STRUCTURES OF HYDROXY/ALKOXY SUBSTITUTED CARBENIUM ION SYSTEMS

By

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ABSTRACT

The structures of two series of hydroxy/alkoxy substituted carbenium ion systems have been explored in this thesis. The structural effect of systematic substituent changes on cationic geometries has been probed and related to variable charge distributions within these cations.

The structures of three 2-substituted 6-ethoxy-tetrahydropyrylium salts have been determined with use of x-ray crystallographic and NMR spectroscopic techniques. It has been shown that the conformations and structures of the tetrahydropyrylium ions observed in the crystalline state are similar, and that these conformations are also present in solution. The six-membered ring in each cation exists in a shallow half-chair conformation with the cationic centers C_6, C_5, O_1 and O_6 having an approximately planar arrangement. These cations each exhibit a Z-conformation about the O_6-C_6 bonds. Systematic analysis of the bond distances obtained has indicated severe C-O bond length distortions and has suggested variable degrees of positive charge delocalization to C_2 and C_7 in these systems. The conformations, details of C-O bonding and closest cation-anion contacts observed have been discussed in terms of the concept of stereoelectronic control.

The crystal structures of three alkyl-substituted hydroxycyclopropylcarbinyl cations have also been determined. Each cation adopts, or approximately adopts, a bisected conformation. The systematic cyclopropyl bond length distortions observed, namely vicinal bond lengthening, distal bond shortening and C_1-C_2 bond contraction when compared to those observed for neutral cyclopropyl ketones, have been related to the degree of charge delocalization into the cyclopropyl ring in each cation and to variable substituent charge stabilizing ability. Semi-empirical and ab initio calculations have also been performed to further probe the nature of bonding within these systems. The optimized gas phase conformations and structures are very similar to those observed crystallographically. However, theory appears to underestimate the degree of structural distortion experimentally observed.

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for George,

and for Mom, Dad and the Whole Family

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LIST OF ABBREVIATIONS

b.p.	boiling point
CPMAS	Cross Polarization Magic Angle Spinning
c-pr	cyclopropyl
dec.	decomposition
DMSO	Dimethylsulfoxide
IGLO	Individualized Gauge for Localized Orbitals
INDO	Intermediate Neglect of Differential Overlap
LCAO	Linear Combination of Atomic Orbitals
m.p.	melting point
Me	methyl
MNDO	Minimal Neglect of Differential Overlap
MO	Molecular Orbital
MP	Moller Plesset
NMR	Nuclear Magnetic Resonance
OMe	methoxy
Ph	phenyl
ppm	parts per million
PROAIM	Properties of Atoms in Molecules
SCF	Self-Consistent Field
STO	Slater Type Orbital
UV	Ultraviolet

Chapter 1

Introduction

1.1 The Study of Carbenium Ions

The existence of carbenium ions has been recognized since the early 1900's (1). These chemical species, which contain a positively charged, trivalent carbon atom, are important intermediates in a large variety of reactions in organic chemistry. Since knowledge of the structure, conformation, reactivity and stability of carbenium ions is essential for the complete understanding of their reactions, the elucidation of these fundamental properties of carbenium ions has attracted the interest of a large number of organic chemists (2).

The knowledge of the precise molecular geometry of an organic molecule or ion is of vital importance for the complete understanding of not only chemical structure and bonding but also chemical stability and reactivity. In general, direct experimental evidence for the molecular geometry of a chemical system is available through x-ray, neutron, or electron diffraction methods and/or microwave spectroscopic techniques (3). However, as carbenium ions are generally extremely reactive moieties, most of the structural information available to date has been obtained by indirect methods such as NMR and UV spectroscopy and solvolytic studies. In addition, theoretical calculations have been extensively used to obtain structural information. However, comparatively little direct experimental solid state evidence exists for the structure of carbenium ions (2).

1.2 The Study of Carbenium Ion Systems by X-Ray Crystallography

Single crystal x-ray crystallography is at present the most powerful general method available for direct three-dimensional structural determination. This technique has become more important in recent years with the introduction of automated diffractometers and new methods of data acquisition, structure solution and refinement (3). Since any organic molecule normally crystallizes in or close to its ground state geometry or conformation, the conformation observed in the solid state generally corresponds to the favoured, or at least one of the preferred, conformations in solution (4). Thus the solid state structures of organic systems observed by crystallography can be used to provide valuable information pertaining to the structures of these systems in solutions in which they react.

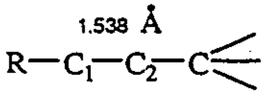
Given the power of single crystal x-ray crystallography in determining structure it would seem natural to apply this technique to the investigation of the structure of carbenium ion systems. Yet, progress using crystallography in this respect has been slow. The reason for this lack of progress is in large measure due to the inherent difficulties associated with the isolation of carbenium ion salts as crystalline materials. In general, where carbenium ion structures have been determined, the relative instability and poor quality of these crystalline samples has led to highly inaccurate structure determinations. The necessary use of complex polyatomic counterions containing heavy metal atoms further reduces the precision associated with the location of the lighter atoms in the crystal structure (4). Consequently, the relatively few reports of x-ray crystallographic structure determinations of carbenium ion systems which exist to date generally have associated standard deviations in bond lengths and angles higher than desirable and higher than those obtainable for similar molecular weight neutral systems (4).

The past 30 years has seen significant advances in the techniques for handling unstable materials such as carbenium ions (5). The use of superacids and non-nucleophilic solvents for preparation of carbenium ion salts in solution, advances in crystal isolation, crystal manipulation and low temperature single crystal diffraction techniques have greatly increased the viability of x-ray crystallography as a tool for the determination of structure, conformation and nature of bonding within carbenium ion systems (5). As such, the time is right to re-enter this field and to provide the badly missing structural information pertaining to some basic carbenium ion salts.

1.2.1 Systematic Structural Studies of a Series of Related Compounds

The utility of x-ray crystallography as a tool for the more complete understanding of structure, reactivity and stability of organic molecules or ions can be amplified considerably by the systematic comparison of the crystal structures of a series of structurally related compounds. For instance, early comparisons of the crystal structures of a variety of vaguely related systems have provided the first evidence for structural variation as a function of large differences in hybridization and environment in these systems (6). These studies have clearly demonstrated that variable hybridization such as that at C_1 in systems such as 1-3 is structurally manifested in terms of significant C_1-C_2 bond length differences in these systems (6).

However, in order to understand more fully subtle differences in chemical phenomena such as the variable stabilities and reactivities observed within a series of



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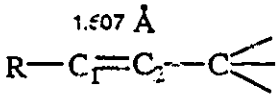

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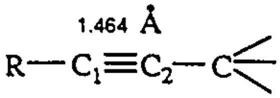

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(6)

structurally related compounds, and the variable regio- and stereo-selectivities observed in their reactions, it is important to analyze systematically the crystal structures of a series of much more closely related systems (6-8). Only via this systematic structural analysis approach can the subtle but consistently observed geometric variations be correlated with varying degrees of electronic delocalization, slight changes in bonding patterns and slight rehybridization (6,9).

Additionally, directed nonbonded contacts seen in each of a series of crystal structures can often be interpreted as structural expressions for incipient reaction stages, such as those of an addition reaction. Such nonbonded contacts of a nitrogen atom with a carbonyl group carbon atom in $R_2C=O$ systems have been experimentally studied (9,10). The nitrogen atom contact in each case showed an approach direction of approximately 105° with concomitant increased nonplanarity of the environment surrounding the carbonyl carbon atom and lengthening of the C=O distance as the N...C(=O) internuclear distance decreased. The implications for the mechanism of addition of a nitrogen atom to a carbonyl functionality and related reactions have been thoroughly discussed (9-11). The structure correlation method has also been used to map out reaction paths for several types of isomerization processes (12). There are also a few examples reported where observed deviations from standard bond lengths and angles along a reaction path have been correlated with the kinetic behavior of molecules in various chemical reactions (13,14).

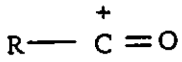
The systematic analysis of a series of related crystal structures is thus a powerful research technique uniquely capable of providing important information pertaining to both the static and dynamic aspects of molecular structure, information which cannot be obtained by any other single experimental method (7,8). However, despite the power of the crystal structure correlation method, as previously mentioned relatively few successful attempts have been made to date in the application of this approach toward the better understanding of carbenium ion systems (15-22).

1.2.2 The X-Ray Structure Correlation Method Applied to Oxygen-Containing Carbenium Ion Systems

Oxygen-containing carbenium ions are an important class of carbenium ions for they are frequently encountered intermediates in a wide variety of useful organic reactions (23). The chemistry of these ions has been extensively studied by a variety of techniques and the results obtained have been comprehensively reviewed (24). However, to date the structure and charge distributions within oxygen-containing carbenium ions is not fully understood. It would therefore appear attractive to apply the x-ray crystallographic structure correlation method toward the achievement of a better understanding of the structure and reactions of these important ions.

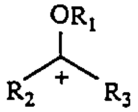
A single oxygen atom can be incorporated into a carbenium ion system in any of three ways as depicted by the structures 4-6 shown following. 4, which contains a formal carbon-oxygen atom double bond adjacent to the carbenium ion center, illustrates the general structure of oxocarbenium ions (24). Alternatively, oxonium ions of the type 5, generally referred to as carboxonium ions, contain a formal C-O single bond adjacent to the carbenium ion center (20). Oxonium ions of the type 6, which incorporate a trivalent, positively charged oxygen atom (24), have not been studied by the x-ray crystal structure correlation approach and thus will not be further discussed.

In order to focus and lay the grounds for further discussion encompassed by this thesis, a brief survey of



$R—\overset{+}{C}=O$

4



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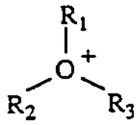

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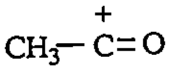
some representative oxocarbenium ion and carboxonium ion systems that have been systematically studied by x-ray diffraction techniques will be presented in the following pages. Although a variety of other oxygen-containing carbenium ions containing additional heteroatoms other than oxygen have also been studied (24), these systems are outside the scope of the present review and will not be herein discussed. In Sections 1.3 and 1.4.4 particular focus will be turned to two important sub-classes of carboxonium ions, namely dialkoxy/hydroxy substituted carbenium ions and protonated cyclopropyl ketone systems.

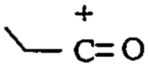
1.2.2.1 Oxocarbenium Ions

The structures of a variety of alkyl- and aryl-substituted oxocarbenium ion derivatives of the type 4, including ions 7a-7e, have been studied by x-ray crystallography. The structure of 7a has been determined independently by Boer and LeCarpentier and coworkers as its SbF_6^- (25), $SbCl_6^-$ (26) and $AlCl_4^-$ (26) salts. Alternatively, the $GaCl_4^-$ salt of 7b (27) and the $SbCl_6^-$ salts of 7c-7e (27-29) have been the subjects of crystallographic investigations.


$CH_3-\overset{+}{C}=O$

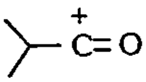
7a

(25,26)



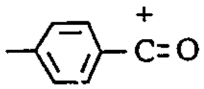
7b

(27)



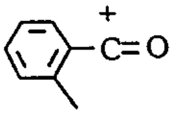
7c

(27)



7d

(28)



7e

(29)

On first inspection of the structural data obtained for 7a-7e, the average $C-C^+$ bond length in the aryl-substituted ions 7d and 7e (1.392(17) Å) appears to be shorter than that observed for the alkyl-substituted derivatives 7a-7c (1.427(23) Å). For comparison, partial LCAO-MO-SCF (Linear Combination of Atomic Orbitals-Molecular Orbital-Self Consistent Field) *ab initio* level calculations for 7a and 7c have calculated an average $C-C^+$ distance of 1.45 Å (30). This would suggest slightly stronger conjugation of the aromatic versus alkyl substituents with the carbenium ion center in these systems. Additionally, the planar phenyl rings of 7d and 7e appear distorted from hexagonal symmetry such that a considerable fraction of positive charge appears to reside on the methyl-substituted aromatic carbon atoms in each case (28,29).

However, the large errors associated with the structure determinations of 7a-7e complicate the systematic structural comparison of these ions. On application of the statistical criterion used throughout this thesis for determination of the significance of experimentally observed structural differences[1], the average C-C$^+$ bond distance in the aryl-substituted ions 7d and 7e is found not to be significantly shorter than that corresponding to the alkyl-substituted ions 7a-7c (difference only 1.2σ), and no significant aryl group bond length distortions from hexagonal symmetry are evident. Additionally, within experimental error no significantly different $^+$C=O bond distances are observed throughout the series of ions 7a-7e. The $^+$C=O bond length values of 1.118 Å (average), 1.099(20) Å, 1.116(10) Å, 1.111(13) Å and 1.097(9) Å

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[1] The statistical criterion used throughout this thesis to determine the difference between two directly comparable bond length or angle values $n_1(\sigma_1)$ and $n_2(\sigma_2)$ is as follows:

$$\sigma = \sqrt{(\sigma_1)^2 + (\sigma_2)^2}$$

where σ_1 and σ_2 are the standard deviations of the two observed values being compared, n_1 and n_2, and σ is the standard deviation associated with the difference between the two values.
The values of n_1 and n_2 are significantly different at the 99% confidence level if the following inequality holds:

$$| n_1 - n_2 | > 3\sigma.$$

respectively obtained for 7a-7e are not different from the corresponding average value of 1.111(13) Å obtained for this series of ions (differences 0.4σ, 0.5σ, 0.3σ, 0.0σ and 0.9σ, respectively) (25-29). Indeed good precision is required in order to detect systematic structural changes within any series of differentially substituted cations. Substituent induced structural changes in these ions 7a-7e may be further masked by the presence of counter-anionic atoms within the crystal lattices of these salts; in each case closest interionic contacts are found between the carbonyl carbon atom of the cation and one or more nucleophilic atoms of the counter-anion (25-29).

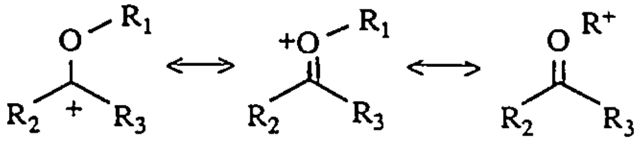
The average carbon-oxygen atom internuclear distance of 1.111 (13) Å in 7a-7e is significantly shorter than the C=O bond in systems of the type $(CR_3)_2-C=O$ (1.210(8) Å) (difference 6.5σ) (3). This average carbon-oxygen bond distance observed for 7a-7e is comparable to that found in $C\equiv O$ (41), and corresponds well with the carbon-oxygen atom bond length in the HF/4-31G level optimized structure of $CH_3-C\equiv O^+$ (1.107 Å) (31). Near 180° $C-C^+=O$ angles are also seen in each of 7a-7e. These structural features provide evidence for considerable oxygen atom participation in positive charge stabilization and for considerable triple bond character in the formal C=O bond in these species. The indicated heteroatomic stabilization suggests the importance of canonical form 4(ii), depicting acyl carbenium ions, to the overall structural description of these oxocarbenium ions.

$$\underset{\underline{4(i)}}{R-\overset{+}{C}=O} \longleftrightarrow \underset{\underline{4(ii)}}{R-C\equiv\overset{+}{O}} \qquad \text{eqn. 1-1}$$

1.2.2.2 Carboxonium Ions

There have been many reports of the preparation of stable solutions of carboxonium ions of the type 5 and their characterization by a wide variety of techniques such as spectroscopic studies in solution (32), gas phase measurements (33), theoretical studies (31,34), thermodynamic measurements (35) as well as studies of their thermal and photochemical rearrangements (36,37). Despite the numerous studies that have been performed, there are relatively few reported direct determinations of the structures of protonated carbonyl compounds (20,38-43), alkoxy-substituted carbenium ions (44-51) or Lewis Acid complexes of carbonyl groups (52).

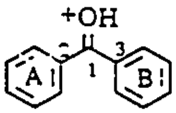
The distribution of positive charge over the $^{+}C-O$ moiety of carboxonium ions, which was a formal C=O double bond before cation formation, is still not fully understood. Precise geometrical parameters relating to these ions could show the relative importance of the various resonance structures 5(i)-5(iii) that can be drawn for this class of carbenium ions, equation 1-2.



5(i) 5(ii) 5(iii)

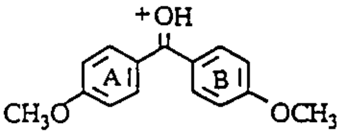
eqn. 1-2

In order to provide a better understanding of both the structure and the nature of electronic delocalization in carboxonium ions in general, the crystal structures of the series of protonated benzophenones 8a-8c have recently been determined by Childs et al (20). 8a and 8c were studied as their SbF_6^- salts whereas the FSO_3^- salt of 8b was investigated.



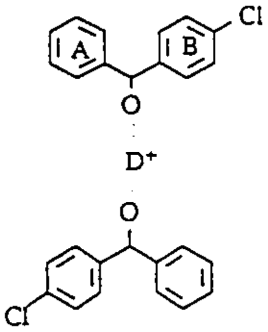
8a

(20)



8b

(20)



8c

(20)

In both 8a and 8b, an electronegative atom of the counter-anion present was found to be situated in or close to the plane of the protonated carbonyl moiety so as to form a strong hydrogen bond with the hydroxyl proton (20). As such, the cations 8a–8c could be considered to be "hemi-protonated" to varying extents (20). In each case additional significant counter-anionic atom contacts to C_1 were observed above and/or below the protonated carbonyl plane.

Similar twist angles of the aryl rings in 8a and 8b from the C_2–C_1–C_3 plane are observed (20). These twist angles of magnitudes 32° (ring A, 8a), 28° (ring B, 8a), 24° (ring A, 8b) and 30° (ring B, 8b) indicate the preferred geometries of these aryl rings which enable maximum conjugation with the adjacent formal carbenium ion center in consideration of the steric constraints present in these systems. In the unsymmetrically substituted ion 8c larger differences in the corresponding twist angles are observed (20). The twist angle of ring A (18°) is considerably smaller than that of ring B (43°) which contains an additional electron withdrawing p-Cl substituent. However, the high degree of disorder seen within the crystal structure of 8c precludes any interpretation of this observation.

The crystallographic bond lengths involving the formal carbenium ion center in each of 8a-8c are listed in Table 1-1 (20). The C_1-O bond in each of these ions is intermediate in length between that found in systems of the type $(C_{ar})_2$-C=O (1.230(15) Å) and those of the type $(CR_3)_2$-C(H)-OH (1.432(11) Å) (3). As such, a C_1 hybridization intermediate between sp^2 and sp^3 is implied. C_1-C_2 and C_1-C_3 bond contraction is also suggested in each of 8a-8c. However, within the error limits of the structure determinations these bond lengths in 8a-8c are not significantly shorter than the average $C(sp^2)$-C_{ar} bond length of 1.480(17) Å observed in neutral systems of the type $(C_{ar})_2$-C=O (3).

Nevertheless, a linear correlation between increasing C_1-O and decreasing C_1-C_{ar} bond distances has been shown to exist within the series of cations 8a-8c and the corresponding neutral systems (20). Childs and coworkers have related these systematic changes to the amount of charge residing on the carbon framework, to variable substituent positive charge stabilizing ability and to the overall stability of each cationic system as a whole (20). On this basis, the suggested relative stabilities of 8a-8c were:

8b > 8a > 8c (20).

Table 1-1. Bond Lengths (Å) Involving the Carbenium Carbon Atom in 8a-8c (20)

CATION	BOND C(1)-O	C(1)-C(2)	C(1)-C(3)
8a	1.296(8)	1.444(9)	1.437(9)
8b	1.314(12)	1.420(13)	1.413(20)
8c	1.260(9)	1.470(11)	1.470(12)

This relative ordering is as expected considering the presence of the electron-donating p-methoxy groups on the aryl rings of **8b** and the electron-withdrawing p-Cl substituent on the aryl rings of **8c**.

1.3 Dihydroxy/Dialkoxy Substituted Carbenium Ions

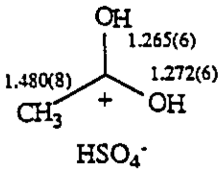
1.3.1 Importance of Dioxygen Substituted Carbenium Ions

Trivalent carbenium ions having two divalent oxygen atom substituents bonded to the positively charged carbon atom center are further examples of carboxonium ions (24). These ions are most commonly referred to as dialkoxy/hydroxy carbenium ions. The immense interest in these ions stems from their intermediacy in a wide variety of acid mediated transformations of carboxylic acids and related derivatives (24,53-55). They are formed, for example, during the acid catalyzed reactions of carboxylic acids and esters such as ester hydrolysis and trans-esterification; reactions which are fundamental transformations of these important functional groups.

Due to the numerous reactions in which dialkoxy/hydroxy carbenium ions participate, it is of considerable interest to determine precisely the structures of these ions in order to more fully understand their modes of reaction. Despite the large number of studies describing the properties of these ions, there have been few reports of their structural determination by direct methods (35,53,54,56-59). However, with the appropriate choice of conditions, relatively stable dialkoxy/hydroxy carbenium ions can be prepared by standard methods as moisture sensitive, but otherwise stable, salts (54). Crystalline samples of such salts can then be studied by x-ray crystallography to provide direct unequivocal structural evidence pertaining to these systems. Following is a discussion of the structures of all known acyclic and cyclic dialkoxy/hydroxy carbenium ions which have been determined by x-ray diffraction techniques. It is intended that the utility of crystallography for direct structure determination will be further demonstrated within these various types of dioxygen substituted carbenium ion systems.

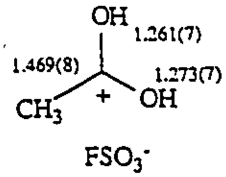
1.3.2 Structural Studies of Protonated Carboxylic Acids

Protonated carboxylic acids are examples of acyclic dihydroxy-substituted carbenium ions. Crystal structural data pertaining to these species are scarce, most likely due to the instability of these cations and the subsequent problems associated with crystallizing these cations as salts. However, over 20 years ago the structures of the 1:1 adducts of acetic acid with sulfuric acid 9a, and acetic acid with fluorosulfuric acid 9b, were determined by Jönnson and coworkers (38).



9a

(38)



9b

(38)

The structures of 9a and 9b were found to be identical within experimental error (38). In both structures the non-hydrogen atoms and hydroxyl hydrogen atoms are coplanar, with one hydroxyl hydrogen atom oriented *cis*, and the other *trans* to the methyl group. This conformation observed for 9a and 9b is also that preferred for protonated carboxylic acids in solution (60,61).

Within experimental error the $^{+}$C-O bond lengths in each of 9a and 9b are equivalent (average value of 1.268 Å), providing evidence for equal positive charge delocalization over the O-C^{+}-O framework of these ions. However, this average bond distance is not significantly different from that observed for either a C=O bond (1.214(19) Å) or a C-OH bond (1.308(19) Å) in neutral carboxylic acids (3).

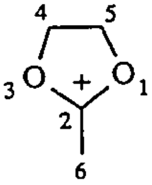
Within experimental error the average C-C^{+} bond length of 1.474 Å obtained for 9a and 9b is not significantly shorter than the corresponding bond in neutral carboxylic acids (1.502(14) Å) (3). This observation suggests the absence of any significant interaction between the methyl group and the formal carbenium ion center in both 9a and 9b.

1.3.3 Structural Studies of Dioxolanylium Ions

Dioxolanylium ions provide an example of relatively stable, cyclic dialkoxy-substituted carbenium ions. These ions have been extensively studied owing to their increased stabilities afforded by the five membered ring system (45-50,54). Yet, dioxolanylium ions are sufficiently reactive to give rise to interesting and selective rearrangements and reactions with nucleophiles (54). In order to more fully understand these reactions, it is important to know the precise structure of these cations and the structural effects of differential substitution.

Paulsen and coworkers have obtained the x-ray structures of the series of differently substituted 2-methyl-1,3-dioxolan-2-ylium ions 10a-10d as their $SbCl_6^-$, ClO_4^- or BF_4^- salts as indicated following (45-48). The x-ray structure of the related 2-phenyl substituted ion 10e has also been studied by Caira and de Wet as its ICl_2^- salt (49). Selected bond lengths obtained for this series of ions are given in Table 1-2.

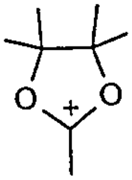
The dioxolanylium rings in each of the cations 10a-10c and 10e are essentially planar, whereas that in 10d adopts a slight twist conformation (70-74). In each of 10a-10d, the acetoxonium methyl group is also coplanar with the



$SbCl_6^-$

10a

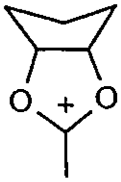
(45)



ClO_4^-

10b

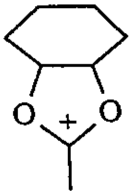
(46)



BF_4^-

10c

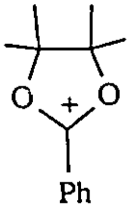
(47)



ClO_4^-

10d

(48)



ICl_2^-

10e

(49)

dioxolanylium ring (45–48). An approximate coplanarity also exists between the planar phenyl substituent of 10e and the adjacent dioxolanylium ring (49).

The five membered ring of 10c exists in an endo-envelope geometry whereas the cyclohexane ring in 10d is twisted toward a half-chair conformation, a conformation which would have been expected had total dioxolanylium ring planarity been observed (48). The methyl groups in 10b are forced to adopt a sterically unfavorable two-fold eclipsed configuration due to the planarity of the dioxolanylium ring system to which they are attached. The presence of this sterically unfavorable configuration provides evidence for the strong resonance energy of the dioxolanylium system which requires total ring planarity for maximum stabilizing orbital overlap (46).

Table 1-2. Selected Bond Lengths (Å) for the Dioxolan-2-ylium Ions 10a-10e (45-49)

			CATION		
BOND	10a	10b	10c	10d	10e
O(1)-C(2)	1.250(6)	1.277(18)	1.257(3)	1.269(2)	1.29(1)
O(1)-C(5)	1.477(6)	1.521(15)	1.496(3)	1.497(6)	1.52(1)
C(2)-O(3)	1.263(6)	1.241(2)	1.253(3)	1.280(8)	1.29(1)
C(2)-C(6)	1.452(9)	1.504(18)	1.481(4)	1.479(7)	1.47(2)
O(3)-C(4)	1.470(7)	1.520(19)	1.479(2)	1.481(4)	1.52(1)
C(4)-C(5)	1.497(6)	1.566(10)	1.516(4)	1.535(4)	1.56(2)

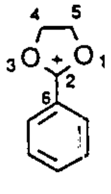
Within experimental error the C_2-O_1 and C_2-O_3 bond lengths in each of 10a-10e are the same (differences 1.5σ, 2.0σ, 1.3σ, 1.3σ and 0.0σ respectively). The average C_2-O bond distances obtained for each of the ions 10a-10d are significantly shorter (differences 5.0σ, 3.4σ, 5.6σ and 3.8σ respectively) than the average $C(sp^2)$-O single bond length of 1.336(14) Å found in alkyl substituted esters (3). Furthermore, these average C_2-O bond distances are significantly longer than the average $C(sp^2)$=O double bond length of 1.196(10) Å found in alkyl esters (differences 4.7σ, 3.1σ, 5.5σ and 5.9σ respectively) (3). These observations indicate a substantial degree of symmetric positive charge delocalization over the O_1-$^+C_2$-O_3 moiety of each of these ions.

The average C_2-O bond in 10e is similarly significantly longer than the $C(sp^2)$=O bond length of 1.202(9) Å typically found in aryl substituted esters (difference 6.5σ) (3). However, this average bond length in 10e is not significantly shorter than the comparable average $C(sp^2)$-O bond distance of 1.337(13) Å found in aryl esters (difference only 2.8σ) (3). It could be argued that less positive charge is delocalized over the O_1-$^+C_2$-O_3 fragment of the 2-phenyl substituted ion 10e than is delocalized over the same fragment of the 2-methyl substituted ions 10a-10d.

One might have expected to observe C_2-C_6 bond lengths in each of the cations 10a-10e which are considerably shorter than those observed in comparable neutral systems. Yet, within experimental error the C_2-C_6 bond lengths in each of 10a-10d are not significantly shorter than the average corresponding $C(sp^3)$-$C(sp^2)$ bond length of 1.497(18) Å in alkyl esters (differences 2.2σ, 0.3σ, 0.9σ and 0.9σ respectively) (3). Similarly, the C_2-C_6 bond distance in 10e is insignificantly different (difference only 0.7σ) from the corresponding C_{ar}-$C(sp^2)$ bond length of 1.487(12) Å typically found in aryl esters (3). Furthermore, one might have expected to observe symmetrically lengthened O_3-C_4 and O_1-C_5 bonds in each of 10a-10e. Indeed, with the exception of 10c, there is no significant difference in the O_3-C_4 and O_1-C_5 bond lengths observed for these ions (45-49). The average O-$C(sp^3)$ bond length in these ions is significantly longer than the corresponding O-$C(sp^3)$ bond length of 1.450(14) Å typically observed in alkyl esters of carboxylic acids (difference 3.1σ) (3). As such, the structures of 10a-10e suggest that a considerable amount of positive charge resides at C_4 and C_5 of these systems.

The crystallographic results described above are in agreement with theoretical results obtained by Pittman and coworkers pertaining to charge delocalization within 1,3-dioxolan-2-ylium ions (62). Calculated π-bond orders for the C_2-O bonds of C_2-substituted derivatives with R=NH_2, OH, CH_3, and H ranged between 0.5-0.65 respectively (62). Atomic charge density calculations for the cations <u>10a</u> and <u>10c</u> have also been performed by Paulsen and Schüttpelz at the semi-empirical MNDO/3 level (47). However, the results of these calculations, which suggest the presence of a considerable amount of positive charge density at C_4 and C_5 in these ions, are questionable in consideration of the low level of the calculations performed.

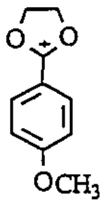
Further information pertaining to the structural effects of systematic substituent changes in 1,3-dioxolan-2-ylium ion derivatives has been obtained by Orgias who has determined the x-ray crystal structures of the series of ions <u>11a</u>-<u>11e</u> (50). Systematic comparison of the structures of these ions can indicate the structural effect of variable substitution at the C_2 and C_4-positions of the dioxolanylium ring in these systems. Representative bond lengths obtained for <u>11a</u>-<u>11e</u> are listed in Table 1-3.



$CF_3SO_3^-$

<u>11a</u>

(50)



SbF_6^-

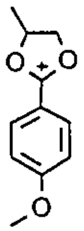
<u>11b</u>

(50)

SbF_6^-

<u>11c</u>

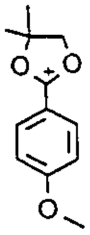
(50)



SbF_6^-

<u>11d</u>

(50)



SbF_6^-

<u>11e</u>

(50)

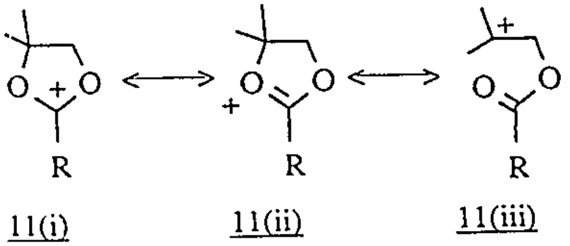
Table 1-3. Selected Bond Lengths (Å) for the Dioxolan-2-ylium Ions 11a-11e (50)

	CATION				
BOND	11a	11b	11c	11d	11e
O(1)-C(2)	1.281(3)	1.292(8)	1.288(5)	1.291(10)	1.286(15)
O(1)-C(5)	1.480(3)	1.466(9)	1.472(5)	1.476(13)	1.486(17)
C(2)-O(3)	1.282(3)	1.293(9)	1.290(5)	1.274(11)	1.306(16)
C(2)-C(6)	1.442(3)	1.414(9)	1.417(5)	1.441(14)	1.409(17)
O(3)-C(4)	1.472(3)	1.474(9)	1.469(5)	1.503(13)	1.546(15)
C(4)-C(5)	1.505(5)	1.503(11)	1.515(7)	1.567(14)	1.574(19)

The average C_2-O bond lengths and the relatively planar conformations of the dioxolanylium rings of 11a-11e are similar to those observed for the related series of ions 10a-10e (50). Furthermore, in each of 11a-11e the aryl ring or alkyl substituent attached to C_2 is also planar. In each case this substituent at C_2 is oriented approximately coplanar with the dioxolanylium system so as to give a small twist angle (in the range 1.4°-9.0°) between the planes of the dioxolanylium ring and aryl or alkyl substituent (50).

Enhanced conjugation of the p-methoxyphenyl ring with the positively charged center in 11b is suggested by the shorter C_2-C_6 bond length observed in 11b when compared to the corresponding bond in 11a (difference 4.6σ). In addition, significant quinoid type distortion of the aryl ring, which is not seen in 11a, is also observed in 11b (50). However, due to the relatively large errors associated with the structure determinations of the similarly substituted cations 11d and 11e, no such significant quinoid type distortion of the p-methoxyphenyl rings is evident. Similarly, the conjugated polyene substituent of 11c might have been expected to participate extensively in charge delocalization; however no evidence for this occurrence is given by the observed bond distances in this cation (50). Results of low level INDO calculations and NMR chemical shift correlations with Hammett σ values have previously suggested that this type of conjugative interaction involving a C_2-substituent is relatively unimportant (62,63). Yet, the evidence obtained for substantial aryl ring participation in positive charge delocalization within 11b suggests that the results of these studies are questionable.

The effect of asymmetric substitution at C_4 of the dioxolanylium ring in these systems can be probed by comparison of the structures of 11b, 11d and 11e (50). An observed clear systematic increase in the O_3-C_4 bond length might be expected with increasing degree of methyl substitution on C_4 and consequent enhanced positive charge on C_4 in these cations, as illustrated in equation 1-3. Such an observed trend would be in agreement with a diverse body of evidence encompassing theoretical calculations (62), ^{13}C NMR and ESCA spectroscopic studies (48) and calorimetric studies (64).



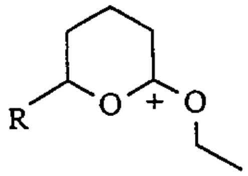
eqn. 1-3

Indeed the O_3-C_4 bond length in the dimethyl substituted cation <u>11e</u> is longer than the corresponding bond in <u>11b</u> which is unsubstituted at the C_4 position (difference 4.1σ). However, taking into account the relatively high errors associated with the structure determinations, no significant difference can be detected on comparison of the O_3-C_4 bond distances in <u>11b</u> and <u>11d</u> (difference only 1.8σ) nor of those in <u>11d</u> and <u>11e</u> (difference only 2.2σ). It should further be noted that within experimental uncertainty the O_3-C_4 and O_1-C_5 bond distances observed in <u>11a</u>-<u>11e</u>, with the exception of the O_3-C_4 bond in <u>11e</u>, are not significantly longer than the C(sp^3)-O bond length of 1.450(14) Å typically found in alkyl esters (3).

Overall, the errors associated with the structure determinations of <u>11a</u>-<u>11e</u> make quantitative comparison of individual bond lengths difficult. Nevertheless, evidence for variable charge distributions as a function of substitution at C_2 and C_4 in these cations has been obtained. It appears that the C_2-O bond lengths are sensitive to substituent changes at C_2, as are the O_3-C_4 bond distances to the degree of methyl substitution at C_4.

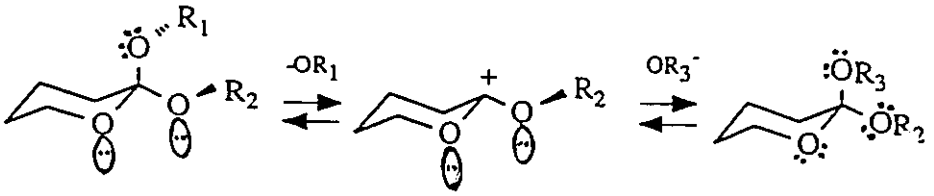
1.3.4 <u>Objectives of the Present Study</u>

In order to further probe the effect of variable substitution on the structure and charge distribution within dialkoxy-substituted carbenium ions, it is the purpose of this thesis to extend the x-ray crystal structure correlation method above discussed for the five-membered ring dioxolanylium ion systems to six-membered ring dialkoxy-substituted carbenium ion systems. Although several candidate systems were available for study, the model system chosen was the 2-substituted 6-ethoxy-2,3,4,5-tetrahydropyrylium ion system 12. Additional interest in these ions stems from the remarkable selectivity exhibited in the reactions of these ions and the consequent development of the concept of stereoelectronic control to explain this selectivity (65-72). This concept, primarily put forth by Deslongchamps and known as the "Kinetic Stereoelectronic Theory", is also subject to direct experimental test in this thesis. As such a brief overview of this theory is warranted.



12

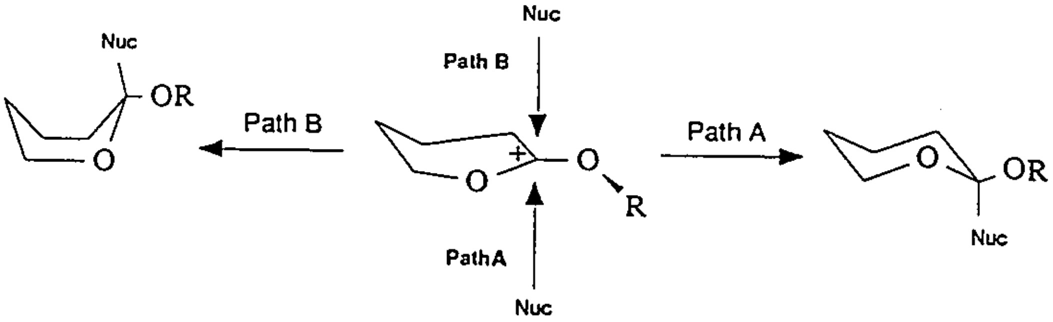
According to the kinetic stereoelectronic theory, in the ionization reactions of acetyl tetrahydropyranyl systems of the type 13, the stereospecific axial C-O bond cleavage observed is thought to be facilitated by n-σ^* orbital overlap of the lone pairs of electrons on the two remaining oxygen atoms with the σ^* orbital of the C-O bond being cleaved, equation 1-4 (65-69).



eqn. 1-4

13 14 15

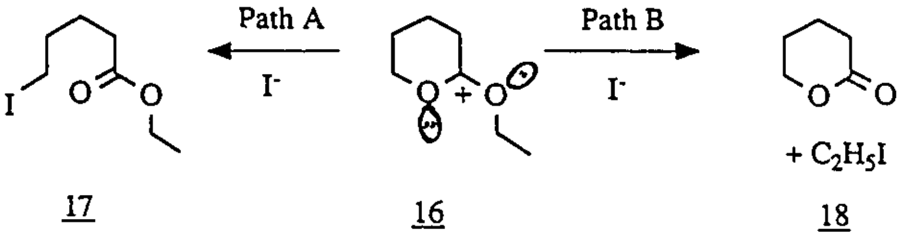
Deslongchamps has also suggested that nucleophilic attack on a tetrahydropyranyl ion such as 14 is governed by the same stereoelectronic effects as the corresponding ionization reactions involved in its formation and that the reaction proceeds via specific pseudo-axial attack at the anomeric carbon atom to generate an orthoester such as 15, equation 1-4 (65-69). Nucleophilic attack is proposed to occur preferentially from the face of the ring which leads directly to the more stable chair (Path A) rather than boat (Path B) conformation of the tetrahydropyran ring, Scheme 1-1.



Scheme 1-1

Deslongchamps and coworkers have also shown that the reaction of the tetrahydropyrylium ion 16 with iodide ion gives a high proportion of the ring opened product 17 via Path A, and lesser amounts of lactone 18 and ethyliodide, the products which would be formed by Path B, Scheme 1-2 (67). Deslongchamps has suggested, on the basis of the known conformational preferences of esters, that 16 exists in the Z rather than E conformation as shown in Scheme 1-2 (67). In this conformation, selective cleavage of the endocyclic C-O bond would be facilitated by the maximum overlap which exists between one lone pair of electrons on the exocyclic oxygen atom and the σ^* orbital of the adjacent endocyclic C-O bond.

In order to understand more fully any underlying electronic basis for the preferred modes of reaction of acetyl tetrahydropyranyl ions, it is important to define



Scheme 1-2

precisely the structures of these ions. As such, it was hoped that the conformation and structures of the 2-substituted 6-ethoxy-2,3,4,5-tetrahydropyrylium ions herein determined by x-ray crystallography would answer some of the questions raised within the kinetic stereoelectronic theory.

Throughout this thesis, close attention is also given to the extent and structural effect of any nearest contact cation - counter-anion interactions present within the crystalline lattices of the tetrahydropyrylium ion salts studied. Any such significant interactions observed can be viewed as a point on the reaction coordinate for nucleophilic addition, and can provide further evidence for preferred sites and modes of nucleophilic attack on these ions.

A further aim of the work described in this thesis is to provide direct experimental evidence for the conformational and structural effects of systematic substituent changes within the homologous series of 2-substituted 6-ethoxy-tetrahydropyrylium ions. Systematically observed trends can taken as structural expressions for variable charge delocalization over the carbon and oxygen framework of the tetrahydropyrylium ring, as well as for variable cationic stability. Overall, detailed structural analysis of this series of ions is intended to provide direct experimental evidence for the electronic basis responsible for both static and dynamic aspects of acetyl tetrahydropyrylium ions; for preferred conformations and geometries and for the degree of regio- and stereo-specificity involved in nucleophilic attack on these ions.

1.4 Substituted Cyclopropylcarbinyl Cations

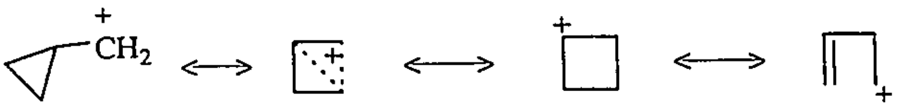
1.4.1 Interest in Cyclopropylcarbinyl Cations

Cyclopropylcarbinyl cations are another important subclass of carbenium ions. These ions are unusually stable and materials which can ionize to form these ions solvolyze with markedly enhanced rates (73,74). Although the reactions and energetics of isomeric interconversion of the parent primary cyclopropylcarbinyl cation 20 and its substituted derivatives have been extensively studied and reviewed (75-80), much interest pertaining to the structures of these systems remains. Although much early evidence for cyclopropyl ring orbital delocalization has been reported from solvolytic (74,81), NMR (82), UV (83) and theoretical studies (84-87), the nature of cyclopropyl group positive charge stabilization and the effect of this stabilization on the structure of cyclopropylcarbinyl cations is still not fully understood. Much of this lack of understanding results from the scarcity of direct x-ray crystal structural information for these systems available to date.

20

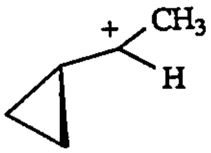
1.4.2 The Structure of 20 and its Secondary and Tertiary Methyl-Substituted Analogues

Over the past 20 years the structure of the parent cyclopropylcarbinyl cation 20 has been extensively, but indirectly studied, particularly in relation to the potential energy surface for the well known facile cyclopropylcarbinyl-bicyclobutonium-cyclobutyl-allylcarbinyl interconversion, Scheme 1-3 (75,76,88-92). The techniques that have been used include solvolytic studies (75-81), isotopic tracer experiments (91,92), detailed NMR studies of solutions of the stable ions (91-95), gas phase studies (96) and theoretical calculations (97-106). Since the cyclopropylcarbinyl cation 20 is relatively unstable, most experimental studies pertaining to 20 have been, of necessity, related to the more stable methyl-substituted secondary and tertiary cyclopropylcarbinyl cations 21 and 22. Hence, a brief description of these ions is warranted.

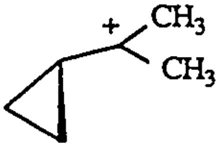


Scheme 1-3

The generation of ions 21 and 22 in superacid media at low temperature has enabled their observation by NMR spectroscopy under stable ion conditions (107-109). Indeed the majority of experimental evidence pertaining to the less stable cyclopropylcarbinyl derivatives has been obtained by this spectroscopic technique. The ^{1}H and ^{13}C NMR spectra for 21 and 22 indicate a symmetrical bisected structure for both of these ions and demonstrate the remarkable ability of the three-membered ring in the bisected conformation to stabilize the positively charged center to which it is attached (107-109). In this conformation, in which the protonated methylene moiety bisects the plane of the cyclopropyl ring, maximum and equal conjugation between the two vicinal cyclopropyl C-C bonds and the empty p-orbital at C_1, the formal center of positive charge is possible.



21

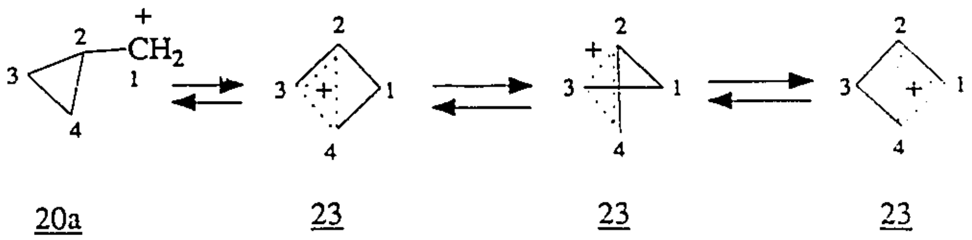


22

The existence of 21 and 22 in solution as static, cyclopropylcarbinyl cations in the bisected geometry has been recently supported by results of IGLO calculations (111). Schindler had obtained good agreement between observed and calculated ^{13}C NMR chemical shifts when a single, bisected cyclopropylcarbinyl cation was assumed in each case (111).

The ^{1}H and ^{13}C NMR spectra obtained by Olah and coworkers for 20 are considerably different than those obtained for 21 and 22 under the identical conditions (94,95). Although the NMR spectra of each of 20, 21 and 22 indicate charge delocalization by the cyclopropyl ring in each case, with 20 a unique behavior has been observed. The chemical shifts obtained for 20 differ markedly from that predicted on the basis of extrapolation from the shifts of 21 and 22, and have been used to suggest dramatically enhanced σ-delocalization in this cation (94,95).

Olah and coworkers have interpreted the experimental evidence for the structure of 20 in terms of two populated cations in rapid equilibrium (94,95). The bisected cyclopropylcarbinyl cation 20a has been postulated as the minor species in equilibrium with a rapidly equilibrating set of $C_{2,3}$ and $C_{2,4}$ nonclassical bicyclobutonium ions 23, which are formed by C_2-C_3 or C_2-C_4 bond delocalization via two-electron, three-center bond formation with the empty p-orbital at C_1 in 20a, Scheme 1-4. More conclusive evidence for this contention has been recently obtained by Myhre and coworkers through their CPMAS ^{13}C NMR studies of methylene carbon labelled $C_4H_7^+$ in amorphous SbF_5 at variable temperatures in the range 170 K to 5 K (112). As the temperature was reduced below 60 K a slowing of a rapid equilibrium between cations 20a and 23 was indicated by comparison of the NMR spectra obtained with corresponding IGLO calculated NMR parameters obtained by Schindler (111). On the basis of these studies, Myhre and coworkers have concluded that the energy surface connecting 20a and 23 is very flat and that the enthalpy difference between these cations is very small (112).



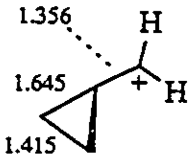
Scheme 1-4

The existence of the nonclassical behavior of 20 is further substantiated by the results of the highest level calculations performed to date using the extended basis set

6-311G** and full fourth order Moller-Plesset perturbation theory (104). These calculations have indicated that both 23 and 20a are equally stable, minimum energy isomers, which lie 9.0 kcal mol^{-1} above the global minimum corresponding to the 1-methylallyl cation (104).

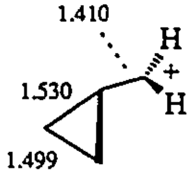
Geometry calculations have also been performed recently by Wiberg and coworkers on both the fixed bisected (20a) and perpendicular conformations (20b) of 20 in order to evaluate the degree of cyclopropyl group participation in charge stabilization, and the structural consequences of these interactions (85). In the bisected conformation 20a, maximum conjugation between the two vicinal cyclopropyl C-C bonds and the empty p-orbital at C_1 is possible. Conversely, in the perpendicular form 20b, no such stabilizing π-overlap of the cyclopropyl ring with the carbenium ion center can occur. The structural effect of maximum cyclopropyl group conjugation versus lack of conjugation with the adjacent carbenium ion center in the bisected and perpendicular conformations 20a and 20b respectively is shown below (85).

The marked bond length changes calculated within 20a, in particular the severely elongated vicinal cyclopropyl C-C bonds and the severely contracted C_1-C_2 and distal cyclopropyl C-C bonds, provide evidence for extensive conjugation and charge delocalization in the bisected form



20a

(85)



20b

(85)

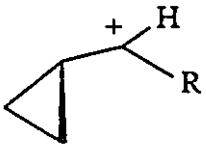
20a. In contrast, the less distorted structure calculated for 20b is indicative of hyperconjugation of normal magnitude (86). The magnitude of the highly stabilizing conjugative interaction present in 20a is evident on comparison of the energies calculated for the bisected and perpendicular conformations of 20; 20a is calculated to be 26.3 kcal mol^{-1} more stable than 20b (87).

It should be stressed however that the above discussed calculations performed by Wiberg and coworkers have indicated the structures of 20 when confined to either the bisected or perpendicular conformation (85). In order to more fully understand the chemistry of the parent cyclopropylcarbinyl cation 20 and its substituted derivatives, experimentally observed or calculated minimum energy structures of these cations are of primary importance.

1.4.3 The Structures of Further Carbon-Substituted Cyclopropylcarbinyl Cations

The structures and stabilities of 1-substituted cyclopropylcarbinyl cations have also been extensively studied by indirect methods. A variety of solvolytic, NMR and UV spectroscopic studies have provided evidence for the conjugative ability of the cyclopropyl ring with the adjacent carbenium ion center in these systems, and for the subsequent enhanced stabilization of these cations (93,96-100).

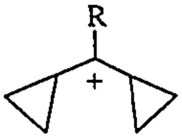
Only a small number of conformationally unrestricted cyclopropylcarbinyl cations containing a single substituent at C_1 have been studied by NMR spectroscopy; representative ions that have been studied by Olah and coworkers are listed below (76,113,114). NMR spectroscopic results have suggested that each of the ions 24a-24d exists in the bisected conformation in which the cyclopropyl group participates considerably in positive charge stabilization (76,113,114).



24

24a R=CH_3
24b R=c-pr
24c R=Phenyl
24d R=2,5-dimethylbenzene

A large variety of the more stable tertiary carbon-substituted cyclopropylcarbinyl cations have been prepared and studied by numerous workers, and the chemistry of these ions has been extensively reviewed (75,76). Included in this class of cyclopropylcarbinyl cations are those that remain relatively conformationally unrestricted, such as the dicyclopropyl, the cyclopropylmethyl, and the cyclopropylphenyl derivatives 25-27 respectively listed below. The NMR spectra of these ions have provided additional evidence both for a bisected conformational preference and for significant positive charge delocalization by the cyclopropyl ring in each case (108,76).



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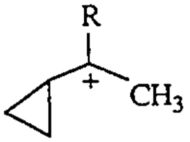
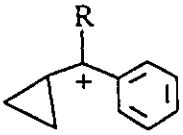


26



27

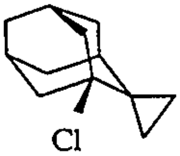
R = c-pr
Me
phenyl
1-Me-c-pr
cyclohexyl
$CH(CH_3)_2$
CCH
$CCCH_3$
2,2,2',2'-tetra-Me-c-pr

R = Me
phenyl
p-OMe-phenyl

R = phenyl

1.4.3.1 Conformationally Restricted Cyclopropylcarbinyl Derivatives

Although ample evidence exists for the stability of bisected cyclopropylcarbinyl cationic structures, geometric factors or substituent effects in some systems may favor or impose other conformations. The study of conformationally restricted cyclopropylcarbinyl cations thus allows investigation of the nature and extent of cyclopropyl ring interaction with the adjacent positively charged center as a function of overall geometry. In this respect, the early solvolytic and NMR studies pertaining to the relatively conformationally rigid adamantyl systems 28-31 have enabled evaluation of the nature and extent of interaction of the cyclopropyl ring oriented perpendicular to the developing empty p-orbital of the formal positively charged center (115,116).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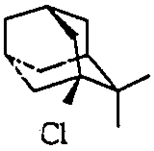
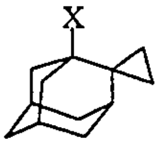
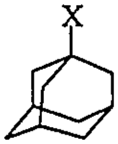
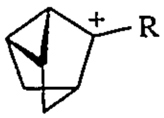

29


30


31

In contrast to the extreme solvolytic rate enhancements usually associated with bisected cyclopropylcarbinyl systems (76), the solvolyses of 28 and 30 have been shown to occur more than 10^2 times more slowly than that of the model compounds 29 and 31 (115,116). The solvolytic rate depressions observed for 28 and 30 have been attributed to the approximately perpendicular conformation with respect to the developing cationic center to which the cyclopropyl groups in these systems are restricted (115,116). A fully perpendicular conformation in these systems would preclude any cyclopropyl group conjugation with the developing cationic center. Furthermore, in the absence of such conjugation, inductive electron withdrawal of the adjacent cyclopropyl bonds would further destabilize these developing cations.

A variety of other conformationally restricted cyclopropylcarbinyl cations such as 32-36 have also been studied by NMR spectroscopy (109,117-119). Olah and Liang have suggested that each of the rigid 3-nortricyclyl cations 32a-32c exist as static entities in FSO_3H-SbF_5 solution at -78°C (109). Although in each of these cations the cyclopropylcarbinyl moiety is restricted to a bisected conformation, the existence of extremely limited bridging interactions between the strained vicinal cyclopropyl bonds and the empty p-orbital at the formal carbenium ion center in each case has been indicated (109). Olah and Liang have thus interpreted their spectroscopic results in terms of considerable hyperconjugative positive charge stabilization by the cyclopropyl groups in each of these systems.

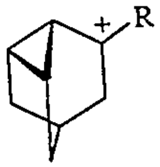


32

32a R = H

32b R = CH_3

32c R = C_2H_5



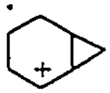
33

33a R = H

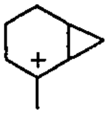
33b R = CH_3

Olah and coworkers have also indicated that the less conformationally restricted 3-homonortricyclyl cations 33a and 33b undergo degenerate cyclopropylcarbinyl rearrangements in SO_2ClF-SbF_5 solutions as the temperature is raised above -100°C (117). These workers have suggested that in cyclopropylcarbinyl systems the barriers to rearrangement observed are proportional to the degrees of geometrical rigidity imposed and hence, to the degrees of non-classical behavior exhibited by these ions (117).

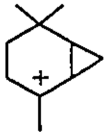
Olah and coworkers have further shown, on the basis of NMR spectroscopic results, that the more sterically hindered bicyclic cations 34 and 35 are stable in SO_2ClF-SbF_5 solutions up to -85°C and 0° respectively (118). For each cation, evidence for considerable charge delocalization by the cyclopropyl ring has been obtained. The enhanced stability of 35 versus 34 observed indicates the additional positive charge stabilization afforded by the 1-methyl substituent present in 35 (118). Kelly and coworkers have also similarly shown that 36 exists as a static entity in SO_2ClF-FSO_3H/SbF_5 (1:1) solutions up to -80°C (119). Comparison of the NMR spectroscopic data obtained for 36 with those obtained for 35 suggests that the geminal dimethyl group of 36 exerts no detectable influence upon the structures of these cations.



34

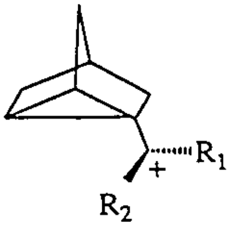


35



36

More recently the results of the NMR spectroscopic analysis of the primary nortricyclylcarbinyl cation 37a and the related secondary and tertiary cations 37b-37d were interpreted by Schmitz and Sorensen to provide the first experimental evidence for the existence in solution of a static primary cyclopropylcarbinyl cation in a bisected conformation (87). The spectra obtained for 37a-37d have suggested a bisected conformation of the cyclopropylcarbinyl moieties contained within each of these cations (87). Progressive electron delocalization changes as would be expected within this series of ions have also been indicated (87). These results suggest that the primary ion 37a is not structurally unique. However, results of semi-empirical calculations involving the MNDO level geometry optimization of 37a have suggested that 37a is marginally closer in structure to a vinyl-bridged 2-norbornyl cation, than to the classical primary cyclopropylcarbinyl cation shown below (87).

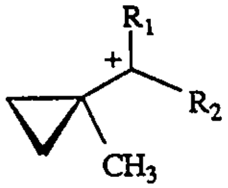


37

37a	$R_1=R_2=H$
37b	$R_1=H$; $R_2=CH_3$
37c	$R_1=CH_3$; $R_2=H$
37d	$R_1=CH_3$; $R_2=CH_3$

1.4.3.2 The Structural Effect of Cyclopropyl Substitution

The series of conformationally mobile α-methyl cyclopropylcarbinyl cations 38a-38e have been investigated by NMR spectroscopy in order to probe the structural effect of an α-methyl cyclopropyl substituent (95,120,121). On the basis of these studies as well as *ab initio* calculations at the 4-31G level, it has been suggested that the primary cation 38a is best represented in terms of a dynamic equilibrium involving both the planar 1-methylcyclobutyl cation and a set of three equivalent bisected 1-methylcyclopropylcarbinyl cations (95). Conversely, NMR data for both 38d and 38e are characteristic of classical tertiary cyclopropylcarbinyl cations in the bisected geometry (120,121). The inability to detect ions 38b and 38c, or any equilibrium mixture of these ions, has been taken to suggest a greater ease of ring opening of the α-methyl-cyclopropyl group in these systems when compared to that in corresponding cyclopropylcarbinyl systems lacking an α-methyl substituent (95,120,121).

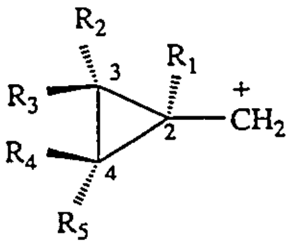


38

38a	$R_1=R_2=H$
38b	$R_1=H$; $R_2=CH_3$
38c	$R_1=CH_3$; $R_2=H$
38d	$R_1=CH_3$; $R_2=CH_3$
38e	$R_1=Ph$; $R_2=CH_3$

Comparison of ^{13}C NMR data for 38d and 22 suggests that the α-methylcyclopropyl group in 38d is slightly more charge stabilizing than the unsubstituted cyclopropyl ring in 22. This conclusion is consistent with the results of solvolysis studies performed by several research groups (122-124). Although characteristically large rates of solvolysis have been measured for cyclopropylcarbinyl derivatives containing an unsubstituted cyclopropyl ring (76), methyl group substitution at either C_α or C_β of the cyclopropyl ring of these derivatives has been shown to lead to large solvolytic rate enhancements (122-124).

More recently the geometries and energies of a comprehensive set of primary cyclopropylcarbinyl cations 39a-39k, having methyl substituents bonded to the α and/or β cyclopropyl carbon atoms, have been theoretically determined by Schmitz and Sorensen at the MNDO//STO-3G basis set level (87). The results obtained have been compared to similarly calculated parameters for the parent primary and methyl substituted secondary and tertiary cyclopropylcarbinyl cations 20-22 (87). For reference, selected bond lengths calculated for these cations are listed in Table 1-4. However, owing to the semi-empirical nature of these calculations it is perhaps most informative to analyze the general geometrical trends that have become evident rather than the absolute geometrical values calculated.



39

39a $R_1=CH_3$; $R_2=R_3=R_4=R_5=H$
39b $R_3=CH_3$; $R_1=R_2=R_4=R_5=H$
39c $R_2=CH_3$; $R_1=R_3=R_4=R_5=H$
39d $R_2=R_3=CH_3$; $R_1=R_4=R_5=H$
39e $R_2=R_4=CH_3$; $R_1=R_3=R_5=H$
39f $R_3=R_4=CH_3$; $R_1=R_2=R_5=H$
39g $R_2=R_5=CH_3$; $R_1=R_3=R_4=H$
39h $R_1=R_2=R_5=CH_3$; $R_3=R_4=H$
39i $R_2=R_3=R_4=CH_3$; $R_1=R_5=H$
39j $R_2=R_3=R_5=CH_3$; $R_1=R_4=H$
39k $R_2=R_3=R_4=R_5=CH_3$; $R_1=H$

For each of the ions containing symmetrical cyclopropyl group substitution, 39a, 39f-39h, 39k and 20-22, the bisected geometry has been calculated to be the global minimum on the potential energy surface (134). Distorted bisected ground states have been calculated for the unsymmetrically substituted ions 39b-39e, 39i and 39j. Furthermore, relative to the structures calculated for 21 and 22, which contain highly charge stabilizing C_1 methyl substituents, highly distorted structures have been calculated for the primary ions 39a-39k and 20 studied (87).

As the degree and unsymmetrical nature of methyl substitution at C_3 and/or C_4 increases within this series of primary ions, the C_1-C_2 bond lengths in these ions have been calculated to shorten (87). In each case, concomitant C_2-C_3 and C_2-C_4 vicinal cyclopropyl bond lengthening and C_3-C_4 distal bond shortening has also been calculated. The degree of either C_2-C_3 or C_2-C_4 vicinal cyclopropyl bond lengthening

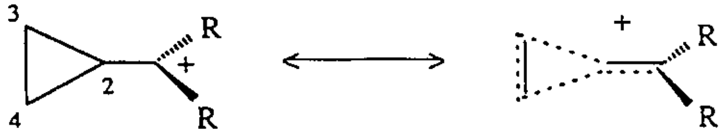
Table 1-4. Selected Calculated Bond Lengths (Å) for the Cyclopropylcarbinyl Cations 39a-39k, and 20-22 (87)

	BOND			
CATION	C(1)-C(2)	C(2)-C(3)	C(2)-C(4)	C(3)-C(4)
39a	1.407	1.630		1.472
39b	1.396	1.657	1.591	1.478
39c	1.397	1.651	1.592	1.480
39d	1.393	1.701	1.576	1.483
39e	1.396	1.632	1.623	1.482
39f	1.395	1.629		1.483
39g	1.397	1.624		1.486
39h	1.407	1.644		1.482
39i	1.393	1.681	1.599	1.492
39j	1.393	1.691	1.595	1.492
39k	1.394	1.640		1.505
20	1.400	1.615		1.474
21[a]	1.416	1.600		1.481
21[b]	1.418	1.601		1.481
22	1.436	1.590		1.486

a) methyl substituent *trans* to hydrogen atom at C_2
b) methyl substituent *cis* to hydrogen atom at C_2

calculated for each ion appears to be proportional to the degree of methyl substitution at the individual carbon atoms C_3 or C_4. Conversely, methyl-substitution at C_2 in the ions 39a and 39h versus 20 and 39g respectively has been calculated to lead to both elongated C_1-C_2 and vicinal cyclopropyl bond lengths.

On the basis of these calculations, Schmitz and Sorensen have reasoned that C_2-methyl substitution in each of the primary cyclopropylcarbinyl cations studied would stabilize resonance structure 40(i), whereas substitution at C_3 and/or C_4 would stabilize the vinyl bridged resonance contributor 40(ii) shown below (87). Calculated energies of isomerization from the bisected to perpendicular form of each of these cations have further provided evidence for the increasing importance of canonical form 40(ii) upon destabilization of the parent cation 20 by methyl group substitution at C_3 and/or C_4 of these cations (87).

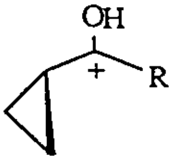


40(i) 40(ii)

The results obtained by Schmitz and Sorensen can be correlated with the results of much earlier solvolytic studies performed by Schleyer and Van Dine (81). These early studies have suggested that the solvolytic reactivity of derivatives of 20, 39b, 39d, 39f and 39k is an approximate linear function of the degree of methyl substitution in these systems, and that approximately symmetrical cyclopropylcarbinyl cationic structures exist in each case (81). It therefore appears that enhanced contributions of the resonance form 40(ii) to the structures of substituted cyclopropylcarbinyl cations are responsible for the enhanced solvolytic reactivities much earlier observed by Schleyer and Van Dine (81).

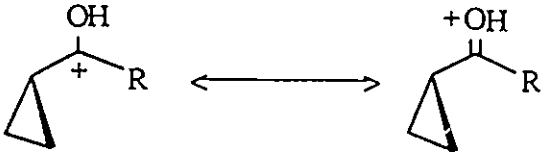
1.4.4 The Structures of Hydroxy-Substituted Cyclopropylcarbinyl Cations

One might expect that a considerable amount of experimental evidence exists for the structures of and bonding within the heteroatom stabilized substituted hydroxycyclopropylcarbinyl cations 41. However, although the structures of a variety of substituted hydroxycyclopropylcarbinyl cations have been studied by indirect methods (95,108,114,125) and theoretical calculations (111,126,127), direct x-ray crystallographic structural evidence pertaining to these ions is scarce.



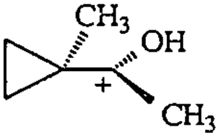
41

Solution state ^1H and ^{13}C NMR studies have indicated that the preferred conformation of these cations is again bisected so as to enable maximum cyclopropyl group participation in positive charge stabilization (95,108,114, 125). The NMR spectra obtained for a variety of protonated cyclopropyl ketones such as 41a, R=CH_3; 41b, R=c-pr; and 41c, R=phenyl, in strong acid or superacid solution at low temperature have provided evidence for both the *s-cis* and *s-trans* bisected geometries as well as for both the E and Z configuration of the hydroxyl proton with respect to the cyclopropyl moiety (95,108,114,125). These studies have also indicated a significant contribution of the resonance contributor 41(ii) to the overall structural description of these ions (108).

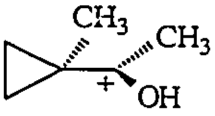


41(i) 41(ii)

Protonated methyl-2-methylcyclopropyl ketone **42** has also been studied by NMR spectroscopy (95). The spectra for **42** obtained by Olah and coworkers on dissolution of the corresponding neutral ketone in FSO_3H-SO_2ClF solution at -78°C has provided evidence for rotation about the C_1-C_2 bond of this ion (95). However, on decreasing the solution temperature to -95°C, evidence for the presence of the two bisected conformers **42a** and **42b** in a 3.5:1 ratio has also been obtained (95).



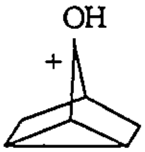
42a



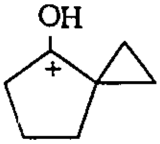
42b

A similar NMR spectroscopic temperature dependency has also been observed by Olah and coworkers for **41a**; decreasing the FSO_3H-SO_2ClF solution temperature from -78°C to -90°C has led to the "freezing-out" of the corresponding *s-trans* and *s-cis* rotomeric pairs for **41a** in a 4:1 ratio (95). On comparison of the spectra obtained for **42** with those obtained for **41a**, the carbenium ion center in **42** is indicated to be more shielded, and the distal cyclopropyl carbon atoms C_3 and C_4 less shielded, than the corresponding atoms in **41a**. Although it should be stressed that quantitative comparisons cannot be made on the basis of these spectroscopic observations (128), these results do however suggest enhanced positive charge stabilization by the α-methylcyclopropyl group in 42 relative to the unsubstituted cyclopropyl group in 41a.

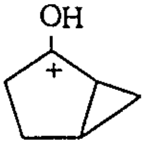
Conformationally restricted systems such as 43-45, which each contain a hydroxycyclopropylcarbinyl subsystem, have also been studied by NMR spectroscopy (75). It has been found from the spectra obtained that the cyclopropyl atoms in 43 and 44 exhibit higher deshielding effects than do those in 45. These results have been interpreted in terms of enhanced conjugation in the bisected cyclopropylcarbinyl geometry to which cations 43 and 44 are restricted, and to decreased conjugation of the cyclopropyl ring of 45 which is constrained to a tilted geometry (75). However, the structures of these cations are not known. Furthermore, the environments of the cyclopropylcarbinyl moieties in each of these cations are expected to be greatly different. As such, this interpretation based on NMR spectroscopic results appears not to be justified.



43

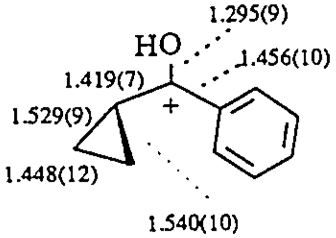


44



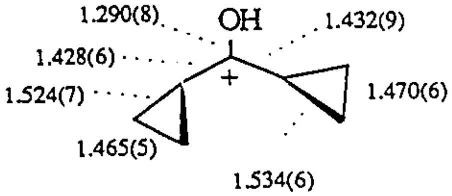
45

Recently the crystal structures of two substituted hydroxycyclopropylcarbinyl cations, 46 and 47 have been published (40). The geometries of these cations are very similar, and each exhibits a geometry which is close to bisected. The bond lengths (Å) observed for each of these cations are shown below (40). The bond length parameters given for 46 correspond to the average values obtained for each of the two independent cations found within the unit cell of 46.



46

(40)



47

(40)

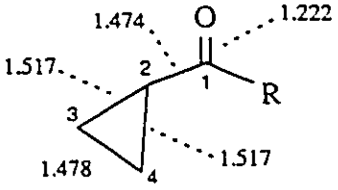
It should be noted that within the crystal lattices of both 46 and 47, or indeed any protonated carbonyl cation whose structure has been determined (20), hydrogen bonding interactions have been shown to exist between the hydroxyl proton and a counter-anionic atom present (40). In most cases, neglecting the positions of the hydroxyl hydrogen atoms which are not known with great precision (4), the interatomic distances between the carbonyl oxygen atoms and the closest contact counter-anionic atoms indicate the presence of strong hydrogen bonding interactions. In addition to these in-plane hydrogen bonding interactions, in most cases two additional counter-anionic atoms have been found to be situated above and below the plane of the protonated carbonyl moiety of these systems so as to form a significant closest contact with the formal carbenium ion center in these systems (20). As such, although it is unlikely that a full positive charge exists on these cations, it is nevertheless informative to discuss the systematic geometrical trends observed within these systems.

For each of the two independent cations in the unit cell of 46, the cyclopropyl ring is oriented *cis* to the protonated carbonyl group (40). The respective angles made between the plane of the cyclopropyl ring and the plane defined by the atoms adjacent to the formal cationic center are 83.4° and 87.8°. Conversely, the same dihedral angles involving the phenyl rather than cyclopropyl rings in 46 are reduced to 25.3° and 28.6°, and clearly demonstrate the different conformations required by cyclopropyl and phenyl groups for effective charge stabilization (40).

In 47, one bisected cyclopropyl group is oriented *cis*, and the other *trans* to the protonated carbonyl bond. This geometry, which is in contrast to the *cis,cis* cyclopropyl geometry suggested by Olah for this ion based on NMR spectroscopic analysis of the parent dicyclopropylmethylium ion 24b (114), can be attributed to increased steric interaction in the *cis,cis* conformation of 47 between the β-cyclopropyl hydrogen atoms and the relatively bulky, hydrogen bonded counter-anionic grouping (40).

Comparison of the bond lengths found for 46 and 47 with those of a typical neutral cyclopropyl ketone, 48 shown below, reveals several systematic trends (129). In each of 46 and 47, the C_1-O bond is substantially lengthened (differences 8.1σ and 8.5σ respectively) and the C_1-C_2 bond is concomitantly shortened (differences 7.9σ and 7.7σ respectively) relative to the corresponding bond lengths observed on average in the neutral systems 48. Substantial C_1-C_5 bond shortening is also observed in each of the protonated species (40). These bond length differences when compared to the neutral systems provide evidence for significant positive charge conjugation by both the cyclopropyl and phenyl rings in these systems.

Bond length variations within the cyclopropyl groups of both 46 and 47 are also systematic. Symmetric vicinal bond lengthening and distal bond diminution relative to the



48

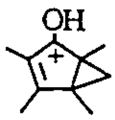
(129)

D_{3h} symmetric C–C bond length of 1.512 Å found in free cyclopropane (110) is seen in each case. Despite the large individual cyclopropyl bond distortions in **46** and **47**, the average cyclopropyl bond lengths of 1.506(29) Å and 1.509(13) Å respectively obtained for **46** and **47** are not significantly different from that found in cyclopropane itself (differences 0.21σ and 0.23σ respectively) (40).

The pattern of cyclopropyl bond length changes seen in each of **46** and **47**, namely vicinal bond lengthening by magnitude δ relative to the average cyclopropyl bond length in the cation, and distal bond contraction by a corresponding value 2δ, has also been observed by Allen in his systematic analysis of the structures of neutral cyclopropyl ketones (129). In the cationic systems however, higher degrees of cyclopropyl distortions are seen; the magnitude of the distortions in **46** and **47** are respectively

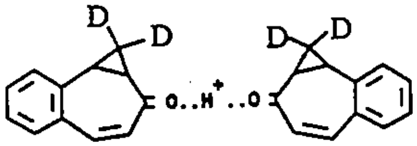
2.3 and 1.6 (average) times that found on average in the corresponding neutral systems (129). The magnitudes of the cyclopropyl bond distortions observed in 46 and 47 appear to be proportional to the extent to which the cyclopropyl groups in these systems participate in positive charge stabilization.

The crystal structures of the related systems 49-52 have also recently been determined (41-43,51). Although in these structures the cyclopropylcarbinyl cation is incorporated into an unsaturated ring, which raises questions pertaining to cyclic delocalization, both 49 and 50 appear to have a cyclopropylcarbinyl-like structure.



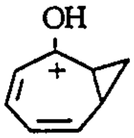
49

(41)



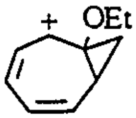
50

(42)



51

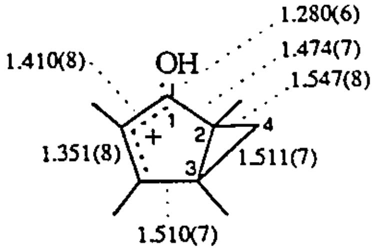
(43)



52

(51)

Selected bond distances (A) obtained for 49 are shown below (41). Whereas the observed pattern of bond length changes within the protonated enone fragment are as

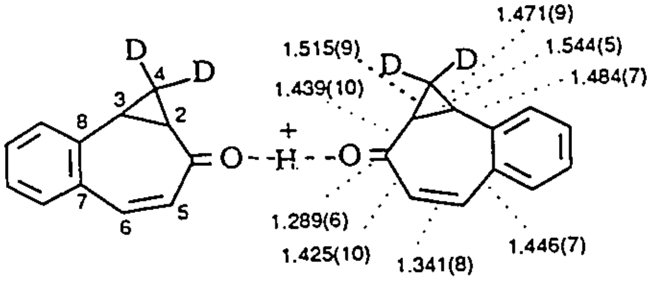


49

(41)

expected (51), the pattern of bond lengths in the cyclopropylcarbinyl moiety differ considerably from that seen in 46 and 47. Particularly noticeable are the C_2-C_3 and C_3-C_4 cyclopropyl bond lengths which are not significantly different than the bond length of 1.512 Å found in free cyclopropane (differences only 0.1σ and 1.4σ respectively) (110). Furthermore, the internal cyclopropyl ring adopts a *trans* gauche rather than the characteristic bisected conformation. Conjugative overlap with the positively charged center is thus reduced, as indicated by the abnormally long C_1-C_2 bond distance in 49 when compared to the corresponding bond length in each of 46 and 47.

The dimer 50 exists as two very strongly hydrogen bonded ketone monomers related to each other by an inversion center passing through the proposed position of the central hydrogen atom (42). As such, each monomer is hemiprotonated. The benzene rings in 50 are essentially planar and steric restrictions of these rings force slight nonplanarity into the seven membered rings (42).

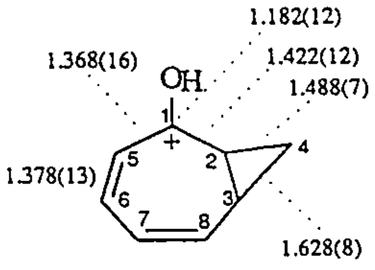


50

(42)

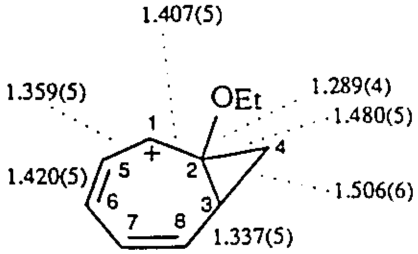
The observed bond lengths within 50 are not significantly different from that expected for the corresponding neutral ketone (42). The short C_5–C_6 bond length indicates inextensive double bond delocalization, and the cyclopropyl group distortions are only marginally amplified when compared to other similar neutral molecules (130). The observed C_1–O bond length, which is significantly longer than the average C=O bond length of 1.222 Å found in neutral cyclopropyl ketone systems (difference 11σ) (129), most likely results from the very strong hydrogen bond present between the carbonyl groups in this dimeric system. Yet, the inequality in cyclopropyl bond lengths, with the longest unbridged cyclopropyl C_2-C_4 bond being that nearest the carbonyl functionality does suggest that some conjugation exists with the hemi-protonated carbonyl group (42). The extent of positive charge conjugation suggested to exist in 50 is however much smaller than that suggested from the structures of 46, 47 and 49.

The crystal structures of the related homotropylium derivatives 51 and 52, for which selected observed bond lengths (Å) are given below, do not contain cyclopropyl bond distortions characteristic of the cyclopropylcarbinyl cations previously mentioned (43,51). Indeed these structures were initially examined to directly study homoaromatic stabilization in cationic systems (43,51).



51

(43)



52

(51)

The seven-membered ring of 51 exists in a shallow boat conformation with the bridging C_4 carbon atom positioned over this ring such that the cyclopropyl ring is approximately perpendicular to, rather than bisecting the C_1-O bond (43). The C_2-C_3 bond distance in 51 is significantly longer (difference 14σ), and the C_2-C_4 bond is significantly shorter (difference 3.4σ), than the C-C bonds in cyclopropane itself (110). Substantial C_1-C_2 bond shortening is also seen relative to the comparable bond in neutral cyclopropyl ketone systems (difference 4.3σ) (129). The distinct geometrical changes seen in 51, in stark contrast to those seen in the hydroxy-substituted cyclopropylcarbinyl cations in the bisected geometry, provide evidence for homoaromatic positive charge delocalization involving only the internal C_2-C_3 cyclopropyl bond in this system (43).

Although the overall conformation of 52 is similar to that of 51, the much larger C_2,C_3 internuclear distance of 2.284 Å observed in 52 indicates an open, cyclooctatrienylium ion in which nonhomoaromatic charge delocalization occurs (51). The structures of both 51 and 52 are in excellent agreement with the two lowest energy structures calculated for the parent homotropenylium cation 53 at both *ab initio* and semi-empirical levels (105,130,131). The presence of an electron donating ethoxy substituent at C_2 in 52 stabilizes the open form of the homotropenylium ion, which has been calculated at the HF 6-31G+5D level to be the lower energy minimum (105,130,131). However, with the inclusion of electron correlation effects, a single minimum energy C_2-C_3 internuclear distance of 1.913 Å (MP2 level) and 1.949 Å (MP3 level) has been calculated (131). The large differences in the C_2-C_3 internuclear distances obtained by crystallographic methods for the C_1- and C_2-substituted homotropenylium ions 51 and 52 indicate the extreme sensitivity of molecular structure to electronic effects (131).

53

1.4.5 Objectives of the Present Study

The questions of structure, nature and degree of cyclopropyl group participation in the cyclopropylcarbinyl cation and its substituted derivatives have indeed received much attention from organic and theoretical chemists over the past few decades. A sample of the wide variety of cyclopropylcarbinyl cation systems that have been studied by various techniques were discussed in some detail earlier in Section 1.4.

An important advance in the area of cyclopropylcarbinyl cation structure has been recently achieved by Childs and coworkers in their determination of the crystal structures of salts containing a cyclopropylcarbinyl moiety (40-43,51). The structures of the cations 46, 47 and 49-52 were presented in section 1.4.4. Of particular interest are the structures of 46 and 47, for in these systems the cyclopropylcarbinyl moieties are conformationally unrestricted and not fused into an unsaturated ring system. As such, the structures of the cyclopropylcarbinyl subsystems of these cations would appear to most directly relate to the structure of the parent cyclopropylcarbinyl cation.

The crystal structure determinations of 46 and 47 have provided direct solid state structural evidence for the preferred *s-cis* and *s-trans* bisected geometries of the cyclopropyl rings with respect to the adjacent formally vacant p-orbital at the carbenium ion center in these ions (40). The structures of 46 and 47 have also provided direct experimental evidence for systematic cyclopropyl bond distortions to varying extents in the solid state (40). The extent of geometrical distortion seen in these ions appears to be related to the extent to which the cyclopropyl group participates in positive charge stabilization. However, due to the lack of further related crystal structures, only a qualitative assessment of the underlying electronic basis for such structural differences has been afforded (40).

The purpose of the related work described in this thesis is to provide further direct x-ray crystallographic information pertaining to the conformation and structure of hydroxy-substituted cyclopropylcarbinyl cations of the type 41. Although gross conformational and geometrical trends are realized upon examination of the structures of cations 46 and 47 (40), analysis of such trends over a larger homologous set of related ions is intended to provide a more systematic view of the structural changes in these systems as a function of differential substitution.

It is also the aim of this thesis to obtain the crystal structures of substituted hydroxycyclopropylcarbinyl salts sufficiently small so as to allow high level *ab initio* calculations to be performed on these cations. A comparison of experimentally observed solid state structures and theoretically calculated gas phase structures could then be afforded.

The particular substituted hydroxy-cyclopropylcarbinyl cations herein studied were chosen in order to systematically evaluate the structural effect of varying substituents adjacent to the protonated carbonyl functionality, of substitution at the α and β cyclopropyl carbon atoms, C_2 and C_3 and/or C_4, and of restricted conformational mobility. Any systematically observed structural trends within this series of cations could then be taken as structural expressions for variable positive charge delocalization over the framework of these systems.

Previous solvolytic and NMR studies pertaining to the related cationic systems 38 have suggested that the presence of an α-methyl cyclopropyl substituent will enhance positive charge delocalization into the cyclopropyl ring (95,120-124). Yet, semi-empirical calculations pertaining to systems such as 39 have conversely predicted diminished cyclopropyl group charge delocalization in the presence of an α-methyl substituent (87). The effect of an additional α-methyl substituent in a representative substituted hydroxy-cyclopropylcarbinyl cation is herein subject to direct experimental and theoretical test.

Similarly, the structural determination of a β-substituted hydroxy-cyclopropylcarbinyl cation should indicate the structural effect of β-cyclopropyl substitution. On the basis of previous theoretical studies (87), it could be expected that β-methyl group substitution will enhance vicinal cyclopropyl bond lengthening and reduce cationic resistance to rearrangement. Similar investigations pertaining to a conformationally restricted homologue are intended to indicate the degree of preference for the bisected geometry of the cyclopropyl ring in this system. Structural parameters observed within this ion could be viewed in light of the overall conformation adopted by this cation.

Analysis of the crystal structures of a homologous set of substituted hydroxycyclopropylcarbinyl cation salts can also enable evaluation of the significance of any directed nearest counter-anion contacts observed within the crystalline lattices of these systems. It was intended that any such interactions observed could be correlated with structural changes and could be related to the dynamic aspects of chemical structure, in a manner as previously discussed for systems involving the interaction of a nearest nitrogen atom contact to a carbonyl carbon atom (9-11).

CHAPTER 2

STRUCTURAL STUDIES IN CONDENSED PHASES OF SUBSTITUTED TETRAHYDROPYRYLIUM SYSTEMS

The structure determinations of a series of substituted 6-ethoxy-tetrahydropyrylium ion salts are presented in this chapter. Direct solid state structural evidence pertaining to these ions has been obtained with the use of single crystal x-ray diffraction techniques. ^{1}H and both solid and solution state ^{13}C NMR spectroscopy have also been utilized for structural characterization.

The goal of this work was to determine systematic structural trends which exist within a series of 2-substituted 6-ethoxy-tetrahydropyrylium ions and to relate the observed solid state structures of these cations to those of the corresponding ions and neutral lactone precursors in solution.

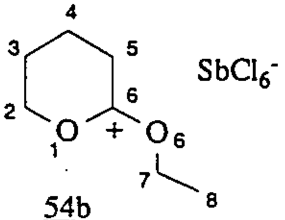
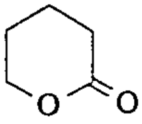
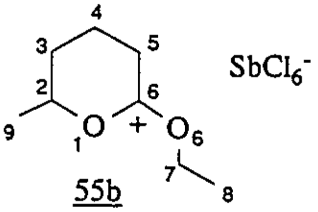
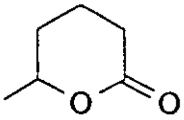
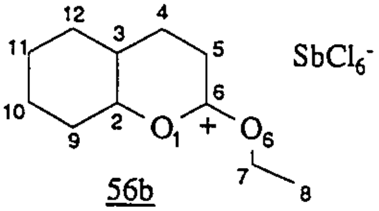
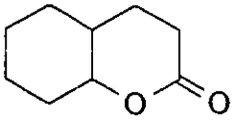
RESULTS

2.1 Preparation of Substituted 6-Ethoxy-tetrahydropyrylium Ions and Their Neutral Precursors

Three differentially substituted 6-ethoxy-tetrahydropyrylium ions were prepared as crystalline salts suitable for x-ray crystallographic structural analyses. These carbenium ion salts, 54b-56b, and their corresponding precursor neutral lactones, 54a-56a, are shown in Table 2-1. 54b contains an unsubstituted and conformationally mobile 6-ethoxy-tetrahydropyrylium cation. The cation of 55b was studied in order to determine the structural effect of methyl group substitution β to the formal carbenium ion center in this system. The cation in 56b, containing a *trans*-fused cyclohexane ring, provided an example of a conformationally restricted system having alkyl substituents both β and τ to the carbenium ion center.

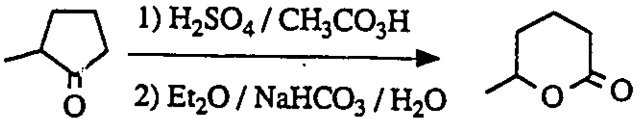
For the purpose of the forthcoming discussion, the numbering system adopted for these cationic and neutral systems has been kept constant as is shown in Table 2-1.

Table 2-1. 6-Ethoxy-tetrahydropyrylium Ions Studied and their Neutral Precursors

Carbenium Ion	Lactone Precursor
 54b	 54a
 55b	 55a
 56b	 56a

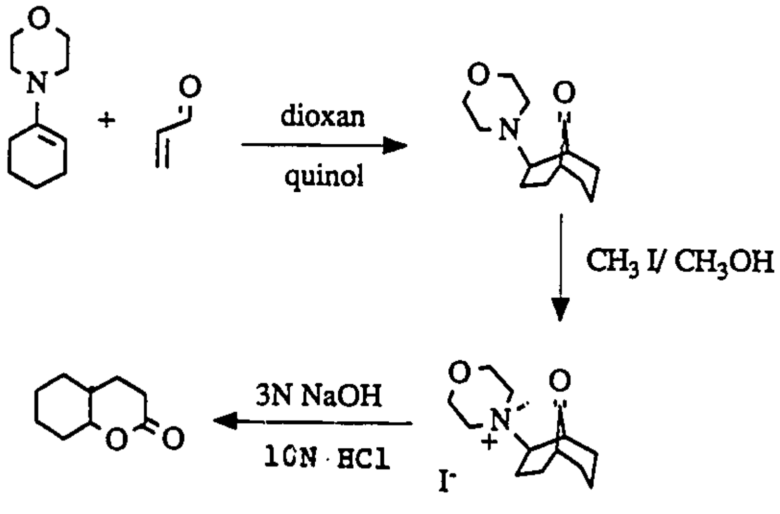
2.1.1 Lactone Precursors

δ-valerolactone 54a was commercially available. Lactone 55a was prepared by an acid catalyzed Baeyer-Villiger oxidatio of commercially available 5-methylcyclopentanone as indicated in equation 2-1 (132).



eqn. 2-1

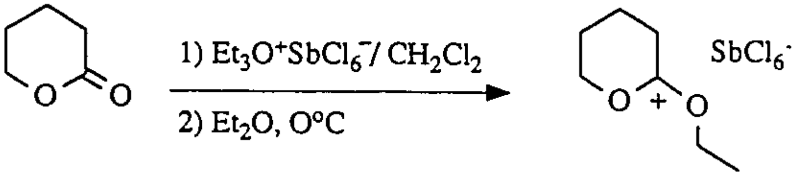
Trans-octahydrocoumarin 56a was prepared from propenal and 1-(N-morpholinyl)cyclohexene according to a modified procedure of Graham et al, Scheme 2-1 (133).



Scheme 2-1

2.1.2 Substituted 6-Ethoxy-tetrahydropyrylium Ion Salts

The hexachloroantimonate salts 54b-56b were prepared according to the same general procedure, as illustrated in equation 2-2 for the preparation of 54b. The precursor lactone and triethyloxonium hexachloroantimonate (Meerwein's reagent) were dissolved in dry CH_2Cl_2 and allowed to react over 3 hours. Precipitation of the crystalline salts was affected with cold, dry diethyl ether. Single crystals suitable for x-ray crystallographic study were obtained by recrystallization of the salts from CH_2Cl_2 at -20°C. The salts were extremely moisture and moderately temperature sensitive. All manipulations were thus carried out under a controlled atmosphere.



54a

54b

eqn. 2-2

2.2 Characterization of 54a-56a and 54b-56b by Solution and Solid State NMR Spectroscopy

The ^1H NMR spectra obtained for lactones 54a-56a were similar to those previously reported (68,133,134). Solution ^{13}C and ^1H NMR data for 54b-56b are listed in Tables

2-2 and 2-3 respectively. Solid state ^{13}C NMR spectral data for the salts 54b and 55b were obtained with use of cross polarization, magic angle spinning (CPMAS) methods, and chemical shift data for these compounds are also listed in Table 2-2. Assignments of the various NMR resonances of 54b-56b were made by comparison with previously published data (68,133,134).

2.3 X-ray Crystallographic Structure Determinations of the Salts 54b-56b

Single crystal x-ray diffraction techniques were used to determine the crystal structures of the salts 54b-56b. All crystals were moisture sensitive and as such, were sealed under a dry N_2 atmosphere in Lindemann capillary tubes for crystallographic investigation. In addition, crystals of 54b and 55b were temperature sensitive and decomposed over several hours on standing sealed at 21°C. All manipulations involving crystals of 54b and 55b were therefore carried out at low temperature and intensity data sets for these crystals were collected at -65°C. The low temperature crystal environment maintained during intensity data collection also offered the advantage of suppressing the magnitude of internal atomic motions within the crystals, and hence led to more precise structural determinations than could otherwise be obtained at room

Table 2-2. Solution and Solid State ^{13}C NMR Chemical Shift Data for Neutral and Protonated Systems 54a, 55a, 54b-56b[a]

		CHEMICAL SHIFT (ppm)							
SYSTEM	PHASE[b]	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
54a	A	64.2	28.5	21.8	34.2	173.5			
54b	A	82.7	21.5	16.4	29.2	189.6	75.1	13.7	
54b	B	82.7	21.6	17.1	30.3	189.7	74.6	15.7	
55a	A	70.6	29.9	21.2	34.5	173.0			20.0
55b	A	95.1	28.5	16.2	28.5	189.0	74.2	13.5	20.7
55b	B	96.2	30.0	18.2	30.0	189.5	74.4	13.9	22.7
56b	A	99.3	29.6[c]	24.7[c]	38.5	189.6	74.8	23.5[c]	31.5[c]

a) Solution State spectra acquired at 125.7 MHz (500 MHz for ^{1}H);
Solid State spectra acquired at 25.1 MHz; acquisition temperature 21°C
b) A, CD_2Cl_2 solution; B, Solid State
c) assignments may be reversed

Table 2-3. ^{1}H NMR Data for 54b–56b[a,b,c]

SYSTEM	H_2	H_3	H_4	H_5	H_7	H_8	OTHER
				CHEMICAL SHIFT (ppm)			
54b	5.04m 3H		2.00m 4H	3.42m 2H	4.70q 2H	1.40t 3H $J_{7,8}$=7.0	
55b	5.55m 1H		2.0–2.5m 4H	3.21m 2H	4.90dq[d] 2H	1.44t 3H $J_{7,8}$=7.1	H_9; 1.77d 3H J=6.5
56b	2.4–3.4m 1H		2.0–2.4m[e] 13H		4.90q 2H	1.45t 3H $J_{7,8}$=7.0	[e]

a) in CD_2Cl_2 at 21°C
b) 500 MHz; ref. CH_2Cl_2 at 5.32 ppm; shifts in ppm; coupling constants in Hz
c) d=doublet; t=triplet; q=quartet; m=multiplet; H values denote number of hydrogen atoms to which resonance corresponds
d) $J_{7,7'}$ = 3.5 Hz
e) peak at 2.0–2.4 corresponding to all remaining ring protons could not be resolved

temperature. Crystals of 56b appeared less temperature sensitive and x-ray diffraction data for 56b were collected at 21°C.

Intensity data sets for crystalline samples of 54b-56b were collected on either a Syntex $P2_1$ or a Nicolet P3 automatic 4-circle diffractometer and structure solutions and refinements were carried out with use of the computer program SHELX (135). The methods of crystal selection, sealing, unit cell and space group determination, data set collection, structure solution and refinement can be found in the Experimental section, Chapter 5.

2.3.1 The Crystal Structure of 54b

Buerger type precession photographs in conjunction with axial photographs and crystal density measurements were used to determine the low symmetry triclinic space group P1 for 54b. The position of the high molecular weight antimony atom was located by direct methods. Remaining atomic positions were determined from subsequent electron density difference maps in conjunction with a series of full matrix least-squares refinement cycles. The crystal structure of 54b was refined to a R_w factor of 0.0370. Further details pertaining to the final structure solution of 54b can be found in Table 5-1.

Table 2-4 lists selected interatomic distances and angles for 54b. The standard deviation associated with each value is enclosed within parentheses immediately following the value to which it corresponds. Selected best fit planes for 54b and atomic distances from each plane are given in Table 2-5. SNOOPI plots of the cation and the stereoscopic view of the unit cell contents for 54b are shown in Figures 2-1 and 2-2 respectively. Ellipses shown in these figures correspond to the magnitude of the anisotropic temperature factors associated with each atom.

2.3.2 The Crystal Structure of 55b

Precession and axial photographs indicated an orthorhombic unit cell for 55b and intensity data were collected in the space group Pmnb. This non standard space group can be transformed into the standard space group Pnma by multiplication of the symmetry elements for Pmnb by the matrix (0 1 0 / 1 0 0 / 0 0 -1). The crystal structure of 55b was solved and refined using a combination of direct and difference methods to a R_w factor of 0.0424. Additional details pertinent to the final structure solution of 55b are listed in Table 5-1.

Selected bond length and angle data, as well as best fit planes data for 55b can be found in Tables 2-4 and 2-5. Figures 2-3 and 2-4 respectively display SNOOPI diagrams of the carbenium ion and stereoview of the unit cell contents

Table 2-4. Selected Bond Lengths (Å) and Angles (°) for 54b-56b

Bond	54b	55b	56b
C(6)-O(1)	1.267(7)	1.266(7)	1.254(8)
C(6)-O(6)	1.273(8)	1.292(8)	1.257(8)
O(1)-C(2)	1.474(7)	1.519(7)	1.538(8)
O(6)-C(7)	1.488(7)	1.489(8)	1.500(10)
C(2)-C(3)	1.514(9)	1.500(9)	1.439(11)
C(3)-C(4)	1.504(9)	1.521(10)	1.491(12)
C(4)-C(5)	1.521(10)	1.517(10)	1.482(12)
C(5)-C(6)	1.483(8)	1.444(8)	1.516(10)
C(7)-C(8)	1.511(10)	1.469(11)	1.475(12)
C(2)-C(9)		1.482(9)	1.533(10)
C(9)-C(10)			1.495(11)
C(10)-C(11)			1.470(13)
C(11)-C(12)			1.472(12)
C(12)-C(3)			1.511(11)
Sb(1)-Cl(11)	2.378(1)	2.383(1)	
Sb(1)-Cl(1)			2.360(2)
Sb(1)-Cl(12)	2.366(1)	2.340(2)	
Sb(1)-Cl(2)			2.365(2)
Sb(1)-Cl(13)	2.366(1)	2.368(2)	
Sb(1)-Cl(3)			2.355(2)
Sb(2)-Cl(21)	2.363(2)	2.379(1)	
Sb(1)-Cl(4)			2.369(2)
Sb(2)-Cl(22)	2.361(2)	2.359(2)	
Sb(1)-Cl(5)			2.373(2)
Sb(2)-Cl(23)	2.366(1)	2.343(2)	
Sb(1)-Cl(6)			2.358(2)
Sb(1)-Cl(14)		2.365(2)	
Sb(1)-Cl(15)		2.358(2)	
Sb(2)-Cl(24)		2.349(2)	
Sb(2)-Cl(25)		2.346(2)	

Angle	54b	55b	56b
C(2)-O(1)-C(6)	122.4(5)	121.4(5)	120.5(5)
C(6)-O(6)-C(7)	120.1(5)	119.2(5)	120.5(6)
C(3)-C(2)-O(1)	111.6(5)	110.4(5)	111.8(7)
C(2)-C(3)-C(4)	110.5(5)	110.6(5)	113.5(7)
C(3)-C(4)-C(5)	108.6(5)	109.4(5)	114.4(7)
C(4)-C(5)-C(6)	112.3(6)	113.7(6)	115.5(6)
C(5)-C(6)-O(1)	125.2(6)	126.2(6)	123.9(6)

Table 2-4 (Con't).

Angle	54b	55b	56b
C(5)-C(6)-O(6)	116.9(6)	116.3(6)	116.4(6)
O(1)-C(6)-O(6)	117.9(5)	117.5(5)	119.6(7)
O(6)-C(7)-C(8)	110.7(5)	107.8(6)	106.0(6)
O(1)-C(2)-C(9)		104.5(5)	104.1(5)
C(3)-C(2)-C(9)		115.7(6)	116.4(7)
C(2)-C(9)-C(10)			109.8(7)
C(9)-C(10)-C(11)			116.5(8)
C(10)-C(11)-C(12)			116.2(8)
C(11)-C(12)-C(3)			115.0(7)
C(2)-C(3)-C(12)			110.4(7)
C(4)-C(3)-C(12)			118.5(7)
Cl(11)-Sb(1)-Cl(12)	89.7(1)	90.5(1)	
Cl(11)-Sb(1)-Cl(13)	90.5(1)	89.5(1)	
Cl(11)-Sb(1)-Cl(14)		89.5(1)	
Cl(11)-Sb(1)-Cl(15)		90.4(1)	
Cl(12)-Sb(1)-Cl(13)	90.6(1)	90.0(1)	
Cl(12)-Sb(1)-Cl(14)		179.8(1)	
Cl(12)-Sb(1)-Cl(15)		90.8(1)	
Cl(13)-Sb(1)-Cl(14)		89.7(1)	
Cl(13)-Sb(1)-Cl(15)		179.2(1)	
Cl(14)-Sb(1)-Cl(15)		89.4(1)	
Cl(21)-Sb(2)-Cl(22)	89.9(1)	90.0(1)	
Cl(21)-Sb(2)-Cl(23)	89.2(1)	90.3(1)	
Cl(21)-Sb(2)-Cl(24)		89.7(1)	
Cl(21)-Sb(2)-Cl(25)		90.0(1)	
Cl(22)-Sb(2)-Cl(23)	89.6(1)	90.0(1)	
Cl(22)-Sb(2)-Cl(24)		89.6(1)	
Cl(22)-Sb(2)-Cl(25)		179.1(1)	
Cl(23)-Sb(2)-Cl(24)		179.6(1)	
Cl(23)-Sb(2)-Cl(25)		90.9(1)	
Cl(24)-Sb(2)-Cl(25)		89.5(1)	
Cl(1)-Sb(1)-Cl(2)			178.6(1)
Cl(1)-Sb(1)-Cl(3)			90.1(1)
Cl(1)-Sb(1)-Cl(4)			89.9(1)
Cl(1)-Sb(1)-Cl(5)			89.6(1)
Cl(1)-Sb(1)-Cl(6)			90.6(1)
Cl(2)-Sb(1)-Cl(3)			89.9(1)
Cl(2)-Sb(1)-Cl(4)			90.1(1)
Cl(2)-Sb(1)-Cl(5)			89.1(1)
Cl(2)-Sb(1)-Cl(6)			90.8(1)
Cl(3)-Sb(1)-Cl(4)			178.5(1)
Cl(3)-Sb(1)-Cl(5)			91.3(1)
Cl(3)-Sb(1)-Cl(6)			90.2(1)
Cl(4)-Sb(1)-Cl(5)			90.2(1)
Cl(4)-Sb(1)-Cl(6)			88.3(1)
Cl(5)-Sb(1)-Cl(6)			178.5(1)

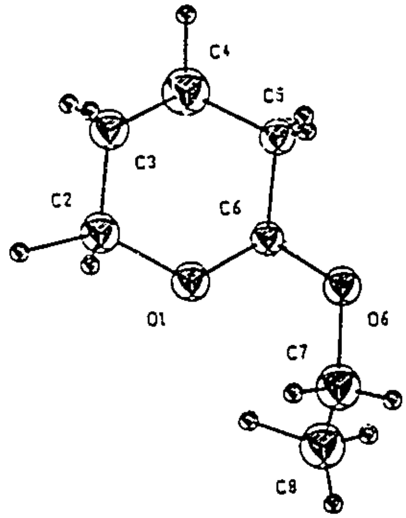
Table 2-5. <u>Selected Least Squares Planes Data for 54b-56b</u>

COMPOUND		Distance (A) of atoms from Plane[a]			Distance of nearest anion contact to C(6) from Plane A
		A	B	C	
54b	O(1)	0.002(7)	0.006(7)	0.000(8)	Cl(21) -3.194(5)
	C(2)	-0.02(1)	-0.01(1)	-0.02(1)	
	C(3)	0.42(2)	0.43(2)	0.42(2)	
	C(4)	-0.32(2)	-0.31(2)	-0.33(2)	
	C(5)	0.01(1)	0.01(1)	0.00(1)	
	C(6)	-0.015(9)	-0.01(1)	-0.018(9)	
	O(6)	0.002(8)	0.00(1)	0.000(8)	
	C(7)	0.13(1)	0.13(2)	0.13(1)	
	C(8)	-1.22(2)	-1.22(2)	-1.22(2)	
55b	O(1)	-0.001(6)	-0.011(6)	0.000(6)	Cl(21) -3.340(6) Cl(11) 3.530(6)
	C(2)	0.11(1)	0.012(9)	0.11(1)	
	C(3)	-0.36(1)	-0.50(1)	-0.36(1)	
	C(4)	0.32(1)	0.21(1)	0.32(1)	
	C(5)	0.00(1)	-0.02(1)	0.00(1)	
	C(6)	0.008(7)	0.032(8)	0.010(8)	
	O(6)	-0.001(6)	0.10(1)	0.000(6)	
	C(7)	0.03(1)	0.17(2)	0.03(1)	
	C(8)	0.21(2)	0.44(2)	0.21(2)	
	C(9)	-0.65(1)	-0.77(1)	-0.65(1)	
56b	O(1)	0.001(7)	0.007(7)	0.000(7)	Cl(4) 3.259(4) Cl(5) -3.592(6)
	C(2)	-0.06(1)	-0.01(1)	-0.06(1)	
	C(3)	0.55(1)	0.62(2)	0.55(1)	
	C(4)	0.05(2)	0.10(2)	0.05(2)	
	C(5)	0.00(1)	0.01(1)	0.00(1)	
	C(6)	-0.006(8)	-0.016(9)	-0.007(8)	
	O(6)	0.001(7)	-0.04(1)	0.000(7)	
	C(7)	0.06(1)	0.00(2)	0.06(1)	
	C(8)	0.85(2)	0.75(3)	0.85(2)	
	C(9)	0.56(1)	0.62(1)	0.56(1)	
	C(10)	0.69(2)	0.78(2)	0.69(2)	
	C(11)	1.16(2)	1.28(3)	1.16(2)	
	C(12)	0.63(2)	0.73(2)	0.63(2)	

a) Plane A: plane of the atoms O(1), C(5), C(6) and O(6)
Plane B: plane of the atoms O(1), C(2), C(5) and C(6)
Plane C: plane of the atoms O(1), C(5) and O(6)

Figure 2-1. The Conformation of 54b

a. Top View of 54b



, b. Edge View of 54b

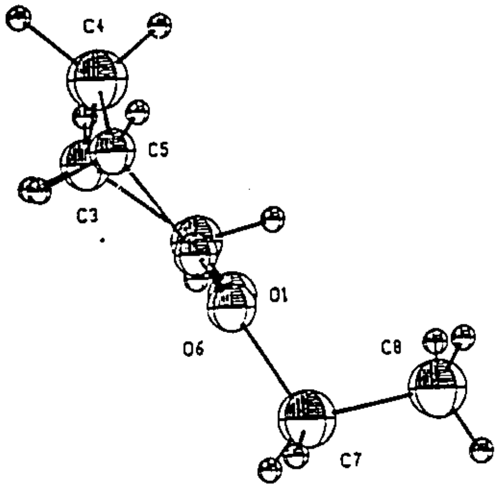
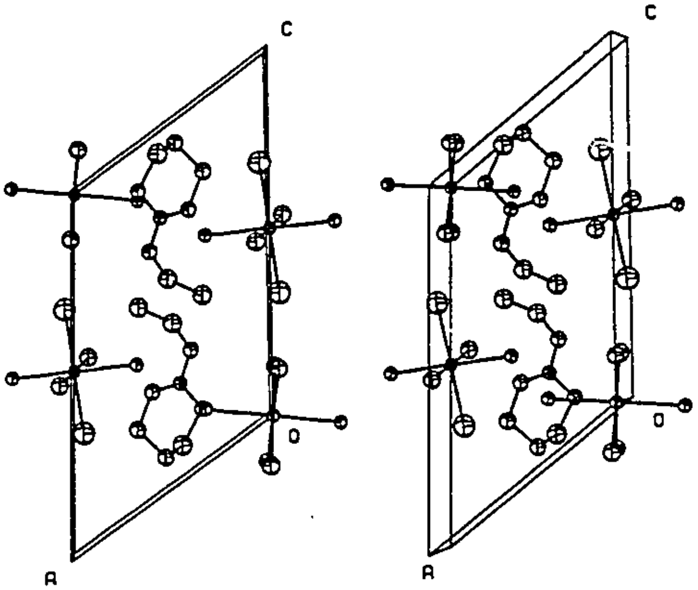


Figure 2-2. <u>Stereoscopic View of Unit Cell Contents for 54b</u>



for 55b.

2.3.3 The Crystal Structure of 56b

The orthorhombic space group $Pca2_1$ was determined for 56b from analysis of precession and axial photographs in combination with crystal density measurements. The structure of 56b was solved in this space group with use of a Patterson synthesis in conjunction with difference methods, and refined to a final R_w value of 0.0349. Table 5-1 lists further details pertaining to the final structure solution of 56b.

Tables 2-4 and 2-5 respectively contain selected interatomic distances and bond angles, and best fit planes data for 56b. The structure of the carbenium ion and stereoscopic view of the unit cell contents for 56b appear in Figures 2-5 and 2-6 respectively.

Figure 2-3. The Conformation of 55b

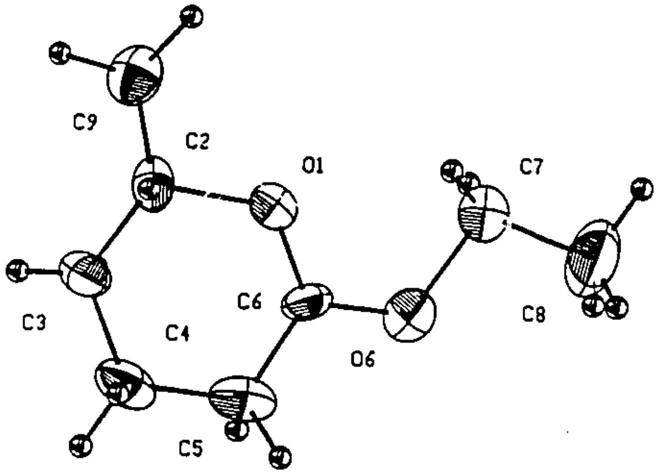


Figure 2-4. Stereoscopic View of Unit Cell Contents for 55b

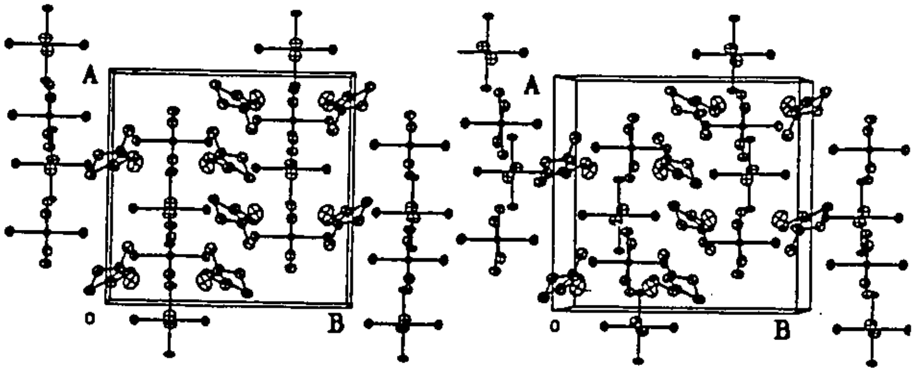


Figure 2-5. The Conformation of 56b

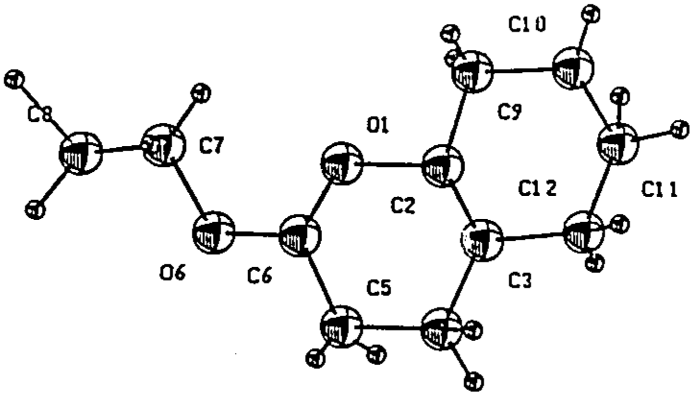
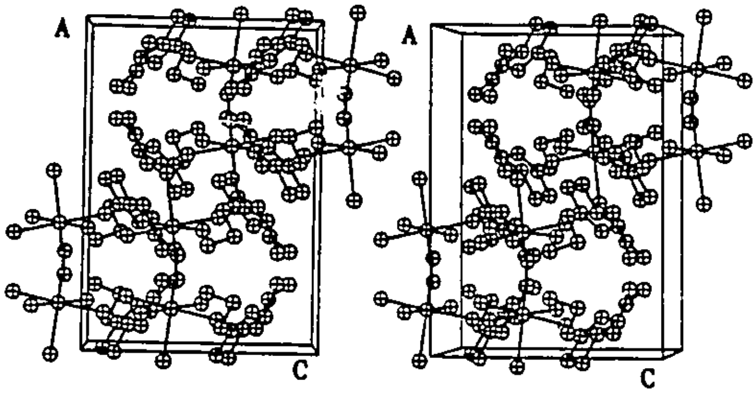


Figure 2-6. Stereoscopic View of Unit Cell Contents for 56b



DISCUSSION

2.4 Comparative Structural Analysis of the 6-Ethoxytetrahydropyrylium Ions 54b-56b

The structures of 54b-56b illustrated in Figures 2-1, 2-3 and 2-5 indicate that each of the precursor lactones 54a-56a has been alkylated at the carbonyl oxygen atom[1]. Comparison of the ^{13}C NMR chemical shift data for 54a, 55a and 54b-56b, Table 2-2 further substantiates this claim. Within the corresponding crystalline lattices, each of these cations 54b-56b is associated with a $SbCl_6^-$ counter-anion having octahedral symmetry, as illustrated in Figures 2-2, 2-4 and 2-6 respectively. The octahedral nature of the $SbCl_6^-$ counterions is further evident on inspection of the bond length and angle data given in Table 2-4.

2.4.1 Conformation

The solid state conformations of cations 54b-56b, which differ in substitution at C_2 and/or C_3, are remarkably similar. This can be seen by comparison of the respective

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[1] Since the following discussion is primarily focussed on the conformations and geometries of the carbenium ions contained in salts 54b-56b,, for brevity the carbenium ions are simply referred to by system number of the corresponding salt. For example, 54b will herein be used to denote the cation of the hexachloroantimonate salt 54b unless otherwise noted.

SNOOPI diagrams, Figures 2-1, 2-3 and 2-5 and the associated best fit planes data given in Table 2-5. In each of 54b-56b the atoms surrounding C_6, the formal carbenium ion center are in an approximately planar arrangement, as shown by the zero or small deviations of the atoms O_1, C_5, C_6 and O_6 from the plane which they define, Plane A in Table 2-5. Comparison of the bond angles surrounding the formal cationic center C_6, as listed in Table 2-4, also indicates an approximate trigonal planar, sp^2 hybridized geometry about C_6 in each of the systems 54b-56b.

The tetrahydropyrylium rings in each of 54b-56b exist in flattened half-chair conformations due to the presence of the positively charged carbon atom center at C_6. The representative conformation of 54b is clearly illustrated in the edge view of 54b, Figure 2-1b. In 54b, significant deviations are observed for the tetrahydropyrylium ring atoms C_3 and C_4 from the plane defined by the remaining ring atoms O_1, C_2, C_5 and C_6, Plane B, Table 2-5. In the series of cations 54b-56b as a whole, the largest deviation of a ring atom from Plane B occurs for C_3 in 56b (0.62(2) Å). This large atomic deviation from planarity can be attributed to the presence of the *trans*-fused cyclohexane ring in 56b which slightly restricts conformational mobility and further flattening of the tetrahydropyrylium ring.

The substituents at C_2 and/or C_3 in both 55b and 56b show relatively large atomic deviations from Planes A through C, Table 2-5. For example, the methyl group carbon atom C_9 of 55b is situated 0.77(1) Å from Plane B. Similarly, C_9 and C_{12} in 56b are oriented 0.62(1) Å and 0.73(2) Å respectively from this same plane, Plane B. These distance values indicate that these substituents adopt pseudo-equatorial positions on the tetrahydropyrylium ring, as illustrated in Figures 2-3 and 2-5 respectively.

As can be seen from the data in Table 2-4, the directly comparable bond angles involving the tetrahydropyrylium ring atoms in 54b-56b are, with a few exceptions, all identical within experimental error. The only significant differences which exist pertain to the angles C_2-C_3-C_4, C_3-C_4-C_5 and C_4-C_5-C_6 in cation 54b versus 56b and to the angles C_2-C_3-C_4 and C_3-C_4-C_5 in 55b versus 56b. For 54b these C_2-C_3-C_4, C_3-C_4-C_5 and C_4-C_5-C_6 angles, of magnitude 110.5(5)°, 108.6(5)° and 112.3(6)° respectively, are significantly smaller than the corresponding angles in 56b (113.5(7)°, 114.4(7)° and 115.5(6)°) (differences 3.5σ, 6.7σ and 3.8σ respectively). Similarly, significantly smaller C_2-C_3-C_4 and C_3-C_4-C_5 bond angles of 110.6(5)° and 109.4(5)° are observed in 55b when compared to those seen in

56b (respective differences 3.4σ and 6.8σ). The smaller bond angles observed in 54b and 55b relative to 56b can be attributed to the increased steric requirements of the *trans*-fused cyclohexane ring in 56b.

The orientation of the ethoxy group side chain in each of 54b-56b are of particular interest. Within each cation, the C_5-C_6-O_6-C_7 moiety exists in an E-conformation and the O_1-C_6-O_6-C_7 subsystem exists in a Z-conformation. A similar E,Z or *trans,cis* conformation about the two C^+-OR bonds in acyclic dialkoxy carbenium ions has been previously indicated on the basis of NMR spectroscopic studies (35,54,56,57). The structures 54b-56b presently described provide the first direct experimental evidence for this same conformational preference in cyclic cations.

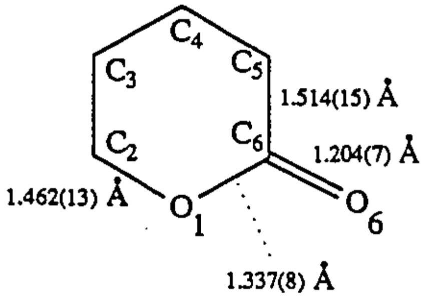
The methyl group (C_8) in each of the cations 54b-56b adopts a variety of orientations. In 55b and 56b, C_8 is oriented at distances of 0.44(2) Å and 0.75(3) Å respectively to Plane B defined by the atoms O_1, C_2, C_5 and C_6, Table 2-5. In 54b C_8 is oriented at a considerably larger distance of 1.22(2) Å from this same plane. However, in each case the hydrogen atoms bonded to C_8 adopt a staggered conformation with respect to the hydrogen atoms of the adjacent methylene center (C_7) and the C_7-O_6 bond.

Comparison of the solution and solid state NMR chemical shift data for 54b and 55b given in Table 2-2 indicates that the solid state conformational preferences above described are also preferred by these ions in solution. For either 54b or 55b, maximum atomic chemical shift differences of only 2 ppm are seen on comparison of the spectra acquired in the two phases and no systematic atomic chemical shift differences are evident. The similarity of the individual carbon atom resonances observed suggests that not only the conformation but also the charge distribution within each of these cations is invariant between solution and solid states.

2.4.2 Carbon-Oxygen Bond and Angle Distortions

A substantial change in geometry accompanies alkylation of the carbonyl oxygen atom of the precursor lactones 54a-56a to form cations 54b-56b. Comparison of the C-O bond length and angle data obtained for 54b-56b as presented in Table 2-4 and corresponding data obtained for the parent, neutral six-membered ring δ-lactones as shown in Figure 2-7 (136) reveals several significant structural differences. The C_6-O_6 bonds in each of 54b-56b having lengths 1.273(8) Å, 1.292(8) Å and 1.257(8) Å respectively are significantly elongated (differences 6.5σ, 8.3σ and 5.0σ, respectively) relative to the average distance of the corresponding bond in the parent δ-lactone systems (1.204(7)

Figure 2-7. <u>The Structure of Neutral Six-Membered Ring Lactones</u> (136)



BOND ANGLES

O(1)-C(6)-C(5)	118.4(1.7)°
O(1)-C(6)-O(6)	118.5(1.0)°
C(5)-C(6)-O(6)	123.0(1.2)°
C(2)-O(1)-C(6)	122.9(2.9)°

Å) (136). A similar comparison of the C_6-O_1 bonds indicates that the C_6-O_1 bonds in each of **54b**-**56b** are significantly shortened to 1.267(7) Å, 1.266(7) Å and 1.254(8) Å, respectively (respective differences 6.6σ, 6.7σ and 7.3σ). The C_6-O_1 and C_6-O_6 bond distances in **54b**-**56b**, which are intermediate between C-O single and double bond lengths (3), are comparable to those found in other oxygen substituted carbenium ions (20,37,38,45-50,58).

Significant O_1-C_2 bond elongations are also seen in **55b** and **56b** relative to the comparable average bond length of 1.462(13) Å in neutral six-membered ring δ-lactones (differences 3.9σ and 5.0σ respectively) (136). However, the O_1-C_2 bond distance of 1.474(7) Å observed for cation **54b** is not significantly different from that observed on average in the parent δ-lactone systems. Nevertheless, both the O_1-C_2 and O_6-C_7 bond distances contained within each of **54b**-**56b** are significantly longer than those of comparable bonds in neutral esters (137). The average $O-CH_2$ distance of 1.488(5) Å in **54b**-**56b** is larger than the corresponding average value of 1.452(2) Å found by Allen and Kirby in their detailed analysis of the structures of esters (difference 6.7σ) (137).

Comparison of the C-O containing bond angles obtained for **54b**-**56b** (Table 2-4) with the average values obtained for neutral six-membered ring δ-lactones shown in

Figure 2-7 (136) reveals some differences. For 54b-56b the average C_5-C_6-O_1 angle of 125.1(7)° is larger (difference 3.6σ) and the average C_5-C_6-O_6 angle of 116.5(2)° is smaller (difference 5.3σ) than the corresponding values of 118.4(1.7)° and 123.0(1.2)° observed in the parent δ-lactone systems. Such systematic O_1-C_6-C_5 bond angle increases and concomitant C_5-C_6-O_6 bond angle decreases in the lactonium ion systems can be attributed to the formal carbenium ion center present at C_6, to a change in electronegativity at O_6, to repulsion between O_1 and C_7, and to the strain of the tetrahydropyrylium rings due to the planar arrangement of the ring atoms O_1, C_2, C_5 and C_6 in each of 54b-56b.

Despite the large and systematic C-O bond length and angle differences evident on comparison of the structures of 54b-56b with the parent, six-membered ring δ-lactone (136) and neutral ester (137) systems, no significant differences exist at the 99% confidence level between any of the individual C_6-O_1, C_6-O_6 or O_6-C_7 bond lengths observed within the cations 54b-56b themselves. However, the length of the O_1-C_2 bond in cations 54b-56b is very dependent on substitution at C_2, Table 2-4. Significant O_1-C_2 bond elongations are seen in the C_2-substituted ions 55b and 56b when compared to the unsubstituted ion 54b; the O_1-C_2 bond lengths of 1.519(7) Å and 1.538(8) Å respectively seen in 55b and 56b are larger than that observed in 54b (1.474(7)

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Despite the large and systematic C-O bond length and angle differences evident on comparison of the structures of 54b-56b with the parent, six-membered ring δ-lactone (136) and neutral ester (137) systems, no significant differences exist at the 99% confidence level between any of the individual C_6-O_1, C_6-O_6 or O_6-C_7 bond lengths observed within the cations 54b-56b themselves. However, the length of the O_1-C_2 bond in cations 54b-56b is very dependent on substitution at C_2, Table 2-4. Significant O_1-C_2 bond elongations are seen in the C_2-substituted ions 55b and 56b when compared to the unsubstituted ion 54b; the O_1-C_2 bond lengths of 1.519(7) Å and 1.538(8) Å respectively seen in 55b and 56b are larger than that observed in 54b (1.474(7)

Å) (differences 4.5σ and 6.0σ respectively). Coupled with the systematic O_1-C_2 bond elongations observed in <u>55b</u> and <u>56b</u>, the C_3-C_2-C_9 and O_1-C_2-C_9 bond angles are significantly distorted from those expected for a carbon atom with tetrahedral geometry, Table 2-4. The C_3-C_2-C_9 bond angles of 115.7(6)° and 116.4(7)° respectively observed in <u>55b</u> and <u>56b</u> are significantly larger than the normal 109.4° tetrahedral angle, whereas the corresponding O_1-C_2-C_9 angles are significantly smaller than 109.4°.

2.4.3 <u>Charge Delocalization in 54b-56b</u>

The conformations and systematic bond length and angle changes observed in the crystal structures of cations <u>54b</u>-<u>56b</u> can be used to qualitatively assess the degree of positive charge delocalization in these cations. The approximately planar arrangement of the O_1, C_5, C_6 and O_6 atoms in <u>54b</u>-<u>56b</u> in conjunction with the observed corresponding C-O and C-C bond distances and angles suggest positive charge delocalization to varying extents over the framework of these atoms.

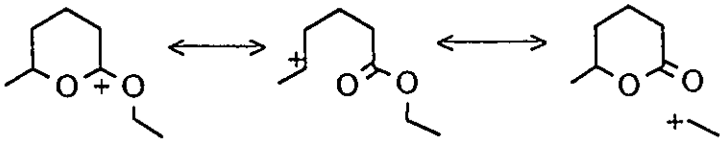
The significantly elongated O-CH_2 bonds, namely O_1-C_2 in <u>54b</u> (difference 3.0σ) and O_6-C_7 in <u>54b</u>-<u>56b</u> (differences 4.5σ, 4.7σ and 4.9σ, respectively) when compared to the corresponding average O-CH_2 bond length of 1.452(2) Å in neutral esters (137) suggests that the electronic distribution within the cationic and neutral systems is considerably different. Similar O-CH_2 bond lengths to those observed here for 54b-56b have been obtained for the dioxolan-2-ylium cations 10a and 11a-11e as well as for the 1-ethoxyhomotropylium cation 52 and these structural results have been explained on a similar basis (45,50,51).

The O_1-C_2 bond distances in the C_2-substituted ions 55b and 56b are remarkable in that they represent some of the longest known C-O bonds. Substitution at the carbon atom of a C-O bond in esters of the form R-CH_2-O-C(=O)-R to give esters of the type R_2-CH-O-C(=O)-R has been shown to cause negligible C-O bond elongation (1.460(2) Å versus 1.452(2) Å, difference 2.8σ) (137). It has been suggested that this trend toward C-O bond elongation results from increased substituent steric requirements (137). However, the O_1-C_2 bond lengthening to 1.519(7) Å and 1.538(8) Å respectively seen in 55b and 56b relative to the O_1-C_2 bond distance of 1.474(7) Å in 54b is too extreme to be explained solely on the basis of steric effects resulting from additional substitution at C_2 (differences 4.5σ and 6.0σ, respectively).

Allen, Kirby and coworkers have shown that the C-O bond in a variety of neutral molecules is systematically lengthened upon substitution of an electron withdrawing group, EW at the oxygen atom (137,138,139). This effect has been attributed to greater involvement of the ionic resonance contributor shown in equation 2-6.

$$R_3C\text{-}OEW \longleftrightarrow R_3C^+ \quad OEW^- \qquad \text{eqn. 2-6}$$

The formal carbenium ion center at C_6 in each of the systems 54b-56b herein studied can be regarded as a strongly electron withdrawing substituent attached to both O_1 and O_6. Elongation of the O_1-C_2 and O_6-C_7 bonds can be interpreted in terms of variable contributions of resonance contributors of the type 55b' and 55b'' as shown in equation 2-7. The presence of methyl and alkyl substituents respectively at C_2 in ions 55b and 56b would be expected to enhance the relative importance of canonical forms of the type 55b'.



55b 55b' 55b''

eqn. 2-7

When compared to <u>54b</u>, the elongation of the O_1-C_2 bonds observed in <u>55b</u> and <u>56b</u> and the greater O_1-C_2-C_9 and C_3-C_2-C_9 bond angle distortions from tetrahedral symmetry observed for these ions suggest an enhanced contribution of resonance form <u>55b'</u> to the overall description of these ions. In each case, enhanced sp^2 character of the formally sp^3 hybridized C_2 center is suggested. A similar correlation between O-C bond length and angle distortions with varying substitution has been seen on analysis of the structural changes ensuing the ionization of 1-arylethanol derivatives (140).

Positive charge transfer to C_2 and C_7 in <u>54b</u>-<u>56b</u> should be accompanied by a contraction of the C_2-C_3, C_2-C_9 and C_7-C_8 bonds. However, relative to the average $C(sp^3)$-$C(sp^3)$ bond length of 1.526(2) Å obtained by Allen and coworkers for esters of the type $(C^*)_2$-CH-O-C(=O)-C^*, where C^* is an sp^3 hybridized carbon atom having only carbon or hydrogen atom substituents (137), only in <u>56b</u> is the C_2-C_3 bond significantly shorter (difference 7.8σ) and only in <u>55b</u> is the C_2-C_9 bond contracted (difference 4.8σ). Furthermore, relative to the average $C(sp^3)$-$C(sp^3)$ bond distance of 1.503(7) Å in esters of the type C^*-CH_2-O-C(=O)-C^* (137), the C_7-C_8 bonds in each of <u>54b</u>-<u>56b</u> are insignificantly shortened. Although the errors associated with the structure determinations make such a correlation difficult to assess, it is clear that any contractions of these bonds seen in 54b-56b are small.

The existence of a considerable fraction of positive charge at C_2 in 54b-56b is further substantiated by the ^{13}C NMR spectroscopic data listed in Table 2-2. Owing to the close similarity between solution and solid state chemical shift data obtained for 54b and 55b, which indicate that the conformations, structures and electronic distributions within these cations are essentially identical in solution and the solid phase, discussion pertaining to charge delocalization within 54b-56b in solution can be directly applied to the solid state as well.

Comparison of the solution state chemical shift data for 54b-55b and 54a-55a indicates that large downfield shifts of the C_2 atom resonances occur on alkylation of the neutral lactones 54a and 55a to form 54b and 55b respectively. The magnitude of the downfield shift of C_2 resulting from conversion of 55a to 55b (24.5 ppm) is larger than that corresponding to the formation of 54b (18.5 ppm), and further suggests the presence of a larger proportion of positive charge on C_2 in 55b. A similar transfer of positive charge to the carbon atoms of C-O bonds adjacent to a formal carbenium ion center has been systematically observed in the dioxolan-2-ylium cations 10a and 11a-11e (45,50).

2.4.4 Interactions Within the Crystal Lattices

Regio- and stereo-specific cation-anion non-bonded interactions are observed within the crystalline lattices of 54b-56b. In each system, closest contacts of a chlorine atom of the $SbCl_6^-$ counterion occur at C_5, the formal carbenium ion center in 54b-56b, and no other specific interactions appear to be present. In 55b and 56b, two chlorine atoms are in closest contact to C_6. In each case, the chlorine atoms are situated above and below the O_1, C_5, C_6, O_6 plane, Plane A as indicated in Table 2-5, so as to form an approximate 90° angle to both the C_6-O_6 and C_6-O_1 bonds. Only one close Cl..C_6 interaction is observed in 54b. The Cl..C_6 internuclear distances in each of 54b-56b are short, with some of them being less than the sum of the Van der Waal radii of neutral chlorine and carbon atoms (3.50 Å) (141).

In 55b the closest contact chlorine atoms, Cl_{21} and Cl_{11}, are situated 3.347(6) Å and 3.541(6) Å from C_6. These contact atoms are oriented at distances of 3.340(6) Å and 3.530(6) Å respectively above and below the plane of the atoms O_1, C_5, C_6 and O_6, designated as Plane A in Table 2-5. The closest of these chlorine atom contacts is positioned so as to give Cl_{21}-C_6-O_6 and Cl_{21}-C_6-O_1 angles of 93.5(3)° and 94.0(3)° respectively. Cl_{11} is likewise oriented so as to give Cl_{11}-C_6-O_6 and Cl_{11}-C_6-O_1 angles of 90.9(3)° and 83.7(3)°.

In **56b**, chlorine atoms Cl_4 and Cl_5 are located at similar distances of 3.272(4) Å and 3.704(6) Å from the formal center of positive charge, C_6, and are also situated at an approximate angle of 90° to both the C_6–O_6 and C_6–O_1 bonds. The Cl_4–C_6–O_6 and Cl_4–C_6–O_1 angles involving the closest of these chlorine atom contacts are respectively 83.0(7)° and 91.3(7)°. Corresponding Cl_5–C_6–O_6 and Cl_5–C_6–O_1 angles of 107.8(7)° and 80.8(7)° are respectively observed.

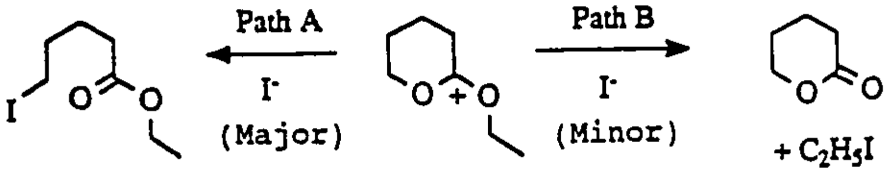
Within the crystal lattice of **54b**, only one chlorine atom, Cl_{21}, is in close proximity to C_6 at 3.208(5) Å. Cl_{21} is situated so as to give a significantly shorter, 3.194(5) Å, contact distance to Plane A, Table 2-5, with Cl_{21}–C_6–O_6 and Cl_{21}–C_6–O_1 angles of 88.5(3)° and 97.3(4)° respectively. The presence of such a single interaction between a nucleophilic species and a carbonyl carbon atom in similar systems has previously been correlated with a significant displacement of the carbonyl carbon atom from the carbonyl plane in the direction of the interacting nucleophile (9,10). Indeed, in **54b** the observed displacement (0.018(9) Å) of C_6 from the plane of the atoms O_1, C_5 and O_6, Plane C in Table 2-5, is significant at the 99% confidence level when a statistical χ^2 test is performed.

2.5 Stereoelectronic Control in the Reactions of Substituted Tetrahydropyrylium Ions

Deslongchamps and coworkers have suggested that the O_6-C_7 bond of the ethoxy group in cation 54b is oriented *cis* with respect to the internal C_6-O_1 bond (67). They have suggested that such a *cis* or Z-conformation of the exocyclic O_6-C_7 bond with respect to the endocyclic C_6-O_1 bond in systems such as 54b-56b would be preferred over the corresponding E-form due to the presence of a stabilizing n-σ^* secondary electronic effect in the Z-conformation (67). The results described in this thesis show that each of the cations 54b-56b adopt such a Z-conformation. These results therefore lend support to Deslongchamps' theory.

However, the presence of a n-σ^* significant stereoelectronic effect in 54b-56b would involve effective orbital overlap of the lone pair of electrons on O_6 and the σ^* antibonding orbital of the endocyclic C_6-O_1 bond in each of these systems. As such, this interaction could be expected to be structurally expressed in terms of a shorter C_6-O_6 bond and a longer C_6-O_1 bond in each of these cations. No such structural effect is observed on examination of the data listed in Table 2-4; in each of 54b-56b the C_6-O_6 and C_6-O_1 bond distances are not significantly different.

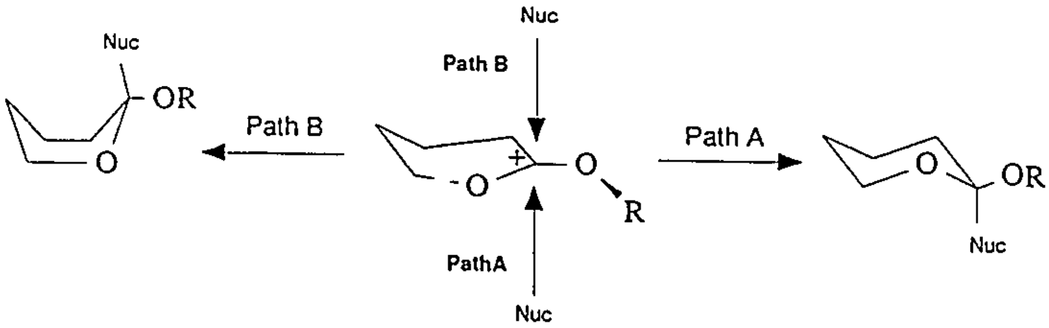
The position of the significant nearest counter-anion contacts within the crystalline lattices of 54b-56b can also be viewed in light of the regioselectivities seen in the reaction of nucleophiles with such cations, as illustrated in Scheme 2-2 (67). The systematically elongated O_1-C_2 and O_6-C_7 bonds as well as the considerable fraction of positive charge on C_2 and C_7 as deduced from the crystal structures of 54b-56b could reflect a significant interaction between both C_2 and C_7 and a chlorine atom of the counterion. Yet, as mentioned in Section 2.4.4, no significant chlorine atom interactions with either C_2 or C_7 are observed in each of the systems 54b-56b; in each case the only significant contacts observed are to C_6, the formal center of positive charge in these cations. Therefore, examination of the nearest chlorine atom contacts to each of the cations within the crystalline lattices of 54b-56b fails to provide supporting evidence for regiospecific nucleophilic attack at C_2 and/or C_7 of these cations.



17 16 18

Scheme 2-2

The crystallographically observed significant chlorine atom contacts to C_6 in systems 54b-56b can also be viewed in light of nucleophilic attack at C_6 in such cations. As illustrated in Scheme 2-3, nucleophilic attack at C_6 of tetrahydropyrylium ions has been proposed to occur stereospecifically, by axial attack from the face of the cation which leads directly to the more stable chair rather than boat conformation of the six-membered ring (65-69). While the closest significant chlorine atom contacts to C_6 in each of 54b-56b are indeed oriented as if they were undergoing specific axial nucleophilic attack at C_6, Table 2-5, there appears to be no preference for attack from the face of the cations which lead directly to the chair conformation.



Scheme 2-3

In 54b the sole nearest nucleophilic contact appears to approach via Path A, Scheme 2-3, so as to give the preferred chair conformation of the product. Such a clear preference is not evident in systems 55b and 56b which each contain two significant chlorine atom contacts to C_6. In both 55b and 56b these nearest contacts are oriented approximately 180° to each other so as to approach via both Path A and Path B, Scheme 2-3. However, the closest chlorine atom to C_6 in 55b appears to approach via Path A whereas conversely, that in 56b appears to approach by Path B.

The observed lack of preference for mode of specific axial nucleophilic attack at C_6 in the systems 54b-56b as deduced from nearest cation-anion interactions observed within the crystal lattices can be explained in terms of the relatively low nucleophilicity of the $SbCl_6^-$ counterion present in the salts 54b-56b. As a consequence, long C_6..Cl internuclear distances and weak C..Cl interactions are involved. It could be argued that a more specific placement of anions or solvent with cations such as 54b-56b occurs in solution. Yet the previously mentioned close similarity of solution and solid state ^{13}C NMR spectra obtained for 54b and 55b suggests that the environment of each of these cations in solution is very similar to that seen in the crystalline state. Thus, if a preference indeed exists in these systems for specific axial attack to give the more stable chair conformation of the product, then differentiation between Paths A and B, Scheme 2-3, must occur at a point farther along the reaction coordinate for nucleophilic addition than is herein represented for 54b-56b.

2.6 Summary

The structures of a series of substituted 6-ethoxytetrahydropyrylium salts were determined with use of single crystal x-ray diffraction and NMR spectroscopic techniques. The work described represents not only the first reported direct structural determinations of these systems, but also the first direct comparison between solid and solution state cationic geometries and environments of such ions.

It has been observed that the conformations and structures of these substituted tetrahydropyrylium ions in the crystalline state are very similar, and that the conformations seen within the crystalline lattices are also present in solution. In each cation, the six-membered ring exists in a shallow half-chair conformation so as to facilitate positive charge delocalization over the entire O_1,C_2,C_5,O_6,C_7 subsystem. The O_6-C_7 bond of the 6-ethoxy group in each ion was found to adopt the Z-conformation with respect to the endocyclic C_5-O_1 bond. This observation has provided the first direct conformational evidence in support of Deslongchamps' theory of stereoelectronic control in the reactions of such ions.

Systematic analysis of the bond distances observed in the crystal structures of the substituted tetrahydropyrylium ions has indicated severe C-O bond length distortions and has suggested positive charge delocalization to C_2 and C_7 in these systems. Such a systematic analysis has also enabled qualitative determination of the effect of variable substitution at C_2 of these cations. Upon substitution at C_2 with an electron-donating group, the O_1-C_2 bond has been observed to further elongate and concomitant hybridization changes at C_2 further toward sp^2 symmetry have been indicated. These structural changes are consistent with increasing positive charge density at C_2 in these systems.

The close similarity of the solution and solid state ^{13}C NMR spectra of the series of tetrahydropyrylium ions has indicated that the geometry and environment of the cations are essentially identical within the crystal lattices and in CD_2Cl_2 solution. However, no evidence has been obtained for explanation of the observed preference for specific nucleophilic attack at C_2 over C_7 in solutions of such tetrahydropyrylium ions. Examination of the closest contacts to the cations within the crystal lattice of each tetrahydropyrylium ion has also failed to explain such observed regioselectivities. In each case the only significant chlorine atom contacts seen are to C_6, the formal carbenium ion center in these cations. Although these nearest contacts are oriented as if they are undergoing specific axial attack at C_6 as predicted in solution, the postulated stereospecificity of attack to give the chair conformation of the 6-membered ring was not observed.

Further examination of the origin of the regio- and stereo-specificities observed in the reactions of substituted tetrahydropyrylium ions would be facilitated by the synthesis of additional salts involving these cations in which closer, more significant nucleophile..$C^{\delta+}$ non-bonded interactions exist. Although these systems are predicted to be difficult to prepare and crystallize in forms suitable for x-ray crystallographic analysis, they offer the capability of clearly depicting not only the preferred modes of nucleophilic attack on these cations, but also, the bonding changes associated with such reactions. Only then will it be possible to uncover the origin of the stereo- and regio-specificities exhibited in the reactions of these systems.

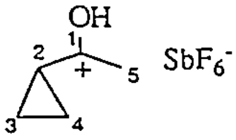
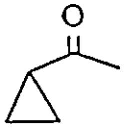
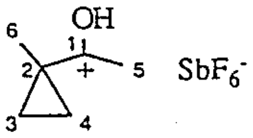
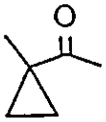
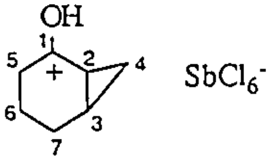
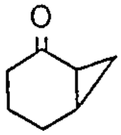
CHAPTER 3

STRUCTURAL STUDIES IN CONDENSED PHASES OF HYDROXY-CYCLOPROPYLCARBINYL CATION SYSTEMS

The structures of a series of substituted hydroxy-cyclopropylcarbinyl cations as determined by low temperature single crystal x-ray crystallography are presented in this chapter. Solution state ^{13}C and ^{1}H NMR spectroscopy has also been utilized for structural characterization of these cations.

The series of hydroxy-cyclopropylcarbinyl cations studied here were chosen to systematically evaluate the conformational and structural effect not only of variable substitution at the carbinyl carbon atom and α- and β-cyclopropyl carbon atoms, but also of restricted conformational mobility in these cationic systems, Table 3-1. **57b** was chosen as the parent, conformationally unrestricted system to which systems **58b** and **59b** could be compared. **58b** is an example of a hydroxy-cyclopropylcarbinyl cation salt having an α-cyclopropyl carbon atom substituent whereas **59b** is a more conformationally restricted hydroxy-cyclopropylcarbinyl cation system. In addition, **59b** contains substitution at one of the β-cyclopropyl carbon atoms.

Table 3-1. Hydroxy-cyclopropylcarbinyl Cations Studied and their Neutral Precursors

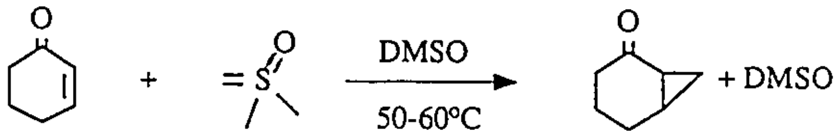
Carbenium Ion	Cyclopropyl Ketone Precursor
 57b	 57a
 58b	 58a
 59b	 59a

RESULTS

3.1 Preparation of Substituted Hydroxy-cyclopropylcarbinyl Cations and their Neutral Precursors

3.1.1 Cyclopropyl Ketone Precursors

Cyclopropylmethyl ketones 57a and 58a, which are commercially available, were distilled before use. The bicyclic material 59a was prepared from 2-cyclohexenone according to a modified procedure of Kuhn and Trischmann as illustrated in equation 3-1 (142).

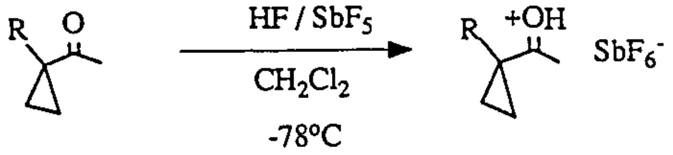


59a

eqn. 3-1

3.1.2 Hydroxy-cyclopropylcarbinyl Cation Salts

The hexafluoroantimonate salts 57b and 58b were prepared by addition at low temperature of a 1:1 mixture of HF/SbF_5 to a dry CH_2Cl_2 solution of the corresponding ketone, equation 3-2. The hexachloroantimonate salt 59b was synthesized by addition of a HCl saturated CH_2Cl_2 solution of $SbCl_5$ to a CH_2Cl_2 solution of the corresponding ketone 59a, equation 3-3. Crystals of salts 57b-59b suitable for crystallographic study were obtained by recrystallization from CH_2Cl_2. These compounds were extremely moisture and temperature sensitive and all manipulations were carried out at low temperature under a dry N_2 atmosphere.



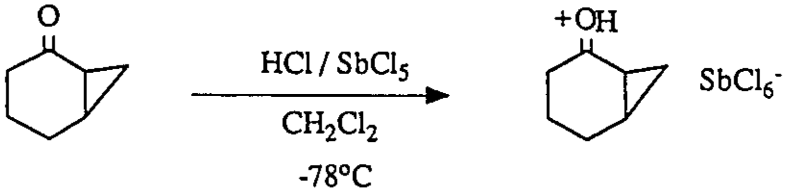
eqn. 3-2

57a R = H

58a R = CH_3

57b R = H

58b R = CH_3



eqn. 3-3

59a

59b

3.2 Characterization of 57b-59b by NMR Spectroscopy

57b-59b were characterized by ^{13}C (125.7 MHz), Table 3.2, and ^{1}H (500 MHz), Table 3.3, NMR spectroscopic techniques. The NMR spectra observed for 57b and 58b were very similar to those previously reported (143). The carbon and hydrogen atom labelling scheme used for NMR spectroscopic analyses and x-ray crystallographic structure determinations of these systems is shown in Figure 3-1.

3.3 X-Ray Crystallographic Structure Determinations of the Salts 57b-59b

X-ray diffraction techniques were used to determine the crystal structures of 57b-59b. Due to the extreme sensitivity of 57b-59b to moisture and temperature, suitable single crystals were sealed in Lindemann capillary tubes and intensity data for these compounds were collected at -65°C.

3.3.1 The Crystal Structure of 57b

Low temperature axial photography was used to determine orthorhombic unit cell parameters for 57b and intensity data were collected in the non-standard space group **Pmnb**. The position of the heavy antimony atom was found by direct methods and remaining non-hydrogen atom positions were determined from subsequent electron density difference maps. The structure of 57b was anisotropically refined by a series of full matrix least-squares refinement

Table 3-2. Spin-Decoupled ^{13}C NMR Chemical Shift Data for 57b-59b[a,b,c]

	CHEMICAL SHIFT (ppm)						
SYSTEM	C_1	C_2	C_3	C_4	C_5	C_6	C_7
57b	242.91	29.83	31.35	31.35	28.10	–	–
58b	238.43	36.88	33.96	33.96	23.87	17.56	–
59b	234.01	34.48	31.64	25.04	33.51	19.09	14.68

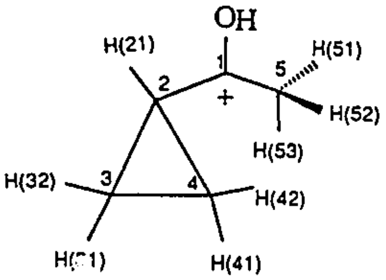
a) 125.721 MHz (500 MHz for ^1H)
b) reference: CD_2Cl_2 at 53.7 ppm; shifts in ppm
c) crystalline samples of 57b-59b dissolved in CD_2Cl_2 at -78°C; spectra acquired at -78°C

Table 3-3. ^{1}H NMR Spectroscopic Data 57b-59b[a,b,c]

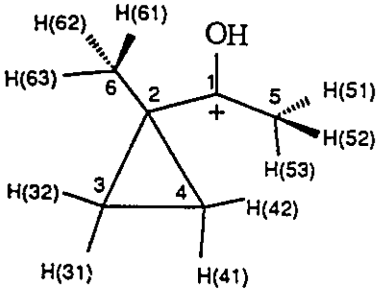
	CHEMICAL SHIFT (ppm) CATION		
ATOM	57b	58b	59b
H(0)	–[d]	7.78bs	–[d]
H(21)	2.30p J=4.5	–	2.77m
H(31)	1.53bs	1.62bs	2.98dd
H(41)	1.53bs	1.62bs	2.60m
H(32)	1.53bs	1.92bd	–
H(42)	1.53bs	1.92bd	2.33dd $J_{H(42)H(31)}$= $J_{H(42)H(21)}$=15.5
H(51)	2.57s	2.45s	3.04bd
H(52)	2.57s	2.45s	2.68m
H(53)	2.57s	2.45s	–
H(61)	–	1.38s	1.92m
H(62)	–	1.38s	1.92m
H(63)	–	1.38s	–
H(71)	–	–	1.78m
H(72)	–	–	2.18bd $J_{H(72)H(62)}$=15.4

a) 500 Mhz; ref. CH_2Cl_2 at 5.32 ppm; shifts in ppm; coupling constants in Hz
b) s=singlet; d=doublet; p=pentet; m=multiplet; b=broad
c) hexafluoroantimonate crystal dissolved in CD_2Cl_2 at −78°C; spectra acquired at −78°C
d) peak not recorded

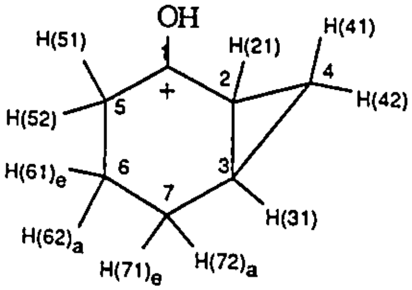
Figure 3-1. Atomic Labelling Scheme Used for 57b-59b



57b



58b



59b

cycles to convergence and a final R_w factor of 0.0374. Further information pertaining to the data collection and final structure solution of <u>57b</u> is presented in Table 5-5.

Table 3-4 lists selected interatomic distances and angles for <u>57b</u> and corresponding best fit planes data is given in Table 3-5. SNOOPI plots of the top and side view of the cation, and stereoscopic view of the unit cell contents for <u>57b</u> are displayed in Figures 3-2 and 3-3 respectively.

3.3.2 The Crystal Structure of 58b

Monoclinic unit cell parameters for <u>58b</u> were determined from axial photographs and reflection intensity data were collected in the uniquely defined space group $P2_1/c$. The structure was solved and refined with the use of a combination of direct and difference methods to a final R_w value of 0.0678. Additional information pertinent to the structure solution of <u>58b</u> is listed in Table 5-5.

Bond length and angle data pertaining to <u>58b</u> are given in Table 3-4. Corresponding selected planes data are presented in Table 3-5. Plots illustrating the cationic geometry and stereoscopic view of the unit cell contents for <u>58b</u> are shown in Figures 3-4 and 3-5 respectively.

Table 3-4. Selected Bond Lengths (Å) and Angles (°) For 57b-59b

Bond Distance	Compound			Angle	Compound		
	57b	58b	59b		57b	58b	59b
C(1)-O	1.256(8)	1.268(8)	1.293(8)	C(2)C(1)C(5)	122.6(6)	124.6(6)	124.5(7)
C(1)-C(2)	1.405(10)	1.461(9)	1.403(10)	OC(1)C(2)	116.5(6)	115.0(6)	114.7(7)
C(2)-C(3)	1.516(8)	1.529(9)	1.534(11)	OC(1)C(5)	120.9(7)	120.4(7)	120.7(6)
C(2)-C(4)	1.516(8)	1.545(8)	1.559(12)	C(1)C(2)C(3)	118.8(5)	116.0(6)	116.4(7)
C(3)-C(4)	1.418(12)	1.448(9)	1.433(13)	C(1)C(2)C(4)	118.8(5)	113.8(6)	119.8(7)
C(1)-C(5)	1.482(9)	1.461(10)	1.461(19)	C(3)C(2)C(4)	55.8(3)	56.2(4)	55.2(6)
C(2)-C(6)		1.491(10)		C(2)C(3)C(4)	62.1(4)	62.5(4)	63.3(6)
C(5)-C(6)			1.534(11)	C(2)C(4)C(3)	62.1(4)	61.3(4)	61.6(6)
C(6)-C(7)			1.540(11)	C(2)C(3)C(7)			116.6(7)
C(3)-C(7)			1.502(11)	C(3)C(7)C(6)			112.7(7)
				C(7)C(6)C(5)			112.0(6)
				C(6)C(5)C(1)			116.0(8)
				C(4)C(3)C(7)			120.5(7)
				C(1)C(2)C(6)		117.7(6)	
				C(3)C(2)C(6)		119.7(7)	
				C(4)C(2)C(6)		119.0(6)	
Anions (57b and 58b, X=F; 59b, X=Cl)							
Sb-X(1)	1.848(4)	1.916(4)	2.356(2)	X(1)SbX(2)	92.7(2)	88.7(2)	89.7(1)
Sb-X(2)	1.841(4)	1.858(4)	2.402(2)	X(1)SbX(3)	88.9(2)	84.4(2)	177.9(1)
Sb-X(3)	1.856(5)	1.871(4)	2.370(2)	X(1)SbX(4)	89.6(2)	88.5(2)	90.4(1)
Sb-X(4)	1.837(5)	1.872(4)	2.351(2)	X(1)SbX(5)		179.6(1)	90.1(1)
Sb-X(5)		1.856(4)	2.368(2)	X(1)SbX(6)		87.8(2)	91.6(1)
Sb-X(6)		1.861(4)	2.341(2)	X(2)SbX(3)	90.5(2)	89.7(2)	88.3(1)
				X(2)SbX(4)	90.9(2)	89.8(2)	89.6(1)
				X(2)SbX(5)		91.0(2)	88.0(1)
				X(2)SbX(6)		176.5(2)	177.7(1)
				X(3)SbX(4)	178.0(3)	90.1(2)	90.2(1)
				X(3)SbX(5)		91.8(2)	89.3(1)
				X(3)SbX(6)		89.9(2)	90.4(1)
				X(4)SbX(5)		91.3(2)	177.5(1)
				X(4)SbX(6)		90.5(2)	92.3(1)
				X(5)SbX(6)		92.5(3)	90.1(1)

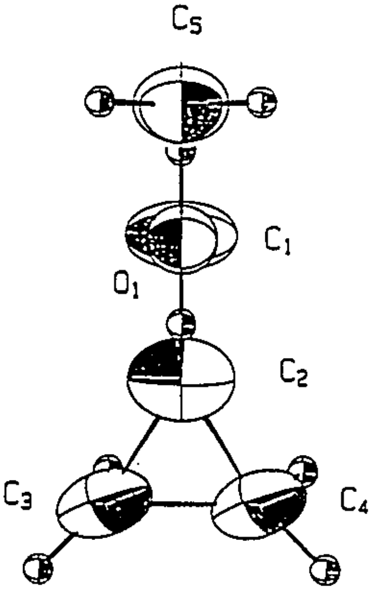
Table 3-5. <u>Selected Least Squares Planes Data For 57b-59b</u>

	Distance[a] of atoms from plane				Dihedral angle[b] between planes A and B	Distance from plane D[f] of nearest contacts to			
COMPOUND		A[c]	B[d]	C[e]		C(1)		H(0)	
<u>57b</u>	O	0.00(1)	2.26(1)		90.0(4)	F(1)	2.99(1)	F(4)	0.00(2)
	C(1)	0.00(1)	1.18(1)			F(1)'	-2.99(1)		
	C(2)	0.00(1)	0.00(1)						
	C(3)	0.71(1)	0.00(1)						
	C(4)	-0.71(1)	0.00(1)						
	C(5)	0.00(1)	1.17(2)						
<u>58b</u>	O	0.00(1)	1.20(2)		90.3(5)	F(4)	2.91(1)	F(1)	-0.133(9)
	C(1)	0.005(9)	1.28(3)			F(2)	-3.010(9)		
	C(2)	0.00(1)	0.00(1)						
	C(3)	0.59(1)	0.00(1)						
	C(4)	-0.85(1)	0.00(1)						
	C(5)	0.00(1)	2.59(1)						
	C(6)	0.68(2)	-1.24(2)						
<u>59b</u>	O	0.000(8)	0.000(8)	0.53(1)	82.2(6)	Cl(1)	-2.56(3)	Cl(2)	-1.10(5)
	C(1)	0.027(9)	-1.18(2)	-0.01(1)		Cl(4)	2.41(3)		
	C(2)	0.00(1)	0.00(1)	0.20(1)					
	C(3)	0.61(2)	0.00(1)	-0.01(1)					
	C(4)	-0.81(2)	0.00(2)	-1.20(1)					
	C(5)	0.00(1)	-2.51(1)	-0.53(2)					
	C(6)	0.31(2)	-2.52(1)	-0.86(2)					
	C(7)	1.17(2)	-1.24(2)	0.10(1)					

a) all distances in Angstroms
b) all angles in Degrees
c) plane of C(2)-C(5)-O
d) plane of C(2)-C(3)-C(4)
e) plane of C(1)-C(2)-C(3)-C(7)
f) plane of C(1)-O-H(O)

Figure 3-2. <u>The Conformation of 57b</u>

a. <u>Top View of 57b</u>



b. <u>Edge View of 57b</u>

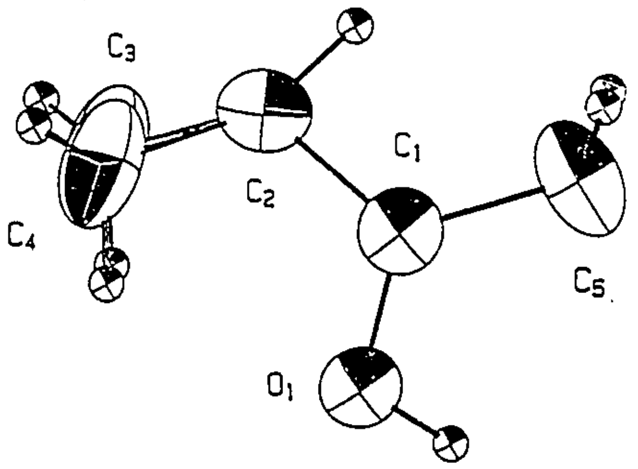


Figure 3-3. <u>Stereoscopic View of Unit Cell Contents for 57b</u>

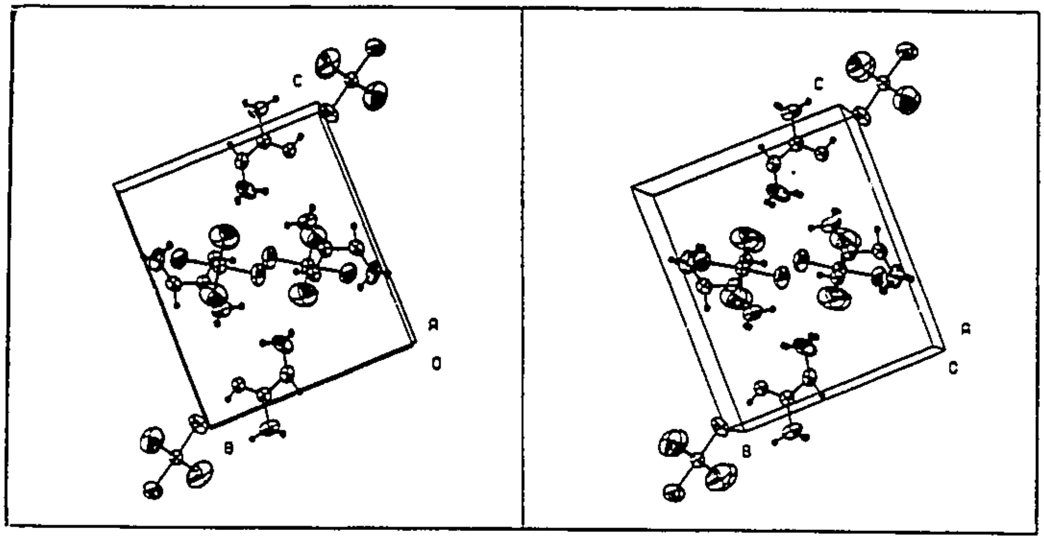


Figure 3-4. <u>The Conformation of 58b</u>

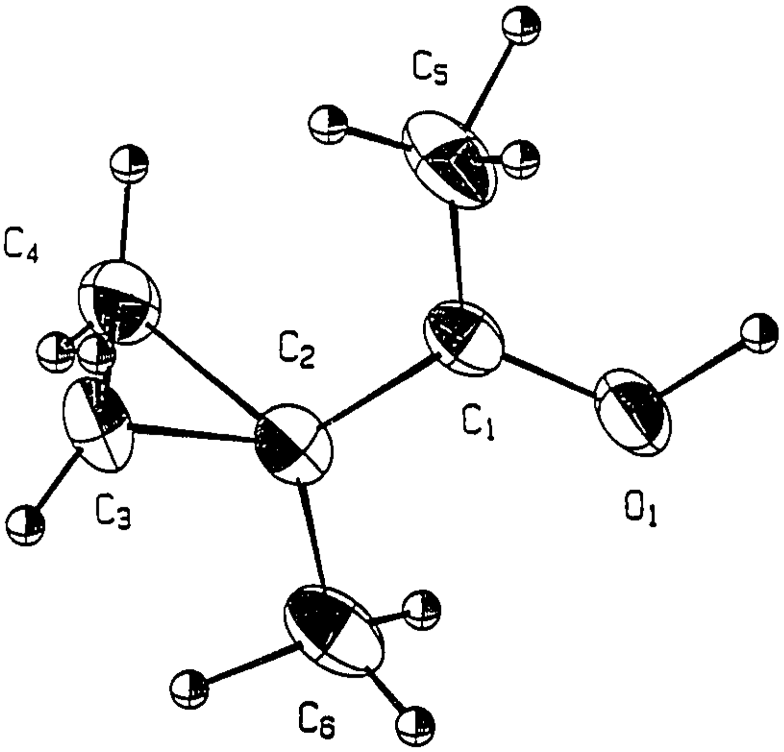
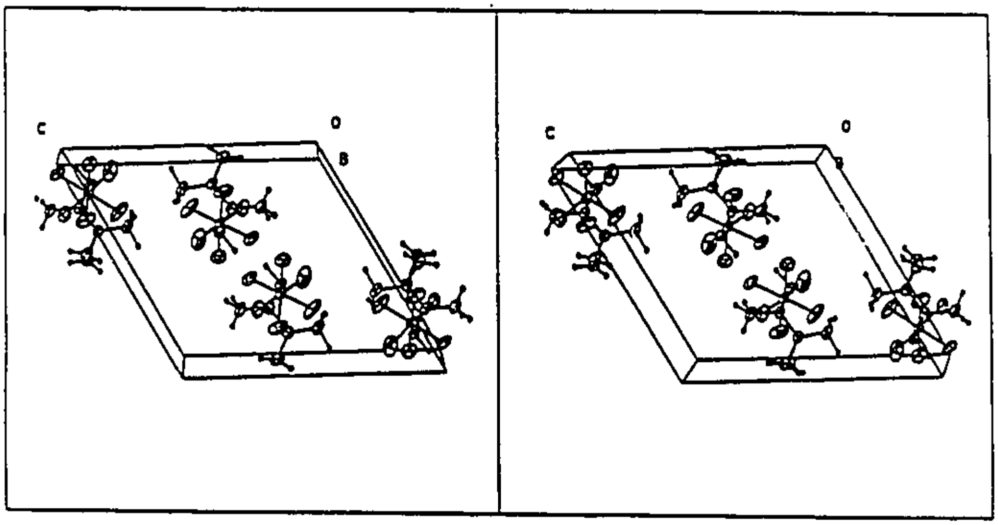


Figure 3-5. Stereoscopic View of Unit Cell Contents for 58b



3.3.3 The Crystal Structure of 59b

Low temperature axial photography was used to determine orthorhombic unit cell parameters for 59b and its structure was solved in the non-standard space group $Pc2_1b$. A three-dimensional Patterson synthesis was used to reveal the position of the antimony atom. The remaining atomic positions were determined and refined using a series of electron density difference maps in conjunction with full matrix least squares refinement cycles. Structure refinements converged to give a final R_w value of 0.0337.

Selected interatomic distances and angles as well as best fit planes data for 59b are listed in Tables 3-4 and 3-5. Figures 3-6 and 3-7 in turn show the cationic geometry and stereoscopic view of the unit cell contents for 59b.

Figure 3-6. The Conformation of 59b

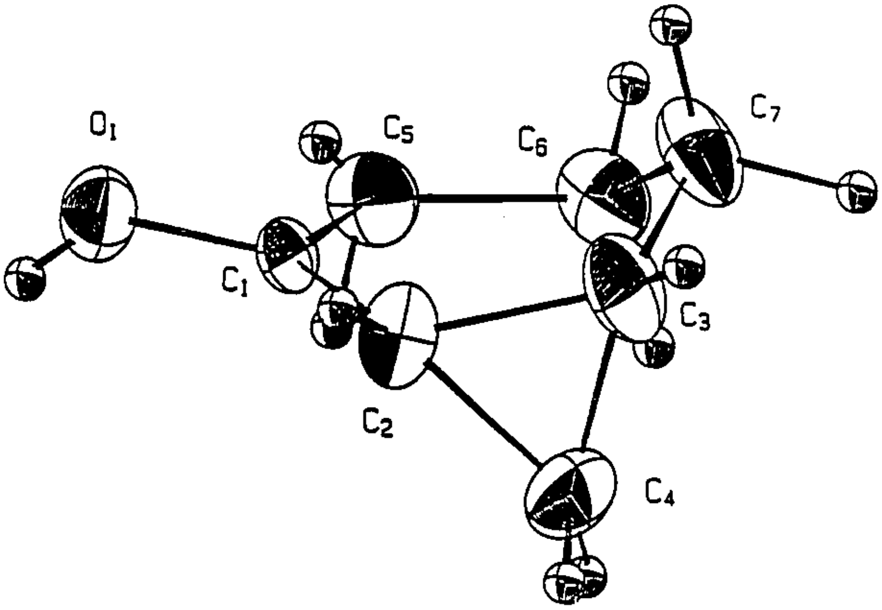
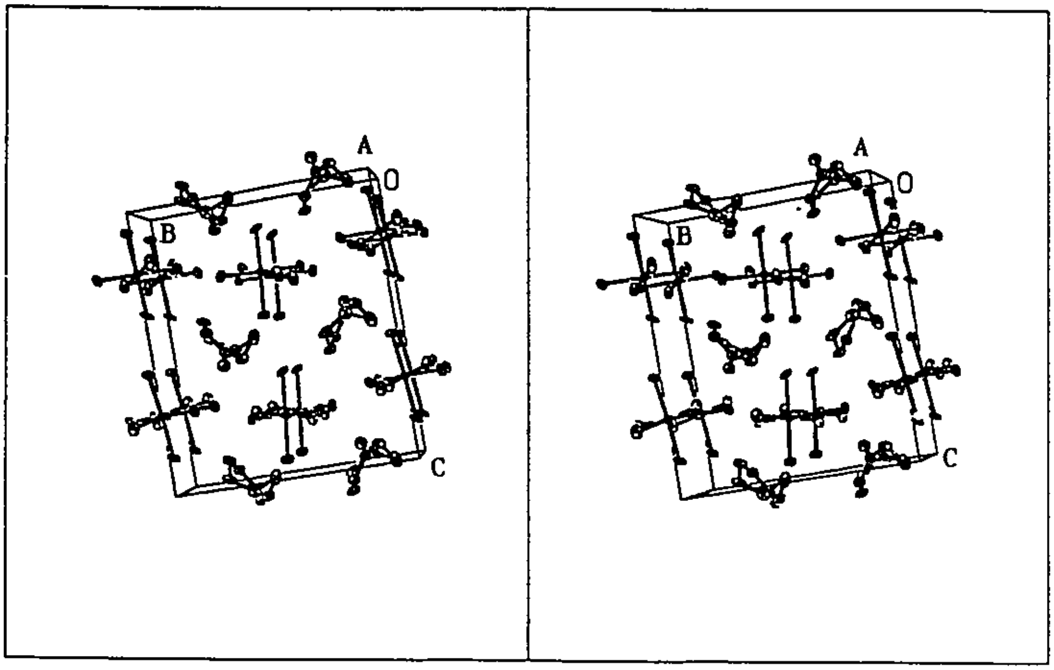


Figure 3-7. Stereoscopic View of Unit Cell Contents for 59b



DISCUSSION

3.4 Comparative X-Ray Structural Analysis of the Hydroxy-Cyclopropylcarbinyl Cations 57b-59b

The structures of 57b-59b shown in Figures 3-2, 3-4 and 3-6 respectively indicate that in each case protonation of the carbonyl carbon atom of 57a-59a has occurred and that the structures are correctly represented as the hydroxy-cyclopropylcarbinyl cations 57b-59b. Associated with each of these cations within the crystal lattices of 57b-59b is a SbF_6^- or $SbCl_6^-$ counter-anion having octahedral symmetry. This association is illustrated in the corresponding stereoscopic views of the unit cell contents for 57b-59b, Figures 3-3, 3-5 and 3-7 respectively.

3.4.1 Conformation

The conformations of the cations observed within the crystal lattices of 57b-59b are similar, as evidenced by comparison of Figures 3-2, 3-4 and 3-6 respectively, and the associated best fit planes and conformational data, Tables 3-5 and 3-6 respectively. In each cation the cyclopropyl ring adopts, or nearly adopts, a bisected geometry with respect to the empty p-orbital at the formal carbenium ion center C_1, Table 3-6.

Table 3-6. Crystallographic Conformations of Various Hydroxy-cyclopropylcarbinyl Cations

		Angle (°)	
Compound	θ^a	τ_1^b	τ_2^c
57b	90.0	0.0	180.0
58b	90.0	-173.5	179.9
59b	82.2	176.3	-7.9
46[d,e]	85.6	-7.0	-180.0
47[e]	90.0 90.0	180.0 0.0	0.0 180.0

a) dihedral angle between the plane defined by the cyclopropyl carbon atoms C_2, C_3, C_4 and the plane defined by O, C_2, C_5

b) torsion angle $O-C_1-C_2$-(midpoint C_3-C_4)

c) torsion angle $H(O)-O-C_1-C_2$

d) average values obtained from the two independent cations which exist within the asymmetric unit of 46

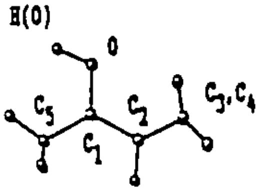
e) Reference 40

As shown in Table 3-6, 57b adopts a completely bisected conformation. The dihedral angle, θ, defined as the angle between the plane of the cyclopropyl group and the C_2-C_5-O plane is 90.0(4)° and the torsion angle, τ_1, defined by the angle O-C_1-C_2-midpoint(C_3-C_4) is 0.0°. (A perfectly bisected geometry is characterized by a dihedral angle θ of 90.0° and a corresponding τ_1 value of 0 or ±180°.) A τ_1 value of 0° indicates an *s-cis* bisected conformation of the cyclopropyl ring with respect to the carbonyl moiety whereas τ_1 values of ±180 indicate corresponding *s-trans* bisected conformations, Figure 3-8.

58b also displays a θ angle of 90° (Table 3-6) but is not completely bisected for the angle τ_1, as defined above, in this cation is -173.5(5)°, a value significantly different (difference 13.0σ) from -180° at the 99% confidence level. However these dihedral and torsion angle values indicate an approximately *s-trans* bisected conformation for 58b.

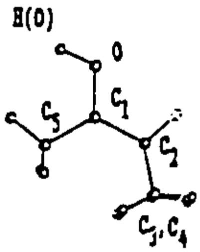
In the more conformationally restricted cation 59b, the fused cyclopropyl ring still adopts an approximately bisected geometry in which the angle θ between the cyclopropyl and carbonyl planes is 82.2(6)°, Table 3-6. The corresponding torsion angle τ_1 is 176.3(8)° indicating that the cyclopropyl ring in this cation, as is observed in 58b, is oriented *trans* about the C_1-C_2 bond to the protonated

Figure 3-8. The *Possible s-cis* and *s-trans* Bisected Conformations of 57b



s-cis

$\tau_1 = 0°$



s-trans

$\tau_1 = \pm 180°$

where τ_1 is the angle defined by $O-C_1-C_2$-midpoint(C_3-C_4)

carbonyl bond. In order to adopt this preferred geometry, the cyclohexane ring of 59b adopts a pseudo-boat conformation similar to those deduced on the basis of NMR studies for the related [4.1.0] bicyclic cations 34 and 35 discussed earlier in Chapter 1 (118).

In both 57b and 58b planar configurations about the protonated carbonyl carbon atom C_1 are observed and C_1 is not significantly displaced from the plane defined by the atoms C_2, C_5 and O, Plane A, Table 3-5. Conversely, in 59b C_1 is situated 0.027(9) Å (3.0σ) from this same plane.

It is also interesting to note the orientation of the hydroxyl proton in each of 57b-59b. In both 57b and 58b the hydroxyl proton is oriented *trans* about the O-C_1 bond to the C_1-C_2 bond, as displayed by the corresponding H(O)-O-C_1-C_2 torsion angles, τ_2 of 180.0° and 179.9° respectively listed in Table 3-6. However, the τ_2 value of -7.9° in 59b indicates a corresponding *s-cis* orientation.

The conformations found for 57b-59b can be compared to those observed for the two other substituted hydroxycyclopropylcarbinyl cations 46 and 47 whose structures have been determined by x-ray crystallography (40). Θ, τ_1 and τ_2 data for 46 and 47 are also summarized in Table 3-6. For each of the two independent cations within the asymmetric unit for 46, the average dihedral angles Θ and torsion angles τ_1 of 85.6° and -7.0° respectively indicate an approximately bisected *s-cis* conformation of the cyclopropyl ring relative to the protonated carbonyl moiety. Similarly, the two cyclopropyl rings of 47 adopt completely bisected geometries as evidenced by the θ values of 90.0° and τ_1 values of 180.0° and 0.0° involving each of the cyclopropyl rings respectively. In this cation, one cyclopropyl ring is oriented *trans*, and the other *cis* about the C_1-C_2 bond to the protonated carbonyl bond. Furthermore, the τ_2 values obtained for 46 (-180.0°) and 47 (0.0° and 180.0°) indicate that in each case, the hydroxyl proton is oriented *trans* to the *cis*-bisected cyclopropyl ring, as is observed for 57b.

The data listed in Table 3-6 indicate a clear preference for the adoption of both a bisected (or nearly bisected) conformation of the cyclopropyl group with respect to the formal center of positive charge and also for an approximately coplanar H(O)-O-C_1-C_2 subsystem in these cations. In each of 57b, 58b, 46 and 47, the *s-trans* orientation of the O-H(O) bond with respect to the C_1-C_2 bond appears to minimize steric interactions between the O-H grouping and the cyclopropyl ring in these systems. As will be discussed in more detail in Section 3.4.6, within the crystal lattices of 57b-59b in-plane hydrogen bonding interactions between the hydroxyl proton and a fluorine or chlorine atom of the SbF_6^- or $SbCl_6^-$ counter-anion are observed. This cation-stabilizing interaction is facilitated by the observed *trans* orientation of the hydroxyl proton with respect to the cyclopropyl ring in each of 57b and 58b. The unique *s-cis* orientational preference of the O-H(O) bond relative to the C_1-C_2 bond seen in 59b can be attributed to crystal packing and to the presence of the methylene groupings on the six-membered ring of this ion.

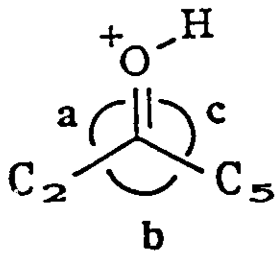
Although the bisected (or nearly bisected) conformations observed for every hydroxy-cyclopropylcarbinyl cation so far studied are also the preferred conformations for cyclopropyl ketones of the type 48, x-ray crystallographic investigations have suggested that a much broader conformational energy minimum exists for these neutral ketones (129). The potential well of this energy minimum is shallow in the region corresponding to τ_1 ranges of ±30° (129). As more examples become available, it is likely that in the cationic systems this potential well will be definitively shown to be steeper and narrower than that of the corresponding neutral systems.

3.4.2 Distortions About the Protonated Carbonyl Group

Bond length and angle data for the series of cations 57b-59b which appear in Table 3-4 provide evidence for a high degree of positive charge delocalization over the carbon and oxygen atom framework of these systems. In each of 57b-59b, oxygen atom protonation results in significant C_1-O bond elongation to 1.256(8) Å, 1.268(8) Å and 1.293(8) Å respectively relative to that found on average (1.22 Å) for neutral cyclopropyl ketone systems 48 (differences 4.5σ, 5.8σ and 8.9σ, respectively) (129). Associated with these C_1-O bond lengthenings are systematic distortions in the angles about C_1, Table 3-7. In each case the C_2-C_1-C_5 bond angle is significantly larger than that observed on average in the crystal structures of neutral compounds containing a cyclopropyl ketone moiety in the *s-cis* or *s-trans* bisected conformation (115.2(6)°) (differences 8.7σ, 10.8σ and 10.0σ, respectively for 57b-59b) (144,145). Concomitant O-C_1-C_2 bond angle diminutions from that seen on average in the neutral systems (122.8(4)°) are also observed (144,145).

In each of the cations 57b-59b, elongation of the C_1-O bond is accompanied by a contraction of the adjacent C_1-C_2 bond. The C_1-C_2 bonds in 57b and 59b (1.405(10) Å and 1.403(10) Å respectively) are significantly shorter (differences 6.3σ and 6.5σ, respectively) than the corresponding value of 1.474(4) Å observed on average in the related cyclopropyl ketone systems 48 (129). The C_1-C_2 bond length of 1.461(9) Å in 58b is not significantly shortened as compared to the neutral ketones. The C_1-C_2 bond lengths in 57b and 59b, which are directly comparable to the average

Table 3-7. Bond Angles Around C_1 of Various Hydroxycyclopropylcarbinyl Cations



Compound	Angle (°) a	b	c
57b	116.5(6)	122.6(6)	120.9(7)
58b	115.0(6)	124.6(6)	120.4(7)
59b	114.7(7)	124.5(7)	120.7(6)
46[a]	116.1(6) 117.2(6)	123.8(6) 122.1(7)	120.1(6) 120.7(6)
47	115.6(4)	123.7(6)	120.8(6)
50	116.2(7)	124.1(5)	119.5(7)

a) values for each of the two independent cations within the asymmetric unit of 46

C_{ar}–C_{ar} bond distance of 1.397(9) Å in aromatic compounds (3), suggest considerable C_1–C_2 double bond character in each of these ions. The relatively long C_1–C_2 bond in 58b can possibly be attributed to steric effects resulting from the additional α-cyclopropyl carbon atom methyl substituent in 58b. The presence of this additional methyl substituent in 58b results in a smaller extent of flattening about C_2 when compared to that observed within 57b; the C_1–C_2–C_3 and C_1–C_2–C_4 angles in 58b (116.0(6)° and 113.8(6)°) are significantly smaller than those found in 57b (each 118.8(5)°) (differences 3.5σ and 8.0σ, respectively).

Within the error limits of the structure determinations, the C_1–C_5 bond distance obtained for each of 57b–59b (1.482(9) Å, 1.461(10) Å and 1.461(9) Å respectively) is not shorter than that in the corresponding neutral systems 48 (1.511(15) Å) (129). As such, these bond lengths obtained fail to indicate any significant charge induced contraction of the C_1–C_5 bond or enhanced conjugation of C_5 with the formal carbenium ion center, C_1, in each of these cationic systems.

3.4.3 Cyclopropyl Bond and Angle Distortions

Large and systematic cyclopropyl bond length and bond angle distortions away from the D_{3h} symmetrical structure observed for free cyclopropane are seen in the crystal structures for each of <u>57b</u>-<u>59b</u>, Tables 3-4 and 3-8. In each case, the magnitude of these distortions away from a symmetrical structure is larger than that observed in the parent neutral systems of the type <u>48</u> (129). The distal C_3-C_4 cyclopropyl bonds in each of <u>57b</u>-<u>59b</u> are significantly shorter (differences 5.0σ, 3.3σ and 3.5σ, respectively) than the corresponding average bond length of 1.478 Å found in neutral cyclopropyl ketones (129). The vicinal cyclopropyl C_2-C_3 and C_2-C_4 bonds in <u>58b</u> and <u>59b</u> are longer than the corresponding average value (1.517 Å) observed in the parent neutral systems (129). These cyclopropyl bond distortions in <u>57b</u>-<u>59b</u> are naturally coupled with changes in the C_2-C_3-C_4 and C_2-C_4-C_3 bond angles. Although similar bond angle distortions are seen in the neutral systems <u>48</u>, the degree of distortion observed in each of <u>57b</u>-<u>59b</u> is consistently larger.

The degree of distortion in the cyclopropyl bond lengths observed in <u>57b</u> is remarkably large. The magnitude of these distortions seen in this cation is larger than that observed in any of the other cyclopropylcarbinyl cations or indeed any cyclopropyl compounds whose structures have been determined. The severely contracted distal cyclopropyl C_3-C_4 bond length of 1.418(12) Å observed in <u>57b</u> is within experimental error the same as that observed for the C-C bonds in benzene and suggests that the C_3-C_4 bond order in

Table 3-8. Selected Crystallographic Bond Lengths Within Various Hydroxy-cyclopropylcarbinyl Cations

Compound	Average C-C Cyclopropyl	Bond (Å) C_3-C_4	C_1-C_2
57b	1.483	1.418(12)	1.405(10)
58b	1.509	1.448(9)	1.461(9)
59b	1.509	1.433(13)	1.403(10)
46[a]	1.506	1.448(4)	1.417(8)
47	1.509	1.468(3)	1.430(2)
49	1.52	1.501(8)	1.474(7)
50	1.51	1.471(9)	1.439(10)
Neutral 48	1.504	1.478	1.474

a) average values obtained from the two independent cations which exist within the asymmetric unit of 46

57b approaches 1.5. This contracted C_3-C_4 bond is coupled with a C_3-C_2-C_4 angle (55.8(3)°) which is significantly smaller (difference 8.3σ), and C_2-C_3-C_4 and C_2-C_4-C_3 angles (each 62.1(4)°) which are considerably larger (differences 3.1σ), than the corresponding average angles of 58.3° and 60.8° respectively found in neutral cyclopropyl ketone systems (129). These observations suggest a high degree of cyclopropyl group participation in stabilization of the adjacent carbenium ion center, C_1 in 57b.

The cyclopropyl bond distortions seen in 57b and 58b are of interest in terms of the structural effect of the additional α-cyclopropyl carbon methyl substituent in 58b. Several theoretical calculations have suggested that the effect of the C_2-methyl substituent in 58b as compared to 57b would result in both C_1-C_2 and vicinal cyclopropyl bond elongation (87,94,120,146,147). In this work, the C_1-C_2 bond in 58b (1.461(9) Å) is significantly longer than that found in 57b (1.405(10) Å) (difference 4.2σ). However, no significant differences in cyclopropyl C-C bond lengths and angles in these two cations can be detected.

The bisected conformation of the bicyclic cation 59b has been previously noted in this thesis. The pattern of cyclopropyl bond length distortions observed within 59b is also of considerable interest. Relative to the parent neutral system 48, the vicinal cyclopropyl C_2-C_4 bond in 59b is significantly elongated to 1.559(12) Å (difference 3.5σ) and the distal C_3-C_4 bond is contracted to 1.433(13) Å (difference 3.5σ). Cation 59b, which formally contains an alkyl substituent at one of the β-cyclopropyl carbon atoms, would have been expected to display a considerable difference in the C_2-C_3 and C_2-C_4 vicinal cyclopropyl bond lengths (87). However, the C_2-C_3 and C_2-C_4 bond lengths of 59b are the same within experimental error. It is not clear whether the presence of the fused cyclohexane ring in 59b is causing these two bonds to be equivalent. As such, further β-substituted cyclopropylcarbinyl cations need to be examined in order to more fully determine the structural effect of such β-substitution.

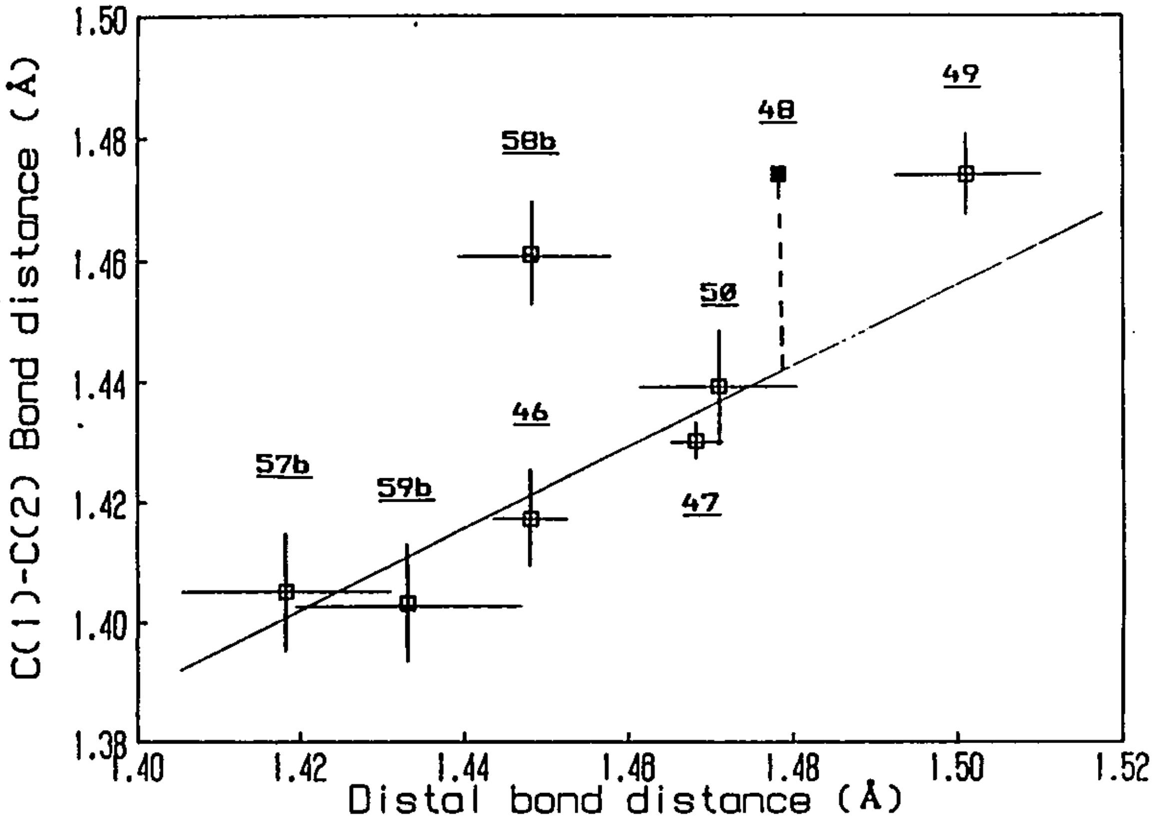
The cyclopropyl C-C bond distortions and shortened C_1-C_2 distances observed here for 57b-59b can be compared to those previously reported for 46-50 (data are summarized in Table 3-8). Examination of this expanded series of cations shows that there is a considerable variation in both the degree of C_1-C_2 bond contraction and cyclopropyl bond distortions away from a D_{3h} symmetrical structure. However, within each cation the average cyclopropyl bond length is approximately equivalent to that found in the composite neutral systems 48. In general, the magnitude of each of the vicinal bond lengthenings observed is half that of the distal bond contraction seen in each of the systems studied.

3.4.4 Correlation Between Cyclopropyl Bond Distortions and C_1-C_2 Bond Lengths; Charge Delocalization in the Solid State

The magnitude of the cyclopropyl bond distortions observed for each of the series of compounds 57b-59b and 46-50 can be related to the degree of C_1-C_2 bond contraction in these systems, Table 3-8. The relationship between C_1-C_2 and distal C_3-C_4 bond lengths in these systems is shown in Figure 3-9. This figure illustrates that, apart from the points corresponding to 58b and 49, a good linear correlation exists between these two structural parameters for the cationic systems plotted. The two cations which deviate from the correlation line, 58b and 49 both possess a methyl substituent at C_2, the α-cyclopropyl carbon atom. As such, these cations might not be expected to fall on the same line as the other cations 57b, 59b, 46, 47 and 50 which are unsubstituted at the C_2 position (3). The unusually long C_1-C_2 bond length of 1.474(7) Å in 49 has been previously rationalized to result from an unfavorable cyclic 4-π electron configuration (41). However, this explanation is questionable given the observation that a similar C_1-C_2 bond length of 1.451(9) Å is also observed in 58b (difference 1.1σ).

The linear correlation observed in Figure 3-9 between the extent of cyclopropyl bond distortion and the

Figure 3-9. The Correlation Between C(1)-C(2) and Distal Cyclopropyl Bond Lengths in Hydroxy-cyclopropylcarbinyl Cations



magnitude of C_1–C_2 bond contraction observed for 57b, 59b, and 46, 47 and 50 can be interpreted in terms of variable cyclopropyl group participation in positive charge delocalization. Larger cyclopropyl group distortions can be taken as indicative of greater electron delocalization involving the three-membered ring in these systems.

The variable factor in these cations is the substituent on C_1. As the charge stabilizing ability of the C_1-substituent in each of these cations increases, the degree of cyclopropyl group participation in electron delocalization would decrease. As a result, the degree of cyclopropyl group structural distortions observed would also decrease. In this context, the correlation shown in Figure 3-9 could be used to rank the relative charge stabilizing abilities of the various C_1-substituents presented in this series of hydroxy-cyclopropylcarbinyl cations as follows:

methyl (57b) < phenyl (46) < cyclopropyl (47).

There appears to be no simple order of the relative positive charge stabilizing ability of methyl, phenyl and cyclopropyl substituents (114,148,149). However, the relative order determined from Figure 3-9 has been commonly found by other experimental techniques including thermodynamic measurements in the gas phase (150).

The correlation observed in Figure 3-9 between systematic cyclopropyl group distortions and the degree of electron demand at the adjacent positively charged carbenium ion center to which it is conjugated is the structural analogue of a similar correlation earlier established by Gassman and Fentiman (151). These workers correlated increasing neighboring group participation with increasing electron demand at the carbenium ion center formed during the solvolytic reactions of C_7-substituted norbornenyl derivatives (151).

The degrees of structural change observed as a function of substituent in these hydroxy-cyclopropylcarbinyl cations are much larger than those typically observed for neutral molecules. Indeed, it has been recently contended that clear, substituent induced structural changes in neutral, ground state molecules do not exist (6,152). It has been shown that, in the absence of steric factors and hybridization changes, the bond lengths in a variety of substituted, saturated and unsaturated neutral compounds usually do not vary by more than 0.02 Å (6,152).

The overall C_1-C_2 bond contraction observed in each of the series of cations 57b-59b, 46, 47, 49 and 50 relative to that observed in the corresponding neutral systems 48 is the result of two effects; enhanced cyclopropyl group positive charge conjugation as discussed above and charge induced contraction resulting from the presence of positive charge at C_1. For a more quantitative analysis of the structural consequences of variable cyclopropyl group participation in positive charge stabilization, it would be attractive to isolate and determine the relative magnitudes of these two effects in each of the cations studied.

Comparison of the C_1-C_2 bond distances obtained experimentally for each of these bisected cyclopropylcarbinyl cations of interest here with those observed for the same systems held in perpendicular conformations, in which conjugative effects would be eliminated, would enable determination of the magnitude of C_1-C_2 bond contractions effected solely by the charge effect. Allen has used such an approach successfully in order to determine the relative conjugative abilities of vinyl and cyclopropyl groups in neutral systems (129). However, this experimental approach is not feasible for the systems herein of interest for no crystal structures of cyclopropylcarbinyl cations held in unstable perpendicular conformations have yet been determined nor are they expected to become available.

An alternative estimate of the magnitude of charge induced C_1-C_2 bond contraction in the cations **57b**-**59b**, **46**, **47**, **49** and **50** herein studied can be obtained upon further analysis of Figure 3-9. In these cations, any charge effect present will lead to dominant C_1-C_2 bond shortening but have comparatively little effect on the more remote C_3-C_4 bond. Conversely, any conjugative effect present will more equally impact both bond lengths. As such, the vertical displacement of the point corresponding to the neutral cyclopropyl ketone 48, in which charge induced bond contraction is absent, from the best-fit correlation line for the cationic systems can be used to estimate the magnitude of the charge induced C_1-C_2 bond contraction observed in these cations. Although large errors are associated with such an analysis, the vertical displacement seen in Figure 3-9 corresponds to a charge induced C_1-C_2 bond shortening of approximately 0.035 Å, roughly half the total observed shortening of this bond in either of 57b or 59b relative to that in 48. As expected, the estimated magnitude of the charge induced shortening of the C_1-C_2 bonds in these tertiary, hydroxy-substituted cyclopropylcarbinyl cations is significantly less than that calculated for the less stabilized, primary parent cation 20a (85). Recall that Wiberg and coworkers have suggested that this charge effect in 20a leads to a C_1-C_2 bond diminution of 0.064 Å (85).

A similar charge induced contraction of the C_1-C_5 bonds in 57b-59b, 46, 49 and 50 might also be expected. Yet, when compared to the corresponding C_1-C_5 bond lengths of 1.45(1) Å in 2-(p-nitrophenyl)-cyclopropylmethyl ketone

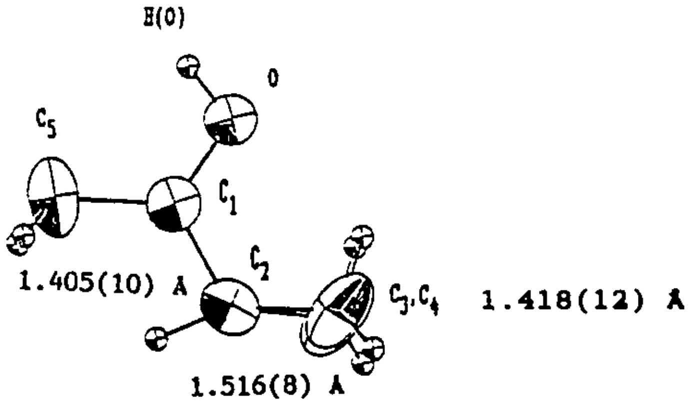
(145) or 1.480(17) Å in aryl-substituted ketones (3), no such statistically significant bond length differences are observed for any of 57b-59b, 46 or 50. Although the C_1-C_5 bond length in 49 is shorter than that seen in 2-(p-nitrophenyl)-cyclopropylmethyl ketone (difference 3.1σ), the presence of the unsaturated C=C double bond involving C_5 in 49, rather than charge induced contraction, more likely accounts for this observed bond diminution.

3.4.5 Comparison of the Crystal Structure of 57b and the Calculated Structure of Cyclopropylcarbinyl Cation 20

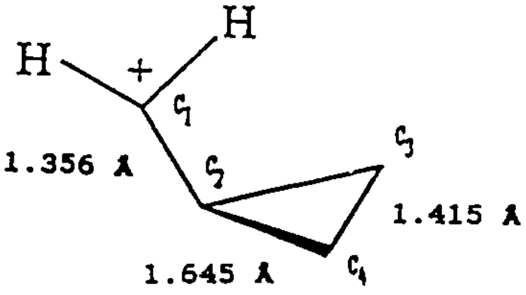
The crystallographically observed structure for 57b, the simplest cyclopropylcarbinyl cation described here, can be compared to results of the highest level theoretical calculations performed to date on the parent unsubstituted cyclopropylcarbinyl cation in the bisected conformation 20a (85), Figure 3-10. Considerable differences are observed on comparison of these two structures.

The C_1-C_2 bond in 57b (1.405(10) Å) is significantly longer than that calculated for 20a (1.356 Å) (difference 4.9σ). Although there is good agreement between the cyclopropyl distal C_3-C_4 bond lengths in 57b and 20a (1.418(12) Å versus 1.415 Å), the vicinal bonds in 57b, having lengths of 1.516(8) Å are substantially shorter than those calculated for 20a (1.645 Å). These observations can

Figure 3-10. Comparison of the Structures of 57b and 20a



57b



20a

possibly be attributed to the charge stabilizing hydroxyl and methyl substituents at C_1 in 57b. A similar elongation of the C_1-C_2 bond and contraction of the vicinal cyclopropyl bonds in 20a has been theoretically calculated upon sequential substitution at C_1 with one and two methyl groups to give 21 and 22 respectively (84,99,153).

The average cyclopropyl bond length of 1.568 Å in the calculated structure of 20a is significantly larger than that observed not only in 57b, but also in any of the other cations that have been discussed here, Table 3-8. It further appears that the type of correlation shown in Figure 3-9 does not apply to 20a and consequently, that the nature of charge delocalization in 20a is considerably different from that observed in any of the hydroxy-cyclopropylcarbinyl cations herein studied.

3.4.6 Interactions Within the Crystal Lattices

Within each of the crystalline lattices of the salts 57b-59b directed and significant contacts between the cations and an atom of the counter-anion are observed. The closest of such contacts in each of 57b-59b are hydrogen bonding interactions between the hydroxyl proton of the cation and a fluorine or chlorine atom of the SbF_6^- or $SbCl_6^-$ counterion. The O-H, H-F or H-Cl internuclear distances are imprecise owing to the uncertainty associated with the positions of crystallographically determined hydrogen atom positions. However, the corresponding O-F or O-Cl internuclear distances can be determined with good precision. These closest O-F interactions at 2.557(6) Å and 2.601(6) Å, in 57b and 58b respectively, and the closest observed O-Cl contact distance of 3.286(7) Å in 59b are all shorter than the sum of the Van der Waal radii of the respective neutral atoms, and suggest the presence of strong hydrogen bonds in each case (140). The C_1-O-F (or Cl) angles (57b; C_1-O-F_4 115.3(2)°, 58b; C_1-O-F_1 119.6(2)°, 59b; C_1-O-Cl_2 112.9(1)°) and C_2-C_1-O..F (or Cl) torsion angles (57b; C_2-C_1-O..F_4 180.0(2)°, 58b; C_2-C_1-O..F_1 -179.3(2)°, 59b; C_2-C_1-O..Cl_2 17.4(1)°) indicate that in each of these systems the oxygen atom is sp^2 hybridized and that the nearest Lewis base contact to the hydroxyl proton is oriented so as to be approximately coplanar with the C_2-C_1-O sub-system.

The occurrence of a similar nearest contact hydrogen bonding interaction is also seen within the crystalline lattices of 46, 47 and 50 (40,42). The presence of such a cation-anion interaction in each of the systems 57b-59b, 46, 47 and 50 appears to cause a distortion of the various bond angles around the carbonyl carbon atom, C_1. As mentioned in section 3.4.2, the C_2-C_1-O angle, angle a, and the C_2-C_1-C_5 bond angle, angle b, Table 3-7, in each of 57b-59b, 46, 47 and 50 are respectively smaller and larger than the comparable angles observed in neutral cyclopropyl ketone systems 48 (144,145). However, in each case the C_5-C_1-O angle, angle c, Table 3-7, remains insignificantly different from the comparable average angle of 122.1(5)° observed in systems of the type 48 (144,145).

In these cations, the angle a, which is *anti* to the H..Anion interaction, is always smaller than angle b, regardless of whether the cation adopts an *s-cis* or *s-trans* bisected conformation, or whether the hydroxyl proton is oriented *trans* or *cis* to the cyclopropyl ring. Such a systematic distortion about the carbonyl carbon atom is not seen in the related neutral cyclopropyl ketones systems 48 (129,144,145). However, this systematic distortion appears to be a general property of protonated ketones as a whole (140). For example, similar distortions have been observed from HF/6-31G* level geometry calculations for protonated formaldehyde in which H-C^+-O(H) bond angles of 115.8° (*trans* to O-H bond) and 121.6° (*cis* to O-H bond) were calculated (33a,33b).

Within the crystalline lattices of 57b-59b additional nearest fluorine or chlorine atom contacts are observed above and/or below the plane of the protonated carbonyl moiety as listed in Table 3-5. In each of 57b and 58b the two fluorine atom contacts to C_1 are located at similar distances from C_1 (57b; F_1-C_1 = $F_{1'}$-C_1 = 3.109(5) Å, 58b; F_4-C_1 = 2.915(5) Å, F_2-C_1 = 3.012(6) Å) on opposite sides of, and approximately perpendicular to, the protonated carbonyl plane (57b; F_1-C_1-O = $F_{1'}$-C_1-O 97.4(2)°, 58b; F_4-C_1-O 92.1(2)°, F_2-C_1-O 89.1(2)°). The orientations of these nearest contacts to C_1 in 57b and 58b, above and below the plane of the protonated carbonyl moiety, are similar to those which have been observed for 46 and 47 (40).

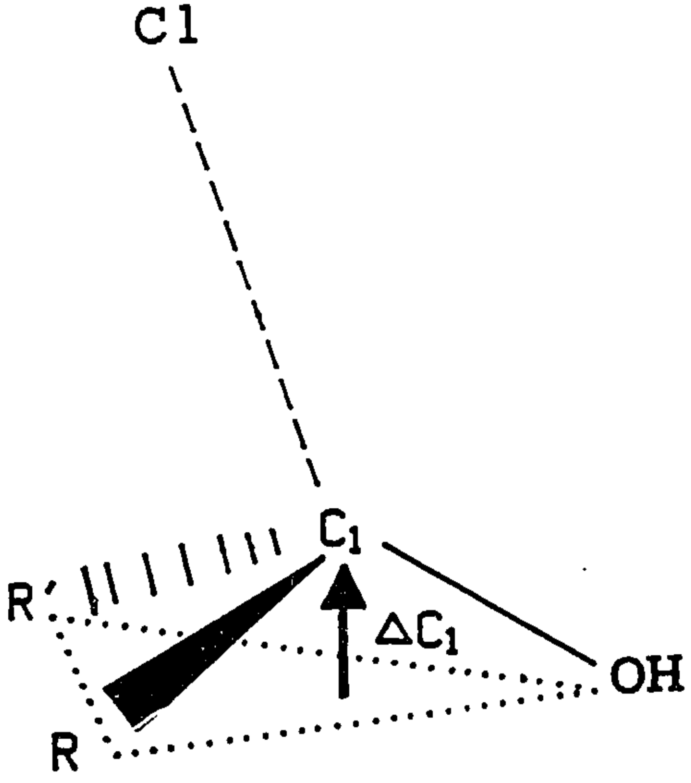
In 59b only one close chlorine atom contact to C_1 is observed, namely Cl_1 at 3.465(7) Å, an internuclear distance significantly shorter than the sum of the Van der Waal radii of neutral chlorine and carbon atoms (3.50 Å) (141). This nearest contact is oriented in a similar manner as those discussed above for 57b and 58b so as to give a Cl_1-C_1-O angle of 84.6(1)°. Cl_4, the second observed nearest contact to C_1 is oriented on the opposite side of the protonated carbonyl plane considerably further removed at an internuclear distance of 3.586(7) Å, a contact distance which is not chemically significant. In addition, Cl_4 is oriented somewhat differently, so as to give a Cl_4-C_1-O angle of only 69.8(1)°.

The one significant Cl..C_1 interaction in 59b gives rise to a non-planar arrangement around the carbonyl carbon atom. C_1 is significantly displaced by 0.027(9) Å from the plane defined by the adjacent atoms O, C_2 and C_5, Plane A in Table 3-5, in the direction of the nearest chlorine atom contact as illustrated in Figure 3-11. Recall that, as discussed in Chapter 1, a similar interaction between a nitrogen atom and a carbonyl group in neutral ketone systems has been shown to lead to increasing non-planarity of the carbonyl carbon atom as the N..C=O internuclear distance decreased (7,9,10). These systems have been used to analyze the structural changes resulting from attack of a nitrogen atom on a neutral carbonyl functionality (9-11). In this context, the nearest Cl..C_1 interaction observed here in 59b can be considered a representative model for a nucleophilic attack on a protonated carbonyl functionality.

3.5 Summary

The crystal structure determinations of 57b-59b described in this chapter have greatly enhanced the range of hydroxy-cyclopropylcarbinyl cations whose structures have been determined. Furthermore, these studies have provided the first direct experimental evidence for the structures of alkyl-substituted hydroxy-cyclopropylcarbinyl cations. Systematic structural analysis of the series of related cations 57b-59b as well as 46-50 as a whole has indicated basic structural similarities indicative of similar bonding patterns and electronic distributions within each of these cations. It has also been shown that the systematic structural changes observed within this series of cations

Figure 3-11. The Deviation From Planarity of C_1 in the Presence of a Significant Nucleophilic Contact



are a function of substitution and variable substituent charge stabilizing ability. The degree of cyclopropyl group structural distortion observed in each case has also been correlated with the degree of involvement of the three-membered ring in electron delocalization and positive charge stabilization.

It would be interesting to extend the work herein described to the x-ray crystal structural determinations of further cyclopropylcarbinyl cations which, relative to those studied here, have less highly charge stabilizing substituents at C_1. The experimentally determined structures of such cations will more directly relate to the calculated structure of the elusive unsubstituted parent cyclopropylcarbinyl cation. However, since these less substituted cyclopropylcarbinyl cations will be more highly unstable and more prone to rearrangement than the cations herein studied, it is expected that further investigation of these systems will prove difficult.

CHAPTER 4

GAS PHASE STRUCTURAL STUDIES OF SUBSTITUTED HYDROXY-CYCLOPROPYLCARBINYL CATION SYSTEMS

The x-ray crystallographic and NMR spectroscopic analyses of the series of substituted hydroxy-cyclopropylcarbinyl cations discussed in Chapter 3 have provided much evidence for the preferred conformations and structures of these cations. The observed changes in bond lengths and angles seen as a function of substitution as well as the observed changes in NMR spectroscopic chemical shifts have suggested varying degrees of positive charge delocalization into the cyclopropyl ring of these cations.

However, systematic geometrical changes and spectroscopic analyses as such provide only indirect and qualitative evidence for variable electronic distributions within these systems. Unfortunately, neither x-ray crystallography nor NMR spectroscopy can be routinely used to calculate quantitative atomic charge populations which are ultimately desired. Furthermore, the crystallographic observation of both the *s-cis* and *s-trans* bisected conformations for substituted hydroxy-cyclopropylcarbinyl cations raises questions of the relative stabilities of these two conformers.

In order to quantify the relative stabilities and energetics of interconversion of the *s-cis* and *s-trans* bisected conformations observed crystallographically for cations <u>57b</u>-<u>59b</u> as well as for the hydroxy-substituted dicyclopropylcarbinyl cation <u>47</u>, a series of semi-empirical AM1 geometry optimizations and heat of formation (ΔH_f) calculations have been performed as a function of cationic conformation. Results of these calculations will be viewed in light of the observed crystallographic conformations of these ions.

Ab initio geometry optimization calculations have also been performed in order to compare the observed crystal structure geometries of the cations <u>57b</u> and <u>58b</u> with their optimized geometries at various basis set levels. The experimentally determined structures of <u>57b</u> and <u>58b</u> will also be compared with the optimized geometries of the parent neutral system <u>57a</u> as well as that of <u>57b..F</u>$^-$ the optimized geometry of <u>57b</u> in the presence of a hydrogen bonded fluoride ion. Quantum mechanical treatment of crystallographic data for <u>57b</u> and <u>58b</u> as well as data obtained from the various geometry optimizations will provide quantitative information regarding the nature of bonding and charge distribution within these systems. Atomic charge populations, bond orders and bond ellipticities calculated from the crystallographic geometries of 57b and 58b will be systematically compared not only to those values obtained from their corresponding optimized geometries but also to those values calculated from the neutral systems 57a and 57b..F^-.

RESULTS

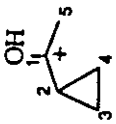
4.1 Semi-Empirical AM1 Calculations

AM1 geometry optimizations were performed on cations 57b, 58b and 47 as well as the parent neutral system 57a. Fractional coordinates corresponding to the crystal structure geometries of the above cations were first converted into cartesian orthogonal coordinates for input into the geometry optimization program AMPAC (154). The cationic systems were each assigned an overall charge of +1. Input parameters for the optimization of 57a were identical to those used for 57b, with the omission of the hydroxyl hydrogen atom and an overall molecular charge of zero. An additional system, 57b..F^- containing a F^- ion hydrogen bonded to the hydroxyl proton of 57b, was also studied in an attempt to mimic the crystalline environment of 57b. The input location of the F^- ion corresponded to the experimentally observed position of the nearest significant fluorine atom (of the counter-anion SbF_6^-) contact to the hydroxyl proton of cation 57b. In this calculation, geometrical parameters involving the O-H(O)-F^- moiety were fixed to values observed in the crystal structure of 57b, and the system was assigned an overall charge of zero. Further details pertaining to the methods used in these calculations are described in the Experimental section, Chapter 5.

In each of the **AM1** calculations, the torsion angle O-C_1-C_2-C_3 was systematically increased in 15° increments from that observed in the corresponding crystal structure. After each incremental change the geometry of the system as a whole was fully re-optimized and ΔH_f for the system was calculated. For each system the torsion angle O-C_1-C_2-C_3 was varied through a full 360°.

The heat of formation, ΔH_f, was plotted versus O-C_1-C_2-C_3 torsion angle for each of the systems 57b, 58b, 47, 57a and 57b..F^- and the resulting rotational coordinate diagrams are shown in Figures 4-1 to 4-5 respectively. Included on these plots are SNOOPI diagrams of the minimum and maximum energy conformations. Bond length data corresponding to the minimum energy conformers of 57b and 58b are listed in Tables 4-1 and 4-3 respectively.

Figure 4-1. AM1 Rotational Coordinate Diagram for 57b



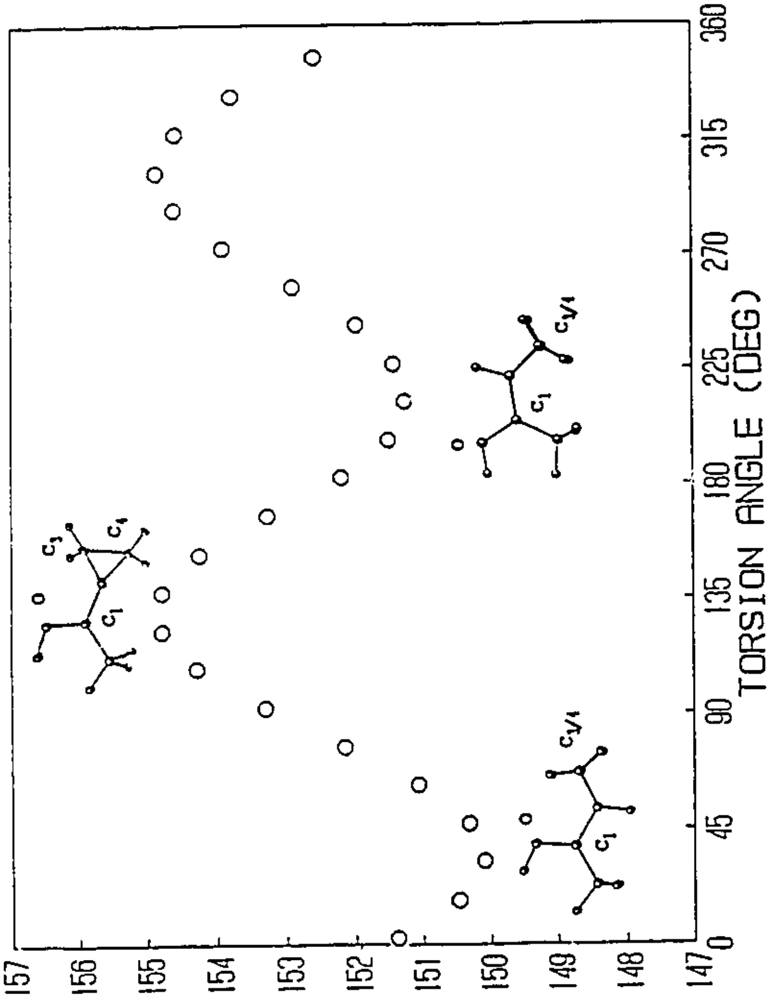
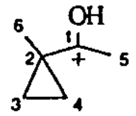


Figure 4-2. AM1 Rotational Coordinate Diagram for 58b



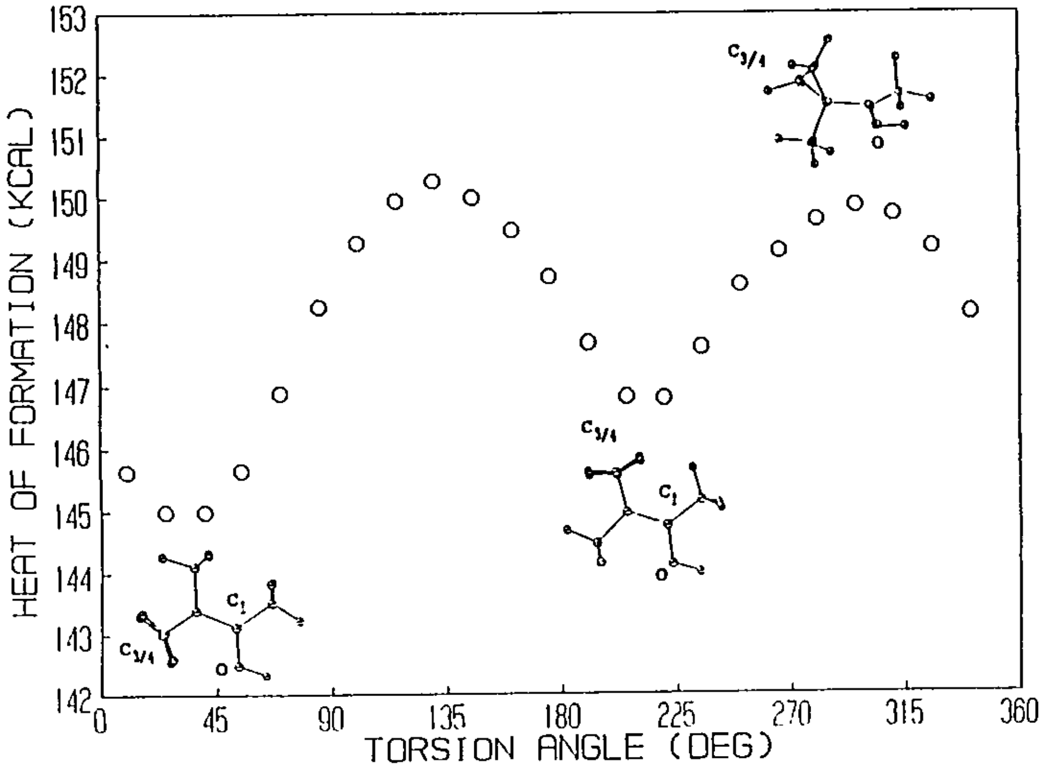
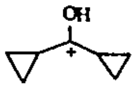


Figure 4-3. AM1 Rotational Coordinate Diagram for 47



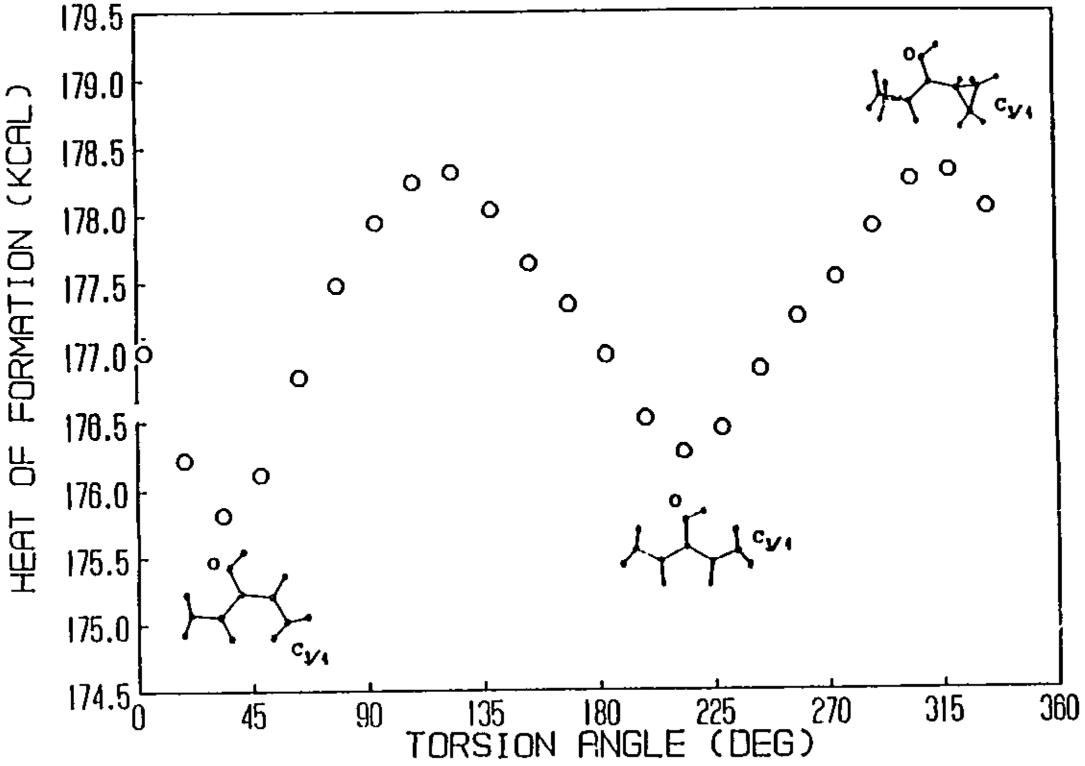
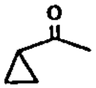


Figure 4-4. <u>AM1 Rotational Coordinate Diagram for 57a</u>



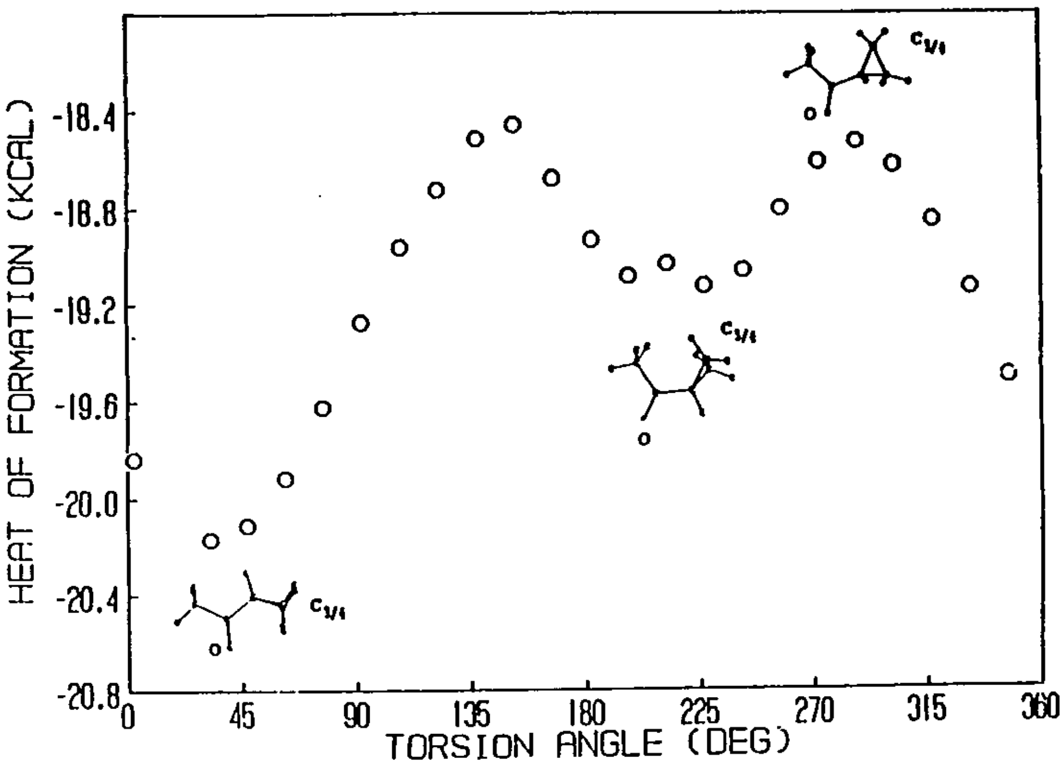
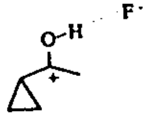
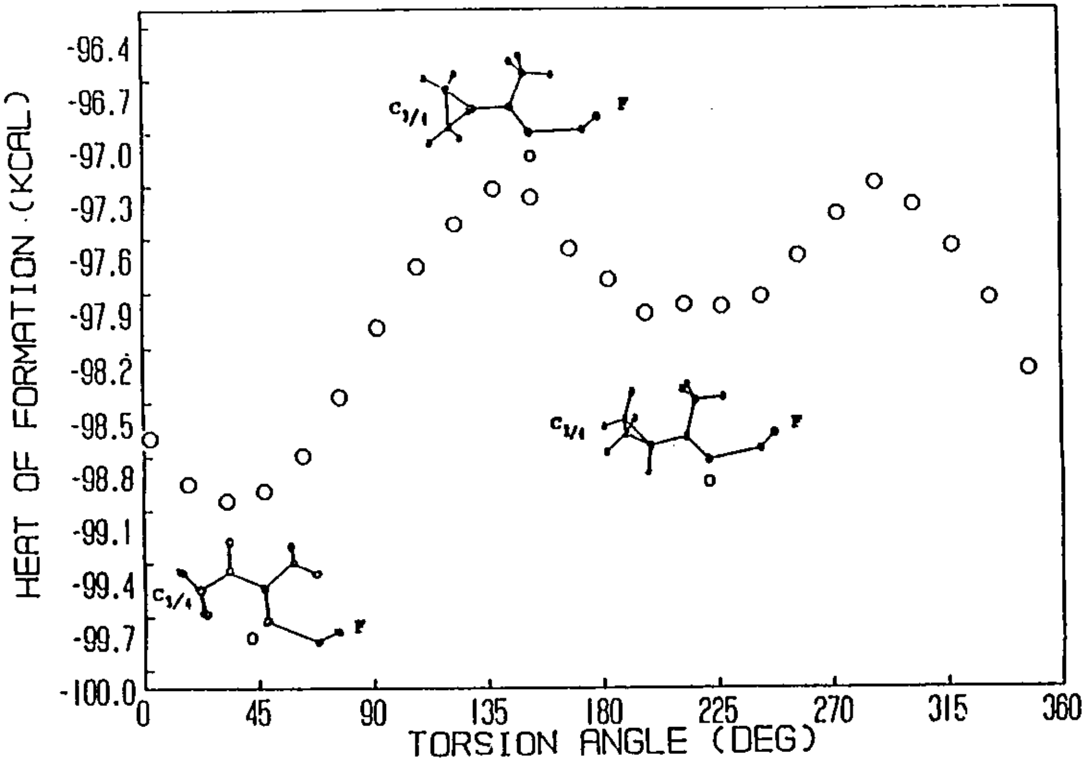


Figure 4-5. AM1 Rotational Coordinate Diagram for 57b..F⁻





4.2 *Ab Initio* GAUSSIAN 86 and PROAIM Calculations

4.2.1 Geometry Optimizations for 57b, 58b, 57b..F$^-$ and 57a

The program GAUSSIAN 86 (155) has been used for the geometry optimizations of the cations 57b and 58b in order that the experimentally observed crystal structure geometries could be compared with high level theoretical results. Two different types of 6-31G** basis set level optimizations were performed on 57b; in one calculation the cation was fully optimized in the absence of any constraints, and in the other, the cationic geometry was optimized holding torsion angles fixed at previously optimized AM1 values. This latter constraint was also used for the optimization of 57b at the 4-31G level. It was intended that this series of geometry optimizations pertaining to system 57b would enable determination of the differences in optimized cationic geometries as a function of basis set level and degree of optimization. Selected bond length and angle data for the various optimized geometries of 57b have been summarized in Tables 4-1 and 4-2. Snoopi plots of the various optimized conformations of 57b are shown in Figure 4-6.

The geometry of 58b has also been optimized at the 6-31G** level. In this calculation the torsion angles involved were fixed to corresponding AM1 optimized values in

Table 4-1. Comparison of Optimized Bond Lengths and Atomic Charge Populations[a] for 57b

			BOND LENGTH (Å) SYSTEM			
BOND	I^b	II^c	III^d	IV^e	V^f	VI^g
O-C(1)	1.256(8)	1.256	1.273	1.272	1.295	1.321
C(1)-C(2)	1.405(10)	1.405	1.422	1.424	1.407	1.441
C(1)-C(5)	1.482(9)	1.482	1.488	1.488	1.483	1.471
C(2)-C(3)	1.516(8)	1.516	1.553	1.543	1.560	1.538
C(2)-C(4)	1.516(8)	1.516	1.553	1.543	1.571	1.539
C(3)-C(4)	1.418(12)	1.418	1.449	1.452	1.452	1.476
O-H(O)	0.826(4)	0.826	0.951	0.951	0.958	0.984
C(2)-H(21)	0.979(7)	1.068	1.072	1.073	1.068	1.113
C(3)-H(31)	0.976(6)	1.071	1.074	1.074	1.070	1.109
C(3)-H(32)	0.876(5)	1.070	1.074	1.074	1.070	1.108
C(4)-H(41)	0.979(6)	1.070	1.074	1.074	1.070	1.109
C(4)-H(42)	0.876(5)	1.070	1.074	1.074	1.070	1.108
C(5)-H(51)	0.989(3)	1.083	1.082	1.082	1.079	1.120
C(5)-H(52)	--	1.084	1.085	1.085	1.084	1.127
C(5)-H(53)	--	1.085	1.086	1.086	1.084	1.127

ATOM		ATOMIC CHARGE POPULATION[a]			
O	-1.323	-1.334	-1.333	-1.331	-1.085
C(1)	0.718	0.746	0.756	0.754	0.687
C(2)	0.016	0.035	0.009	-0.018	-0.124
C(3)	0.723	0.172	0.162	0.161	0.089
C(4)	0.723	0.170	0.162	0.161	0.096
C(5)	0.636	0.223	0.220	0.220	0.059
H(O)	0.690	0.693	0.703	0.704	0.624
H(21)	-0.088	0.023	0.032	0.031	0.076
H(31)	-0.384	0.023	0.035	0.033	0.080
H(32)	-0.101	0.038	0.044	0.042	0.079
H(41)	-0.384	0.024	0.036	0.034	0.081
H(42)	-0.101	0.037	0.044	0.044	0.081
H(51)	-0.240	0.065	0.057	0.059	0.096
H(52)	—	0.067	0.058	0.059	0.095
H(53)	—	0.004	0.007	0.007	0.049
E_{SCF} (a.u.)		-269.17	-269.20	-269.17	-268.78

a) atomic charge densities were calculated with use of a wavefunction generated at the $6\text{-}31G^{**}$ basis set level

b) SYSTEM I: observed crystal structure geometry

c) SYSTEM II: crystal structure geometry with C-H bonds optimized at the $6\text{-}31G^{**}$ level

d) SYSTEM III: fully optimized $6\text{-}31G^{**}$ level geometry

e) SYSTEM IV: optimized $6\text{-}31G^{**}$ level geometry; torsion angles fixed at optimized AM1 values

f) SYSTEM V: optimized 4-31G level geometry; torsion angles fixed at optimized AM1 values

g) SYSTEM VI: optimized AM1 level geometry

Table 4-2. Selected Angles for Optimized Geometries of 57b, 57b..F$^-$, 58b and 57a

	SYSTEM					
		57b				
ANGLE	III^a	IV^b	V^c	57b..F^{-d}	58b ^{e}	57a^f
H(O)-O-C(1)-C(2)	180.00	179.93	179.93	179.93	179.92	--
F-O-C(1)	--	--	--	116.59	--	--
O-C(1)-C(2)-MP(C3,C4)^g	0.17	-0.10	0.29	-0.39	8.33	-1.44
C(2)-C(1)-O	117.92	117.88	117.39	119.41	117.17	121.54
C(5)-C(1)-O	120.65	120.73	120.52	117.17	119.63	121.72
C(2)-C(1)-C(5)	121.44	121.38	122.09	123.42	123.20	116.73
C(1)-C(2)-C(3)	118.84	118.45	118.45	117.83	118.23	117.46
C(1)-C(2)-C(4)	118.92	119.98	120.16	119.46	116.41	118.57
C(3)-C(2)-C(4)	55.62	55.94	55.27	56.91	57.44	58.88
C(2)-C(3)-C(4)	62.19	62.37	62.76	61.66	61.86	60.68
C(2)-C(4)-C(3)	62.19	61.70	61.98	61.43	60.70	60.44
C(6)-C(2)-C(1)	--	--	--	--	116.76	--
C(6)-C(2)-C(3)	--	--	--	--	117.56	--
C(6)-C(2)-C(4)	--	--	--	--	117.25	--
H(21)-C(2)-C(1)	115.26	115.11	115.04	123.75	--	115.48
H(21)-C(2)-C(3)	117.66	117.35	117.13	109.93	--	116.95
H(21)-C(2)-C(4)	117.63	117.74	117.80	110.54	--	117.78

a) SYSTEM III: fully optimized 6-31G** level geometry of 57b

b) SYSTEM IV: optimized 6-31G* level geometry of 57b; torsion angles fixed at optimized AM1 values

c) SYSTEM V: optimized 4-31G level geometry of 57b; torsion angles fixed at optimized AM1 values

d) SYSTEM 57b..F$^-$: 4-31G level optimized geometry of 57b..F$^-$; 57b in the presence of a nearest contact F$^-$ ion fixed as seen in the crystal structure; torsion angles fixed at optimized AM1 values

e) SYSTEM 58b: 6-31G** level optimized geometry of 58b; torsion angles fixed at optimized AM1 values

f) SYSTEM 57a: 6-31G** level optimized geometry of 57a; torsion angles fixed at optimized AM1 values

g) midpoint of the C_3-C_4 bond

Table 4-3. <u>Comparison of Optimized Bond Lengths and Atomic Charge Populations[a] for 58b</u>

	BOND LENGTH (Å)			
		SYSTEM		
BOND	I[b]	II[c]	III[d]	IV[e]
O-C(1)	1.265(8)	1.268	1.273	1.323
C(1)-C(2)	1.461(9)	1.461	1.437	1.447
C(1)-C(5)	1.461(10)	1.461	1.487	1.470
C(2)-C(3)	1.529(10)	1.529	1.526	1.544
C(2)-C(4)	1.545(8)	1.545	1.543	1.549
C(2)-C(6)	1.491(10)	1.491	1.524	1.495
C(3)-C(4)	1.448(9)	1.448	1.475	1.461
O-H(O)	1.136(4)	1.107	0.951	0.984
C(3)-H(31)	1.107(8)	1.074	1.074	1.108
C(3)-H(32)	0.831(7)	1.073	1.074	1.109
C(4)-H(41)	0.921(7)	1.074	1.074	1.107
C(4)-H(42)	0.897(7)	1.073	1.074	1.108
C(5)-H(51)	0.828(8)	1.083	1.084	1.127
C(5)-H(52)	1.075(7)	1.083	1.084	1.127
C(5)-H(53)	0.924(7)	1.082	1.082	1.120
C(6)-H(61)	0.879(8)	1.082	1.081	1.120
C(6)-H(62)	0.928(8)	1.084	1.084	1.118
C(6)-H(63)	1.093(9)	1.084	1.084	1.118
ATOM	ATOMIC CHARGE POPULATION[a]			
O	-1.268	-1.266	-1.331	
C(1)	0.794	0.777	0.749	
C(2)	-0.059	-0.055	-0.047	
C(3)	0.779	0.149	0.126	
C(4)	0.928	0.131	0.105	
C(5)	0.894	0.224	0.220	
C(6)	0.977	0.272	0.248	
H(O)	0.658	0.657	0.702	
H(31)	-0.551	0.037	0.027	
H(32)	-0.066	0.015	0.034	
H(41)	-0.404	0.037	0.026	
H(42)	-0.341	0.020	0.034	
H(51)	-0.463	0.046	0.057	
H(52)	0.083	0.044	0.059	
H(53)	-0.245	0.000	0.005	
H(61)	-0.440	-0.025	-0.013	
H(62)	-0.297	-0.021	-0.041	
H(63)	-0.022	-0.023	-0.039	
E_{SCF} (a.u.)		-308.20	-308.23	

a) atomic charge populations were calculated with use of a wavefunction generated at the $6\text{-}31G^{**}$ basis set level

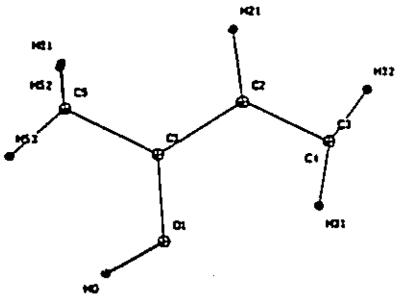
b) SYSTEM I: observed crystal structure geometry

c) SYSTEM II: crystal structure geometry with C-H bonds optimized at the $6\text{-}31G^{**}$ level

d) SYSTEM III: $6\text{-}31G^{**}$ level optimized geometry; torsion angles fixed at AM1 optimized values

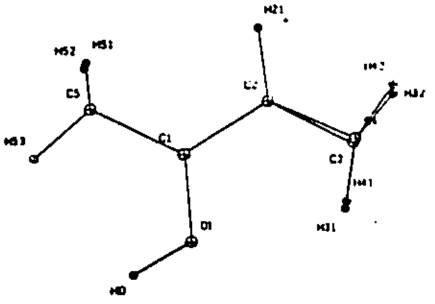
e) SYSTEM IV: optimized AM1 level geometry

Figure 4-6. The Conformations of 57b as Optimized at Various Levels



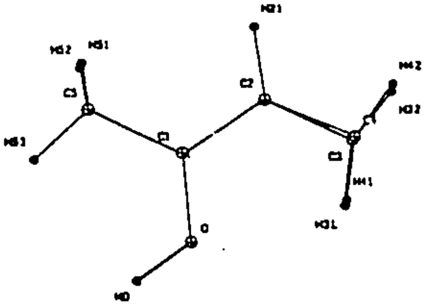
System III

6-31G** Level: Fully Optimized



System IV

6-31G** Level: Torsion Angles Fixed to AM1 values



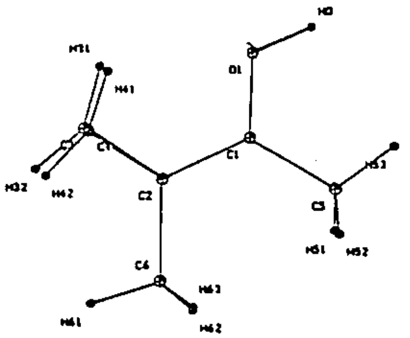
System V

4-31G Level: Torsion Angles Fixed to AM1 values light of the negligible differences observed on comparison of such "partially" and fully optimized geometries of 57b. Tables 4-3 and 4-2 respectively list optimized bond length and angle data for 58b and the optimized conformation of this cation is illustrated in Figure 4-7.

An additional system 57b..F^- was similarly optimized at the 4-31G basis set level in an attempt to model the structural changes within 57b resulting from the crystallographically observed hydrogen bonding interaction between the hydroxyl proton of 57b and a counter-anionic fluorine atom. Resulting optimized bond lengths and angles for 57b..F^- are given in Tables 4-4 and 4-2 respectively and the optimized conformation of this system is shown in Figure 4-7.

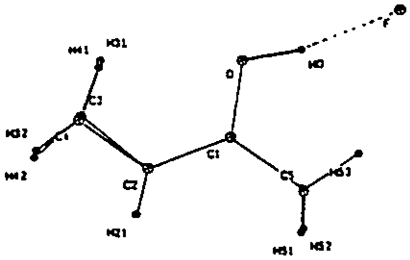
In order to provide a reference for comparison of the optimized geometries of cations 57b and 58b, the parent neutral system 57a was also optimized at the 6-31G** basis set level. Similarly, geometry optimization was performed in the presence of torsion angles fixed at the corresponding AM1 optimized values. Optimized bond length and angle parameters for 57a are given in Tables 4-5 and 4-2 respectively and a plot of the corresponding optimized conformation appears in Figure 4-7.

Figure 4-7. The Optimized Conformations of 58b, 57b..F⁻ and 57a



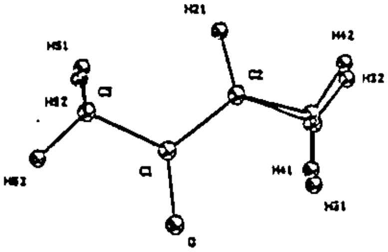
58b: System III

6-31G** Level:
Torsion Angles
Fixed to AM1
Values



57b..F⁻: System III

4-31G Level:
Parameters Involving
F⁻ Fixed to Crystal
Structure Geometry



57a

6-31G** Level:
Torsion Angles
Fixed to AM1
values

Table 4-4. The Effect of an F^- Counterion on Calculated[a] Geometries and Atomic Charge Populations for 57b

BOND	II[b]	V[c]	57b..F^-[d]
		BOND LENGTH (Å) SYSTEM	
O-C(1)	1.256(8)	1.295	1.269
C(1)-C(2)	1.405(10)	1.407	1.430
C(1)-C(5)	1.482(9)	1.483	1.491
C(2)-C(3)	1.516(8)	1.560	1.537
C(2)-C(4)	1.516(8)	1.571	1.540
C(3)-C(4)	1.418(12)	1.452	1.467
O-H(O)	0.826(4)	0.958	0.934
C(2)-H(21)	1.068	1.068	1.068
C(3)-H(31)	1.071	1.070	1.070
C(3)-H(32)	1.070	1.070	1.070
C(4)-H(41)	1.070	1.070	1.070
C(4)-H(42)	1.070	1.070	1.070
C(5)-H(51)	1.083	1.079	1.083
C(5)-H(52)	1.084	1.084	1.083
C(5)-H(53)	1.085	1.084	1.085

ATOM		ATOMIC CHARGE POPULATION	
O	-1.334	-1.085	-1.119
C(1)	0.746	0.687	0.757
C(2)	0.035	-0.124	-0.106
C(3)	0.172	0.089	0.067
C(4)	0.170	0.096	0.069
C(5)	0.223	0.059	0.033
H(O)	0.693	0.624	0.674
H(21)	0.023	0.076	0.043
H(31)	0.023	0.080	0.071
H(32)	0.038	0.079	0.039
H(41)	0.024	0.081	0.067
H(42)	0.037	0.081	0.040
H(51)	0.065	0.096	0.047
H(52)	0.067	0.095	0.049
H(53)	0.004	0.049	0.045

---

a) calculated at the 4-31G basis set level except for system II in which atomic charge populations were calculated with use of the 6-31G** basis set

b) SYSTEM II: crystal structure geometry of 57b with C-H bonds optimized at the 6-31G** level

c) SYSTEM V: 4-31G optimized geometry of 57b; torsion angles were fixed at optimized AM1 values

d) SYSTEM 57b..F^-: 4-31G optimized geometry of 57b..F^-: 57b in the presence of a nearest contact F^- ion fixed as seen in the crystal structure; torsion angles fixed at optimized AM1 values

Table 4-5. Comparison of 6-31G** Optimized Bond Lengths and Atomic Charge Populations for 57b, 58b and 57a

	BOND LENGTH (Å)		
BOND	57b[a]	58b[a]	57a[b]
O-C(1)	1.273	1.273	1.196
C(1)-C(2)	1.422	1.437	1.494
C(1)-C(5)	1.489	1.487	1.511
C(2)-C(3)	1.553	1.526	1.506
C(2)-C(4)	1.553	1.543	1.509
C(2)-C(6)	--	1.524	--
C(3)-C(4)	1.449	1.475	1.470
O-H(O)	0.951	0.951	--
C(2)-H(21)	1.072	--	1.076
C(3)-H(31)	1.074	1.074	1.086
C(3)-H(32)	1.074	1.074	1.086
C(4)-H(41)	1.074	1.074	1.081
C(4)-H(42)	1.074	1.074	1.074
C(5)-H(51)	1.082	1.084	1.076
C(5)-H(52)	1.085	1.084	1.075
C(5)-H(53)	1.086	1.082	1.075
C(6)-H(61)	--	1.081	--
C(6)-H(62)	--	1.084	--
C(6)-H(63)	--	1.084	--

ATOM	ATOMIC CHARGE POPULATION		
O	-1.333	-1.331	-1.367
C(1)	0.756	0.749	1.220
C(2)	0.009	-0.047	-0.031
C(3)	0.162	0.126	0.123
C(4)	0.162	0.105	0.096
C(5)	0.220	0.220	0.186
C(6)	--	0.248	--
H(O)	0.703	0.702	--
H(21)	0.032	--	-0.031
H(31)	0.035	0.027	-0.005
H(32)	0.044	0.034	-0.044
H(41)	0.036	0.026	-0.008
H(42)	0.044	0.034	-0.042
H(51)	0.057	0.057	-0.046
H(52)	0.058	0.059	-0.045
H(53)	0.007	0.005	-0.023
H(61)	--	-0.013	--
H(62)	--	-0.041	--
H(63)	--	-0.039	--

a) fully optimized

b) torsion angles were fixed at optimized AM1 values

4.2.2 Calculation of Atomic Charge Populations, Bond Orders and Bond Ellipticities

GAUSSIAN 86 (155) single point calculations using the high level 6-31G** basis set were performed for the crystal structure geometries of cations 57b and 58b in order to generate the corresponding molecular wavefunctions. These wavefunctions in turn enabled calculation of quantitative atomic charge populations, bond orders and bond ellipticities using the series of programs collectively known as PROAIM (156). Atomic charge populations as calculated from the crystal structure geometries of 57b and 58b are shown in Tables 4-1 and 4-3 respectively.

Upon analysis of atomic charge densities calculated from crystal structure geometries of 57b and 58b, it immediately became apparent of the need to correct crystallographic hydrogen atom positions, which are well known to be subject to a high degree of uncertainty (4). Consequently, hydrogen atom positions for each of 57b and 58b were optimized using GAUSSIAN 86 at the 6-31G** basis set level while holding the remainder of the cationic systems fixed as seen in the corresponding crystal structures. Better representative atomic charge populations were then calculated and results for these calculations are also listed in Tables 4-1 and 4-3 respectively.

One additional single point 4-31G level calculation was performed on the system 57b..F^- in an attempt to model the electronic redistribution within 57b resulting from the presence of the nearest contact fluorine atom seen within the crystal lattice of 57b. Results of charge population analysis for 57b..F^- are given in Table 4-4. Atomic charge populations for each of the optimized systems 57b, 58b, 57b..F^- and 57a have also been calculated. Results of these calculations are listed in Tables 4-1 and 4-3 to 4-5, respectively.

Bond orders (n) for the C-C and C-H bonds contained in the crystal structure geometries of 57b and 58b as well as various optimized systems have also been calculated using equation 4-1, where ρ_B represents the charge density at the bond critical point in question. The constants involved are obtained by a least squares best-fit of bond orders to a standard set of bonds as optimized at the 6-31G*/6-31G* level. The values of ρ_B associated with the bonds analyzed were calculated using the program EXTREME (156). Bond order data for the various systems are presented in Table 4-6.

$$n = e\{\, 6.46\, (\rho_B - 0.252)\, \} \qquad \text{eqn. 4-1}$$

Bond ellipticities (ϵ) have also been calculated for each system studied. These values are presented in Table 4-7. The general equation used for the calculation of

Table 4-6. Calculated C-C and C-H Bond Orders for the Various Systems 57b, 57b..F^-, 58b and 57a

BOND	BOND ORDER[a]					
	SYSTEM 57b			SYSTEM 58b		
	II[b]	III[c]	57b..F^-[d]	II[e]	III[f]	57a[g]
C(2)-C(3)	0.87	0.79	0.72	0.87	0.79	0.94
C(2)-C(4)	0.87	0.79	0.72	0.82	0.81	0.93
C(3)-C(4)	1.34	1.20	0.94	1.19	1.09	1.04
C(1)-C(2)	1.58	1.47	1.20	1.28	1.39	1.20
C(1)-C(5)	1.20	1.18	0.96	1.30	1.18	1.13
C(2)-C(6)	--	--	--	1.12	1.01	--
C(2)-H(21)	1.39	1.37	1.16	--	--	1.32
C(3)-H(31)	1.39	1.37	1.16	1.36	1.37	1.34
C(3)-H(32)	1.39	1.37	1.15	1.36	1.36	1.31
C(4)-H(41)	1.39	1.37	1.16	1.36	1.37	1.34
C(4)-H(42)	1.39	1.37	1.15	1.36	1.37	1.32
C(5)-H(51)	1.28	1.30	1.11	1.30	1.29	1.23
C(5)-H(52)	1.27	1.26	1.05	1.27	1.26	1.23
C(5)-H(53)	1.27	1.26	1.05	1.26	1.26	1.29
C(6)-H(61)	--	--	--	1.29	1.30	--
C(6)-H(62)	--	--	--	1.29	1.27	--
C(6)-H(63)	--	--	--	1.28	1.27	--

a) bond order (N) = exp $\{A(p_B - B)\}$ where p_B is the calculated charge density at the bond critical point and A=6.46, B=0.252 as determined by least squares best-fit to a standard set of bonds, calculated at the $6\text{-}31G^{*}/6\text{-}31G^{*}$ level

b) SYSTEM II: crystal structure geometry of 57b with $6\text{-}31G^{**}$ optimized C-H bonds; wavefunction generated at the $6\text{-}31G^{**}$ level

c) SYSTEM III: fully optimized $6\text{-}31G^{**}$ geometry of 57b

d) 57b..F^-: optimized 4-31G geometry of 57b with torsion angles fixed at optimized AM1 values, in the presence of a closest contact F^- ion fixed as seen in the crystal structure

e) SYSTEM II: crystal structure geometry of 58b with $6\text{-}31G^{**}$ optimized C-H bonds; wavefunction generated at the $6\text{-}31G^{**}$ level

f) SYSTEM III: optimized $6\text{-}31G^{**}$ geometry of 58b with torsion angles fixed at optimized AM1 values

g) 57a: optimized $6\text{-}31G^{**}$ geometry of 57a; torsion angles fixed at AM1 optimized values

Table 4-7. Calculated Ellipticity of Bonds for the Various Systems 57b, 57b..F^-, 58b and 57a

	ELLIPTICITY					
	SYSTEM 57b			SYSTEM 58b		
BOND	II[a]	III[b]	57b..F^-[c]	II[d]	III[e]	57a[f]
C(2)-C(3)	1.185	0.947	0.404	0.757	0.707	0.581
C(2)-C(4)	1.188	1.104	0.423	0.948	0.917	0.606
C(3)-C(4)	0.283	0.265	0.137	0.292	0.320	0.426
O-C(1)	0.211	0.221	0.311	0.200	0.224	0.055
C(1)-C(2)	0.233	0.215	0.082	0.188	0.204	0.090
C(1)-C(5)	0.044	0.048	0.005	0.044	0.048	0.038
C(2)-C(6)	--	--	--	0.052	0.027	--
O-H(O)	0.012	0.012	0.011	0.014	0.012	--
C(2)-H(21)	0.001	0.051	0.047	--	--	0.043
C(3)-H(31)	0.047	0.021	0.018	0.021	0.023	0.030
C(3)-H(32)	0.098	0.020	0.020	0.020	0.021	0.028
C(4)-H(41)	0.047	0.022	0.019	0.022	0.023	0.030
C(4)-H(42)	0.098	0.021	0.021	0.022	0.022	0.025
C(5)-H(51)	0.059	0.018	0.023	0.019	0.017	0.010
C(5)-H(52)	0.053	0.021	0.037	0.023	0.022	0.009
C(5)-H(53)	0.053	0.021	0.037	0.024	0.022	0.006
C(6)-H(61)	--	--	--	0.016	0.015	--
C(6)-H(62)	--	--	--	0.018	0.021	--
C(6)-H(63)	--	--	--	0.018	0.020	--

a) SYSTEM II: crystal structure geometry of 57b with 6-31G** optimized C-H bonds

b) SYSTEM III: fully optimized 6-31G** geometry of 57b

c) 57b..F^-: optimized 4-31G geometry of 57b with torsion angles fixed at optimized AM1 values, in the presence of a closest contact F^- ion fixed as seen in the crystal structure

d) SYSTEM II: crystal structure geometry of 58b with 6-31G** optimized C-H bonds

e) SYSTEM III: optimized 6-31G** geometry of 58b with torsion angles fixed at optimized AM1 values

f) 57a: optimized 6-31G** geometry of 57a; torsion angles fixed to AM1 optimized values ellipticities is shown in equation 4-2. λ_1 and λ_2 correspond to the two negative curvatures of ρ at the bond critical point, with λ_2 being the curvature of smallest magnitude (157).

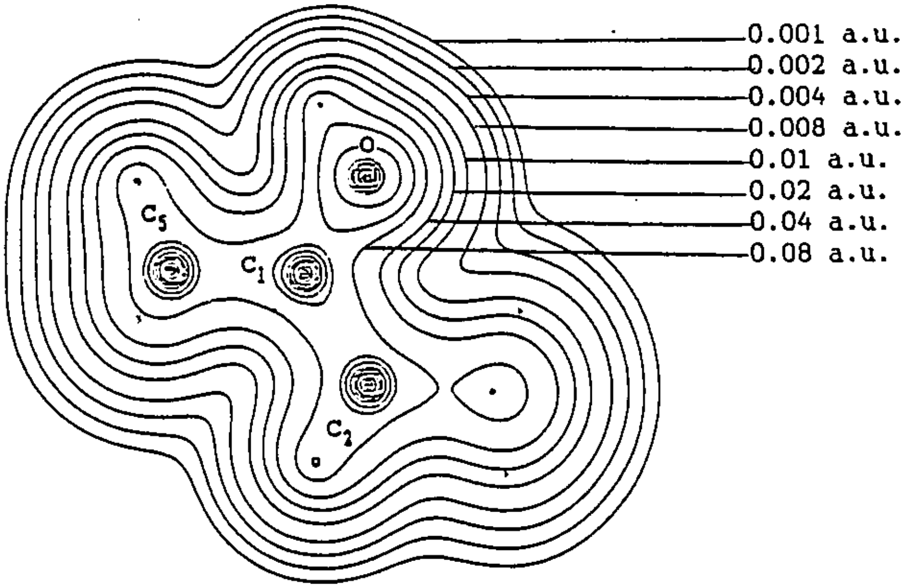
$$\epsilon = (\lambda_1/\lambda_2 - 1) \qquad \text{eqn. 4-2}$$

4.2.3 Charge Density Contour Plots for 57b, 58b and 57a

Charge density contour plots for the highest level 6-31G** optimized geometries of 57b, 58b and 57a have also been obtained. In each case the plane of the O-C_1-C_2 moiety and the corresponding perpendicular plane passing through the C_1-O bond were plotted, as shown in Figures 4-8 to 4-10 respectively. These plots map out the electronic distribution over each of the systems 57b, 58b and 57a.

Figure 4-8. Electron Density Contour Maps for the 6-31G** Basis Set Level Optimized Geometry of 57b

a. Plane of O, C(1) and C(2) Atoms



b. Perpendicular Plane Passing Through O and C(1) Atoms

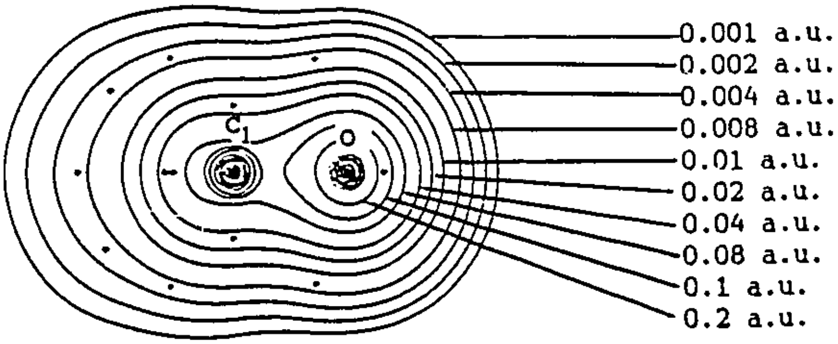
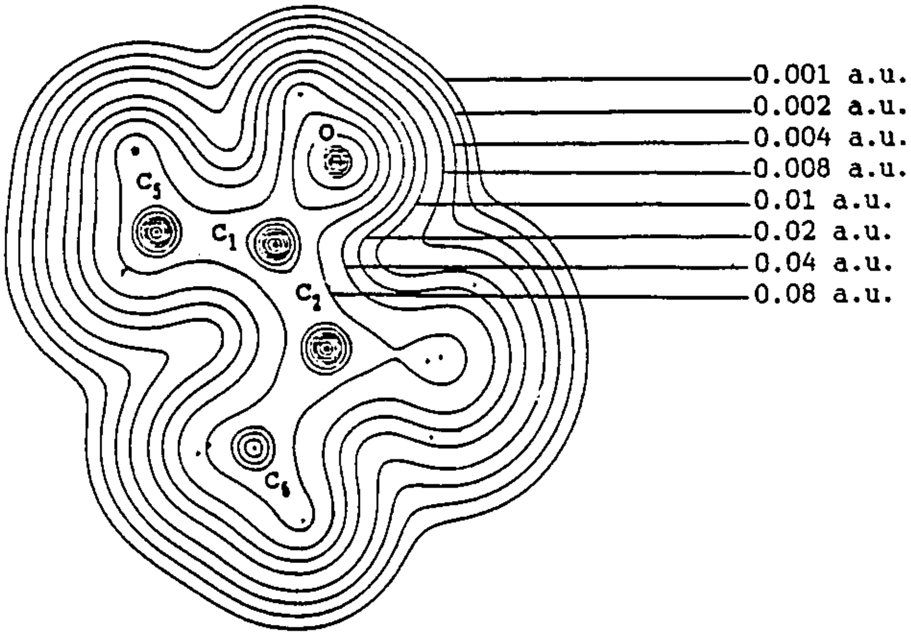


Figure 4-9. Electron Density Contour Maps for the 6-31G** Basis Set Level Optimized Geometry of 58b

a. Plane of O, C(1) and C(2) Atoms



b. Perpendicular Plane Passing Through O and C(1) Atoms

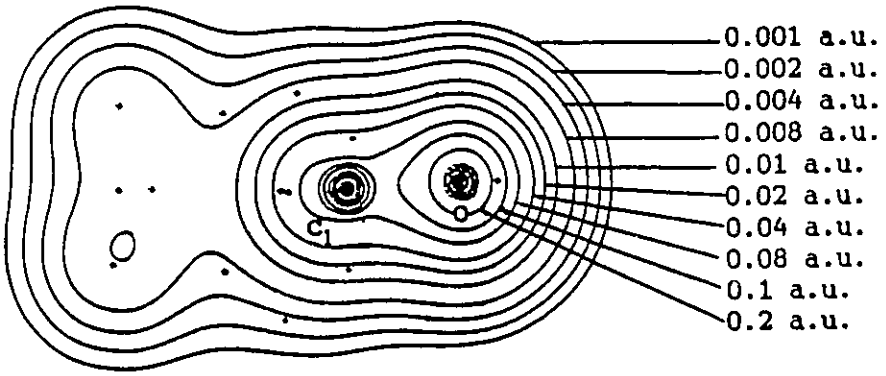
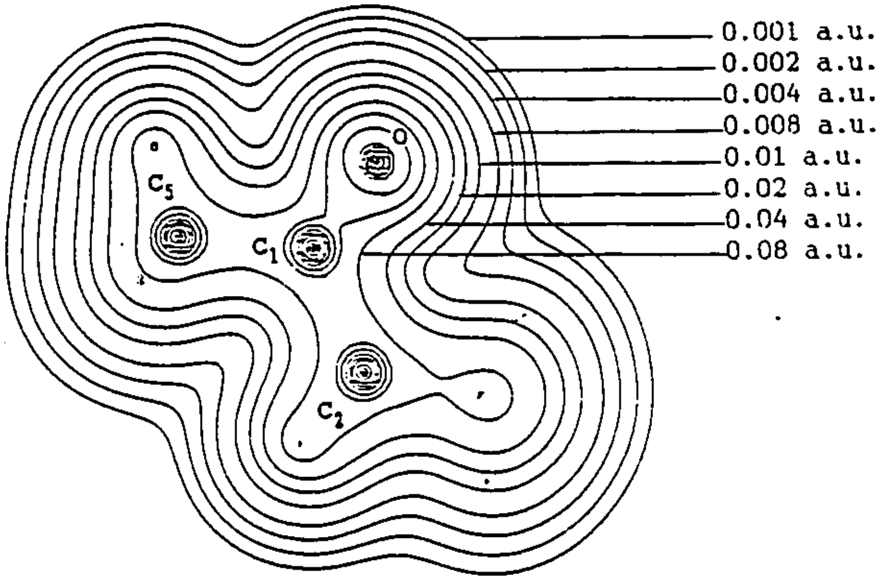
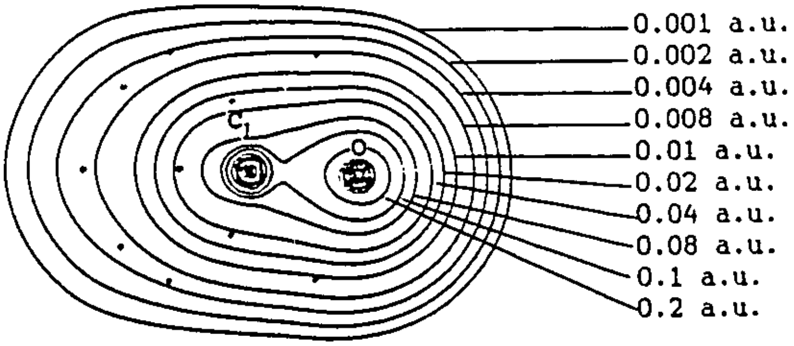


Figure 4-10. Electron Density Contour Maps for the 6-31G** Basis Set Level Optimized Geometry of 57a

a. Plane of O, C(1) and C(2) Atoms



b. Perpendicular Plane Passing Through O and C(1) Atoms



DISCUSSION

4.3 Comparison of AM1 Optimized Geometries and ΔH_f Calculations Systems 57b, 58b, 47, 57b..F$^-$ and 57a

Analysis of the AM1 optimized geometries and calculated ΔH_f values for 57b, 58b and 47 as a function of $O-C_1-C_2-C_3$ torsion angle reveals several consistent trends within this series of cations. In each cyclopropyicarbinyl system a sine wave-type curve is obtained on plotting calculated heat of formation for the optimized structure versus $O-C_1-C_2-C_3$ torsion angle, Figures 4-1 to 4-3. Two energy minima, corresponding to the *s-cis* and *s-trans* bisected geometries of the cyclopropyl ring with respect to the protonated carbonyl moiety, are situated 180° apart. In these bisected geometries maximum positive charge conjugation between the bent σ-type vicinal cyclopropyl C-C bonds and the formally vacant p-orbital at C_1 can occur, thereby stabilizing the system as a whole. The *s-cis* and *s-trans* bisected conformational minima are separated by rotational barriers through "perpendicular" conformations in which the plane of the cyclopropyl ring is perpendicular to the formal cationic center at C_1. In such a conformation no stabilization of the positive charge by the cyclopropyl group can occur (115,116).

In each of 57b, 58b, 57a and 57b..F$^-$ the *s-cis* bisected geometry of the cyclopropyl ring with respect to the carbonyl group is calculated to be the lowest energy conformation, Figures 4-1, 4-2, 4-4 and 4-5. As such, one cyclopropyl ring in 47 was fixed in a similar *s-cis* conformation prior to acquisition of the rotational coordinate diagram for this cation. The second cyclopropyl ring in 47 is shown to preferentially adopt the corresponding *s-trans* bisected geometry, Figure 4-3.

For each of the cationic systems studied the minimum energy conformation obtained contains an H(O)-O bond which is oriented *trans* with respect to the C_1-C_2 bond and the *s-cis* bisected cyclopropyl group. This favoured geometry can be attributed to reduced steric interactions between the relatively bulky hydrogen bonded grouping and the cyclopropyl ring in these systems.

In the cationic systems 57b and 58b, each of which contains a single cyclopropyl group, the *s-cis* conformation of the cyclopropyl group with respect to the carbonyl functionality is respectively 1.2 and 1.8 kcal mol^{-1} more stable than the corresponding *s-trans* form, Table 4-8. Minimum barriers to rotation about the C_1-C_2 bond from the *s-cis* bisected conformations are calculated to be 4.7 and 4.9 kcal mol^{-1} respectively. When compared to 57b, the more sterically hindered α-methyl-substituted cyclopropyl ring of

Table 4-8. AM1 Calculated Relative Energies for the *s-cis* and *s-trans* Bisected Geometries of 57b, 58b, 47, 57a and 57b..F$^-$

COMPOUND	Relative Energy (kcal mol^{-1}) *s-cis*	Relative Energy (kcal mol^{-1}) *s-trans*	Rotational Barrier from *s-cis* Form (kcal mol^{-1})	Rotational Barrier from *s-trans* Form (kcal mol^{-1})
57b	0	1.2	4.7	3.5
58b	0	1.8	4.9	3.1
47	0	0.45	2.5[a]	2.05[b]
57a	0	1.0	1.7	0.7
57b..F$^-$	0	1.0	1.8	0.8

a) minimum rotational barrier from *s-cis,s-trans* form
b) minimum rotational barrier from *s-cis,s-cis* form

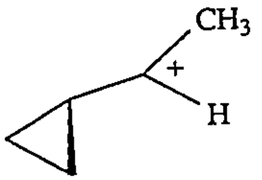
58b leads to relatively greater *s-cis* conformational stability and slightly higher rotational barriers from the *s-cis* form. Conversely, the presence of such α-methyl cyclopropyl substitution leads to a lower barrier to rotation from the *s-trans* conformation (3.1 kcal mol^{-1}) in 58b when compared to that in 57b (3.5 kcal mol^{-1}). Overall, the small activation barriers to rotation about the C_1-C_2 bond herein calculated for 57b and 58b can be used to explain the inability to detect by NMR spectroscopy a single conformer at low temperature, as discussed in Chapter 3.

Rotational coordinate diagrams similar to those obtained for 57b and 58b have been previously reported for the cationic systems 20-22 (85,99,121,158). In the unsymmetrically substituted secondary ion 21, as seen here for 57b, the *s-trans* bisected orientation of the methyl substituent with respect to the cyclopropyl ring was calculated at the STO-3G level to be more stable (by 2.2 kcal mol^{-1}) than the alternative *s-cis* orientation, Figure 4-11 (99). This observation was accounted for in terms of the increased steric requirements of the methyl group when compared to that of the hydrogen atom substituents at C_1 in 21.

Within the series of ions 20-22, the barrier to rotation about the C_1-C_2 bond has been shown to decrease as alkyl substituents are added to C_1 (99). For 20, an energy

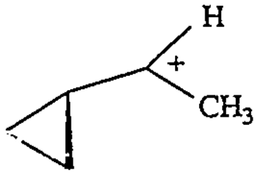
Figure 4-11. The *s-trans* and *s-cis* Bisected Geometries of 21 (99)

RELATIVE ENERGY
(kcal mol^{-1})



0.0

Methyl Group *s-trans* to
Bisected Cyclopropyl Group



2.2

Methyl Group *s-cis* to
Bisected Cyclopropyl Group

barrier of 25.7 kcal mol^{-1} has been calculated at the STO-3G level (85). At the higher MP4SDTQ/6-31G*//MP2(FULL)/6-31G* level of theory this barrier to rotation in 20 has been found to be greater than 35 kcal mol^{-1} (85). Corresponding rotational barriers for 21 have been calculated at the STO-3G and 4-31G basis set levels to be 23.0 and 26.1 kcal mol^{-1} respectively (99). A much lower rotational barrier of 15.0 kcal mol^{-1} has been calculated for 22 at the 4-31G level of theory (99). A similar value of 13.7 ± 0.4 kcal mol^{-1} has been measured for 22 by NMR spectroscopic techniques (87).

It appears that as cyclopropyl group participation in positive charge stabilization increases, the barrier to rotation about the C_1-C_2 bond in these cyclopropylcarbinyl cation systems also increases. As such, the relative rotational barriers from the *s-cis* bisected conformations herein calculated for 57b and 58b can be taken as indicative of similar extents of cyclopropyl group positive charge stabilization in each case.

However, recall that crystallographic analyses of 57b and 58b have indicated that 57b exists in the *s-cis* bisected conformation whereas 58b exists in the corresponding *s-trans* geometry (Chapter 3). As such, it may be more informative to compare the rotational energy barrier calculated to exist from the *s-cis* bisected conformation of

<u>57b</u> (4.7 kcal mol^{-1}) with that calculated to exist from the corresponding *s-trans* geometry of <u>58b</u> (3.1 kcal mol^{-1}). These relative rotational barriers suggest that the cyclopropyl ring in the crystallographically observed conformation of <u>57b</u> participates in positive charge stabilization to a larger extent than does that in <u>58b</u>. This conclusion is in agreement with that made earlier in Chapter 3 on the basis of C_1-C_2 and cyclopropyl group structural distortions observed within each of these cations.

The *s-cis,s-trans* bisected conformation of <u>47</u> is calculated to be marginally (0.45 kcal mol^{-1}) more stable than the corresponding *s-cis,s-cis* conformer. Relative to the rotational barriers calculated for either <u>57b</u> or <u>58b</u>, the barrier to rotation about the C_1-C_2 bond from this minimum energy conformation of <u>47</u> is reduced to 2.05 kcal mol^{-1}. It appears that effective positive charge stabilization by the second (fixed) cyclopropyl ring upon rotation about the C_1-C_2 bond in this cation accounts for these observations.

The rotational coordinate diagrams obtained for the neutral systems <u>57b..F</u>$^-$ and <u>57a</u> are qualitatively very similar. In both cases the *s-cis* bisected geometries are calculated to be 1.0 kcal mol^{-1} more stable than the corresponding *s-trans* conformations. Additionally, in each case the C_1–C_2 rotational barriers from the minimum energy conformation are reduced considerably (to 1.7 and 1.8 kcal mol^{-1} respectively for 57a and 57b..F) when compared to those obtained for 57b and 58b. Extremely low barriers to rotation from the *s-trans* bisected geometries (0.7 and 0.8 kcal mol^{-1} respectively) are also obtained. The small C_1–C_2 rotational barriers calculated here for 57a and 57b..F$^-$ when compared to those obtained for the cations studied suggest a weaker cyclopropyl group conjugative interaction with C_1 in both of these neutral systems. It further appears that the fluoride ion hydrogen-bonding contact present in 57b..F$^-$ considerably depletes the positive charge available for delocalization within cation 57b.

Although the **AM1** minimum energy conformations for 57b and 47 calculated here agree well with the crystallographic conformations of these cations, as previously noted the *s-cis* bisected conformation of 58b is calculated to be 1.8 kcal mol^{-1} more stable than the corresponding *s-trans* bisected conformer which is observed crystallographically. Furthermore, the **AM1** optimized bond length data do not correlate well with experimentally determined data, as shown in Tables 4-1 and 4-3 respectively for systems 57b and 58b. In order to achieve better agreement between such theoretical and experimental values a series of high level *ab initio* geometry optimizations have been performed.

4.4 Comparison of GAUSSIAN 86 Optimized Conformations and Geometries and PROAIM Atomic Charge Populations

4.4.1 The Conformations and Energies of 57b, 58b, 57b..F$^-$ and 57a as Optimized at Various Levels

As is illustrated in Figures 4-6 and 4-7, the optimized conformations of 57b, 58b, 57b..F$^-$ and 57a at the 6-31G** and 4-31G basis set levels both in the presence and absence of torsion angle constraints are nearly identical. The 6-31G** optimized torsion angle O-C_1-C_2-midpoint(C_3-C_4) of 0.17° obtained for 57b is similar to the corresponding AM1 optimized values in each of 57b, 58b, 57b..F$^-$ and 57a, Table 4-2. These values which approach 0° indicate a preference for the *s-cis* bisected (or nearly bisected) conformation of the cyclopropyl ring with respect to the C_1-O bond in each system. The hydroxyl proton in the 6-31G** optimized system 57b is oriented *trans* to the C_1-C_2 bond, so as to give a H(O)-O-C_1-C_2 torsion angle of 180°. Similar H(O)-O-C_1-C_2 torsion angles have been calculated at the AM1 level for the other systems studied, Table 4-2.

The minimum SCF energies obtained from the various optimizations involving 57b are similar, however, the lowest energy structure is that obtained using 6-31G** basis set level full optimization, as denoted by System III, Table 4-1. As such, the quantitative results obtained from this highest level geometry optimization of 57b can be used as a reference point for comparison of the adequacy of the corresponding results of lower level optimizations of 57b which are also listed in Table 4-1.

The various bond lengths and angles obtained from the two 6-31G** basis set level optimizations of 57b in the absence and presence of torsion angle constraints are essentially identical, Tables 4-1 and 4-2. This observation suggests that adequate preliminary torsion angle optimizations have been achieved at the semi-empirical AM1 level. Therefore, for the purpose of conserving computing time, it is suggested that future calculations involving full-scale *ab initio* geometry optimizations of cyclopropylcarbinyl cations could best be performed in the presence of such torsion angle constraints.

As is evident from the data given in Tables 4-1 and 4-2, the bond length and angle values obtained for 57b from the lower 4-31G basis set level calculation are quite different from those obtained at the higher 6-31G** level. Owing to the lower total energy calculated for the 6-31G** versus 4-31G level optimized geometry of 57b, it is thus further suggested that if quantitative rather than qualitative bond length and angle data are required from ab initio geometry optimizations of related cationic systems, calculations are better performed at the 6-31G** basis set level.

4.4.2 Comparison of Optimized Conformations and Geometries for 57b, 58b, 57b..F⁻ and 57a with Crystallographic Results for 57b and 58b

Comparison of the optimized geometries of 57b, 58b, 57b..F⁻ and 57a and corresponding electronic distributions with crystallographic results for 57b and 58b should enable determination of the affect of crystalline environment on the experimentally observed conformations and geometries of 57b and 58b. For the purpose of such a comparison, the results of the highest level calculations performed are of primary interest.

It should be noted that the theoretically calculated and experimentally observed bond lengths and angles involving hydrogen atoms in 57b and 58b, respectively, are quite different, Tables 4-1 and 4-3. It is well known that hydrogen atom positions cannot be determined with great precision using x-ray diffraction methods (4). As such, the crystallographic hydrogen atom positions have been optimized at the 6-31G** level in order to facilitate comparison of experimentally and theoretically determined structures and atomic charge populations for 57b and 58b, Tables 4-1 and 4-3 respectively.

As shown by the data given in Table 4-9, neglecting the position of H_{21}, the 6-31G** fully optimized conformation of 57b is essentially identical to that experimentally observed in the crystalline state. In each case the *s-cis* bisected conformation of the cyclopropyl ring with respect to the carbonyl bond is seen, as is the *trans* orientation of the H(O)-O bond with respect to the C_1-C_2 bond, as indicated by the respective O-C_1-C_2-Midpoint(C_3-C_4) torsion angles of approximately 0° and the H(O)-O-C_1-C_2 torsion angles of 180°.

The trends in C-O and C-C bond length and angle distortions observed crystallographically for 57b are, in general, reproduced theoretically. Relative to the optimized structure of the parent neutral system 57a, both the optimized and crystal structures of 57b contain considerably elongated C_1-O bonds and significantly contracted C_1-C_2 and C_1-C_5 bonds, Table 4-5. Systematic cyclopropyl bond length and angle distortions as seen in the crystal structure of 57b are also calculated. Associated with these bond length distortions are considerably higher atomic positive charge populations at the vicinal cyclopropyl carbon atoms C_3 and C_4 in the optimized and crystal structures of 57b when compared to the corresponding values in the optimized structure of 57a, Tables 4-1 and 4-5.

However, relatively large differences are seen on comparison of the calculated and experimental bond angles

Table 4-9. Comparison of Crystal Structural and Optimized Angles Within 57b, 58b and 57a

ANGLE	ANGLE (°) SYSTEM 57b I[a]	 III[b]	 SYSTEM 58b I[c]	 III[d]	 57a[e]
H(O)-O-C(1)-C(2)	180.0	180.00	179.9	179.92	--
O-C(1)-C(2)-MP(C3,C4)	0.0	0.17	-173.5	8.23	-1.44
C(2)-C(1)-O	116.5	117.92	115.0	117.17	121.54
C(5)-C(1)-O	120.9	120.65	120.4	119.63	121.72
C(2)-C(1)-C(5)	122.6	121.44	124.6	123.20	116.73
C(1)-C(2)-C(3)	118.8	118.84	116.0	118.23	117.46
C(1)-C(2)-C(4)	118.8	118.92	113.8	116.41	118.57
C(3)-C(2)-C(4)	55.8	55.62	56.2	57.44	58.88
C(2)-C(3)-C(4)	62.1	62.19	62.5	61.86	60.68
C(2)-C(4)-C(3)	62.1	62.19	61.3	60.70	60.44
C(6)-C(2)-C(1)	--	--	117.7	116.76	--
C(6)-C(2)-C(3)	--	--	119.7	117.56	--
C(6)-C(2)-C(4)	--	--	119.0	117.25	--
H(21)-C(2)-C(1)	84.2	115.26	--	--	115.48
H(21)-C(2)-C(3)	141.8	117.66	--	--	116.95
H(21)-C(2)-C(4)	141.8	117.63	--	--	117.78

a) SYSTEM I: crystal structure geometry of 57b
b) SYSTEM III: fully optimized $6\text{-}31G^{**}$ geometry of 57b
c) SYSTEM I: crystal structure geometry of 58b
d) SYSTEM III: optimized $6\text{-}31G^{**}$ geometry of 58b with torsion angles fixed at optimized AM1 values
e) 57a: optimized $6\text{-}31G^{**}$ geometry of 57a; torsion angles fixed at optimized AM1 values

about the carbonyl carbon atom C_1 in <u>57b</u>. As mentioned in Chapter 3, the presence of an anionic atom hydrogen bonded to the hydroxyl proton of <u>57b</u>, <u>58b</u> and <u>59b</u>, as observed within each of the corresponding crystal lattices, appears to effect distortion of the geometry about the carbonyl carbon atom, C_1. Indeed, in <u>57b</u> the crystallographic C_2-C_1-C_5 angle of 122.6° appears larger and the corresponding C_2-C_1-O angle (which is *anti* to the nearest fluorine atom-hydroxyl proton contact) of 116.5° appears smaller than those angles theoretically calculated for <u>57b</u>. However, the maximum deviation of 1.4° between calculated and experimental C_2-C_1-O bond angles is not statistically significant (difference 2.3σ) in consideration of the errors associated with crystallographic determination of these angles (0.6°). These results suggest that the affect of crystalline environment on the structure of cation <u>57b</u> is at most weak.

As a result of the errors associated with the crystallographic determination of bond lengths of these ions, the only significant differences between calculated and experimental bond lengths for <u>57b</u> occur for the two vicinal cyclopropyl bonds C_2-C_3 and C_2-C_4 (differences respectively 4.6σ). Calculations also appear to underestimate the degree of distal C_3-C_4 bond shortening observed in the crystal structure of <u>57b</u> (difference 2.6σ).

Indeed the 1.516(8) Å vicinal bond lengths in 57b observed crystallographically are surprisingly short in consideration of the extremely contracted distal C_3-C_4 bond length (1.418(12) Å) also observed. Although the magnitude of errors associated with individual atomic charge populations are not fully known, comparison of the atomic charge populations at C_1, C_2, C_3 and C_4 calculated for 57b from experimental and theoretical geometries (Table 4-1) further suggests that theory slightly underestimates the degree of cyclopropyl group participation in positive charge stabilization in this system.

Comparison of the 4-31G level optimized bond lengths, angles and atomic charge populations for 57b..F^- with crystallographic results for 57b (Tables 4-2 and 4-4) indicates that this system is not a good model for the interaction of the fluorine atom and hydroxyl proton of 57b seen crystallographically. System 57b..F^- severely underestimates the degree of bond distortion and charge delocalization seen in the crystal structure of 57b. Indeed, the structural data obtained from the optimization of 57b..F^- approach those calculated for the parent neutral system 57a, Tables 4-2, 4-4 and 4-5. Coupled with the less severe cyclopropyl bond length and angle distortions away from D_{3h} symmetry calculated for 57b..F^- relative to 57b are very small average positive charge populations of 0.068

which are calculated to reside at both C_3 and C_4 in 57b..F^-. Overall, these observations can be attributed to the charge stabilizing ability of the F^- ion, having a full -1 charge, and the resultant decreased positive charge available for delocalization over the carbon and oxygen atom framework of this system. Perhaps an improved model for 57b..F^- for simulation of this hydrogen bonding interaction observed within the crystal lattice of 57b would involve a similar placement of a fluoride ion having a fractional, rather than a full -1, negative charge.

Nearly bisected conformations in which the hydroxyl proton adopts a *trans* orientation with respect to the cyclopropyl ring about the C_1-C_2 bond have been both calculated and observed for 58b. This is shown by the O-C_1-C_2-Midpoint(C_3,C_4) torsion angles of approximately 0° or ±180° and by the H(O)-O-C_1-C_2 torsion angles very close to 180°, Table 4-9. However, while theory, both at the *ab initio* and semi-empirical levels, calculates the approximate *s-cis* bisected (O-C_1-C_2-Midpoint(C_3,C_4) torsion angle of 8.23°) conformer to be the more stable conformation of 58b, the *s-trans* conformer (O-C_1-C_2-Midpoint(C_3,C_4) torsion angle of -173.5°) has been observed by x-ray crystallography. The crystal packing of 58b could possibly account for this observed preference in the solid state.

Comparison of optimized and experimental bond angles for 58b are not as meaningful owing to the different bisected conformations involved. However, trends in geometrical parameters can be analyzed. As seen on comparison of theoretical and experimental results for 57b, the systematic bond length and angle distortions observed within the crystal structure of 58b are in general reproduced theoretically, Tables 4-3 and 4-9.

However, as in system 57b, theory appears to underestimate the degree of cyclopropyl group participation in the overall stabilization of 58b. The distal cyclopropyl C_3-C_4 bond length of 1.448(9) Å observed within the crystal structure of 58b is significantly shorter (difference 3.0σ) than the corresponding optimized value of 1.475 Å. Coupled with this shorter C_3-C_4 bond length, larger atomic charge populations on C_3 and C_4 (0.149 and 0.131, respectively) are calculated from the crystal structure geometry of 58b. For comparison, atomic charge populations of 0.126 and 0.105, respectively are obtained for C_3 and C_4 in the theoretically optimized geometry of 58b, Table 4-3.

A relatively large discrepancy exists between calculated and observed C_1-C_2-C_3 and C_1-C_2-C_4 angles in 58b, Table 4-9. These angles calculated (118.2° and 116.4°) are significantly larger than those observed within the crystal structure of 58b (116.0(6)° and 113.8(6)°) (differences 3.7σ and 4.3σ, respectively). It appears that theory overestimates the extent of flattening about C_2 observed crystallographically in 58b.

In both the calculated and observed structures of 58b, a high degree of positive charge (0.248 and 0.272, respectively) is calculated to reside on the α-cyclopropyl methyl carbon atom C_6. These observations, in conjunction with the relatively smaller cyclopropyl bond distortions calculated and observed for 58b versus 57b, suggest that the presence of the α-methyl group lowers the charge stabilizing role of the cyclopropyl ring in 58b relative to that in 57b. As a result, less positive charge resides on C_3 and C_4 in 58b. This effect was expected in light of the fact that the additional α-cyclopropyl methyl group in 58b was shown by crystallography both to significantly increase the C_1-C_2 bond length and to hinder flattening of the geometry about C_2, and hence, to prevent more effective cyclopropyl group positive charge conjugation. A similar effect has been calculated at the STO-3G level for the related pair of systems 39g and 39h (87). These calculations, as well as others, have also predicted that the presence of an additional α-methyl cyclopropyl substituent would lead to increased C_1-C_2 bond distances and decreased positive charge densities at C_3 and C_4 in these systems (87,62,63,94,120).

As seen in cation 57b, the presence of the nearest fluorine atom-hydroxyl proton contact within the crystalline lattice of 58b appears to cause slight bond angle distortions about the carbonyl carbon atom C_1; the C_2-C_1-O and C_2-C_1-C_5 bond angles of 115.0(6)° and 124.6(6)° observed in the crystal structure of 58b are respectively smaller (difference 3.7σ) and larger (difference 2.3σ) than those in the corresponding optimized structure, Table 4-9.

4.5 Comparison of PROAIM Calculated Bond orders and Ellipticities for 57b, 58b, 57..F^- and 57a

C-C and C-H bond orders (**n**) and bond ellipticities (ϵ) are additional properties of the charge distribution which can be used to provide information pertaining to the nature and degree of bonding within protonated and neutral cyclopropyl ketone systems. The value of n measures the extent to which charge is preferentially accumulated between two bonded nuclei and hence, gives a measure of the degree of interaction of two such bonded nuclei. Bond orders have been calculated using ρ_B, the value of ρ at the bond critical point, the point lying in the bond path connecting the two bonded nuclei at which ρ is a minimum (157,158). Bond ellipticity measures the spatial distribution of such charge; it defines the plane between two bound atoms in which charge is preferentially accumulated (158,159). C-C and C-H bond order data and bond ellipticity data pertaining to the crystal structures of 57b and 58b as well as to the various optimized systems 57b, 58b, 58..F⁻ and 57a can be found in Tables 4-6 and 4-7 respectively.

C-C and C-H bond order data for the highest basis set level optimized geometries of 57b and 58b correspond relatively well with those calculated from crystallographic data, Table 4-6. As expected on the basis of cyclopropyl bond distortions seen in each of these cations, vicinal C-C bond orders are calculated to be less than unity while the distal cyclopropyl bond orders are calculated to be greater than unity. For comparison, in the more stable and less distorted optimized neutral system 57a both vicinal and distal cyclopropyl C-C bonds are calculated to have bond orders much closer to 1.0.

Although the vicinal cyclopropyl C-C bonds in the crystal structures of 57b and 58b have approximately equal bond orders of 0.87, as expected, the distal cyclopropyl bond in the crystal structure geometry of 57b is calculated to possess a relatively higher order than that of 58b (1.34 versus 1.19). Crystallographic C_3-C_4 bond orders for both 57b (1.34) and 58b (1.19) are calculated to be slightly higher than those calculated for the corresponding optimized cationic geometries (1.20 and 1.09 respectively). These observations support the conclusion made earlier that cyclopropyl group participation in positive charge delocalization is greater in 57b and that theory underestimates the degree of such participation in both 57b and 58b.

As anticipated, larger C_1-C_2 and C_1-C_5 bond orders are calculated for each of the cationic systems when compared to those calculated for the neutral system 57a. The higher C_1-C_2 bond orders calculated from both the crystal structure (1.58) and optimized geometries (1.47) of 57b relative to those similarly calculated for 58b (1.28 and 1.39, respectively) are consistent with slightly increased positive charge conjugation of C_2 in 57b as indicated by the smaller C_1-C_2 bond length and the higher C_2 positive·charge population observed and calculated for 57b.

The bond ellipticity data for crystallographic and theoretically optimized geometries for 57b, 58b, 57b..F$^-$ and 57a, listed in Table 4-7, indicate that in each of the cationic systems 57b and 58b the vicinal cyclopropyl C-C bond paths, as defined by the line of maximum charge density between the two carbon nuclei, are extremely ellipsoid in shape. In each case, the vicinal cyclopropyl bond ellipticities, ϵ, are much greater than zero. Corresponding ellipticity values for the two overall neutral systems 57a and 57b..F$^-$ while significantly different from zero, are considerably reduced on average to 0.594 and 0.414 respectively. In each of 57b and 58b the vicinal cyclopropyl C-C bond paths are extremely curved toward the ring critical point found within, and in the plane of, the three-membered ring. As such, the three cyclopropyl C-C bond critical points are in extremely close proximity to the electronic charge minimum which exists in the plane of the ring joining these three bond critical points. The proximity of the cyclopropyl C-C bond and ring critical points reduces the energy required to achieve coalescence of these critical points (158). Hence, the vicinal cyclopropyl bond ellipticities calculated can be used to measure not only the lability of these bonds, but also the overall stability of the three-membered ring structure in each case (105,158).

The larger ellipticity values of 1.185 and 1.188 obtained for the vicinal cyclopropyl bonds in the crystal structure of 57b when compared to those similarly obtained for 58b (0.757 and 0.948) parallel the larger distal cyclopropyl bond distortions and the higher positive charge densities at C_3 and C_4 observed in the crystal structure geometry of 57b. Similarly, the slightly larger vicinal cyclopropyl bond ellipticities obtained from the crystallographic results for both 57b and 58b relative to those obtained from the corresponding theoretically optimized geometries (Table 4-7) were also expected in consideration of the relatively more severe cyclopropyl bond distortions experimentally observed.

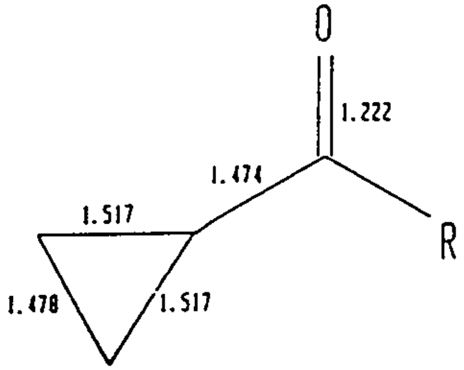
Since ellipticity gives a measure of the extent to which positive charge is preferentially distributed in any one plane, ellipticity values in conjunction with bond order and bond length values can also be used to qualitatively differentiate between through-bond conjugative and through-space hyperconjugative effects (158). This approach has been used to determine similar effects in a variety of simple hydrocarbon and three-membered ring cationic and neutral systems (157,158). Upon collective analysis of the data presented in Tables 4-1, 4-3, 4-6 and 4-7, C_1-C_2 bond positive charge conjugation in both the crystal structure and optimized geometries of 57b and 58b is indicated by the significantly enhanced C_1-C_2 bond ellipticity and bond order values and the significantly decreased C_1-C_2 bond distances in 57b and 58b relative to the corresponding values obtained for 57a. On the other hand, hyperconjugation of the C_5 methyl group with the formal center of positive charge in the crystal structure and optimized geometries of both 57b and 58b is suggested by the extremely small, but significantly enhanced, C_1-C_5 bond ellipticity and bond order values, as well as the slightly decreased C_1-C_5 bond lengths observed and calculated for 57b and 58b in comparison to those values obtained for 57a.

Results of the calculations described here for the simplest cationic system 57b can be compared to similar results obtained at the 4-31G//6-31G* level of theory for the parent unsubstituted cyclopropylcarbinyl cation 20a shown in Figure 4-12 (105). Considerable differences exist between the optimized geometries of 20a and 57b. In 20a much more extreme conjugation between C_2 and the positively charged center C_1 is indicated by the severely shortened C_1-C_2 bond length of 1.347 Å. The C_1-C_2 bond order of 1.91 approaches that of a double bond and its substantial ellipticity of 0.28 provides additional proof for this extreme conjugative interaction in 20a (105). The weaker conjugative interaction herein indicated to exist in 57b can be explained by the presence of two additional charge stabilizing substituents bonded to C_1, including a highly charge stabilizing hydroxyl group in 57b.

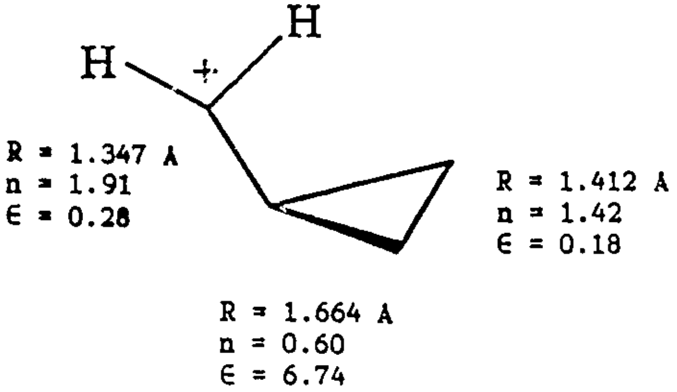
The severe vicinal cyclopropyl bond elongations to 1.664 Å calculated for 20a give rise to extremely low vicinal bond orders (0.60) and correspondingly high bond ellipticities (6.74) when compared to those values calculated for 57b. However, it is interesting to note that the distal cyclopropyl C_3-C_4 bond length of 1.412 Å and bond order of 1.42 calculated for 20a is similar to that calculated from the crystal structure geometry of 57b. The nature of cyclopropyl group participation in positive charge delocalization in 20a appears to be considerably different from that observed in 57b, or in any of the tertiary

Figure 4-12. Bond Length (Å), Bond Order and Ellipticity Data for "Extreme" Systems

A. Neutral Cyclopropyl Ketones (129)



B. The Cyclopropylcarbinyl Cation 20a (105)



hydroxy-substituted cyclopropylcarbinyl cations herein studied.

4.6 Comparison of Charge Density Contour Plots for 57b, 58b and 57a

Charge density contour plots for the theoretically optimized geometries of 57b, 58b and 57a are shown in Figures 4-8 to 4-10 respectively. In each case the plane of the nuclei O, C_1 and C_2 as well as the corresponding perpendicular plane passing through the carbonyl carbon and oxygen atoms is shown. As such, charge density distribution differences in these planes associated with the presence of the additional α-cyclopropyl methyl substituent in 58b can be ascertained (188). Furthermore, similar charge density distribution differences upon protonation of 57a to give 57b can be analyzed.

Comparison of the contour plots for 57b, 58b and 57a in the plane of O, C_1 and C_2, Figures 4-8a to 4-10a respectively, shows remarkable similarity in the charge distribution surrounding the $O-C_1(-C_2)-C_3$ subsystem. In each case the C_1-O bond is strongly polarized in the direction of the oxygen atom, but in the neutral system higher electron density is seen between the C_1 and O nuclei, as shown by the continuous 0.1 a.u. contour enveloping these nuclei in 57a which is discontinuous in both 57b and 58b. Upon protonation of 57a to give 57b electronic density is polarized in the direction of the in-plane hydroxyl proton.

The 0.001 a.u. contour encompassing C_3, C_4 and C_5 in the neutral molecule 57a as shown in Figure 4-10a encompasses a slightly larger volume than do the same limiting contours in each of the cationic systems 57b and 58b, Figures 4-8a and 4-9a respectively. This observation further supports the contention of positive charge delocalization over the entire framework of these systems. It is interesting to note the discontinuity in the 0.08 a.u. contour in the region of space between C_2 and the midpoint of the distal cyclopropyl C_3-C_4 bond in 57b which is not observed in 58b nor 57a. This observation provides additional evidence for a slightly higher degree of positive charge in this plane for 57b and hence, for more labile vicinal cyclopropyl C-C bonds in 57b when compared to those in 58b or 57a.

The charge density contour plots for the perpendicular plane passing through the C_1 and O nuclei of 57b and 58b are essentially identical in the C_1-O bond region shown in Figures 4-8b and 4-9b. The corresponding plot for 57a, Figure 4-10b exhibits slightly more diffuse contours indicative of a smaller amount of positive charge in this region of space.

In each of Figures 4-8b to 4-10b, the line drawn to the 0.001 a.u. contour perpendicular to the plane of the C_2-C_1-O linkage indicates the direction of the formal p-orbital at C_1 in each of these systems. In the cationic systems, the formal p-orbital at the carbenium ion center C_1, is vacant whereas in the neutral system, this orbital is filled. Measurement of the length of this line above and below the plane of the nuclei O, C_1 and C_2 will give an indication of the Van der Waal radius of C_1 in each of **57b**, **58b** and **57a** and will indicate the extent to which positive charge is preferentially distributed at C_1 in each of these directions. However, for each of the systems, distances to the limiting 0.001 a.u. contour above and below the C-O plane are found to be equal at 1.724 Å. As such, no evidence for the preferential distribution of positive charge in the direction of the formally vacant p-orbital at C_1 in **57b** and **58b** is obtained by this method.

The distances from C_1 to the 0.001 a.u. limiting contour in the direction perpendicular to the C_2-C_1-O subsystem can also enable determination of the significance of the directed fluorine atom contacts to C_1 observed within the crystalline lattices of **57b** and **58b**. Any such contacts observed at distances less than the sum of the Van der Waal radius of a neutral fluorine atom (1.35 Å) (141) and the corresponding distance to the limiting 0.001 a.u. contour (1.724 Å) will appear to be significant. In this context, the nearest fluorine atom contacts to C_1 in 57b seen above and below the protonated carbonyl plane at 2.99(1) Å appear significant, as do such nearest contacts at 2.91(1) Å and 3.010(9) Å observed within the crystal structure of 58b.

The equal distances obtained from C_1 to the 0.001 a.u. contour above and below the protonated carbonyl plane as well as the overall spatial distribution of electron density observed for 57b, 58b and 57a suggest that there is no underlying electronic reason for any preferred modes of axial nucleophilic attack at C_1 in these systems. Indeed, within the crystal structures of 57b and 58b significant fluorine atom contacts to C_1 were observed both above and below the plane of the protonated carbonyl moiety.

4.7 Summary

Results of the semi-empirical and *ab initio* calculations discussed in this chapter for a series of substituted hydroxy-cyclopropylcarbinyl cations and the corresponding parent cyclopropylmethyl ketone system have further probed the nature and extent of bonding as well as the degree of positive charge delocalization within these systems. The data obtained from these calculations greatly supplement the crystallographic data discussed in Chapter 3.

The **AM1** calculations have provided quantitative results concerning relative conformational stabilities in these systems. The *ab initio* calculations have enabled quantitative correlation between systematic geometry changes, both as seen experimentally and calculated theoretically, with variable electronic distributions and bonding patterns within these systems. However, similar calculations pertaining to less highly substituted cyclopropylcarbinyl cations are required in order to link the structure, bonding and charge delocalization within the substituted hydroxy-cyclopropylcarbinyl cations of interest here with those properties calculated for the parent, unsubstituted cyclopropylcarbinyl cation 20a (105).

CHAPTER 5

EXPERIMENTAL METHODS

5.1 Materials

$HSbF_6$ and $SbCl_5$ (Aldrich) were stored in air tight containers at -40°C and used without further purification. CH_2Cl_2 was refluxed over P_2O_5 and distilled under a dry N_2 atmosphere prior to its use. Similarly, diethyl ether was distilled from $LiAlH_4$, dioxan from Na and DMSO from CaH_2. Dry solvents were stored in a glove bag which was continuously purged with N_2 in the presence of solid P_2O_5. Deuterated CH_2Cl_2, used in all solution state ^1H and ^{13}C NMR experiments, was purchased (MSD Isotopes) in 1 g ampules and used without further purification.

5.2 Instrumentation

5.2.1 ^1H NMR Spectroscopy

^1H NMR spectra were obtained using Varian EM390 (90 MHz), Bruker WM250 (250 MHz) and Bruker AM500 (500 MHz) spectrometers. All solution spectra were referenced with CD_2Cl_2; the residual $C\underline{H}DCl_2$ present appeared as a triplet centered at 5.32 ppm. Spectra were acquired at variable temperatures as individually noted.

5.2.2 Solution State ^{13}C NMR Spectroscopy

All solution state ^{13}C NMR spectra were obtained with use of a Bruker AM500 (125.7 MHz) spectrometer. Unless otherwise noted, spectra were acquired at room temperature. CD_2Cl_2 was used as the internal standard for all spectra and appeared as a quintet centered at 53.8 ppm. Spin-sort and gated decoupled ^{13}C NMR spectra were acquired when needed to facilitate assignment of resonances.

5.2.3 Solid State ^{13}C NMR Spectroscopy

Room temperature solid state ^{13}C NMR spectra of crystalline samples were obtained by cross polarization magic angle spinning (CPMAS) techniques with the use of a Bruker MSL100 (25.1 MHz) spectrometer. Spinning rates were approximately 4000 Hz. Samples were mixed with $CaCl_2$ (approximate 1:2 ratio by volume), finely ground and densely packed into alumina rotors under a dry N_2 atmosphere. Adamantane was used as an external reference, and displayed resonances at 29.50 ppm ($\underline{C}H$) and 38.56 ppm ($\underline{C}H_2$) relative to tetramethylsilane (160).

5.2.4 Single Crystal X-Ray Crystallography

Crystal density measurements were performed in a dry N_2 atmosphere utilizing the crystal "float-no float" method. In each case variable volumes of ice cold CH_2Cl_2 and $CHBr_3$, giving mixtures which were less and more dense than the crystal itself, were used to approximate crystal density.

X-ray crystallographic data were collected at -65°C or 21°C on either a Syntex $P2_1$ or a Nicolet P3 automatic 4-circle diffractometer equipped with a low temperature apparatus. The low temperature crystal environment was maintained by passing a thin stream of cold N_2 gas along the Φ axis of the diffractometer. To prevent frosting of the Lindemann tube, a heater was used to warm the outer periphery of the cold stream. Intensity data were collected with the use of graphite monochromated MoK_α radiation (λ = 0.71069 Å) and a coupled Θ(crystal)-2Θ(counter) scan.

Intensities were measured with an upper 2Θ limit of 50°. Scan rate selection and preliminary data treatment were as previously described (161,162). When necessary, reflections having $75° \leq \chi \leq 90°$ were converted into their Friedel equivalents with available software in order to avoid collision between the χ circle and the low temperature apparatus. For each crystal, two internal standard reflections were measured every 48 reflections to monitor crystal stability.

Structure solution and refinement computations were performed using either a Digital Equipment Corporation VAX-8600 or a VAX-8650 mainframe computer. The **XRAY76** package (163) and the **XTAL** program suite (164) were used for preliminary data treatment. Three-dimensional Patterson syntheses, electron difference syntheses and full matrix least-squares refinement cycles were performed with use of the **SHELX** (135) program. X-ray scattering curves were taken from reference 165. Anomalous dispersion corrections were also applied to the scattering factors of the heavy atoms involved (165).

Crystallographic data were manipulated in order to obtain torsion angles, planes data and dihedral angles, and non-bonded atomic contact distances with use of the computer programs **MOLGEOM** (166), **CHEMX** (167) and **LSQPL** (164). For each crystallographic system, the program **SNOOPI** (168) was used to generate plots of the cationic geometry and the stereoscopic pair view of the unit cell contents. Each of these programs were run on a Digital Equipment Corporation VAX-8600 or VAX-8650 mainframe computer.

5.3. Syntheses

5.3.1 Preparation of Neutral Lactones, 54a-56a

δ-valerolactone 54a was commercially available (Aldrich) and was distilled before use. 6-Methyltetrahydro-2H-pyran-2-one, 55a was obtained by an acid catalyzed Baeyer-Villiger oxidation of commercially available (Lancaster Synthesis Ltd.) 5-methylcyclopentanone (132).

The procedure was as follows. A solution of concentrated H_2SO_4 (1.6 ml), 5-methylcyclopentanone (0.98 g, 0.01 mol) and CH_3COOH (4.0 ml) was cooled to 0°C and 40% CH_3COOOH (1.9 ml) was added dropwise. After the mixture had stood 2 hours in the dark, diethyl ether (100 ml) was added and the resulting solution was poured into a cold solution of $NaHCO_3$ (8.6 g) in H_2O (90 ml). The etheral layer was separated and the aqueous layer was extracted with additional ether. The combined etheral extracts were washed with aqueous $NaHCO_3$ and with H_2O and then dried over $MgSO_4$. Removal of the ether by careful distillation yielded 0.87 g (76%) of the pure colorless liquid <u>55a</u>. <u>55a</u> was used without further purification (132).

Trans-octahydrocoumarin, <u>56a</u> was prepared according to a modified procedure of Graham et al (133). Propenal (7.8 g, 0.14 mol) and quinol (0.05 g, 4.5×10^{-4} mol) in dry dioxan were added over 6 hours to an ice cold solution of 1-(N-morpholinyl)-cyclohexene (23.4 g, 0.14 mol) in dioxan (25 ml) under a N_2 atmosphere. The mixture was left overnight, and the solvent was removed at 20 mm Hg. The residue was distilled to give a viscous pale yellow liquid, 2α-(N-morpholinyl)-bicyclononan-9-one <u>60</u> (22.3 g, 0.10 mol), b.p. 110°C/0.5 mm Hg.

The crystalline methiodide salt <u>61</u>, m.p. 196-198°C, was prepared in quantitative yield by the addition of CH_3I

(15.6 g, 0.11 mol) in CH_3OH (50 ml) to a solution of 60 (22.3 g, 0.10 mol) in CH_3OH (50 ml). The methiodide salt 61 (10.0 g, 0.027 mol) was then refluxed in 3 N NaOH (70 ml) for 48 hours and the cooled solution was acidified with 10 N HCl (25 ml). The product was extracted into $CHCl_3$ and the extracts were washed with 5% $NaHCO_3$. Evaporation of the $CHCl_3$ and purification by distillation, b.p. 96°C/0.4 mm Hg, left the pure trans-fused bicyclic lactone 56a (2.46 g, 0.016 mol).

The ^1H NMR spectra of lactones 54a-56a in CD_2Cl_2 were in accord with those previously reported (68,133,134). The corresponding spin decoupled ^{13}C NMR chemical shift data are listed in Table 2-2.

5.3.2 Preparation of Substituted Ethoxy-tetrahydropyrylium Hexachloroantimonate Salts, 54b-56b

Salts 54b-56b were prepared from the corresponding lactones according to a modified procedure of Deslongchamps et al (68). The general method for preparation of these salts is described below for the synthesis of salt 54b. δ-valerolactone, 54a (0.50 g, 5 mmol) and triethyloxonium hexachloroantimonate (Aldrich) (2.2 g, 5 mmol) were dissolved in anhydrous CH_2Cl_2 (20 ml) and the solution was magnetically stirred at room temperature for 3 hours. Dry diethyl ether at 0°C was then added until the solution became turbid. The resulting solution was maintained at 0°C overnight and the crystals, 54b were allowed to settle. The supernatant liquid was quickly drawn off under a dry N_2 atmosphere and the crystals were washed with a -20°C ether-CH_2Cl_2 (5:1) mixture.

The salts 54b-56b were recrystallized from CH_2Cl_2 at -20°C to give single crystals suitable for x-ray diffraction studies. The salts were extremely hydroscopic and all manipulations were performed under a controlled atmosphere.

a. 6-Ethoxy-2,3,4,5-tetrahydropyrylium Hexachloroantimonate, 54b.

m.p. 108-110°C dec. Room temperature ^{13}C NMR chemical shift data for 54b appear in Table 2-2. ^{1}H NMR data for 54b in CD_2Cl_2 at room temperature are listed in Table 2-3.

b. 6-Ethoxy-2-methyl-2,3,4,5-tetrahydropyrylium Hexachloroantimonate, 55b.

m.p. 127-128°C dec. Room temperature solution and solid state ^{13}C NMR chemical shift data for 55b are given in Table 2-2. The corresponding ^{1}H NMR spectroscopic data for 55b appear in Table 2-3.

c. **2-Ethoxy-3,4,4a,5,6,7,8,8a-octahydro-1-benzopyrylium Hexachloroantimonate, 56b.**

m.p. 120-122°C dec. Tables 2-2 and 2-3 respectively summarize room temperature ^{13}C and ^{1}H NMR spectroscopic data for 56b.

5.3.3 Preparation of Neutral Cyclopropyl Ketones, 57a-59a

Ketones 57a and 58a were commercially available (Aldrich), were dried over 4 Å molecular sieves and were distilled before use. The bicyclic material 59a was prepared from 2-cyclohexenone according to a modified procedure of Kuhn and Trischmann as described following (142). Dry DMSO (35 ml) was added slowly by dropping funnel to a stirred mixture of trimethylsulfoxonium iodide (7.26 g, 33 mmol) and NaH (0.94 g, 39 mmol) contained in a three-necked flask at 5°C under a dry N_2 atmosphere. The resulting solution was stirred for 10 minutes at 0°C then the ice bath was removed. The solution was stirred a further 90 minutes, while allowed to warm to room temperature. 2-Cyclohexenone (2.88 g, 30 mmol) in dry DMSO (10 ml) was added dropwise over 10 minutes. When addition was complete, the solution was stirred 15 minutes at room temperature, and then for 1 hour while the solution temperature was maintained between 50-60°C. The reaction was quenched with water (150 ml) and the bicyclic ketone product 59a was extracted three times with dry ether (75 ml). Combined etheral extracts were dried over $MgSO_4$. The ether was carefully distilled off leaving a clear colorless liquid 59a. 59a had identical spectroscopic properties to those previously reported (169).

5.3.4 Preparation of Protonated Cyclopropyl Ketone Salts, 57b–59b

The hexafluoroantimonate salts 57b and 58b were prepared by slow addition of HF/SbF_5 (1:1. 0.5 eq) to a cooled solution (-78°C) of the corresponding ketone 57a or 58a (2 mmol) in dry CH_2Cl_2 (15 ml) contained in a Schlenk tube under an inert N_2 atmosphere. The hexachloroantimonate salt 59b was prepared by addition at -78°C of a CH_2Cl_2 (10 ml) solution of $SbCl_5$ (1 mmol) which had been saturated with HCl gas to a dry CH_2Cl_2 solution (10 ml) of the corresponding ketone 59a (1 mmol) at -78°C. The salts 57b-59b were recrystallized from CH_2Cl_2 at -20°C. The crystals obtained were very sensitive to moisture and temperature and all manipulations were carried out under a controlled atmosphere.

The ^{13}C and ^{1}H NMR spectra of CD_2Cl_2 solutions of 57b and 58b were very similar to those previously reported (143). ^{13}C NMR chemical shift data for 57b-59b in CD_2Cl_2 solutions at -78°C are given in Table 3-2. Corresponding ^{1}H

NMR spectroscopic data for 57b-59b are listed in Table 3-3.

5.4 Single Crystal X-Ray Crystallography

5.4.1 Crystal Selection and Handling

Single crystals were chosen for x-ray diffraction studies on the basis of clarity, shape and size, with those chosen best approximating a cube having the dimensions 0.3 mm x 0.3 mm x 0.3 mm. In some instances it was necessary to cut the crystals with an exacto knife to obtain crystals of suitable size and shape. The crystals were sealed in 0.3 mm diameter Lindemann capillary tubes in a Vacuum/Atmospheres Company HE 43-2 DRI-LAB dry box equipped with a VAC DC-882 DRI-COLD storage unit, a Bausch and Lomb Stereo Zoom 7 microscope and cold block at -40°C.

5.4.2 Data Collection, Structure Solution and Refinement

For the crystals 54b-56b, Buerger-type precession photography was used to determine potential space groups and to establish approximate unit cell dimensions prior to crystal mounting on the diffractometer. Due to the severe thermal instability of the crystals 57b-59b, it was not possible to obtain precession photographs. Alternatively, axial photographs were taken at low temperature once the sealed crystals had been mounted on the diffractometer.

a. 6-Ethoxy-2,3,4,5-tetrahydropyrylium Hexachloroantimonate, 54b

Precise triclinic unit cell parameters for 54b were determined from a least squares fit of χ, Φ, and 2θ at -65°C for 15 reflections in the range $20° \leq 2\theta \leq 29°$. Intensity data were collected at low temperature in the space group P1 and were then corrected by data reduction for Lorentz and polarization effects but not for absorption. This would lead to a maximum error on F_0 of 3.6%.

The antimony atom was found by direct methods with use of 2674 scaled reflections with $|E| \geq 1.5$ and 20 sets of starting phases. Subsequent full matrix least-squares refinement cycles and electron density difference maps revealed the positions of the remaining atoms. Temperature factors of all non-hydrogen atoms were made anisotropic and refined before hydrogen atom positions were located. Hydrogen atom positional parameters and isotropic temperature factors were then varied through 4 full matrix least-squares cycles before being fixed. A variable weighting scheme which minimized $\Sigma w(|F_0|-|F_c|)^2$ was then imposed and least-squares refinement was terminated when the maximum shift/error was ≤ 0.010.

The information pertinent to the data collection and final structure solution of 54b is comprehensively listed in Table 5-1. Final atomic positional parameters and equivalent temperature factors for the non-hydrogen atoms in <u>54b</u> are given in Table 5-2. Supplementary tables listing hydrogen atom positional parameters and isotropic temperature factors, anisotropic temperature factors for non-hydrogen atoms, and F_0F_c values for <u>54b</u> appear in the Appendix section.

b. 6-Ethoxy-2-methyl-2,3,4,5-tetrahydropyrylium Hexachloroantimonate, <u>55b</u>

The unit cell parameters for <u>55b</u> were obtained at low temperature by a least squares fit of χ, Φ and 2Θ for 15 reflections in the range $20° \leq 2\Theta \leq 26°$. The unit cell was found to be orthorhombic and intensity data were collected in the uniquely defined non-standard space group Pmnb. Data reduction produced scaled intensity data, corrected for Lorentz and polarization effects. An absorption correction was not applied; this omission would lead to a 7.1% maximum error on F_0.

The position of the antimony atom was revealed by direct methods with use of 1633 reflections with $|E| \geq 1.5$ and 20 sets of starting phases. The remaining atoms were located from subsequent electron density difference maps. The temperature factors for all non-hydrogen atoms were made anisotropic and refined before hydrogen atoms were located. Hydrogen atom positional parameters and isotropic

Table 5-1. Crystallographic Data for 54b-56b

Compound	54b	55b	56b
Formula	$C_7H_{14}O_2^+$ $SbCl_6^-$	$C_8H_{15}O_2^+$ $SbCl_6^-$	$C_{11}H_{19}O_2^+$ $SbCl_6^-$
F.W.	464.68	477.68	517.45
Crystal Size (mm)	0.3x0.2x0.5 parallelepiped	0.3x0.3x0.4 parallelepiped	0.3x0.3x0.3 rough cube
Systematic Absences	none	(h0l) h+l=2n (hk0) k=2n	(0kl) l=2n (h0l) h=2n (00l) l=2n
Space Group	$P\bar{1}$	Pmnb'	$Pca2_1$
Unit Cell (Å and °)	a = 9.285(2) b = 8.248(1) c = 15.034(3) α = 118.73(1) β = 108.98(1) γ = 109.30(1)	a = 15.888(5) b = 15.292(4) c = 13.945(3)	a = 10.081(3) b = 13.365(4) c = 14.331(3)
Volume ($Å^3$)	772.9(2)	3388(2)	1931(1)
Z	2	8	4
ρcalc ($g\ cm^{-3}$)	2.00	1.87	1.78
μ (cm^{-1})	28.13	25.04	22.01
F(000)	4478	1856	1016
Max. 2θ, reflctns meas	50°, $0 \leq h \leq 11$ $-9 \leq k \leq 9$ $-17 \leq l \leq 17$	45°, $0 \leq h \leq 13$ $0 \leq k \leq 16$ $-15 \leq l \leq 15$	50.15°, $0 \leq h \leq 8$ $0 \leq k \leq 15$ $-16 \leq l \leq 16$
Std. reflctns (esd)	(-2,-3 2) 1.6% (-3,5,-3) 1.9%	(1,5,6) 3.5% (7,5,4) 3.6%	(1,3,6) 2.1% (1,-3,-5) 2.4%
Temperature (°C)	-65±5	-55±5	21±5
No. unique reflctns	2674	2302	2853
No. with I > 0	2505	4579	3327
Final R, R_w	0.041, 0.037	0.045, 0.042	0.036, 0.035
R_a, R_b	0.050, 0.050	0.045, 0.045	0.039, 0.039
Final shift/error max, average	0.010,0.002	0.002,0.001	0.001,0.000
χ (secondary extinction)	0.00294	0.00034	0.00054
Final Difference Map max ($e/Å^{-3}$), location	0.74 (-0.09,0.15,-0.15)	0.99 (0.75,0.58,0.28)	0.47 (-0.08,0.16,0.74)
min ($e/Å^{-3}$)	-0.70	-0.80	-0.51
Weighting	$(\sigma^2F_o+0.000034F_o^2)^{-1}$	$(\sigma^2F_o+0.000841F_o^2)^{-1}$	$(\sigma^2F_o+0.000413F_o^2)^{-1}$
Err in obs of unit wt, S	3.407	0.862	1.204

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

$\sigma_F = 1/2(k/Lp^{1/2})(\sigma_I/I^{1/2})$ where k is the scale constant

$S = [\Sigma w(|F_o|-|F_c|)^2/(n-m)]^{1/2}$ where m is the number of unique reflections and n is the total number of parameters

' This cell may be transformed into the standard cell, space group Pnma, a=15.292(4), b=15.888(5), c=13.945(3) Å by the matrix (0 1 0/1 0 0/0 0 -1).

Table 5-2. Atomic Positional Parameters (x10^4) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)(x10^4) for Non-Hydrogen Atoms in 54b

Atom	x	y	z	U_{eq}
Sb(1)	0	0	0	11
Sb(2)	0	0	5000	11
Cl(11)	285(2)	-2957(2)	-1136(1)	16
Cl(12)	165(2)	972(3)	-1228(2)	18
Cl(13)	3307(2)	2600(3)	1480(1)	16
Cl(21)	3224(2)	1506(3)	6078(2)	20
Cl(22)	473(3)	2399(3)	6925(2)	25
Cl(23)	703(2)	2909(3)	4896(2)	22
O(1)	4050(6)	-1392(7)	7133(4)	15
O(6)	6026(6)	-153(7)	6755(4)	15
C(2)	3278(10)	-1091(12)	7870(6)	21
C(3)	4705(9)	1169(12)	9201(6)	18
C(4)	5559(11)	3089(12)	9217(7)	23
C(5)	6574(9)	2689(10)	8608(6)	16
C(6)	5463(9)	275(10)	7452(6)	15
C(7)	5113(10)	-2559(11)	5653(6)	20
C(8)	3379(10)	-3404(11)	4532(6)	21

$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{12}\cos\tau + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$

temperature factors were refined through 4 full matrix least-squares cycles before being fixed. Full matrix least-squares refinement which employed a variable weighting scheme, minimized $\Sigma w(|F_0|-|F_c|)^2$ until the maximum shift/error was $\leq$ 0.002.

Details of the data set collection and structure solution of 55b are listed in Table 5-1. Final non-hydrogen atom positions and equivalent temperature factors are presented in Table 5-3. The Appendix section also contains supplementary material involving final hydrogen atom positions and isotropic temperature factors, anisotropic temperature factors for non-hydrogen atoms, and F_0F_c values for 55b.

c. 2-Ethoxy-3,4,4a,5,6,7,8,8a-octahydro-1-benzopyrylium Hexachloroantimonate, 56b

Accurate unit cell parameters for 56b were obtained at 21°C by a least-squares fit of χ, Φ and 2θ for 15 reflections in the range $21° \leq 2\theta \leq 30°$. The unit cell was determined to be orthorhombic and data were collected in the uniquely defined space group $Pca2_1$. Reflection intensities were corrected for Lorentz and polarization effects but not for absorption. This would lead to a maximum error on F_0 of 6.8%.

A three-dimensional Patterson synthesis revealed the position of the antimony atom. All remaining atom positions

Table 5-3. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)($\times 10^3$) for Non-Hydrogen Atoms in 55b

Atom	x	y	z	U_{eq}
Sb(1)	2500	7029.0(4)	1973.3(4)	25.7
Sb(2)	2500	4086.9(3)	7905.9(4)	22.4
Cl(11)	3999(1)	7026(1)	1994(1)	38
Cl(12)	2500	6228(1)	544(2)	42
Cl(13)	2500	5710(1)	2864(2)	41
Cl(14)	2500	7834(2)	3422(2)	42
Cl(15)	2500	8354(1)	1109(2)	47
Cl(21)	3997(1)	4086(1)	7916(1)	41
Cl(22)	2500	5612(1)	8159(2)	38
Cl(23)	2500	4315(2)	6245(2)	51
Cl(24)	2500	3868(2)	9574(2)	54
Cl(25)	2500	2566(1)	7681(2)	56
O(1)	9455(3)	8573(3)	2858(3)	36
O(6)	9817(3)	9114(3)	1466(3)	44
C(2)	9533(4)	8497(4)	3940(4)	41
C(3)	10421(4)	8677(4)	4250(5)	47
C(4)	10733(4)	9532(4)	3820(6)	51
C(5)	10701(4)	9475(4)	2735(5)	46
C(6)	9961(4)	9037(4)	2374(5)	36
C(7)	9057(4)	8690(5)	1047(5)	54
C(8)	8980(6)	8985(6)	48(6)	82
C(9)	9210(4)	7611(4)	4163(5)	50

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$$

were located by subsequent electron density difference maps in conjunction with full matrix least-squares refinement cycles. Hydrogen atoms were given fixed positions and isotropic temperature factors. Full matrix least-squares refinement with a variable weighting scheme minimized $\Sigma w(|F_0|-|F_c|)^2$ and refinement was terminated when the maximum shift/error was ≤ 0.001.

Table 5-1 lists the information pertinent to the intensity data set collection and structure solution of 56b. Final non-hydrogen atom positional parameters and equivalent temperature factors are given in Table 5-4. Supplementary tables involving hydrogen atom positional parameters and isotropic temperature factors, anisotropic temperature factors for non-hydrogen atoms, and F_0F_c values for 56b can be found in the Appendix section.

d. 1-Cyclopropyl-1-hydroxyethylium Hexafluouroantimonate, 57b

The unit cell parameters for 57b were obtained at -65°C by a least squares fit of χ, Φ and 2θ for 15 reflections in the range $19° \leq 2\theta \leq 25°$. The clear colorless crystal 57b was determined to be orthorhombic and intensity data were collected in the uniquely defined non-standard space group Pmnb. Reflection data were then scaled and corrected for Lorentz and polarization effects. No

Table 5-4. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)($\times 10^3$) for Non-Hydrogen Atoms in 56b

Atom	x	y	z	U_{eq}
Sb	-1263.4(4)	2341.4(2)	8879.0(2)	43
Cl(1)	29(2)	3808(1)	8749(2)	66
Cl(2)	-2511(2)	850(1)	9016(2)	78
Cl(3)	-1552(2)	2644(1)	10485(1)	69
Cl(4)	-1025(2)	2060(2)	7255(1)	71
Cl(5)	695(2)	1405(1)	9166(1)	68
Cl(6)	-3205(2)	3260(2)	8549(2)	79
O(1)	2207(4)	1833(3)	6310(3)	54
O(6)	905(5)	633(3)	5860(4)	62
C(2)	2788(9)	2889(5)	6181(5)	67
C(3)	1844(9)	3562(6)	5765(6)	66
C(4)	1225(9)	3162(7)	4897(7)	95
C(5)	741(9)	2118(6)	4974(6)	71
C(6)	1339(7)	1509(5)	5761(5)	53
C(7)	1383(8)	-12(6)	6647(6)	73
C(8)	240(11)	-634(5)	6925(7)	82
C(9)	3297(8)	3170(6)	7154(5)	61
C(10)	3779(10)	4229(6)	7151(7)	87
C(11)	2957(14)	4958(7)	6646(8)	118
C(12)	2386(8)	4616(5)	5755(6)	69

$$U_{eq} = 1/3\ (U_{11} + U_{22} + U_{33})$$

absorption correction was applied. This would lead to a 11.0% maximum error on F_0.

The antimony atom was found by direct methods with use of 943 reflections with $|E| \geq 1.5$ and 20 sets of starting phases. All remaining atoms were found from subsequent electron difference maps and refined by full matrix least-squares refinement cycles. Before the hydrogen atoms were located, the temperature factors of all non-hydrogen atoms were made anisotropic and refined. U_{12} and U_{13} were fixed at 0 Å^3 for those atoms occupying special positions. Hydrogen atoms were then located and their positions and isotropic temperature factors were varied through three least-squares refinement cycles before being fixed. One hydrogen atom on the methyl group carbon atom C_5 was not found. A variable weighting scheme was imposed and refinement which minimized $\Sigma w(|F_0|-|F_c|)^2$ was terminated when the maximum shift/error was $\leq$ 0.001.

Information relevant to the data collection and final structure solution of <u>57b</u> is tabulated in Table 5-5. Final atomic positional parameters and equivalent temperature factors for all non-hydrogen atoms in <u>57b</u> are listed in Table 5-6. The Appendix section contains supplementary tables listing hydrogen atom positions and isotropic temperature factors, anisotropic temperature factors for non-hydrogen atoms, and F_0F_c values for <u>57b</u>.

Table 5-5. Crystallographic Data for 57b-59b

Compound	57b	58b	59b
Formula	$C_5H_9O^+$ SbF_6^-	$C_5H_9O^+$ SbF_6^-	$C_7H_{11}O^+$ $SbCl_6^-$
F.W.	320.75	334.89	445.47
Crystal Size (mm)	0.30x0.25x0.35 rough cube	0.20x0.20x0.10 plate	0.30x0.20x0.35 rough cylinder
Systematic Absences	h0l h+l=2n hk0 k=2n	h0l h+l=2n 0k0 k=2n	0kl l=2n hk0 k=2n
Space Group	Pmnb*	$P2_1/c$	$Pc2_1b$**
Unit Cell (Å and °)	a= 8.516(2) b=10.136(2) c=11.608(1)	a=11.596(3) b= 8.209(1) c=12.621(8) β=119.57(2)	a= 6.824(1) b=13.323(2) c=15.657(2)
Volume (Å^3)	1002(3)	1044.9(4)	1423.6(4)
Z	8	4	4
ρcalc (g cm^{-3})	4.25	2.13	2.08
μ (cm^{-1})	55.92	26.79	29.71
F(000)	1215	639.7	855.7
Max. 2θ, reflctns meas	50°, $0 \le h \le 10$ $0 \le k \le 12$ $-13 \le l \le 13$	50°, $-13 \le h \le 13$ $-9 \le k \le 9$ $-14 \le l \le 14$	50°, $0 \le h \le 8$ $0 \le k \le 15$ $-18 \le l \le 18$
Std. reflctns (esd)	(2,-2,5) 1.66% (1,3,-6) 2.83%	(-4,-4,2) 1.27% (2,-5,-5) 1.40%	(0,5,8) 1.67% (1,7,-8) 1.68%
Temperature (°C)	-65±5	-65±5	-65±5
No. unique reflctns	943	1827	1321
No. with I > 0	1997	1965	2824
Final R, R_w R_a, R_2	0.0371, 0.0374 0.0413, 0.0413	0.0618, 0.0678 0.0846, 0.0846	0.0298, 0.0337 0.0410, 0.0410
Final shift/error max, average	0.001,0.000	0.001,0.000	0.001,0.000
χ (secondary extinction)	-0.0062	0.00655	0.00133
Final Difference Map max (e/Å^{-3}), location	0.553 (0.41,0.66,0.46)	2.304 (0.15,0.79,-0.11)	1.351 (0.01,0.50,0.84)
min (e/Å^{-3})	-0.525	-1.499	-1.027
Weighting	$(\sigma^2(F_o)+0.00014F_o^2)^{-1}$	$(\sigma^2(F_o)+0.0050F_o^2)^{-1}$	$(\sigma^2(F_o)+0.0017F_o^2)^{-1}$
Err in obs of unit wt,S	2.337	1.088	0.865

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

$\sigma_F = 1/2(k/Lp^{1/2})(\sigma_I/I^{1/2})$ where k is the scale constant

$S = [\Sigma w(|F_o|-|F_c|)^2/(n-m)]^{1/2}$ where m is the number of unique reflections and n is the total number of parameters

* This cell may be transformed into the standard cell, space group Pnma, a=10.136(2), b=8.516(2), c=11.608(1) Å by the matrix (0 1 0/1 0 0/0 0 -1).

** This cell may be transformed into the standard cell, space group $Pca2_1$, a=15.657(2), b=6.824(1), c=13.323(2) Å by the matrix (0 0 1/-1 0 0/0 0 1).

Table 5-6. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)($\times 10^3$) for Non-Hydrogen Atoms in 57b

Atom	x	y	z	U_{eq}
Sb	2500	6901(1)	5602(1)	45
F(1)	3990(5)	7628(6)	4635(4)	112
F(2)	4000(5)	6196(5)	6564(4)	130
F(3)	2500	8456(5)	6446(4)	133
F(4)	2500	5395(6)	4721(5)	184
C(1)	2500	2146(6)	4655(6)	45
C(2)	2500	846(8)	4235(6)	68
C(3)	1668(7)	846(8)	4235(6)	68
C(4)	3332(7)	555(5)	3109(5)	78
C(5)	2500	2459(10)	5901(6)	65
O	2500	3048(4)	3913(4)	66

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$$

e. (1'-Methylcyclopropyl)-1-hydroxyethylium Hexafluoroantimonate, 58b

At −65°C, monoclinic unit cell parameters were determined for the clear, colorless crystal 58b from a least-squares fit of χ, Φ and 2θ for 15 reflections in the range $20° \leq 2\theta \leq 30°$. Data were collected a low temperature in the uniquely defined space group $P2_1/c$. The preliminary set of intensity data obtained was corrected for Lorentz and polarization effects. An absorption correction was not performed, and this omission would produce a maximum error on F_0 of 6.1%.

The antimony atom in 58b was located by direct methods using 1827 reflections with $|E| \geq 1.5$ and 20 sets of starting phases. The positions of the remainder of the atoms were revealed from subsequent electron difference maps. All non-hydrogen atoms and their isotropic temperature factors were refined through a series of full matrix least-squares refinement cycles before anisotropic refinement. Hydrogen atoms were then located; their coordinates and isotropic temperature factors were varied over three cycles of least-squares refinement before being fixed. Introduction of a variable weighting scheme did not improve the trial structure and hence, a fixed weighting scheme was employed which led to a value closest to unity for the error in observation of unit weight, S.

A summary of data related to the data set collection and structure solution of 58b is given in Table 5-5. Table 5-7 lists final non-hydrogen positional parameters and equivalent temperature factors. Hydrogen atom positional parameters and isotropic temperature factors, anisotropic temperature factors for all non-hydrogen atoms and F_0F_c values for 58b are tabulated in the Appendix section.

f. 2-Hydroxy-bicyclo[4.1.0]heptanylium Hexachloroantimonate, 59b

Precise unit cell parameters for the clear colorless crystal 59b were obtained at -65°C by a least-squares fit of χ, Φ and 2θ for 15 reflections in the range $19° \leq 2\theta \leq 38°$. The cell was determined to be orthorhombic and reflection intensity data were collected in the uniquely defined non-standard space group $Pc2_1b$. The set of intensity data was scaled and corrected for Lorentz and Polarization effects but not for absorption. This would lead to a maximum 10.5% error on F_0.

A three-dimensional Patterson synthesis revealed the position of the antimony atom. The remaining atomic positions were determined and refined using a series of electron density difference maps and full matrix least-squares refinement cycles. All non-hydrogen atoms were refined anisotropically prior to the location of hydrogen

Table 5-7. Atomic Positional Parameters ($x10^4$) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)($x10^3$) for Non-Hydrogen Atoms in 58b

Atom	x	y	z	U_{eq}
Sb	1496(1)	7827(1)	-456(1)	27
F(1)	644(4)	6841(6)	354(4)	48
F(2)	2326(4)	9268(5)	843(3)	48
F(3)	57(4)	9257(5)	-1212(4)	50
F(4)	2898(4)	6357(5)	354(5)	58
F(5)	2331(5)	8785(6)	-1230(5)	74
F(6)	607(6)	6336(6)	-1712(5)	66
C(1)	2361(7)	7847(6)	-5523(6)	26
C(2)	1205(7)	7668(7)	-5359(6)	26
C(3)	-90(6)	8391(10)	-6364(6)	37
C(4)	78(6)	6643(9)	-6363(6)	37
C(5)	2302(8)	8025(9)	-6700(7)	43
C(6)	1439(9)	7573(10)	-4088(7)	43
O(1)	3470(4)	7823(6)	-4546(4)	34

$U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + U_{13} \cos \beta)$

atoms which were isotropically refined before being fixed. In the final stage of the structure refinement a variable weighting scheme minimizing the quantity $\Sigma w(|F_0|-|F_c|)^2$ was imposed. Refinement was terminated when the maximum shift/error was ≤ 0.001.

Further information pertinent to the intensity data collection and final structure solution of 59b can be found in Table 5-5. Final non-hydrogen atom positions and equivalent temperature factors are listed in Table 5-8. Supplementary tables listing hydrogen atom positional parameters and isotropic temperature factors, anisotropic temperature factors for non-hydrogen atoms and F_0F_c values for 59b are presented in the Appendix section.

Table 5-8. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Atomic Displacement Factors ($Å^2$)($\times 10^4$) for Non-Hydrogen Atoms in 59b

Atom	x	y	z	U_{eq}
Sb	18(1)	5000(0)	7830(1)	17
Cl(1)	454(3)	5206(2)	9312(1)	34
Cl(2)	-1743(2)	6560(2)	7780(1)	27
Cl(3)	-452(4)	4857(2)	6335(1)	44
Cl(4)	-2947(2)	4148(2)	8070(1)	40
Cl(5)	2925(2)	5923(2)	7573(1)	36
Cl(6)	1822(2)	3505(2)	7838(1)	29
O	-8946(7)	7240(4)	10787(3)	35
C(1)	-7354(10)	7218(6)	10339(4)	24
C(2)	-5710(11)	6681(7)	10623(5)	34
C(3)	-3708(12)	7062(7)	10318(5)	39
C(4)	-4376(14)	6131(7)	9965(6)	48
C(5)	-7397(14)	7839(7)	9570(4)	36
C(6)	-5412(13)	8032(8)	9142(5)	39
C(7)	-3710(14)	8002(8)	9787(5)	44

$$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$$

5.5 Gas Phase Calculations

5.5.1 AM1 Calculations

AM1 calculations were performed with use of the program **AMPAC** (154). All calculations were performed on a Digital Equipment Corporation VAX 11-780 computer.

Input geometry parameters for all systems herein calculated were obtained from x-ray crystallographic results. In the case of calculations involving the hydroxydicyclopropylcarbinyl cation 47, input crystallographic data were acquired from Mr. Steven Zweep (170). Fractional crystallographic coordinates were transformed in cartesian orthogonal coordinates and all cationic systems were given a full +1 charge. The neutral methylcyclopropyl ketone system 57a was optimized from the crystal structure geometry of 57b in the absence of the hydroxyl proton. System 57b..F$^-$ involving the cation 57b hydrogen bonded to a fluoride ion, was classified as neutral. The fluoride ion coordinates were obtained from the position of the nearest fluorine atom (of the counter-anion SbF_6^-) contact seen in the crystal structure of 57b. Structural parameters involving this ion were fixed.

For each system, **AM1** calculated ΔH_f versus O-C_1-C_2-C_3 torsion angle rotational coordinate diagrams were plotted using the computer program **ENERGRAPHICS**. Geometries of the various calculated minimum and maximum energy structures were plotted with use of the SNOOPI molecular drawing program (168).

5.5.2 *Ab Initio* Calculations

All *ab initio* computations utilized the GAUSSIAN 86 program (155). Both single point and optimization calculations were performed on a CRAY X-MP supercomputer situated at the Ontario Center for Large Scale Computations (OCLSC) at the University of Toronto. Either the $6\text{-}31G^{**}$ or 4-31G basis set was used for geometry optimization. In each case, final approximate single determinant state functions were then generated at the $6\text{-}31G^{**}$ level. These calculations can be denoted by $6\text{-}31G^{**}//6\text{-}31G^{**}$ and $6\text{-}31G^{**}//4\text{-}31G$ respectively.

Convergence criteria for both geometries and wavefunctions were set to program default values. For geometry, the criteria for convergence were that the residual maximum force exhibited on any particular nucleus was $< 4.5 \times 10^{-4}$ Hartree/Bohr (or Hartree/radian for bending forces), that the root mean square force was $< 3.0 \times 10^{-4}$ Hartree/Bohr while a maximum displacement of $< 1.8 \times 10^{-3}$ Å was projected, and that the root mean square displacement was $< 1.2 \times 10^{-3}$ Å (155). Furthermore, SCF cycles were performed until the root mean square difference between the density matrix elements of consecutive cycles had converged to within 1 x 10^{7} (155).

Data obtained from the above mentioned *ab initio* calculations were input into the series of programs PROAIM (PRoperties Of Atoms In Molecules) developed by Dr. R. F. W. Bader and coworkers at McMaster University (156). Default values were used throughout. Computations were performed with the use of either a Multiflow Trace 300 or Digital Equipment Corporation Microvax 2000 computer. The positions of the critical points within each system studied were obtained using the program **EXTREME** (156) and a Digital Equipment Corporation VAX-8600 or VAX-8650 computer.

Critical points within each system were located to an accuracy of 10^{-12} a_0 (156). Atomic basins, bounded by zero flux surfaces (157-159), were numerically integrated in order to calculate atomic charge populations, bond ellipticities and bond orders. The value of the integral of L(x) gave a measure of the accuracy of each atomic integration; this value would be zero for an exact integration (156). Numerical integrations were accepted for values of $L(x) < 10^{-3}$. The accuracy of computed atomic charge populations was also tested by comparison of the value of the summed atomic electron populations with the total number of electrons in the system. Such differences and hence the uncertainty in calculated charge population for any on atom was of the order 10^{-3}.

Electron density contour plots were obtained courtesy of Mr. Jim Cheeseman, with use of the AIMPAC package of computer programs (171).

GENERAL SUMMARY

The structures of two series of elusive dialkoxy/ hydroxy substituted carbenium ions have been determined in this thesis. The structural effect of substituent changes on cationic geometries, in the crystalline state, in solution and in the gas phase has been probed and related to variable charge delocalization within these cations.

The structural determinations of the 2-substituted 6-ethoxy-tetrahydropyrylium ions discussed in this thesis represent not only the first reported direct x-ray structural determinations of these systems, but also the first direct comparison between solid state and solution phase cationic geometries and environments of such ions. Since it was shown that the solid state structures of these ions are also present in solutions in which they react, the observed structures of these ions were used to test selected assumptions put forth within the theory of stereoelectronic control in the reactions of these ions.

The first direct experimental evidence for systematic structural changes within alkyl-substituted hydroxycyclopropyl carbinyl cations is also discussed in this thesis. Semi empirical and high level *ab initio* calculations performed have further enabled quantitative correlation between systematic geometry changes with variable electronic distributions in these systems.

APPENDIX

Table A-1. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 54b

H(21)-C(2)	0.88	H(22)-C(2)	1.27
H(31)-C(3)	0.79	H(32)-C(3)	0.75
H(41)-C(4)	0.94	H(42)-C(4)	1.12
H(51)-C(5)	0.68	H(52)-C(5)	0.99
H(71)-C(7)	0.87	H(72)-C(7)	0.99
H(81)-C(8)	0.86	H(82)-C(8)	0.94
H(83)-C(8)	1.15		

H(21)-C(2)-O(1)	88	H(21)-C(2)-C(3)	123
H(21)-C(2)-H(22)	89	H(22)-C(2)-O(1)	134
H(22)-C(2)-C(3)	105	H(31)-C(3)-C(2)	109
H(31)-C(3)-C(4)	97	H(31)-C(3)-H(32)	86
H(32)-C(3)-C(2)	116	H(32)-C(3)-C(4)	130
H(41)-C(4)-C(3)	113	H(41)-C(4)-C(5)	111
H(41)-C(4)-H(42)	101	H(42)-C(4)-C(3)	109
H(42)-C(4)-C(5)	114	H(51)-C(5)-C(4)	104
H(51)-C(5)-C(6)	108	H(51)-C(5)-H(52)	115
H(52)-C(5)-C(4)	115	H(52)-C(5)-C(6)	103
H(71)-C(7)-O(6)	105	H(71)-C(7)-C(8)	110
H(71)-C(7)-H(72)	106	H(72)-C(7)-O(6)	107
H(72)-C(7)-C(8)	118	H(81)-C(8)-C(7)	110
H(81)-C(8)-H(82)	101	H(81)-C(8)-H(83)	121
H(82)-C(8)-C(7)	111	H(82)-C(8)-H(83)	113
H(83)-C(8)-C(7)	100		

Table A-2. Atomic Positional Parameters ($x10^3$) for Hydrogen Atoms in 54b

Atom	x	y	z
H(21)	227	-152	724
H(22)	222	-241	793
H(31)	418	154	948
H(32)	510	110	969
H(41)	467	326	883
H(42)	649	475	1020
H(51)	665	333	844
H(52)	777	298	912
H(71)	595	-253	551
H(72)	497	-343	594
H(81)	301	-465	387
H(82)	367	-244	435
H(83)	245	-335	488

Isotropic Atomic Displacement Factors were fixed at 0.0500 $Å^2$

Table A-3. Temperature Factors (Å^2)(x10^3) for Non-Hydrogen Atoms in 54b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	21.1(3)	21.6(3)	19.6(3)	12.9(2)	12.2(2)	13.7(2)
Sb(2)	20.2(3)	17.5(3)	20.2(3)	10.1(2)	11.0(2)	12.9(2)
Cl(11)	34.5(9)	27.7(7)	31.1(8)	21.2(7)	20.6(7)	16.8(7)
Cl(12)	39.3(9)	40.0(9)	34.1(8)	22.7(8)	23.8(7)	29.7(8)
Cl(13)	22.1(8)	29.6(7)	26.7(7)	12.2(6)	11.6(6)	14.9(6)
Cl(21)	23.2(8)	43.1(9)	48(1)	17.8(7)	16.8(8)	33.1(8)
Cl(22)	62(1)	42(1)	30(1)	31(1)	31(1)	20(1)
Cl(23)	40(1)	32(1)	49(1)	17(1)	21(1)	33(1)
O(1)	31(2)	27(2)	27(2)	15(2)	19(2)	18(2)
O(6)	30(2)	32(2)	28(2)	20(2)	23(2)	19(2)
C(2)	34(4)	45(4)	40(4)	18(3)	28(3)	32(3)
C(3)	34(4)	51(4)	38(4)	29(3)	31(3)	31(3)
C(4)	48(4)	33(4)	40(4)	26(4)	25(4)	20(3)
C(5)	27(3)	30(3)	32(3)	17(3)	17(3)	21(3)
C(6)	24(3)	26(3)	29(3)	15(3)	10(3)	20(3)
C(7)	43(4)	34(4)	35(4)	26(3)	24(3)	20(3)
C(8)	45(4)	34(4)	27(3)	21(3)	18(3)	17(3)

Table A-4. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 55b

H(21)-C(2)	0.96	H(31)-C(3)	0.89
H(32)-C(3)	1.10	H(41)-C(4)	0.89
H(42)-C(4)	1.01	H(51)-C(5)	0.91
H(52)-C(5)	0.96	H(71)-C(7)	0.80
H(72)-C(7)	1.13	H(81)-C(8)	0.98
H(82)-C(8)	0.73	H(83)-C(8)	1.08
H(91)-C(9)	1.00	H(92)-C(9)	0.91
H(93)-C(9)	1.13		

H(21)-C(2)-O(1)	101	H(21)-C(2)-C(3)	108
H(21)-C(2)-C(9)	116	H(31)-C(3)-C(2)	112
H(31)-C(3)-C(4)	104	H(31)-C(3)-H(32)	116
H(32)-C(3)-C(2)	105	H(32)-C(3)-C(4)	109
H(41)-C(4)-C(3)	114	H(41)-C(4)-C(5)	112
H(41)-C(4)-H(42)	102	H(42)-C(4)-C(3)	112
H(42)-C(4)-C(5)	109	H(51)-C(5)-C(4)	104
H(51)-C(5)-C(6)	117	H(51)-C(5)-H(52)	99
H(52)-C(5)-C(4)	115	H(52)-C(5)-C(6)	108
H(71)-C(7)-O(6)	104	H(71)-C(7)-C(8)	112
H(71)-C(7)-H(72)	107	H(72)-C(7)-O(6)	107
H(72)-C(7)-C(8)	117	H(81)-C(8)-C(7)	119
H(81)-C(8)-H(82)	88	H(81)-C(8)-H(83)	118
H(82)-C(8)-C(7)	107	H(82)-C(8)-H(83)	120
H(83)-C(8)-C(7)	106	H(91)-C(9)-C(2)	108
H(91)-C(9)-H(92)	110	H(91)-C(9)-H(93)	107
H(92)-C(9)-C(2)	111	H(92)-C(9)-H(93)	113
H(93)-C(9)-C(2)	108		

Table A-5. Atomic Positional Parameters ($\times 10^3$) for Hydrogen Atoms in 55b

Atom	x	y	z
H(21)	919	897	415
H(31)	1046	876	488
H(32)	1079	813	396
H(41)	1046	1000	404
H(42)	1133	967	402
H(51)	1121	924	258
H(52)	1075	1003	241
H(71)	915	818	109
H(72)	852	883	154
H(81)	947	893	-37
H(82)	906	946	5
H(83)	839	874	-21
H(91)	920	754	487
H(92)	955	720	390
H(93)	854	758	390

Isotropic Atomic Displacement Factors were fixed at 0.0500 $Å^2$

Table A-6. Temperature Factors (Å^2)(x10^3) for Non-Hydrogen Atoms in 55b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	25.5(3)	23.7(3)	27.8(3)	0	0	-6.6(2)
Sb(2)	23.7(3)	13.7(3)	30.1(3)	0	0	0.1(2)
Cl(11)	25.3(9)	40.7(9)	47.6(9)	-2.3(7)	2.8(7)	-5.7(8)
Cl(12)	45(1)	45(1)	37(1)	0	0	-20(1)
Cl(13)	39(1)	33(1)	51(1)	0	0	10(1)
Cl(14)	41(1)	49(1)	37(1)	0	0	1(7)
Cl(15)	55(1)	32(1)	53(1)	0	0	7(1)
Cl(21)	24.7(9)	35.6(9)	62(1)	-1.3(6)	1.7(7)	-4.6(8)
Cl(22)	42(1)	17(1)	56(1)	0	0	-7(1)
Cl(23)	66(2)	60(2)	26(1)	0	0	-5(1)
Cl(24)	55(2)	73(2)	35(1)	0	0	20(1)
Cl(25)	39(1)	16(1)	113(2)	0	0	-7(1)
O(1)	34(2)	34(2)	39(2)	-3(2)	-2(2)	-1(1)
O(6)	49(3)	41(3)	43(3)	1(2)	3(2)	2(2)
C(2)	45(4)	49(4)	29(3)	2(3)	-6(3)	2(3)
C(3)	41(4)	47(4)	54(4)	8(3)	-14(3)	-14(4)
C(4)	46(4)	30(3)	76(5)	4(3)	-23(4)	-5(4)
C(5)	32(4)	31(3)	74(5)	-4(3)	4(3)	-1(4)
C(6)	31(4)	30(3)	46(4)	14(3)	1(3)	-7(3)
C(7)	61(5)	58(4)	43(4)	5(4)	-6(4)	-10(4)
C(8)	91(7)	112(8)	44(5)	18(6)	2(4)	-1(5)
C(9)	46(4)	58(4)	45(4)	3(3)	3(7)	4(8)

Table A-7. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 56b

H(21)-C(2)	1.13	H(31)-C(3)	1.30
H(41)-C(4)	1.07	H(42)-C(4)	0.95
H(51)-C(5)	1.12	H(52)-C(5)	1.07
H(71)-C(7)	0.87	H(72)-C(7)	1.20
H(81)-C(8)	1.02	H(82)-C(8)	0.94
H(83)-C(8)	1.09	H(91)-C(9)	0.80
H(92)-C(9)	1.12	H(101)-C(10)	0.93
H(102)-C(10)	1.15	H(111)-C(11)	1.01
H(112)-C(11)	1.26	H(121)-C(12)	1.08
H(122)-C(12)	0.87		

H(21)-C(2)-O(1)	81	H(21)-C(2)-C(3)	72
H(21)-C(2)-C(9)	64	H(31)-C(3)-C(2)	132
H(31)-C(3)-C(4)	89	H(41)-C(4)-C(3)	108
H(41)-C(4)-C(5)	113	H(41)-C(4)-H(42)	116
H(42)-C(4)-C(3)	83	H(42)-C(4)-C(5)	126
H(51)-C(5)-C(4)	128	H(51)-C(5)-C(6)	105
H(51)-C(5)-H(52)	105	H(52)-C(5)-C(4)	66
H(52)-C(5)-C(6)	68	H(71)-C(7)-O(6)	97
H(71)-C(7)-C(8)	113	H(71)-C(7)-H(72)	119
H(72)-C(7)-O(6)	118	H(72)-C(7)-C(8)	105
H(81)-C(8)-C(7)	113	H(81)-C(8)-H(82)	115
H(81)-C(8)-H(83)	103	H(82)-C(8)-C(7)	121
H(82)-C(8)-H(83)	96	H(83)-C(8)-C(7)	105
H(91)-C(9)-C(2)	122	H(91)-C(9)-C(10)	120
H(91)-C(9)-H(92)	87	H(92)-C(9)-C(2)	112
H(92)-C(9)-C(10)	101	H(101)-C(10)-C(9)	113
H(101)-C(10)-C(11)	114	H(101)-C(10)-H(102)	110
H(102)-C(10)-C(9)	118	H(102)-C(10)-C(11)	83
H(111)-C(11)-C(10)	108	H(111)-C(11)-C(12)	116
H(111)-C(11)-H(112)	109	H(112)-C(11)-C(10)	80
H(112)-C(11)-C(12)	122	H(121)-C(12)-C(3)	101
H(121)-C(12)-C(11)	114	H(121)-C(12)-H(122)	127
H(122)-C(12)-C(3)	101	H(122)-C(12)-C(11)	114

Table A-8. Atomic Positional Parameters ($\times 10^3$) for Hydrogen Atoms in 56b

Atom	x	y	z
H(21)	200	306	672
H(31)	68	387	603
H(41)	47	368	469
H(42)	205	337	463
H(51)	-30	183	490
H(52)	74	252	562
H(71)	197	-35	633
H(72)	173	40	735
H(81)	-41	-27	737
H(82)	-16	-107	650
H(83)	65	-122	737
H(91)	363	277	749
H(92)	248	322	768
H(101)	405	445	774
H(102)	456	446	660
H(111)	346	561	663
H(112)	232	491	740
H(121)	335	461	542
H(122)	168	495	558

Isotropic Atomic Displacement Factors were fixed at 0.1000 $Å^2$

Table A-9. Temperature Factors ($Å^2$)($x10^3$) for Non-Hydrogen Atoms in 56b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	41.3(3)	42.4(2)	46.3(2)	3.6(2)	2.8(2)	2.3(3)
Cl(1)	65(1)	52.4(8)	81(1)	-7.9(7)	4(1)	9(1)
Cl(2)	86(1)	60(1)	88(2)	-24(1)	-9(1)	10(1)
Cl(3)	96(2)	63(1)	50(1)	9(1)	15(1)	-2(1)
Cl(4)	75(2)	91(1)	48(1)	4(1)	0(1)	-6(1)
Cl(5)	62(1)	61(1)	81(1)	24(1)	-12(1)	-7(1)
Cl(6)	48(1)	89(1)	100(2)	20(1)	11(1)	30(1)
O(1)	56(4)	44(2)	63(3)	-7(2)	-23(3)	0(2)
O(6)	66(4)	50(3)	70(3)	-6(3)	-18(3)	-13(2)
C(2)	93(7)	48(4)	61(6)	-7(4)	-22(5)	0(3)
C(3)	69(6)	62(5)	67(5)	-7(5)	-18(4)	3(4)
C(4)	102(8)	88(6)	94(6)	-27(6)	-43(6)	30(5)
C(5)	72(6)	80(6)	59(4)	-11(4)	-24(4)	8(4)
C(6)	46(5)	59(4)	54(4)	7(4)	7(4)	-11(3)
C(7)	66(6)	56(4)	98(6)	-4(4)	-21(5)	-5(4)
C(8)	82(7)	52(5)	113(7)	-7(5)	-2(5)	2(4)
C(9)	67(6)	51(5)	65(5)	6(4)	-27(4)	-10(4)
C(10)	105(8)	60(5)	96(7)	-17(5)	-20(6)	-19(5)
C(11)	195(13)	44(5)	116(8)	-17(6)	-38(9)	5(5)
C(12)	67(6)	43(4)	98(7)	-5(4)	-2(5)	14(4)

Table A-10. Observed and Calculated Structure Factors for 54b

F_0, F_c and SIG (σ) values have been multiplied by 10.

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	0	0	690	713	2	-10	5	0	288	290	2	5	-6		104	127	3
5	0	0	481	478	2	-9	5	0	267	252	2	6	-6	1	165	179	2
6	0	0	686	703	3	-8	5	0	446	451	2	7	-6	1	101	113	2
7	0	0	277	282	2	-7	5	0	419	422	2	8	-6	1	18	49	5
8	0	0	134	130	2	-6	5	0	493	474	3	9	-6	1	179	179	2
-9	1	0	242	235	2	-5	5	0	559	565	2	10	-6	1	119	113	2
-8	1	0	191	191	2	-4	5	0	444	444	2	-3	-5	1	68	73	3
-7	1	0	662	669	3	-3	5	0	428	431	2	-2	-5	1	106	110	2
-6	1	0	544	554	3	-2	5	0	266	259	2	-1	-5	1	155	156	1
-5	1	0	684	693	2	-1	5	0	335	333	2	0	-5	1	120	126	1
-4	1	0	1170	1200	3	0	5	0	86	85	2	1	-5	1	131	115	2
-3	1	0	1138	1156	3	1	5	0	149	139	2	2	-5	1	433	445	2
1	1	0	324	332	2	2	5	0	186	188	2	3	-5	1	347	344	2
2	1	0	775	781	2	3	5	0	68	79	3	4	-5	1	174	154	1
3	1	0	669	660	2	-10	6	0	372	369	2	5	-5	1	630	637	3
4	1	0	231	186	2	-9	6	0	389	378	2	6	-5	1	212	207	2
5	1	0	531	530	3	-8	6	0	510	518	2	7	-5	1	135	140	2
6	1	0	464	460	2	-7	6	0	420	422	2	8	-5	1	291	296	2
7	1	0	230	231	2	-6	6	0	429	425	2	9	-5	1	141	109	2
-9	2	0	323	331	2	-5	6	0	510	504	2	10	-5	1	86	80	3
-8	2	0	574	567	3	-4	6	0	257	244	2	-5	-4	1	80	73	3
-7	2	0	885	999	3	-3	6	0	334	344	2	-4	-4	1	47	41	5
-6	2	0	368	384	2	-2	6	0	291	289	2	-3	-4	1	330	319	2
-5	2	0	859	870	3	-1	6	0	213	211	1	-2	-4	1	387	386	2
-4	2	0	876	883	3	0	6	0	246	246	1	-1	-4	1	131	117	1
-3	2	0	173	199	1	1	6	0	244	246	2	0	-4	1	58	54	2
-2	2	0	420	421	2	-9	7	0	172	182	2	1	-4	1	373	382	2
-1	2	0	681	674	2	-8	7	0	207	187	2	2	-4	1	113	112	1
0	2	0	190	184	1	-7	7	0	46	83	6	3	-4	1	86	91	2
1	2	0	287	287	2	-6	7	0	302	319	2	4	-4	1	188	208	1
2	2	0	551	562	2	-5	7	0	200	195	2	5	-4	1	142	151	2
3	2	0	225	225	1	-4	7	0	223	230	2	6	-4	1	244	244	2
4	2	0	315	324	2	-3	7	0	376	387	2	7	-4	1	105	89	2
5	2	0	501	504	2	-2	7	0	372	378	2	8	-4	1	88	80	3
6	2	0	205	199	2	-1	7	0	248	243	2	9	-4	1	174	157	2
-10	3	0	239	246	2	-8	8	0	105	108	3	10	-4	1	80	64	3
-9	3	0	380	381	2	-7	8	0	192	186	2	-6	-3	1	127	140	2
-8	3	0	549	547	3	-6	8	0	287	286	2	-5	-3	1	218	207	2
-7	3	0	404	398	2	-5	8	0	114	115	2	-4	-3	1	88	91	2
-6	3	0	426	425	2	-4	8	0	302	306	2	-3	-3	1	133	125	2
-5	3	0	729	734	2	-3	8	0	282	288	2	-2	-3	1	567	554	2
-4	3	0	488	471	2	2	-8	1	27	30	6	-1	-3	1	174	165	1
-3	3	0	519	525	2	3	-8	1	24	22	5	0	-3	1	122	116	1
-2	3	0	1063	1031	3	4	-8	1	150	153	2	1	-3	1	401	398	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-1	3	0	649	663	2	5	-8	1	60	24	4	2	-3	1	567	570	2
0	3	0	849	837	2	6	-8	1	79	58	3	3	-3	1	251	218	2
1	3	0	884	871	3	7	-8	1	134	151	2	5	-3	1	482	483	2
2	3	0	682	683	3	8	-8	1	19	25	5	6	-3	1	125	143	2
3	3	0	506	504	2	9	-8	1	34	57	7	7	-3	1	94	50	2
4	3	0	497	498	2	0	-7	1	28	34	4	8	-3	1	114	97	2
5	3	0	317	311	2	1	-7	1	69	74	3	9	-3	1	109	115	2
-10	4	0	47	72	6	2	-7	1	142	143	2	-7	-2	1	76	79	3
-9	4	0	191	189	2	3	-7	1	25	13	5	-6	-2	1	216	210	2
-8	4	0	309	302	2	4	-7	1	95	97	2	-5	-2	1	68	78	3
-7	4	0	124	84	2	5	-7	1	182	180	2	-4	-2	1	99	121	2
-6	4	0	462	461	2	6	-7	1	42	12	5	-3	-2	1	252	265	1
-5	4	0	511	528	2	7	-7	1	18	10	5	-2	-2	1	90	93	2
-4	4	0	532	518	2	8	-7	1	177	155	2	-1	-2	1	10	16	3
-3	4	0	768	760	2	9	-7	1	90	86	3	0	-2	1	154	147	1
-2	4	0	925	904	3	-2	-6	1	12	18	3	1	-2	1	212	212	1
-1	4	0	634	644	2	-1	-6	1	128	128	2	2	-2	1	56	26	2
0	4	0	740	740	2	0	-6	1	223	219	1	3	-2	1	318	318	2
1	4	0	600	598	3	1	-6	1	106	108	2	4	-2	1	264	246	2
2	4	0	428	417	2	2	-6	1	72	59	3	5	-2	1	99	95	2
3	4	0	363	355	2	3	-6	1	259	265	2	6	-2	1	276	294	2
4	4	0	288	281	2	4	-6	1	258	243	2	7	-2	1	112	110	2
8	-2	1	32	61	6	5	2	1	372	373	2	-8	8	1	118	110	2
9	-2	1	64	72	4	6	2	1	97	99	3	-7	8	1	138	135	2
-8	-1	1	67	66	4	-10	3	1	13	8	4	-6	8	1	82	77	3
-7	-1	1	36	19	6	-9	3	1	230	248	2	-5	8	1	256	257	2
-6	-1	1	74	79	3	-8	3	1	21	12	5	-4	8	1	178	177	2
-5	-1	1	251	260	2	-7	3	1	301	286	2	5	-9	2	124	127	2
-4	-1	1	88	98	2	-6	3	1	558	541	2	6	-9	2	278	270	2
-3	-1	1	280	261	1	-5	3	1	299	309	2	1	-8	2	279	280	2
-2	-1	1	360	368	2	-4	3	1	333	322	2	2	-8	2	342	345	2
-1	-1	1	15	4	3	-3	3	1	809	789	2	3	-8	2	438	447	2
0	-1	1	22	22	1	-2	3	1	151	133	1	4	-8	2	358	360	2
1	-1	1	26	7	2	-1	3	1	224	229	1	5	-8	2	431	425	2
2	-1	1	300	320	1	0	3	1	170	171	1	6	-8	2	466	468	2
3	-1	1	406	418	2	1	3	1	235	248	2	7	-8	2	305	309	2
4	-1	1	49	35	3	2	3	1	28	29	5	8	-8	2	300	292	2
5	-1	1	227	216	2	3	3	1	29	48	6	9	-8	2	316	318	2
6	-1	1	98	59	3	4	3	1	18	16	5	-1	-7	2	488	484	2
7	-1	1	60	10	3	5	3	1	131	124	2	0	-7	2	396	397	2
8	-1	1	25	17	6	-10	4	1	133	120	2	1	-7	2	489	494	2
-8	0	1	70	45	3	-9	4	1	43	93	6	2	-7	2	737	743	3
-7	0	1	21	25	5	-8	4	1	204	206	2	3	-7	2	554	556	3
-6	0	1	145	28	2	-7	4	1	194	159	2	4	-7	2	600	622	3

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	0	1	20	5	5	-6	4	1	17	110	5	5	-7	2	616	615	3
-4	0	1	10	1	3	-5	4	1	446	470	2	6	-7	2	558	570	3
-2	0	1	161	156	1	-4	4	1	188	190	1	7	-7	2	346	348	2
-1	0	1	38	30	1	-3	4	1	137	142	1	8	-7	2	491	475	2
0	0	1	44	27	0	-2	4	1	831	832	3	9	-7	2	333	337	2
1	0	1	115	120	1	-1	4	1	77	8	2	-2	-6	2	382	380	2
2	0	1	498	507	2	0	4	1	108	97	1	-1	-6	2	419	412	2
3	0	1	234	223	1	1	4	1	352	354	2	0	-6	2	404	408	2
4	0	1	406	406	2	2	4	1	167	150	1	1	-6	2	453	446	2
5	0	1	388	388	2	3	4	1	97	90	2	2	-6	2	402	412	2
6	0	1	270	279	2	4	4	1	83	78	3	3	-6	2	374	367	2
7	0	1	190	182	2	-10	5	1	141	132	2	4	-6	2	423	418	2
8	0	1	201	195	2	-9	5	1	165	169	2	5	-6	2	323	320	2
-9	1	1	25	16	6	-7	5	1	11	10	3	6	-6	2	389	352	2
-8	1	1	16	15	4	-6	5	1	391	377	2	7	-6	2	351	346	2
-7	1	1	149	177	2	-5	5	1	101	103	2	8	-6	2	291	295	2
-6	1	1	100	108	2	-4	5	1	44	50	5	9	-6	2	370	374	2
-5	1	1	186	196	1	-3	5	1	251	253	2	-4	-5	2	370	375	2
-4	1	1	221	227	2	-2	5	1	104	89	2	-3	-5	2	410	410	2
-3	1	1	292	305	2	-1	5	1	152	147	2	-2	-5	2	403	399	2
-2	1	1	185	196	1	0	5	1	160	152	1	-1	-5	2	457	456	2
-1	1	1	82	65	1	1	5	1	24	2	5	0	-5	2	338	340	1
0	1	1	130	123	1	2	5	1	72	79	3	1	-5	2	464	455	2
1	1	1	684	667	2	-10	6	1	58	68	5	2	-5	2	321	321	2
2	1	1	394	404	2	-9	6	1	91	86	3	3	-5	2	431	428	2
3	1	1	131	141	1	-8	6	1	121	129	2	4	-5	2	269	280	2
4	1	1	436	428	2	-7	6	1	35	47	6	5	-5	2	396	404	2
5	1	1	109	111	2	-6	6	1	20	12	5	6	-5	2	317	292	2
6	1	1	26	30	6	-5	6	1	324	320	2	7	-5	2	268	269	2
7	1	1	113	90	2	-4	6	1	201	194	2	8	-5	2	215	222	2
-9	2	1	107	113	3	-3	6	1	46	67	5	9	-5	2	216	213	2
-8	2	1	214	219	2	-2	6	1	297	302	2	-5	-4	2	240	240	2
-7	2	1	170	68	2	-1	6	1	35	67	6	-4	-4	2	370	370	2
-6	2	1	375	367	2	0	6	1	20	35	4	-3	-4	2	309	300	2
-5	2	1	486	499	2	1	6	1	17	40	5	-2	-4	2	388	388	2
-4	2	1	173	207	2	-9	7	1	111	98	2	-1	-4	2	690	688	3
-3	2	1	754	727	2	-8	7	1	94	76	3	0	-4	2	438	428	2
-2	2	1	956	941	3	-7	7	1	122	81	2	1	-4	2	739	722	2
-1	2	1	405	394	2	-6	7	1	46	87	6	2	-4	2	835	825	3
0	2	1	271	273	1	-5	7	1	74	87	3	3	-4	2	664	671	2
1	2	1	506	493	2	-4	7	1	95	93	2	4	-4	2	563	552	2
2	2	1	78	93	2	-3	7	1	75	64	3	5	-4	2	726	741	3
3	2	1	236	238	2	-2	7	1	92	89	2	6	-4	2	356	360	2
4	2	1	179	185	1	-1	7	1	177	184	2	7	-4	2	277	296	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
8	-4	2	445	451	2	-5	1	2	651	655	2	0	5	2	195	195	1
9	-4	2	103	119	3	-4	1	2	968	997	3	1	5	2	270	262	2
-6	-3	2	118	132	2	-3	1	2	35	23	3	2	5	2	68	76	3
-5	-3	2	290	283	2	-1	1	2	803	812	2	-10	6	2	252	259	2
-4	-3	2	187	177	2	0	1	2	77	74	1	-9	6	2	420	428	2
-3	-3	2	220	222	2	1	1	2	536	530	2	-8	6	2	261	258	2
-2	-3	2	618	615	1	2	1	2	691	687	2	-7	6	2	358	359	2
-1	-3	2	247	252	1	3	1	2	135	131	2	-6	6	2	380	383	2
0	-3	2	426	431	1	4	1	2	461	466	2	-5	6	2	354	357	2
1	-3	2	887	867	2	5	1	2	447	457	2	-4	6	2	222	220	2
2	-3	2	158	165	1	6	1	2	236	244	2	-3	6	2	447	459	2
3	-3	2	490	516	2	-10	2	2	256	256	2	-2	6	2	300	305	2
4	-3	2	648	661	2	-9	2	2	372	388	2	-1	6	2	305	300	2
5	-3	2	357	367	2	-8	2	2	676	681	3	0	6	2	359	366	1
6	-3	2	353	345	2	-7	2	2	558	559	3	-9	7	2	137	150	2
7	-3	2	472	488	2	-6	2	2	610	636	3	-7	7	2	256	255	2
8	-3	2	373	371	2	-5	2	2	1110	1130	3	-6	7	2	183	160	2
9	-3	2	202	199	2	-4	2	2	687	694	2	-5	7	2	137	119	2
-7	-2	2	168	158	2	-3	2	2	951	902	3	-4	7	2	325	323	2
-6	-2	2	495	491	2	-2	2	2	1085	1077	3	-3	7	2	276	274	2
-5	-2	2	473	471	2	-1	2	2	983	963	3	-2	7	2	191	200	2
-4	-2	2	299	288	2	0	2	2	667	674	2	-7	8	2	338	343	2
-3	-2	2	593	596	2	1	2	2	1033	1031	3	-6	8	2	272	272	2
-2	-2	2	794	807	2	2	2	2	635	640	3	4	-9	3	18	5	5
-1	-2	2	69	43	2	3	2	2	590	584	3	5	-9	3	24	16	5
0	-2	2	386	380	1	4	2	2	609	615	3	6	-9	3	27	33	6
2	-2	2	692	698	2	5	2	2	388	388	2	7	-9	3	119	119	2
3	-2	2	850	849	2	-10	3	2	247	243	2	1	-8	3	102	109	2
4	-2	2	548	559	2	-9	3	2	406	418	2	2	-8	3	166	162	2
5	-2	2	106	88	2	-8	3	2	329	326	2	3	-8	3	59	52	4
6	-2	2	500	478	3	-7	3	2	493	517	3	4	-8	3	30	4	6
7	-2	2	464	476	2	-6	3	2	547	519	2	5	-8	3	77	80	3
8	-2	2	113	104	2	-5	3	2	852	826	3	6	-8	3	153	151	2
-8	-1	2	182	181	2	-4	3	2	668	679	2	7	-8	3	28	19	6
-7	-1	2	382	385	2	-3	3	2	1066	1074	3	8	-8	3	37	3	6
-6	-1	2	679	664	3	-2	3	2	1023	998	3	-1	-7	3	140	147	2
-5	-1	2	220	235	2	-1	3	2	995	987	3	0	-7	3	89	94	2
-4	-1	2	750	757	2	0	3	2	1035	1037	3	1	-7	3	15	2	4
-3	-1	2	959	962	3	1	3	2	874	873	3	2	-7	3	134	135	2
-2	-1	2	456	454	2	2	3	2	673	669	3	3	-7	3	76	76	3
2	-1	2	483	509	2	3	3	2	623	624	3	4	-7	3	172	171	2
3	-1	2	1326	1375	3	4	3	2	433	427	2	5	-7	3	90	99	2
4	-1	2	491	487	2	-10	4	2	336	335	2	6	-7	3	73	52	3
5	-1	2	434	450	2	-9	4	2	405	414	2	7	-7	3	369	367	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	-1	2	668	671	3	-8	4	2	287	290	2	8	-7	3	148	142	2
7	-1	2	233	229	2	-7	4	2	650	636	3	9	-7	3	82	95	3
8	-1	2	174	176	2	-6	4	2	524	511	2	-3	-6	3	26	12	6
-9	0	2	113	104	2	-5	4	2	647	606	2	-2	-6	3	66	76	3
-8	0	2	123	108	2	-4	4	2	787	782	3	-1	-6	3	375	378	2
-7	0	2	411	414	2	-3	4	2	575	587	2	0	-6	3	211	210	1
-6	0	2	292	309	2	-2	4	2	689	676	3	1	-6	3	143	141	2
-5	0	2	53	45	3	-1	4	2	501	494	2	2	-6	3	109	118	2
-4	0	2	1007	1016	3	0	4	2	441	439	2	3	-6	3	292	292	2
-3	0	2	433	430	2	1	4	2	319	316	2	4	-6	3	48	100	5
-2	0	2	525	532	2	2	4	2	276	272	2	5	-6	3	114	25	2
1	0	2	604	610	2	3	4	2	208	200	2	6	-6	3	172	198	2
2	0	2	1135	1137	3	-10	5	2	410	398	2	7	-6	3	109	114	2
3	0	2	681	689	2	-9	5	2	568	579	3	8	-6	3	119	142	2
4	0	2	407	408	2	-8	5	2	541	538	2	9	-6	3	95	82	3
5	0	2	607	595	3	-7	5	2	656	657	3	-4	-5	3	116	128	2
6	0	2	465	471	2	-6	5	2	660	661	3	-3	-5	3	225	216	2
7	0	2	172	172	2	-5	5	2	664	644	3	-2	-5	3	173	174	2
-9	1	2	86	101	3	-4	5	2	545	509	3	-1	-5	3	158	154	1
-8	1	2	475	481	2	-3	5	2	455	450	2	0	-5	3	755	755	2
-7	1	2	484	481	3	-2	5	2	397	407	2	1	-5	3	68	58	2
-6	1	2	307	289	2	-1	5	2	211	212	2	2	-5	3	286	285	2
3	-5	3	576	575	1	1	-1	3	347	361	2	0	3	3	125	124	1
4	-5	3	218	218	1	2	-1	3	141	148	1	1	3	3	129	121	2
5	-5	3	12	20	3	3	-1	3	62	46	2	2	3	3	240	241	2
6	-5	3	133	136	2	4	-1	3	50	19	3	3	3	3	105	108	2
7	-5	3	296	291	2	5	-1	3	82	53	3	4	3	3	39	44	6
8	-5	3	127	142	2	6	-1	3	119	108	2	-10	4	3	79	97	4
9	-5	3	44	12	6	7	-1	3	17	36	5	-8	4	3	147	134	2
-6	-4	3	70	58	3	-9	0	3	178	176	2	-7	4	3	196	228	3
-5	-4	3	71	80	3	-8	0	3	17	43	5	-6	4	3	124	139	2
-4	-4	3	306	311	2	-7	0	3	22	85	5	-5	4	3	30	152	7
-3	-4	3	38	54	6	-6	0	3	212	220	2	-4	4	3	115	146	3
-2	-4	3	207	212	1	-5	0	3	54	20	3	-3	4	3	161	174	2
-1	-4	3	359	359	2	-4	0	3	228	197	1	-2	4	3	11	34	3
0	-4	3	14	2	2	-3	0	3	379	377	2	-1	4	3	115	123	2
1	-4	3	79	45	2	-2	0	3	208	178	1	0	4	3	145	144	1
2	-4	3	84	77	2	-1	0	3	205	223	1	1	4	3	22	31	5
3	-4	3	66	58	2	0	0	3	459	470	1	2	4	3	106	100	2
4	-4	3	255	253	1	1	0	3	352	357	2	-10	5	3	15	15	4
5	-4	3	122	114	2	2	0	3	49	10	2	-9	5	3	128	140	2
6	-4	3	94	32	2	3	0	3	265	267	2	-8	5	3	403	382	2
7	-4	3	129	123	2	4	0	3	15	7	4	-7	5	3	15	24	4
8	-4	3	163	169	2	5	0	3	128	135	2	-6	5	3	232	225	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
9	-4	3	13	19	4	6	0	3	140	129	2	-5	5	3	403	419	2
-7	-3	3	96	73	3	7	0	3	175	150	2	-4	5	3	74	55	3
-6	-3	3	140	125	2	-10	1	3	47	39	6	-3	5	3	213	223	2
-5	-3	3	70	85	3	-9	1	3	160	120	2	-2	5	3	295	296	2
-4	-3	3	109	90	2	-8	1	3	69	71	3	-1	5	3	83	98	2
-3	-3	3	483	465	2	-7	1	3	140	57	2	0	5	3	35	31	4
-2	-3	3	269	275	2	-6	1	3	192	120	2	1	5	3	198	205	2
-1	-3	3	386	371	2	-5	1	3	21	12	5	-10	6	3	33	33	7
0	-3	3	1087	1056	3	-4	1	3	318	370	2	-9	6	3	27	12	6
1	-3	3	414	403	2	-3	1	3	56	58	2	-8	6	3	128	99	2
2	-3	3	475	467	2	-2	1	3	172	170	1	-7	6	3	124	127	2
3	-3	3	552	554	2	-1	1	3	805	799	2	-6	6	3	185	168	2
4	-3	3	240	248	1	0	1	3	288	272	1	-5	6	3	102	100	2
5	-3	3	79	53	2	1	1	3	303	302	2	-4	6	3	60	76	4
6	-3	3	249	235	2	2	1	3	299	298	2	-3	6	3	195	195	2
7	-3	3	15	0	4	3	1	3	91	94	2	-2	6	3	26	12	6
8	-3	3	60	52	4	4	1	3	104	111	2	-1	6	3	17	13	5
9	-3	3	69	81	4	5	1	3	76	63	3	-9	7	3	62	40	4
-8	-2	3	91	93	3	6	1	3	59	68	4	-8	7	3	46	29	6
-7	-2	3	175	154	2	-10	2	3	37	46	6	-7	7	3	15	53	4
-6	-2	3	14	24	4	-9	2	3	16	36	4	-6	7	3	32	69	6
-5	-2	3	122	81	2	-8	2	3	97	96	2	-5	7	3	109	121	2
-4	-2	3	323	321	2	-6	2	3	105	214	4	-4	7	3	129	143	2
-3	-2	3	276	277	2	-5	2	3	174	177	1	-3	7	3	110	91	2
-2	-2	3	176	117	1	-4	2	3	158	101	1	3	-9	4	228	230	2
-1	-2	3	617	601	2	-3	2	3	370	376	2	4	-9	4	96	113	2
0	-2	3	137	129	1	-2	2	3	194	205	2	5	-9	4	271	268	2
1	-2	3	62	50	2	-1	2	3	162	147	1	6	-9	4	305	310	2
2	-2	3	400	408	2	0	2	3	686	679	2	7	-9	4	219	221	2
3	-2	3	33	7	4	1	2	3	26	20	5	0	-8	4	273	277	1
4	-2	3	196	208	1	2	2	3	21	16	5	1	-8	4	349	365	2
5	-2	3	124	128	2	3	2	3	345	338	2	2	-8	4	551	556	3
6	-2	3	197	205	2	4	2	3	120	108	2	3	-8	4	491	508	2
7	-2	3	108	98	2	5	2	3	24	18	5	4	-8	4	552	551	3
8	-2	3	165	166	2	-10	3	3	13	75	4	5	-8	4	706	694	3
-8	-1	3	42	50	6	-9	3	3	204	211	2	6	-8	4	448	454	2
-7	-1	3	247	237	2	-8	3	3	248	250	2	7	-8	4	498	496	3
-6	-1	3	28	115	6	-7	3	3	15	156	4	8	-8	4	399	396	2
-5	-1	3	128	59	2	-6	3	3	285	179	2	-2	-7	4	326	334	2
-4	-1	3	88	79	2	-5	3	3	236	247	2	-1	-7	4	353	362	2
-3	-1	3	84	15	1	-4	3	3	332	327	2	0	-7	4	460	465	2
-2	-1	3	438	433	2	-3	3	3	77	64	2	1	-7	4	501	518	2
-1	-1	3	148	130	1	-2	3	3	61	76	2	2	-7	4	622	612	3
0	-1	3	120	118	1	-1	3	3	255	248	1	3	-7	4	475	469	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	-7	4	545	544	3	-7	-2	4	608	610	3	-7	2	4	339	363	2
5	-7	4	453	452	2	-6	-2	4	775	772	3	-6	2	4	1066	1054	3
6	-7	4	363	367	2	-5	-2	4	629	622	3	-5	2	4	461	462	2
7	-7	4	332	335	2	-4	-2	4	950	964	3	-4	2	4	802	789	3
8	-7	4	354	359	2	-3	-2	4	1352	1350	4	-3	2	4	981	966	3
9	-7	4	250	242	2	-2	-2	4	451	409	2	-2	2	4	604	610	2
-3	-6	4	489	490	2	-1	-2	4	1074	1032	3	-1	2	4	499	500	2
-2	-6	4	497	504	2	1	-2	4	295	294	2	0	2	4	705	702	2
-1	-6	4	456	459	2	2	-2	4	699	708	2	1	2	4	419	421	2
0	-6	4	561	565	2	3	-2	4	362	388	2	2	2	4	396	391	2
1	-6	4	362	353	2	4	-2	4	42	55	4	3	2	4	463	465	2
2	-6	4	417	422	2	5	-2	4	320	310	2	4	2	4	340	332	2
3	-6	4	252	244	1	6	-2	4	393	403	2	-10	3	4	234	224	2
4	-6	4	331	335	2	7	-2	4	142	137	2	-9	3	4	354	348	2
5	-6	4	242	227	2	8	-2	4	187	170	2	-8	3	4	320	334	2
6	-6	4	344	360	2	-9	-1	4	186	178	2	-7	3	4	284	234	2
7	-6	4	248	245	2	-8	-1	4	271	270	2	-6	3	4	373	402	2
8	-6	4	351	353	2	-7	-1	4	578	582	3	-5	3	4	181	221	2
9	-6	4	295	294	2	-6	-1	4	246	240	2	-4	3	4	198	193	1
-5	-5	4	418	419	2	-5	-1	4	206	258	2	-3	3	4	350	343	2
-4	-5	4	430	438	2	-4	-1	4	569	579	2	-2	3	4	237	233	1
-3	-5	4	427	430	2	-3	-1	4	281	276	2	-1	3	4	400	393	2
-2	-5	4	526	541	3	-2	-1	4	360	335	2	0	3	4	311	304	1
-1	-5	4	558	556	2	-1	-1	4	939	916	2	1	3	4	429	430	2
0	-5	4	457	454	2	0	-1	4	231	240	1	2	3	4	368	369	2
1	-5	4	699	700	2	1	-1	4	87	98	1	3	3	4	300	297	2
2	-5	4	820	810	3	2	-1	4	952	968	3	-11	4	4	349	351	2
3	-5	4	564	555	2	3	-1	4	623	642	2	-10	4	4	280	283	2
4	-5	4	931	923	3	4	-1	4	309	306	2	-9	4	4	333	347	2
5	-5	4	775	780	3	5	-1	4	773	781	3	-8	4	4	404	414	2
6	-5	4	581	585	3	6	-1	4	382	376	2	-7	4	4	334	332	2
7	-5	4	624	622	3	7	-1	4	242	239	2	-6	4	4	488	459	2
8	-5	4	489	489	3	-9	0	4	13	45	4	-5	4	4	452	467	2
9	-5	4	283	286	2	-8	0	4	350	350	2	-4	4	4	468	466	3
-6	-4	4	185	198	2	-7	0	4	179	186	2	-3	4	4	484	465	3
-5	-4	4	330	338	2	-6	0	4	96	146	3	-2	4	4	537	540	3
-4	-4	4	181	169	2	-5	0	4	373	356	2	-1	4	4	442	438	2
-3	-4	4	375	366	2	-4	0	4	205	179	1	0	4	4	386	382	1
-2	-4	4	573	583	2	-3	0	4	240	262	2	1	4	4	359	367	2
-1	-4	4	695	677	2	-2	0	4	584	626	2	2	4	4	302	295	2
0	-4	4	667	665	2	-1	0	4	533	560	2	-10	5	4	242	245	2
1	-4	4	1299	1278	3	0	0	4	208	222	1	-9	5	4	426	421	2
2	-4	4	1115	1098	3	1	0	4	742	768	2	-8	5	4	407	394	2
3	-4	4	809	817	3	2	0	4	663	666	2	-7	5	4	433	449	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	-4	4	1320	1316	4	3	0	4	255	250	2	-6	5	4	760	749	3
5	-4	4	620	637	3	4	0	4	473	474	2	-5	5	4	513	517	2
6	-4	4	539	539	3	5	0	4	392	390	2	-4	5	4	653	658	3
7	-4	4	652	651	3	6	0	4	113	98	2	-3	5	4	698	715	3
8	-4	4	303	296	2	-10	1	4	99	99	3	-2	5	4	500	501	2
9	-4	4	204	198	2	-9	1	4	317	314	2	-1	5	4	452	451	2
-7	-3	4	194	191	2	-8	1	4	422	437	2	0	5	4	509	510	2
-6	-3	4	475	468	2	-7	1	4	288	273	2	-10	6	4	301	291	2
-5	-3	4	504	506	2	-6	1	4	678	693	3	-9	6	4	285	292	2
-4	-3	4	378	378	2	-5	1	4	704	715	2	-8	6	4	321	298	2
-3	-3	4	1100	1080	3	-4	1	4	996	971	3	-7	6	4	426	423	2
-2	-3	4	777	780	2	-3	1	4	752	730	2	-6	6	4	369	373	2
-1	-3	4	879	861	3	-1	1	4	551	567	2	-5	6	4	325	328	2
1	-3	4	745	745	2	0	1	4	803	800	2	-4	6	4	377	391	2
2	-3	4	667	655	2	1	1	4	579	595	2	-3	6	4	371	378	2
3	-3	4	348	364	2	2	1	4	378	393	2	-2	6	4	222	223	2
4	-3	4	627	633	2	3	1	4	211	199	1	-8	7	4	339	344	2
5	-3	4	98	79	2	4	1	4	340	346	2	-7	7	4	407	400	2
6	-3	4	299	308	2	5	1	4	133	136	2	-6	7	4	124	149	2
7	-3	4	259	268	2	-10	2	4	67	106	4	-5	7	4	309	308	2
8	-3	4	24	18	5	-9	2	4	505	510	3	2	-9	5	24	27	5
-8	-2	4	251	249	2	-8	2	4	357	380	2	3	-9	5	58	52	4
4	-9	5	18	6	5	-7	-3	5	117	131	2	-5	1	5	423	453	2
5	-9	5	17	24	5	-6	-3	5	77	58	3	-4	1	5	171	236	3
6	-9	5	147	145	2	-5	-3	5	217	208	2	-3	1	5	164	103	1
7	-9	5	109	101	2	-4	-3	5	112	118	2	-2	1	5	600	598	2
-1	-8	5	106	113	2	-3	-3	5	15	23	4	-1	1	5	115	114	1
0	-8	5	32	38	4	-2	-3	5	155	159	1	0	1	5	46	10	2
1	-8	5	115	116	2	0	-3	5	323	312	1	1	1	5	116	110	2
2	-8	5	236	233	2	1	-3	5	109	112	1	2	1	5	28	29	5
3	-8	5	37	22	6	2	-3	5	49	9	2	3	1	5	185	192	1
4	-8	5	52	76	5	3	-3	5	55	62	2	4	1	5	46	31	5
5	-8	5	175	174	2	4	-3	5	221	208	1	5	1	5	31	52	6
6	-8	5	31	28	6	5	-3	5	66	59	3	-10	2	5	18	49	5
7	-8	5	138	136	2	6	-3	5	95	102	2	-9	2	5	300	320	2
8	-8	5	16	16	4	7	-3	5	17	23	5	-8	2	5	358	353	2
-2	-7	5	156	165	2	8	-3	5	45	37	6	-7	2	5	16	164	5
-1	-7	5	222	218	2	-8	-2	5	80	101	3	-6	2	5	462	404	2
0	-7	5	200	198	1	-7	-2	5	65	93	4	-5	2	5	486	488	2
1	-7	5	68	64	3	-6	-2	5	25	25	6	-4	2	5	162	174	1
2	-7	5	422	424	2	-5	-2	5	12	19	4	-3	2	5	206	211	1
3	-7	5	45	59	5	-4	-2	5	138	131	1	-2	2	5	17	31	4
4	-7	5	20	12	5	-3	-2	5	346	359	2	-1	2	5	394	404	2
5	-7	5	178	188	1	-2	-2	5	338	321	2	0	2	5	90	89	1

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	-7	5	237	237	2	-1	-2	5	664	650	2	1	2	5	45	49	5
7	-7	5	123	123	2	0	-2	5	753	747	2	2	2	5	279	274	2
8	-7	5	17	40	5	1	-2	5	666	678	2	3	2	5	20	25	5
-4	-6	5	77	80	3	2	-2	5	378	386	2	4	2	5	31	50	6
-3	-6	5	61	44	3	3	-2	5	457	480	2	-11	3	5	20	21	5
-2	-6	5	230	223	2	4	-2	5	124	114	2	-10	3	5	101	74	3
-1	-6	5	269	261	2	5	-2	5	77	82	3	-9	3	5	273	279	2
0	-6	5	68	70	2	6	-2	5	26	21	6	-8	3	5	84	91	3
1	-6	5	11	3	3	7	-2	5	107	113	2	-7	3	5	181	54	2
2	-6	5	312	315	2	-9	-1	5	16	19	5	-6	3	5	222	221	2
3	-6	5	264	262	2	-8	-1	5	70	102	4	-5	3	5	41	178	8
4	-6	5	16	26	4	-7	-1	5	34	47	6	-4	3	5	179	96	2
5	-6	5	123	118	2	-5	-1	5	9	34	3	-3	3	5	231	274	2
6	-6	5	191	197	1	-4	-1	5	279	248	2	-2	3	5	127	129	2
7	-6	5	162	173	2	-3	-1	5	151	126	1	-1	3	5	19	48	5
8	-6	5	32	9	6	-2	-1	5	437	445	2	0	3	5	286	284	1
9	-6	5	50	31	5	-1	-1	5	100	99	1	1	3	5	93	100	2
-5	-5	5	19	35	5	0	-1	5	81	80	1	2	3	5	42	41	5
-4	-5	5	221	224	2	1	-1	5	255	266	2	-11	4	5	182	173	2
-3	-5	5	11	24	3	2	-1	5	361	379	2	-10	4	5	15	34	4
-2	-5	5	162	173	2	3	-1	5	128	133	1	-9	4	5	202	205	2
-1	-5	5	548	559	2	4	-1	5	80	88	3	-8	4	5	282	274	2
0	-5	5	244	252	1	5	-1	5	216	211	1	-7	4	5	123	121	2
1	-5	5	199	193	1	6	-1	5	61	65	4	-5	4	5	376	373	2
2	-5	5	632	639	2	-9	0	5	191	190	2	-4	4	5	18	155	5
3	-5	5	11	22	3	-8	0	5	28	71	6	-3	4	5	76	92	3
4	-5	5	94	102	2	-7	0	5	105	69	3	-2	4	5	129	126	2
5	-5	5	213	200	2	-6	0	5	316	278	2	-1	4	5	282	286	2
6	-5	5	16	26	4	-5	0	5	60	28	2	0	4	5	84	78	2
7	-5	5	92	92	2	-4	0	5	307	225	2	-10	5	5	96	97	3
8	-5	5	145	150	2	-3	0	5	235	112	1	-9	5	5	173	140	2
-6	-4	5	75	86	3	-2	0	5	563	546	2	-8	5	5	208	211	2
-5	-4	5	202	215	2	-1	0	5	758	767	2	-7	5	5	27	3	6
-3	-4	5	126	119	2	0	0	5	668	693	2	-6	5	5	99	89	2
-2	-4	5	169	183	2	1	0	5	368	374	2	-5	5	5	90	83	2
-1	-4	5	55	49	2	2	0	5	747	745	3	-4	5	5	99	83	2
0	-4	5	463	443	2	3	0	5	219	218	2	-3	5	5	16	16	4
1	-4	5	66	41	2	4	0	5	120	111	2	-2	5	5	71	49	3
2	-4	5	139	137	1	5	0	5	326	314	2	-1	5	5	15	1	4
3	-4	5	442	441	2	6	0	5	59	51	4	-10	6	5	43	56	6
4	-4	5	177	179	1	-10	1	5	33	74	6	-9	6	5	51	47	5
6	-4	5	29	17	6	-9	1	5	175	186	2	-8	6	5	267	279	2
7	-4	5	149	153	2	-8	1	5	164	154	2	-7	6	5	27	5	6
8	-4	5	186	184	2	-6	1	5	123	48	2	-6	6	5	93	95	3

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	6	5	150	150	2	-1	-4	6	288	272	2	-1	0	6	636	667	2
-4	6	5	64	60	3	0	-4	6	1125	1115	3	0	0	6	684	707	2
-3	6	5	27	13	6	1	-4	6	680	664	2	1	0	6	908	929	3
1	-9	6	299	304	2	2	-4	6	353	348	2	2	0	6	181	185	1
2	-9	6	278	285	2	3	-4	6	1141	1153	3	3	0	6	406	402	2
3	-9	6	227	226	2	4	-4	6	357	365	2	4	0	6	310	315	2
4	-9	6	238	245	2	5	-4	6	390	400	2	5	0	6	84	74	3
5	-9	6	321	324	2	6	-4	6	563	556	3	-10	1	6	345	359	2
6	-9	6	222	228	2	7	-4	6	304	304	2	-9	1	6	358	350	2
7	-9	6	230	224	2	8	-4	6	181	157	2	-8	1	6	489	493	2
-1	-8	6	122	119	2	-8	-3	6	203	197	2	-7	1	6	548	560	3
0	-8	6	102	102	2	-7	-3	6	507	506	3	-6	1	6	767	779	3
1	-8	6	288	293	2	-6	-3	6	543	547	2	-5	1	6	939	906	3
2	-8	6	197	200	1	-5	-3	6	441	453	2	-4	1	6	710	736	2
3	-8	6	301	307	2	-4	-3	6	919	904	3	-3	1	6	1015	1018	3
4	-8	6	337	333	2	-3	-3	6	989	1002	3	-2	1	6	764	760	2
5	-8	6	408	413	2	-2	-3	6	823	817	3	-1	1	6	575	572	2
6	-8	6	268	269	2	-1	-3	6	1098	1058	3	0	1	6	602	611	2
7	-8	6	383	388	2	0	-3	6	1205	1199	3	1	1	6	302	307	2
8	-8	6	269	261	2	1	-3	6	637	639	2	2	1	6	291	297	2
-3	-7	6	158	157	2	2	-3	6	614	636	2	3	1	6	258	257	2
-2	-7	6	236	228	2	3	-3	6	847	856	3	4	1	6	170	172	2
-1	-7	6	210	211	1	4	-3	6	168	178	1	-10	2	6	369	387	2
0	-7	6	285	278	1	5	-3	6	374	361	2	-9	2	6	212	215	2
1	-7	6	327	326	2	6	-3	6	472	473	2	-8	2	6	325	318	2
2	-7	6	274	279	2	7	-3	6	54	80	5	-7	2	6	436	393	2
3	-7	6	335	346	2	-8	-2	6	292	301	2	-6	2	6	278	280	2
4	-7	6	220	215	2	-7	-2	6	664	674	3	-5	2	6	289	253	2
5	-7	6	313	310	2	-6	-2	6	361	371	2	-4	2	6	239	271	2
6	-7	6	156	160	2	-5	-2	6	615	643	3	-3	2	6	17	115	5
7	-7	6	227	232	2	-4	-2	6	1141	1128	3	-2	2	6	182	153	2
8	-7	6	185	184	2	-3	-2	6	592	586	2	-1	2	6	132	124	2
-4	-6	6	367	366	2	-2	-2	6	817	815	2	0	2	6	263	262	1
-3	-6	6	360	357	2	0	-2	6	592	599	2	1	2	6	120	128	2
-2	-6	6	553	562	3	1	-2	6	650	670	2	2	2	6	301	305	2
-1	-6	6	529	520	3	2	-2	6	1069	1088	3	3	2	6	261	257	2
0	-6	6	540	527	2	3	-2	6	540	553	2	-11	3	6	264	255	2
1	-6	6	556	552	3	4	-2	6	514	508	3	-10	3	6	339	344	2
2	-6	6	593	585	3	5	-2	6	742	742	3	-9	3	6	220	240	2
3	-6	6	404	400	2	6	-2	6	419	411	2	-8	3	6	326	329	2
4	-6	6	481	491	2	7	-2	6	272	264	2	-7	3	6	272	241	2
5	-6	6	499	500	2	-9	-1	6	250	253	2	-6	3	6	224	135	2
6	-6	6	258	260	2	-8	-1	6	525	537	3	-5	3	6	290	305	2
7	-6	6	403	409	2	-7	-1	6	339	349	2	-3	3	6	265	244	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
8	-6	6	354	355	2	-6	-1	6	316	316	2	-2	3	6	299	305	2
-6	-5	6	230	231	2	-5	-1	6	717	722	3	-1	3	6	213	213	1
-5	-5	6	348	356	2	-4	-1	6	370	363	2	0	3	6	302	310	1
-4	-5	6	307	315	2	-3	-1	6	431	422	2	1	3	6	330	338	2
-3	-5	6	367	368	2	-2	-1	6	717	720	2	2	3	6	197	190	2
-2	-5	6	598	605	3	-1	-1	6	717	732	2	-10	4	6	256	273	2
-1	-5	6	347	346	2	0	-1	6	388	398	2	-9	4	6	264	270	2
0	-5	6	709	699	2	1	-1	6	979	999	3	-8	4	6	256	262	2
1	-5	6	692	698	2	2	-1	6	617	635	2	-7	4	6	463	452	2
2	-5	6	634	648	2	3	-1	6	525	539	3	-6	4	6	431	442	2
3	-5	6	795	789	3	4	-1	6	593	592	3	-5	4	6	529	528	3
4	-5	6	747	753	3	5	-1	6	492	498	2	-4	4	6	547	542	3
5	-5	6	726	742	3	6	-1	6	238	235	2	-3	4	6	629	642	3
6	-5	6	517	511	2	-10	0	6	253	246	2	-2	4	6	485	491	2
7	-5	6	635	633	3	-9	0	6	408	419	2	-1	4	6	455	452	2
8	-5	6	391	385	2	-8	0	6	692	685	3	0	4	6	439	441	2
-7	-4	6	225	222	2	-7	0	6	323	274	2	-10	5	6	260	263	2
-6	-4	6	412	409	2	-6	0	6	691	686	3	-9	5	6	199	197	2
-5	-4	6	266	258	2	-5	0	6	1116	1109	3	-8	5	6	228	228	2
-4	-4	6	285	290	2	-4	0	6	231	275	2	-7	5	6	443	453	2
-3	-4	6	601	610	3	-3	0	6	1240	1215	3	-6	5	6	368	363	2
-2	-4	6	546	528	2	-2	0	6	1068	1082	3	-5	5	6	287	300	2
-4	5	6	494	490	3	-6	-4	7	128	129	2	-1	0	7	237	231	1
-3	5	6	299	304	2	-5	-4	7	59	64	3	0	0	7	292	296	1
-2	5	6	228	232	2	-4	-4	7	102	37	2	1	0	7	187	188	1
-9	6	6	209	199	2	-3	-4	7	45	78	5	2	0	7	125	118	2
-8	6	6	339	336	2	-2	-4	7	186	179	1	3	0	7	143	149	2
-7	6	6	262	259	2	-1	-4	7	264	259	1	4	0	7	145	132	2
-6	6	6	127	127	2	0	-4	7	153	150	1	-10	1	7	102	133	3
-5	6	6	204	208	2	1	-4	7	71	73	2	-9	1	7	106	118	2
-4	6	6	155	154	2	2	-4	7	159	156	1	-8	1	7	93	83	3
1	-9	7	87	91	3	3	-4	7	138	129	1	-7	1	7	272	239	2
2	-9	7	101	108	2	4	-4	7	35	3	5	-6	1	7	110	132	2
3	-9	7	72	80	3	5	-4	7	148	150	2	-5	1	7	154	157	2
4	-9	7	226	226	1	6	-4	7	25	15	6	-4	1	7	284	305	2
5	-9	7	52	34	5	7	-4	7	27	48	6	-3	1	7	11	7	3
6	-9	7	31	28	6	-8	-3	7	69	61	4	-1	1	7	409	424	2
7	-9	7	124	126	2	-7	-3	7	65	40	4	0	1	7	78	52	2
-1	-8	7	80	86	3	-6	-3	7	312	302	2	1	1	7	122	116	2
0	-8	7	193	195	1	-5	-3	7	181	118	2	2	1	7	273	268	2
1	-8	7	216	213	2	-4	-3	7	174	150	2	3	1	7	76	57	3
2	-8	7	56	64	3	-3	-3	7	424	429	2	-10	2	7	50	6	6
3	-8	7	14	15	4	-2	-3	7	73	89	2	-9	2	7	120	154	2
4	-8	7	214	208	2	-1	-3	7	249	257	2	-8	2	7	125	134	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
5	-8	7	201	219	2	0	-3	7	256	262	1	-6	2	7	213	246	2
6	-8	7	49	38	5	1	-3	7	100	108	1	-5	2	7	23	47	5
7	-8	7	119	115	2	2	-3	7	225	227	1	-3	2	7	379	375	2
-3	-7	7	26	35	6	3	-3	7	121	121	2	-2	2	7	110	96	2
-2	-7	7	147	139	2	4	-3	7	191	200	2	-1	2	7	33	13	6
-1	-7	7	22	25	5	5	-3	7	41	55	5	0	2	7	320	323	1
0	-7	7	82	85	2	6	-3	7	105	100	2	1	2	7	56	56	3
1	-7	7	468	474	2	7	-3	7	64	69	4	2	2	7	82	63	3
2	-7	7	143	151	2	-9	-2	7	33	12	6	-11	3	7	116	102	2
3	-7	7	216	215	1	-8	-2	7	107	29	3	-10	3	7	13	28	4
4	-7	7	504	493	2	-7	-2	7	61	78	4	-9	3	7	135	148	2
5	-7	7	33	64	6	-6	-2	7	13	38	4	-8	3	7	222	225	2
6	-7	7	160	147	2	-4	-2	7	220	227	1	-7	3	7	179	192	2
7	-7	7	205	204	2	-3	-2	7	180	158	1	-6	3	7	326	318	2
8	-7	7	75	56	3	-2	-2	7	116	45	1	-3	3	7	13	56	4
-5	-6	7	28	41	6	-1	-2	7	205	162	1	-2	3	7	86	85	2
-4	-6	7	27	14	6	0	-2	7	156	163	1	-1	3	7	248	240	2
-3	-6	7	291	287	2	1	-2	7	301	306	2	0	3	7	151	163	1
-2	-6	7	173	174	1	2	-2	7	224	237	1	1	3	7	85	80	3
-1	-6	7	20	2	5	3	-2	7	63	77	3	-10	4	7	87	78	3
0	-6	7	314	307	1	4	-2	7	318	313	2	-9	4	7	115	67	3
1	-6	7	143	147	2	5	-2	7	67	68	3	-8	4	7	25	43	6
2	-6	7	182	173	1	6	-2	7	23	19	5	-7	4	7	245	231	2
3	-6	7	103	99	2	-8	-1	7	54	26	5	-6	4	7	202	198	2
4	-6	7	59	54	3	-7	-1	7	88	86	3	-5	4	7	235	224	2
5	-6	7	295	299	2	-6	-1	7	95	82	2	-4	4	7	145	131	2
6	-6	7	116	106	2	-4	-1	7	109	100	1	-3	4	7	83	83	3
7	-6	7	17	17	5	-3	-1	7	114	173	2	-2	4	7	112	123	2
8	-6	7	112	91	2	-2	-1	7	110	84	1	-1	4	7	75	64	3
-6	-5	7	234	226	2	0	-1	7	106	117	1	-10	5	7	114	92	2
-5	-5	7	168	171	2	1	-1	7	122	125	1	-9	5	7	171	171	2
-4	-5	7	269	268	2	2	-1	7	24	63	5	-8	5	7	233	222	2
-3	-5	7	380	376	2	3	-1	7	11	36	3	-7	5	7	159	147	2
-2	-5	7	12	7	4	4	-1	7	33	28	6	-6	5	7	174	158	2
-1	-5	7	280	269	2	5	-1	7	49	61	5	-5	5	7	193	213	2
0	-5	7	77	78	1	-10	0	7	140	147	2	-4	5	7	17	36	5
1	-5	7	61	74	2	-9	0	7	124	110	2	-3	5	7	66	55	3
2	-5	7	65	61	2	-8	0	7	120	110	2	-8	6	7	52	48	6
3	-5	7	86	86	2	-7	0	7	252	228	2	-7	6	7	32	8	6
4	-5	7	171	163	1	-6	0	7	361	391	2	-6	6	7	36	29	6
5	-5	7	85	72	2	-5	0	7	93	84	2	0	-9	8	206	214	1
6	-5	7	89	87	2	-4	0	7	312	326	2	1	-9	8	312	306	2
7	-5	7	133	138	2	-3	0	7	485	497	2	2	-9	8	226	235	2
-7	-4	7	172	187	2	-2	0	7	90	89	2	3	-9	8	162	169	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	-9	8	357	363	2	-8	-3	8	215	222	2	-4	1	8	753	731	3
5	-9	8	228	236	2	-7	-3	8	265	268	2	-3	1	8	544	570	3
6	-9	8	302	310	2	-6	-3	8	71	60	3	-2	1	8	549	559	2
-2	-8	8	105	9[illegible]	2	-5	-3	8	431	420	2	-1	1	8	718	735	3
-1	-8	8	172	168	2	-4	-3	8	634	653	3	0	1	8	479	478	2
0	-8	8	146	141	1	-3	-3	8	379	361	2	1	1	8	503	499	2
1	-8	8	196	194	1	-2	-3	8	925	896	3	2	1	8	421	421	2
2	-8	8	246	252	2	-1	-3	8	1143	1147	3	3	1	8	344	329	2
3	-8	8	306	304	2	0	-3	8	704	719	2	-10	2	8	289	316	2
4	-8	8	334	337	2	1	-3	8	915	920	3	-9	2	8	404	411	2
5	-8	8	352	354	2	2	-3	8	1051	1067	3	-8	2	8	450	446	2
6	-8	8	336	341	2	3	-3	8	444	448	2	-7	2	8	444	464	2
7	-8	8	262	257	2	4	-3	8	572	568	3	-6	2	8	596	592	3
-3	-7	8	312	310	2	5	-3	8	554	545	2	-5	2	8	513	471	3
-2	-7	8	368	365	2	6	-3	8	245	240	2	-4	2	8	600	5[illegible]3	3
-1	-7	8	452	473	2	-9	-2	8	111	100	2	-3	2	8	386	414	3
0	-7	8	517	517	2	-8	-2	8	374	369	2	-2	2	8	476	491	2
1	-7	8	645	647	3	-7	-2	8	313	298	2	-1	2	8	285	295	2
2	-7	8	482	485	2	-6	-2	8	215	203	2	0	2	8	322	322	1
3	-7	8	567	566	3	-5	-2	8	872	876	3	1	2	8	274	280	2
4	-7	8	422	426	2	-4	-2	8	612	608	2	-10	3	8	415	430	2
5	-7	8	302	294	2	-3	-2	8	434	442	2	-9	3	8	551	533	3
6	-7	8	249	249	2	-2	-2	8	1232	1205	3	-8	3	8	518	504	2
7	-7	8	160	161	2	-1	-2	8	618	627	2	-7	3	8	577	573	3
-5	-6	8	292	295	2	0	-2	8	497	512	2	-6	3	8	690	691	3
-4	-6	8	344	342	2	1	-2	8	757	781	3	-5	3	8	442	443	2
-3	-6	8	484	497	2	2	-2	8	581	595	3	-4	3	8	583	596	3
-2	-6	8	628	631	3	3	-2	8	196	191	2	-3	3	8	483	488	2
-1	-6	8	518	509	3	4	-2	8	623	622	3	-2	3	8	364	367	2
0	-6	8	540	545	2	5	-2	8	317	321	2	-1	3	8	342	345	2
1	-6	8	730	737	3	-9	-1	8	604	602	3	0	3	8	326	324	1
2	-6	8	261	255	1	-8	-1	8	475	465	2	-10	4	8	284	297	2
3	-6	8	367	368	2	-7	-1	8	576	583	3	-9	4	8	270	248	2
4	-6	8	501	511	2	-6	-1	8	720	726	3	-8	4	8	237	237	2
5	-6	8	17	44	5	-5	-1	8	850	810	3	-7	4	8	373	376	2
6	-6	8	317	330	2	-4	-1	8	603	594	2	-6	4	8	294	289	2
7	-6	8	301	296	2	-3	-1	8	595	634	2	-5	4	8	239	250	2
-6	-5	8	379	393	2	-2	-1	8	826	812	3	-4	4	8	368	375	2
-5	-5	8	205	207	2	-1	-1	8	230	227	1	-3	4	8	294	286	2
-4	-5	8	294	293	2	0	-1	8	562	578	2	-2	4	8	200	202	2
-3	-5	8	395	404	2	1	-1	8	479	492	2	-9	5	8	131	116	2
-2	-5	8	57	75	3	2	-1	8	253	256	2	-8	5	8	219	226	2
-1	-5	8	141	135	2	3	-1	8	374	382	2	-7	5	8	139	143	2
0	-5	8	184	179	1	4	-1	8	394	393	2	-6	5	8	44	53	6

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	-5	8	22	16	5	5	-1	8	173	178	2	-5	5	8	199	206	2
2	-5	8	98	78	2	-10	0	8	311	324	2	-4	5	8	136	131	2
3	-5	8	214	232	1	-9	0	8	597	622	3	0	-9	9	114	111	2
4	-5	8	299	302	2	-8	0	8	275	275	2	1	-9	9	70	81	3
5	-5	8	97	101	2	-7	0	8	659	685	3	2	-9	9	39	22	6
6	-5	8	476	469	2	-6	0	8	692	707	3	3	-9	9	321	319	2
7	-5	8	268	263	2	-5	0	8	474	472	2	4	-9	9	15	7	4
-7	-4	8	361	357	2	-4	0	8	807	811	3	5	-9	9	24	44	5
-6	-4	8	322	334	2	-3	0	8	779	804	3	6	-9	9	193	191	2
-5	-4	8	87	70	2	-2	0	8	598	622	2	-2	-8	9	18	18	5
-4	-4	8	403	391	2	-1	0	8	763	768	3	-1	-8	9	229	226	2
-3	-4	8	311	296	2	0	0	8	696	705	2	0	-8	9	49	41	3
-2	-4	8	10	42	3	1	0	8	607	617	3	1	-8	9	72	65	3
-1	-4	8	480	486	2	2	0	8	459	449	2	2	-8	9	16	24	4
0	-4	8	465	453	2	3	0	8	543	533	3	3	-8	9	86	88	2
1	-4	8	130	126	1	4	0	8	287	277	2	4	-8	9	271	268	2
2	-4	8	633	647	2	-10	1	8	248	262	2	5	-8	9	99	104	2
3	-4	8	526	536	2	-9	1	8	265	294	2	6	-8	9	90	81	3
4	-4	8	274	268	2	-8	1	8	149	161	2	7	-8	9	263	257	2
5	-4	8	430	430	2	-7	1	8	463	489	3	-4	-7	9	180	170	2
6	-4	8	395	393	2	-6	1	8	374	415	2	-3	-7	9	21	19	5
7	-4	8	124	116	2	-5	1	8	346	357	2	-2	-7	9	80	90	3
-1	-7	9	125	118	2	-5	-2	9	336	352	2	-3	3	9	329	326	2
0	-7	9	235	237	1	-4	-2	9	586	567	2	-2	3	9	121	121	2
1	-7	9	24	11	5	-3	-2	9	371	372	2	-1	3	9	110	99	2
2	-7	9	36	4	5	-2	-2	9	335	346	2	-10	4	9	129	112	2
3	-7	9	203	208	1	-1	-2	9	345	368	2	-9	4	9	80	83	3
4	-7	9	37	30	6	0	-2	9	45	1	2	-7	4	9	137	113	2
5	-7	9	103	114	2	1	-2	9	23	30	5	-6	4	9	35	9	7
6	-7	9	86	69	3	2	-2	9	98	79	2	-5	4	9	25	41	6
7	-7	9	24	1	5	3	-2	9	211	207	1	-4	4	9	110	99	2
-5	-6	9	35	35	6	4	-2	9	86	68	2	-3	4	9	35	5	6
-4	-6	9	314	320	2	5	-2	9	31	38	6	-8	5	9	73	72	3
-3	-6	9	182	178	2	-9	-1	9	94	41	3	-7	5	9	69	49	4
-2	-6	9	91	98	2	-8	-1	9	230	229	2	-6	5	9	127	110	2
-1	-6	9	241	236	2	-7	-1	9	182	179	2	0	-9	10	299	304	1
0	-6	9	245	239	1	-6	-1	9	158	91	2	1	-9	10	266	267	2
1	-6	9	230	231	1	-4	-1	9	352	345	2	2	-9	10	238	237	2
2	-6	9	103	94	2	-3	-1	9	218	245	1	3	-9	10	269	261	2
3	-6	9	129	122	2	-2	-1	9	26	118	6	4	-9	10	325	328	2
4	-6	9	227	229	1	-1	-1	9	436	430	2	5	-9	10	255	251	2
5	-5	9	90	94	2	0	-1	9	241	248	1	-2	-8	10	319	321	2
6	-6	9	26	31	6	1	-1	9	36	0	5	-1	-8	10	381	378	2
7	-6	9	142	127	2	2	-1	9	158	152	1	0	-8	10	378	379	1

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-6	-5	9	87	101	3	3	-1	9	63	51	3	1	-8	10	421	417	2
-5	-5	9	13	25	4	4	-1	9	118	123	2	2	-8	10	488	487	2
-4	-5	9	318	330	2	-10	0	9	15	48	4	3	-8	10	383	380	2
-3	-5	9	54	16	5	-9	0	9	95	73	3	4	-8	10	483	488	2
-1	-5	9	184	183	1	-8	0	9	38	62	7	5	-8	10	394	397	2
0	-5	9	77	68	2	-7	0	9	320	326	2	6	-8	10	285	278	2
1	-5	9	98	88	2	-6	0	9	107	146	3	-4	-7	10	255	254	2
2	-5	9	242	247	2	-5	0	9	272	296	2	-3	-7	10	484	489	2
3	-5	9	40	33	5	-4	0	9	565	551	3	-2	-7	10	489	497	2
4	-5	9	114	112	2	-3	0	9	251	235	2	-1	-7	10	517	523	2
5	-5	9	235	239	2	-2	0	9	172	190	2	0	-7	10	717	721	2
6	-5	9	179	170	2	-1	0	9	394	400	2	1	-7	10	645	661	3
-7	-4	9	66	88	4	0	0	9	59	34	3	2	-7	10	589	586	3
-6	-4	9	44	54	6	1	0	9	24	10	5	3	-7	10	646	636	3
-5	-4	9	106	109	2	2	0	9	205	205	1	4	-7	10	475	481	2
-4	-4	9	246	230	2	3	0	9	39	36	6	5	-7	10	401	398	2
-3	-4	9	107	94	2	-10	1	9	33	7	6	6	-7	10	273	267	2
-2	-4	9	211	185	1	-8	1	9	202	244	2	-5	-6	10	272	281	2
-1	-4	9	35	65	5	-6	1	9	195	143	2	-4	-6	10	355	358	2
0	-4	9	17	20	3	-5	1	9	219	260	2	-3	-6	10	532	533	2
1	-4	9	296	306	2	-4	1	9	294	338	2	-2	-6	10	398	401	2
2	-4	9	201	212	2	-3	1	9	163	130	2	-1	-6	10	418	414	2
3	-4	9	260	260	2	-1	1	9	159	155	2	0	-6	10	593	579	2
4	-4	9	310	305	2	0	1	9	172	152	1	1	-6	10	286	283	2
5	-4	9	122	120	2	1	1	9	105	94	2	2	-6	10	275	277	2
6	-4	9	179	167	2	2	1	9	18	9	5	3	-6	10	454	464	2
-8	-3	9	62	55	4	-10	2	9	11	15	3	4	-6	10	133	127	2
-7	-3	9	11	17	3	-9	2	9	190	169	2	5	-6	10	285	282	2
-6	-3	9	98	96	2	-8	2	9	151	100	2	6	-6	10	293	289	2
-5	-3	9	171	121	2	-7	2	9	90	90	3	-6	-5	10	356	356	2
-4	-3	9	127	140	2	-6	2	9	14	50	4	-5	-5	10	342	345	2
-3	-3	9	340	338	2	-5	2	9	184	191	2	-4	-5	10	579	584	3
-2	-3	9	252	252	2	-4	2	9	363	361	2	-3	-5	10	359	350	2
-1	-3	9	480	481	2	-3	2	9	139	126	2	-2	-5	10	246	213	2
0	-3	9	199	194	1	-2	2	9	72	54	3	-1	-5	10	503	496	2
1	-3	9	239	248	1	-1	2	9	121	134	2	0	-5	10	282	273	1
2	-3	9	159	150	1	0	2	9	97	87	2	1	-5	10	92	67	2
3	-3	9	75	51	3	1	2	9	79	72	3	2	-5	10	440	441	2
4	-3	9	29	12	6	-10	3	9	26	78	6	3	-5	10	316	316	2
5	-3	9	76	80	3	-9	3	9	107	89	3	4	-5	10	98	91	2
-9	-2	9	20	42	5	-7	3	9	115	116	2	5	-5	10	424	420	2
-8	-2	9	200	203	2	-6	3	9	222	215	2	6	-5	10	247	247	2
-7	-2	9	167	174	2	-5	3	9	145	137	2	-7	-4	10	382	384	2
-6	-2	9	370	389	2	-4	3	9	153	152	2	-6	-4	10	172	184	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	-4	10	418	428	2	-10	1	10	203	192	2	-2	-6	11	87	85	2
-4	-4	10	584	588	3	-9	1	10	227	220	2	-1	-6	11	105	102	2
-3	-4	10	212	206	2	-8	1	10	354	329	2	0	-6	11	56	47	3
-2	-4	10	609	610	3	-7	1	10	316	323	2	1	-6	11	13	1	4
-1	-4	10	789	790	3	-6	1	10	419	424	2	2	-6	11	96	99	2
0	-4	10	386	384	2	-5	1	10	562	576	3	3	-6	11	141	149	2
1	-4	10	692	712	3	-4	1	10	408	409	2	4	-6	11	16	23	4
2	-4	10	721	732	3	-3	1	10	668	669	3	5	-6	11	26	24	6
3	-4	10	356	372	2	-2	1	10	425	421	2	-7	-5	11	88	91	3
4	-4	10	401	398	2	-1	1	10	457	460	2	-6	-5	11	123	130	2
5	-4	10	492	488	2	0	1	10	344	348	1	-5	-5	11	53	34	5
-8	-3	10	312	315	2	1	1	10	305	298	2	-4	-5	11	147	150	2
-7	-3	10	32	37	6	-10	2	10	400	399	2	-3	-5	11	143	157	2
-6	-3	10	289	278	2	-9	2	10	510	503	3	-2	-5	11	28	6	6
-5	-3	10	394	397	2	-8	2	10	599	597	3	-1	-5	11	226	220	2
-4	-3	10	391	385	2	-7	2	10	578	589	3	0	-5	11	53	45	3
-3	-3	10	378	396	2	-6	2	10	668	667	3	1	-5	11	117	117	2
-2	-3	10	742	726	3	-5	2	10	635	636	3	2	-5	11	40	43	5
-1	-3	10	555	551	2	-4	2	10	441	456	2	3	-5	11	13	46	4
0	-3	10	325	346	1	-3	2	10	532	532	2	4	-5	11	86	71	2
1	-3	10	699	710	3	-2	2	10	323	317	2	5	-5	11	90	97	3
2	-3	10	295	298	2	-1	2	10	250	250	2	-8	-4	11	18	22	5
3	-3	10	231	228	2	0	2	10	273	271	1	-7	-4	11	34	15	7
4	-3	10	348	336	2	-10	3	10	389	376	2	-6	-4	11	32	69	6
5	-3	10	217	210	2	-9	3	10	269	272	2	-5	-4	11	26	39	6
-9	-2	10	342	350	2	-8	3	10	398	400	2	-4	-4	11	205	204	2
-8	-2	10	380	360	2	-7	3	10	415	421	2	-3	-4	11	176	52	2
-7	-2	10	134	121	2	-6	3	10	296	283	2	-2	-4	11	13	73	4
-6	-2	10	733	736	3	-5	3	10	311	306	2	-1	-4	11	149	152	2
-5	-2	10	274	335	3	-4	3	10	403	417	2	0	-4	11	64	14	2
-4	-2	10	202	211	2	-3	3	10	204	206	2	1	-4	11	67	55	3
-3	-2	10	677	668	3	-2	3	10	286	283	2	2	-4	11	15	14	4
-2	-2	10	215	178	2	-9	4	10	126	108	2	3	-4	11	24	39	5
-1	-2	10	45	58	5	-8	4	10	217	231	2	4	-4	11	46	40	5
0	-2	10	263	274	1	-7	4	10	131	133	2	5	-4	11	27	23	6
1	-2	10	95	84	2	-6	4	10	126	141	2	-7	-3	11	114	122	2
2	-2	10	22	25	5	-5	4	10	219	217	2	-6	-3	11	95	99	2
3	-2	10	188	189	1	0	-9	11	93	92	2	-5	-3	11	317	308	2
4	-2	10	166	165	2	1	-9	11	136	136	2	-4	-3	11	134	75	2
-10	-1	10	306	302	2	2	-9	11	103	109	2	-3	-3	11	150	152	2
-9	-1	10	396	389	2	3	-9	11	24	19	5	-2	-3	11	255	256	2
-8	-1	10	329	332	2	4	-9	11	62	54	4	-1	-3	11	221	232	2
-7	-1	10	352	349	2	5	-9	11	109	105	2	0	-3	11	59	46	2
-6	-1	10	625	603	3	-3	-8	11	64	50	4	1	-3	11	203	201	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	-1	10	244	270	2	-2	-8	11	238	238	2	2	-3	11	77	72	2
-4	-1	10	275	284	2	-1	-8	11	176	179	2	3	-3	11	37	30	6
-3	-1	10	537	563	3	0	-8	11	54	41	3	4	-3	11	24	25	5
-2	-1	10	135	135	2	1	-8	11	249	249	2	-9	-2	11	18	43	5
-1	-1	10	322	327	2	2	-8	11	222	221	2	-8	-2	11	59	3	5
0	-1	10	506	499	2	3	-8	11	85	84	2	-7	-2	11	50	9	5
1	-1	10	217	214	1	4	-8	11	172	172	2	-6	-2	11	18	43	5
2	-1	10	396	390	2	5	-8	11	61	63	4	-5	-2	11	236	182	2
3	-1	10	356	355	2	-4	-7	11	58	71	4	-3	-2	11	33	61	6
-10	0	10	213	215	2	-3	-7	11	24	32	5	-2	-2	11	136	172	2
-9	0	10	118	96	3	-2	-7	11	288	286	2	-1	-2	11	84	9	2
-8	0	10	192	165	2	-1	-7	11	57	30	3	0	-2	11	42	16	2
-7	0	10	245	239	2	0	-7	11	84	79	2	1	-2	11	188	176	1
-6	0	10	21	156	6	1	-7	11	205	204	1	2	-2	11	17	6	4
-5	0	10	317	301	2	2	-7	11	91	98	2	3	-2	11	52	46	5
-4	0	10	354	399	2	3	-7	11	20	10	5	-9	-1	11	32	99	4
-3	0	10	501	500	3	4	-7	11	259	263	2	-8	-1	11	14	7	4
-2	0	10	457	462	2	5	-7	11	61	68	4	-7	-1	11	72	75	3
-1	0	10	698	705	3	6	-7	11	69	64	3	-6	-1	11	75	143	4
0	0	10	529	527	2	-5	-6	11	27	56	6	-5	-1	11	180	133	2
1	0	10	526	525	2	-4	-6	11	14	4	4	-4	-1	11	232	173	2
2	0	10	542	525	3	-3	-6	11	74	57	3	-3	-1	11	186	124	2
-2	-1	11	125	149	2	-6	-6	12	202	205	2	-4	-1	12	533	550	3
-1	-1	11	85	99	2	-5	-6	12	273	271	2	-3	-1	12	308	309	2
0	-1	11	118	119	1	-4	-6	12	556	553	3	-2	-1	12	548	550	3
1	-1	11	22	22	5	-3	-6	12	456	452	2	-1	-1	12	358	355	2
2	-1	11	44	36	6	-2	-6	12	438	433	2	0	-1	12	386	379	2
-10	0	11	223	221	2	-1	-6	12	783	782	3	1	-1	12	308	308	2
-9	0	11	111	106	3	0	-6	12	489	490	2	-10	0	12	203	189	2
-7	0	11	225	229	2	1	-6	12	431	429	2	-9	0	12	215	221	2
-6	0	11	203	234	2	2	-6	12	594	602	3	-8	0	12	262	263	2
-5	0	11	79	44	3	3	-6	12	341	339	2	-7	0	12	299	298	2
-4	0	11	227	217	2	4	-6	12	220	214	2	-6	0	12	146	155	2
-3	0	11	408	418	2	5	-6	12	364	359	2	-5	0	12	303	304	2
-2	0	11	58	74	4	-7	-5	12	427	436	2	-4	0	12	261	274	2
-1	0	11	316	315	2	-6	-5	12	429	437	2	-3	0	12	116	112	2
0	0	11	205	201	1	-5	-5	12	717	719	3	-2	0	12	345	339	2
1	0	11	53	48	5	-4	-5	12	681	683	3	-1	0	12	150	145	2
-10	1	11	116	138	3	-3	-5	12	649	655	3	0	0	12	201	200	1
-9	1	11	79	112	4	-2	-5	12	762	759	3	-10	1	12	271	275	2
-8	1	11	38	106	7	-1	-5	12	732	733	3	-9	1	12	325	333	2
-7	1	11	241	221	2	0	-5	12	478	478	2	-8	1	12	252	238	2
-6	1	11	14	26	4	1	-5	12	550	554	3	-7	1	12	352	382	2
-5	1	11	218	222	2	2	-5	12	540	549	2	-6	1	12	290	302	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-4	1	11	212	218	2	3	-5	12	260	260	2	-5	1	12	238	240	2
-3	1	11	163	158	2	4	-5	12	379	377	2	-4	1	12	286	291	2
-2	1	11	15	31	4	-8	-4	12	434	442	2	-3	1	12	267	263	2
-1	1	11	190	196	2	-7	-4	12	270	272	2	-2	1	12	137	137	2
0	1	11	14	4	3	-6	-4	12	361	380	2	-1	1	12	207	204	2
-10	2	11	69	17	4	-5	-4	12	705	722	3	-9	2	12	155	175	2
-9	2	11	119	148	3	-4	-4	12	165	175	2	-8	2	12	218	225	2
-8	2	11	173	161	2	-3	-4	12	499	510	3	-7	2	12	327	327	2
-7	2	11	94	140	3	-2	-4	12	699	712	3	-6	2	12	210	196	2
-6	2	11	163	173	2	-1	-4	12	220	228	2	-5	2	12	300	310	2
-5	2	11	11	19	3	0	-4	12	511	513	2	-4	2	12	288	289	2
-4	2	11	220	225	2	1	-4	12	603	625	3	-3	2	12	281	266	2
-3	2	11	249	244	2	2	-4	12	321	322	2	-8	3	12	199	204	2
-2	2	11	67	59	3	3	-4	12	373	368	2	-7	3	12	164	157	2
-9	3	11	26	18	6	4	-4	12	502	506	2	-6	3	12	118	103	2
-8	3	11	25	19	6	-8	-3	12	222	239	2	0	-9	13	136	139	1
-7	3	11	130	160	2	-7	-3	12	257	269	2	1	-9	13	70	61	3
-6	3	11	29	69	6	-6	-3	12	364	352	2	2	-9	13	24	34	5
-5	3	11	65	67	4	-5	-3	12	372	373	2	3	-9	13	24	33	5
-4	3	11	215	206	2	-4	-3	12	165	171	2	-3	-8	13	83	77	3
0	-9	12	260	261	1	-3	-3	12	467	452	2	-2	-8	13	80	83	3
1	-9	12	190	198	2	-2	-3	12	425	425	2	-1	-6	13	20	20	5
2	-9	12	159	155	2	-1	-3	12	158	149	2	0	-8	13	102	105	2
3	-9	12	142	148	2	0	-3	12	509	510	2	1	-8	13	193	194	2
4	-9	12	116	126	2	1	-3	12	316	325	2	2	-8	13	61	48	3
-3	-8	12	251	261	2	2	-3	12	165	164	2	3	-8	13	43	38	5
-2	-8	12	257	266	2	3	-3	12	351	338	2	4	-8	13	65	69	3
-1	-8	12	220	217	2	-9	-2	12	334	339	2	-4	-7	13	101	99	2
0	-8	12	306	308	1	-8	-2	12	243	230	2	-3	-7	13	124	122	2
1	-8	12	306	305	2	-7	-2	12	497	511	2	-2	-7	13	157	153	2
2	-8	12	280	276	2	-6	-2	12	519	500	2	-1	-7	13	166	172	2
3	-8	12	410	411	2	-5	-2	12	370	382	2	0	-7	13	27	26	4
4	-8	12	406	395	2	-4	-2	12	590	626	3	1	-7	13	263	257	2
5	-8	12	278	267	2	-3	-2	12	533	547	3	2	-7	13	184	181	2
-4	-7	12	164	171	2	-2	-2	12	452	438	2	3	-7	13	107	95	2
-3	-7	12	245	243	2	-1	-2	12	424	421	2	4	-7	13	61	70	4
-2	-7	12	178	182	2	0	-2	12	498	495	2	-6	-6	13	16	35	5
-1	-7	12	381	382	2	1	-2	12	195	195	1	-5	-6	13	17	36	5
0	-7	12	471	479	2	2	-2	12	271	270	2	-4	-6	13	111	85	2
1	-7	12	442	436	2	-9	-1	12	196	197	2	-3	-6	13	18	16	5
2	-7	12	511	506	2	-8	-1	12	323	316	2	-2	-6	13	252	239	2
3	-7	12	600	591	3	-7	-1	12	462	455	2	-1	-6	13	125	130	2
4	-7	12	428	429	2	-6	-1	12	301	301	2	0	-6	13	29	32	3
5	-7	12	364	353	2	-5	-1	12	478	476	2	1	-6	13	179	180	1

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	-6	13	25	42	5	-1	0	13	136	141	2	0	-3	14	469	465	2
3	-6	13	20	34	5	-9	1	13	64	80	4	1	-3	14	420	405	2
4	-6	13	18	20	5	-8	1	13	23	53	6	-9	-2	14	203	208	2
-7	-5	13	46	33	6	-7	1	13	171	152	2	-8	-2	14	430	422	2
-6	-5	13	93	114	3	-6	1	13	181	170	2	-7	-2	14	507	515	3
-5	-5	13	13	46	4	-5	1	13	30	12	7	-6	-2	14	562	557	3
-4	-5	13	101	83	2	-4	1	13	95	104	3	-5	-2	14	580	585	3
-3	-5	13	136	143	2	-3	1	13	88	79	3	-4	-2	14	785	786	3
-2	-5	13	103	106	2	-2	1	13	100	101	2	-3	-2	14	601	607	3
-1	-5	13	269	264	2	-8	2	13	113	63	2	-2	-2	14	551	550	2
0	-5	13	245	252	1	-7	2	13	52	56	6	-1	-2	14	641	646	3
1	-5	13	317	311	2	-6	2	13	123	114	2	0	-2	14	317	316	1
2	-5	13	236	245	2	-5	2	13	72	55	3	-9	-1	14	290	298	2
3	-5	13	239	230	2	1	-9	14	161	164	2	-8	-1	14	459	455	2
4	-5	13	144	137	2	-2	-8	14	65	64	3	-7	-1	14	336	330	2
-8	-4	13	17	41	5	-1	-8	14	142	134	2	-6	-1	14	446	457	2
-5	-4	13	170	159	2	0	-8	14	242	248	1	-5	-1	14	339	351	2
-4	-4	13	30	50	6	1	-8	14	91	82	3	-4	-1	14	308	317	2
-3	-4	13	315	313	2	2	-8	14	290	280	2	-3	-1	14	281	274	2
-2	-4	13	166	166	2	3	-8	14	321	321	2	-2	-1	14	225	232	2
-1	-4	13	228	233	2	-4	-7	14	175	165	2	-1	-1	14	196	194	2
0	-4	13	212	214	1	-3	-7	14	98	90	2	-9	0	14	381	370	2
1	-4	13	122	124	2	-2	-7	14	220	214	2	-8	0	14	280	287	2
2	-4	13	55	47	3	-1	-7	14	297	290	2	-7	0	14	279	277	2
3	-4	13	128	121	2	0	-7	14	248	248	1	-6	0	14	316	308	2
-8	-3	13	202	198	2	1	-7	14	282	283	2	-5	0	14	152	139	2
-7	-3	13	231	236	2	2	-7	14	374	380	2	-4	0	14	232	223	2
-6	-3	13	203	192	2	3	-7	14	229	233	2	-3	0	14	201	184	2
-5	-3	13	206	210	2	-5	-6	14	437	441	2	-2	0	14	163	151	2
-4	-3	13	251	251	2	-4	-6	14	439	438	2	-8	1	14	213	214	2
-3	-3	13	67	62	3	-3	-6	14	276	278	2	-7	1	14	288	291	2
-2	-3	13	37	3	6	-2	-6	14	638	641	3	-6	1	14	271	266	2
-1	-3	13	37	36	6	-1	-6	14	496	485	2	-5	1	14	283	296	2
0	-3	13	106	103	1	0	-6	14	239	243	1	-4	1	14	378	380	2
1	-3	13	141	133	2	1	-6	14	504	499	2	-2	-8	15	77	64	3
2	-3	13	35	40	6	2	-6	14	289	292	2	-1	-8	15	121	116	2
-9	-2	13	64	17	4	3	-6	14	109	106	2	0	-8	15	23	20	4
-8	-2	13	277	280	2	-7	-5	14	172	172	2	1	-8	15	85	90	3
-7	-2	13	130	150	2	-6	-5	14	412	404	2	2	-8	15	126	122	2
-6	-2	13	58	32	4	-5	-5	14	393	401	2	-4	-7	15	65	39	3
-5	-2	13	116	118	2	-4	-5	14	338	329	2	-3	-7	15	106	120	2
-4	-2	13	160	159	2	-3	-5	14	369	368	2	-2	-7	15	98	110	2
-3	-2	13	142	144	2	-2	-5	14	475	483	2	-1	-7	15	141	140	2
-2	-2	13	17	39	4	-1	-5	14	243	240	2	0	-7	15	135	139	1

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-1	-2	13	137	141	2	0	-5	14	273	273	1	1	-7	15	240	237	2
0	-2	13	165	166	1	1	-5	14	464	463	2	2	-7	15	131	142	2
1	-2	13	100	90	2	2	-5	14	168	165	2	-5	-6	15	19	32	5
2	-2	13	114	106	2	3	-5	14	324	314	2	-3	-6	15	203	194	2
-9	-1	13	88	94	3	-7	-4	14	165	172	2	-2	-6	15	64	35	4
-8	-1	13	70	14	4	-6	-4	14	420	394	2	-1	-6	15	117	105	2
-7	-1	13	246	265	2	-5	-4	14	115	107	2	0	-6	15	32	29	4
-6	-1	13	138	105	2	-4	-4	14	181	179	2	1	-6	15	47	3	5
-5	-1	13	19	32	5	-3	-4	14	352	347	2	2	-6	15	39	31	6
-4	-1	13	210	215	2	-2	-4	14	182	170	2	-6	-5	15	161	175	2
-3	-1	13	39	19	6	-1	-4	14	259	267	2	-5	-5	15	150	151	2
-2	-1	13	21	14	5	0	-4	14	393	391	2	-4	-5	15	76	39	3
-1	-1	13	64	38	3	1	-4	14	384	381	2	-3	-5	15	114	122	2
0	-1	13	32	9	4	2	-4	14	273	265	2	-2	-5	15	12	18	3
-9	0	13	46	32	6	-8	-3	14	210	217	2	-1	-5	15	55	45	4
-8	0	13	49	43	6	-7	-3	14	428	426	2	0	-5	15	34	30	4
-7	0	13	183	201	2	-6	-3	14	412	419	2	1	-5	15	34	32	6
-6	0	13	93	116	3	-5	-3	14	301	293	2	2	-5	15	75	74	3
-5	0	13	21	38	5	-4	-3	14	636	644	3	-7	-4	15	17	54	5
-4	0	13	190	198	2	-3	-3	14	576	579	3	-6	-4	15	71	76	4
-3	0	13	166	154	2	-2	-3	14	432	413	2	-5	-4	15	105	43	2
-2	0	13	95	85	3	-1	-3	14	735	726	3	-3	-4	15	12	3	3
-2	-4	15	133	147	2	-2	-7	16	282	281	2	-1	-3	16	351	346	2
-1	-4	15	61	37	4	-1	-7	16	227	230	2	-7	-2	16	154	160	2
0	-4	15	105	98	2	0	-7	16	146	150	1	-6	-2	16	222	218	2
1	-4	15	161	160	2	1	-7	16	273	274	2	-5	-2	16	324	331	2
-8	-3	15	136	107	2	-5	-6	16	284	275	2	-4	-2	16	153	150	2
-7	-3	15	79	104	3	-4	-6	16	83	93	3	-3	-2	16	283	289	2
-6	-3	15	100	18	3	-3	-6	16	391	384	2	-2	-2	16	289	278	2
-5	-3	15	180	182	2	-2	-6	16	301	304	2	-7	-1	16	219	216	2
-2	-3	15	110	87	2	-1	-6	16	206	205	2	-6	-1	16	276	268	2
-1	-3	15	40	37	6	0	-6	16	364	366	1	-5	-1	16	229	230	2
0	-3	15	23	22	4	1	-6	16	275	275	2	-4	-1	16	247	232	2
-8	-2	15	15	27	4	-6	-5	16	231	239	2	-2	-7	17	90	84	3
-7	-2	15	75	100	4	-5	-5	16	152	139	2	-1	-7	17	162	161	2
-6	-2	15	80	44	4	-4	-5	16	120	120	2	-4	-6	17	45	25	6
-5	-2	15	119	91	2	-3	-5	16	358	363	2	-3	-6	17	36	11	6
-4	-2	15	63	59	4	-2	-5	16	115	100	2	-2	-6	17	68	66	3
-3	-2	15	92	12	3	-1	-5	16	136	138	2	-1	-6	17	117	107	2
-2	-2	15	266	262	2	0	-5	16	338	342	1	-5	-5	17	182	184	2
-1	-2	15	17	7	5	1	-5	16	86	80	2	-4	-5	17	135	129	2
-8	-1	15	72	84	4	-7	-4	16	377	359	2	-3	-5	17	247	248	2
-7	-1	15	12	2	4	-6	-4	16	229	221	2	-2	-5	17	152	158	2
-6	-1	15	159	144	2	-5	-4	16	218	221	2	-1	-5	17	135	130	2

Table A-10 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	-1	15	34	9	7	-4	-4	16	313	306	2	-6	-4	17	114	95	2
-4	-1	15	15	53	4	-3	-4	16	276	284	2	-5	-4	17	11	27	3
-3	-1	15	190	191	2	-2	-4	16	153	148	2	-4	-4	17	40	45	6
-2	-1	15	83	87	3	-1	-4	16	288	290	2	-3	-4	17	37	78	6
-8	0	15	112	90	2	0	-4	16	250	259	1	-2	-4	17	35	12	6
-7	0	15	271	277	2	-7	-3	16	356	342	2	-6	-3	17	64	34	4
-6	0	15	228	221	2	-6	-3	16	201	212	2	-5	-3	17	42	61	6
-5	0	15	93	100	3	-5	-3	16	404	412	2	-4	-3	17	72	74	3
-4	0	15	200	187	2	-4	-3	16	337	332	2	-3	-3	17	119	89	2
-1	-8	16	260	267	2	-3	-3	16	347	351	2	-6	-2	17	47	48	6
0	-8	16	111	105	2	-2	-3	16	353	352	2	-5	-2	17	134	124	2
-3	-7	16	186	181	2												

Table A-11. Observed and Calculated Structure Factors for 55b

F_0, F_c and SIG (σ) values have been multiplied by 10.

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	0	0	4291	4369	125	10	8	0	382	364	32	11	1	1	361	372	52
4	0	0	5899	5953	172	11	8	0	420	403	31	12	1	1	343	353	38
6	0	0	8792	8663	256	12	8	0	984	924	34	13	1	1	66	131	45
8	0	0	5111	5120	150	13	8	0	149	269	72	14	1	1	431	421	25
10	0	0	3141	3221	94	14	8	0	687	676	31	15	1	1	124	171	60
12	0	0	3877	3924	116	15	8	0	511	499	33	0	2	1	2101	1965	150
14	0	0	3372	3325	101	0	10	0	2261	2115	68	1	2	1	3026	2911	133
16	0	0	1785	1715	55	1	10	0	889	849	30	2	2	1	4229	4163	153
0	2	0	1071	951	32	2	10	0	1411	1373	44	3	2	1	1998	2047	60
1	2	0	754	655	24	3	10	0	74	52	48	4	2	1	844	864	26
2	2	0	1156	1140	35	4	10	0	939	913	31	5	2	1	1587	1650	68
3	2	0	1549	1607	47	5	10	0	426	404	28	6	2	1	3000	3087	88
4	2	0	317	310	22	6	10	0	1540	1508	47	7	2	1	2569	2673	82
5	2	0	368	388	22	7	10	0	950	891	32	8	2	1	2406	2488	75
6	2	0	1111	1127	35	8	10	0	2016	1994	61	9	2	1	1365	1377	46
7	2	0	1048	1088	33	9	10	0	106	63	59	10	2	1	698	693	34
8	2	0	586	578	23	10	10	0	159	96	68	11	2	1	603	611	40
9	2	0	287	288	30	11	10	0	111	264	61	12	2	1	1541	1550	69
10	2	0	393	414	28	12	10	0	1214	1222	40	13	2	1	1697	1705	51
11	2	0	521	494	27	13	10	0	411	446	35	14	2	1	1720	1723	52
12	2	0	386	405	32	0	12	0	112	147	60	15	2	1	875	863	50
13	2	0	390	354	34	1	12	0	434	394	28	0	3	1	1426	1332	50
14	2	0	608	619	30	2	12	0	102	204	56	1	3	1	1221	1193	36
15	2	0	319	279	39	3	12	0	210	189	56	2	3	1	579	523	20
0	4	0	3392	3114	100	4	12	0	449	421	29	3	3	1	1621	1598	48
1	4	0	3071	2877	91	5	12	0	327	359	36	4	3	1	1004	1037	30
2	4	0	257	255	24	6	12	0	135	82	65	5	3	1	546	582	27
3	4	0	857	770	27	7	12	0	348	314	35	6	3	1	767	813	24
4	4	0	1301	1250	40	8	12	0	441	403	30	7	3	1	516	537	20
5	4	0	1722	1768	52	9	12	0	180	199	67	8	3	1	460	473	19
6	4	0	707	769	25	10	12	0	53	30	38	9	3	1	79	97	44
7	4	0	2417	2473	73	11	12	0	229	260	61	10	3	1	585	588	25
8	4	0	803	771	27	0	14	0	622	615	29	11	3	1	72	15	50
9	4	0	333	235	29	1	14	0	2385	2335	72	12	3	1	296	258	28
10	4	0	472	470	26	2	14	0	313	335	36	13	3	1	475	478	24
11	4	0	892	901	31	3	14	0	1725	1705	53	14	3	1	503	497	38
12	4	0	315	266	35	4	14	0	375	388	32	15	3	1	52	32	37
13	4	0	1320	1287	42	5	14	0	1693	1635	52	0	4	1	214	158	104
14	4	0	632	599	29	6	14	0	437	472	33	1	4	1	2262	2119	67
15	4	0	802	807	32	7	14	0	2354	2384	72	2	4	1	1292	1232	47
0	6	0	4235	3841	124	8	14	0	231	284	61	3	4	1	570	519	30
1	6	0	1956	1772	59	9	14	0	1259	1282	41	4	4	1	440	455	17
2	6	0	2049	1904	61	0	16	0	538	569	31	5	4	1	1576	1587	50
3	6	0	1653	1594	50	1	16	0	806	874	32	6	4	1	480	502	18
4	6	0	1989	1934	60	2	16	0	76	95	51	7	4	1	1333	1383	51
5	6	0	1065	1060	34	3	16	0	314	359	40	8	4	1	126	158	47
6	6	0	2254	2216	68	4	16	0	183	214	68	9	4	1	553	553	40
7	6	0	2068	2133	62	1	0	1	352	332	12	10	4	1	525	554	41
8	6	0	2216	2248	67	3	0	1	358	361	31	11	4	1	466	443	25
9	6	0	964	983	32	5	0	1	484	482	18	12	4	1	64	61	43
10	6	0	703	678	28	7	0	1	322	317	37	13	4	1	991	997	32
11	6	0	543	512	28	9	0	1	357	343	40	14	4	1	292	208	77
12	6	0	1602	1625	50	11	0	1	192	177	82	15	4	1	552	546	24
13	6	0	1402	1413	45	13	0	1	56	128	41	0	5	1	366	364	18
14	6	0	1039	1046	36	15	0	1	56	47	41	1	5	1	236	218	34
15	6	0	752	759	32	0	1	1	1459	1465	116	2	5	1	664	646	21
0	8	0	1529	1395	47	1	1	1	527	500	16	3	5	1	373	355	32
1	8	0	725	663	25	2	1	1	607	628	19	4	5	1	489	494	20
2	8	0	1486	1387	46	3	1	1	535	565	19	5	5	1	389	399	42
3	8	0	652	616	24	4	1	1	809	833	25	6	5	1	216	172	24
4	8	0	867	841	29	5	1	1	489	524	20	7	5	1	44	107	32
5	8	0	595	564	24	6	1	1	1124	1171	37	8	5	1	70	35	42
6	8	0	1368	1400	43	7	1	1	391	425	33	9	5	1	252	246	27
7	8	0	573	625	26	8	1	1	218	257	26	10	5	1	384	371	22
8	8	0	1189	1205	38	9	1	1	171	153	64	11	5	1	151	202	84
9	8	0	364	400	33	10	1	1	711	717	24	12	5	1	65	11	44

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
13	5	1	72	58	47	1	10	1	567	545	21	7	15	1	175	198	55
14	5	1	122	79	59	2	10	1	357	340	58	0	16	1	1046	1069	40
15	5	1	159	151	59	3	10	1	472	448	20	1	16	1	497	479	52
0	6	1	1550	1451	47	4	10	1	106	100	51	2	16	1	718	729	26
1	6	1	3200	2976	94	5	10	1	405	474	127	3	16	1	41	35	30
2	6	1	106	32	52	6	10	1	672	669	24	4	16	1	443	474	24
3	6	1	1718	1624	52	7	10	1	402	408	25	0	0	2	5757	5784	167
4	6	1	410	419	18	8	10	1	200	211	44	2	0	2	2518	2627	151
5	6	1	2006	1998	68	9	10	1	346	338	25	4	0	2	2555	2650	136
6	6	1	617	615	21	10	10	1	220	239	34	6	0	2	3700	3733	179
7	6	1	2504	2523	79	11	10	1	331	309	26	8	0	2	2815	2902	110
8	6	1	610	613	26	12	10	1	209	240	46	10	0	2	1212	1225	39
9	6	1	1319	1349	40	13	10	1	98	154	54	12	0	2	2157	2135	78
10	6	1	124	143	74	0	11	1	342	336	22	14	0	2	1880	1844	56
11	6	1	833	850	37	1	11	1	104	114	51	16	0	2	971	962	34
12	6	1	257	254	56	2	11	1	256	219	26	0	1	2	1819	1825	103
13	6	1	1692	1727	51	3	11	1	123	6	60	1	1	2	404	400	18
14	6	1	594	592	50	4	11	1	308	291	24	2	1	2	1738	1832	56
15	6	1	750	744	27	5	11	1	134	150	57	3	1	2	1089	1133	43
0	7	1	523	535	18	6	11	1	49	15	35	4	1	2	701	739	27
1	7	1	1150	1101	39	7	11	1	78	97	47	5	1	2	223	241	29
2	7	1	884	820	32	8	11	1	131	116	73	6	1	2	1389	1428	74
3	7	1	764	704	24	9	11	1	62	47	42	7	1	2	668	700	28
4	7	1	160	149	35	10	11	1	231	199	34	8	1	2	1769	1828	52
5	7	1	824	813	26	11	11	1	75	66	49	9	1	2	318	326	21
6	7	1	672	866	27	12	11	1	55	46	39	10	1	2	48	54	34
7	7	1	764	773	25	0	12	1	1573	1528	50	11	1	2	389	358	22
8	7	1	530	528	39	1	12	1	2257	2207	89	12	1	2	1012	1017	38
9	7	1	705	713	24	2	12	1	653	641	23	13	1	2	196	256	52
10	7	1	78	17	50	3	12	1	935	916	30	14	1	2	934	947	30
11	7	1	149	214	56	4	12	1	458	446	22	15	1	2	435	406	27
12	7	1	575	567	24	5	12	1	1807	1741	54	0	2	2	522	499	30
13	7	1	565	588	24	6	12	1	1383	1358	47	1	2	2	464	466	16
14	7	1	246	301	92	7	12	1	1933	1939	58	2	2	2	988	1014	63
15	7	1	356	381	41	8	12	1	518	522	24	3	2	2	456	474	17
0	8	1	3937	3670	135	9	12	1	1015	1013	32	4	2	2	300	314	18
1	8	1	1436	1392	44	10	12	1	531	542	24	5	2	2	416	423	35
2	8	1	2304	2123	69	11	12	1	854	894	29	6	2	2	636	663	21
3	8	1	56	44	36	0	13	1	440	441	28	7	2	2	959	928	32
4	8	1	1295	1222	55	1	13	1	600	561	26	8	2	2	612	607	25
5	8	1	1107	1083	34	2	13	1	438	426	22	9	2	2	325	326	21
6	8	1	3327	3273	108	3	13	1	429	442	23	10	2	2	286	269	37
7	8	1	1076	1044	35	4	13	1	441	420	23	11	2	2	87	26	59
8	8	1	1662	1665	55	5	13	1	455	417	29	12	2	2	257	237	31
9	8	1	155	231	63	6	13	1	372	355	49	13	2	2	363	356	63
10	8	1	1234	1227	38	7	13	1	566	548	23	14	2	2	503	487	24
11	8	1	606	618	25	8	13	1	336	357	28	15	2	2	107	57	72
12	8	1	1397	1373	42	9	13	1	381	384	31	0	3	2	334	341	28
13	8	1	621	601	25	10	13	1	232	213	38	1	3	2	736	734	58
14	8	1	1585	1621	48	0	14	1	403	374	23	2	3	2	456	435	28
0	9	1	1144	1105	46	1	14	1	831	833	28	3	3	2	440	432	17
1	9	1	43	28	31	2	14	1	387	359	63	4	3	2	54	76	35
2	9	1	1347	1258	41	3	14	1	674	669	25	5	3	2	182	193	26
3	9	1	44	44	32	4	14	1	115	79	56	6	3	2	286	305	30
4	9	1	1044	1002	37	5	14	1	592	577	24	7	3	2	943	958	29
5	9	1	163	128	43	6	14	1	556	552	46	8	3	2	325	343	20
6	9	1	1004	1023	34	7	14	1	834	871	28	9	3	2	301	311	23
7	9	1	111	60	67	8	14	1	123	119	60	10	3	2	390	394	53
8	9	1	896	891	29	9	14	1	506	521	71	11	3	2	48	78	34
9	9	1	62	52	42	0	15	1	218	241	36	12	3	2	231	179	33
10	9	1	590	598	23	1	15	1	82	154	49	13	3	2	666	652	25
11	9	1	80	24	48	2	15	1	116	128	56	14	3	2	89	41	53
12	9	1	571	580	25	3	15	1	65	247	44	15	3	2	224	226	59
13	9	1	157	19	59	4	15	1	190	247	71	0	4	2	429	438	29
14	9	1	525	526	25	5	15	1	149	95	72	1	4	2	2399	2319	100
0	10	1	681	676	31	6	15	1	74	115	50	2	4	2	1261	1212	59

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	4	2	429	568	208	5	8	2	568	570	21	2	13	2	420	368	27
4	4	2	574	555	19	6	8	2	1642	1639	63	3	13	2	205	212	100
5	4	2	1319	1376	39	7	8	2	647	610	24	4	13	2	742	723	26
6	4	2	563	553	20	8	8	2	1165	1142	39	5	13	2	763	713	26
7	4	2	2032	2053	62	9	8	2	259	252	31	6	13	2	440	467	24
8	4	2	377	373	30	10	8	2	571	593	23	7	13	2	667	677	26
9	4	2	347	336	49	11	8	2	312	303	27	8	13	2	384	389	26
10	4	2	448	453	28	12	8	2	911	893	30	9	13	2	269	290	32
11	4	2	577	555	25	13	8	2	306	328	52	10	13	2	477	457	32
12	4	2	113	109	68	14	8	2	812	794	28	0	14	2	500	526	23
13	4	2	1200	1205	58	0	9	2	1827	1724	54	1	14	2	1654	1656	54
14	4	2	123	216	60	1	9	2	774	733	45	2	14	2	391	350	24
15	4	2	671	666	25	2	9	2	169	186	72	3	14	2	863	902	30
0	5	2	1359	1302	54	3	9	2	779	754	29	4	14	2	266	238	29
1	5	2	2347	2252	103	4	9	2	372	373	21	5	14	2	1246	1256	43
2	5	2	1676	1586	74	5	9	2	712	678	31	6	14	2	505	488	24
3	5	2	1079	1059	37	6	9	2	841	827	27	7	14	2	1569	1575	47
4	5	2	621	609	23	7	9	2	445	460	47	8	14	2	245	240	119
5	5	2	1426	1427	51	8	9	2	474	474	24	0	15	2	427	465	53
6	5	2	1305	1274	47	9	9	2	676	695	34	1	15	2	928	940	35
7	5	2	2189	2222	67	10	9	2	166	193	52	2	15	2	111	99	60
8	5	2	663	678	26	11	9	2	298	272	46	3	15	2	438	440	24
9	5	2	737	752	25	12	9	2	424	434	25	4	15	2	89	107	49
10	5	2	385	397	23	13	9	2	406	375	33	5	15	2	703	708	26
11	5	2	898	904	31	14	9	2	552	555	50	6	15	2	271	317	31
12	5	2	714	734	28	0	10	2	1993	1901	64	0	16	2	591	646	26
13	5	2	1189	1190	37	1	10	2	147	180	81	1	16	2	551	566	24
14	5	2	88	82	53	2	10	2	926	888	29	2	16	2	220	209	37
15	5	2	835	831	45	3	10	2	364	367	21	3	16	2	230	166	35
0	6	2	2528	2400	77	4	10	2	709	679	38	1	0	3	497	524	30
1	6	2	2130	2045	77	5	10	2	142	104	76	3	0	3	1104	1137	50
2	6	2	1657	1575	52	6	10	2	1344	1325	44	5	0	3	675	698	36
3	6	2	1237	1217	39	7	10	2	160	160	50	7	0	3	165	238	70
4	6	2	1735	1668	67	8	10	2	1363	1373	41	9	0	3	744	741	41
5	6	2	1005	991	34	9	10	2	103	49	67	11	0	3	352	342	44
6	6	2	1459	1457	44	10	10	2	91	140	50	13	0	3	305	223	51
7	6	2	2171	2190	64	11	10	2	149	78	56	15	0	3	460	449	24
8	6	2	1694	1717	50	12	10	2	950	967	31	0	1	3	1985	2068	81
9	6	2	800	812	26	13	10	2	159	147	59	1	1	3	874	918	33
10	6	2	678	692	24	0	11	2	1368	1336	43	2	1	3	453	461	17
11	6	2	574	585	26	1	11	2	855	838	27	3	1	3	125	115	39
12	6	2	1077	1087	39	2	11	2	705	683	24	4	1	3	529	507	25
13	6	2	1304	1320	40	3	11	2	445	411	21	5	1	3	560	571	20
14	6	2	940	925	43	4	11	2	580	560	22	6	1	3	1844	1876	80
15	6	2	661	668	26	5	11	2	573	560	22	7	1	3	584	577	48
0	7	2	897	861	27	6	11	2	1057	1056	33	8	1	3	406	443	19
1	7	2	814	751	25	7	11	2	853	864	28	9	1	3	216	209	28
2	7	2	36	85	26	8	11	2	620	644	73	10	1	3	260	276	82
3	7	2	335	320	32	9	11	2	280	264	29	11	1	3	226	211	34
4	7	2	410	416	18	10	11	2	381	414	29	12	1	3	624	635	55
5	7	2	847	825	39	11	11	2	412	413	44	13	1	3	197	254	84
6	7	2	309	323	22	12	11	2	545	556	57	14	1	3	686	698	25
7	7	2	276	289	28	0	12	2	553	580	29	15	1	3	304	314	81
8	7	2	353	359	23	1	12	2	343	357	41	0	2	3	2757	2795	204
9	7	2	444	436	27	2	12	2	443	453	22	1	2	3	758	755	46
10	7	2	126	130	76	3	12	2	172	207	73	2	2	3	612	623	20
11	7	2	238	268	34	4	12	2	559	573	22	3	2	3	922	921	34
12	7	2	257	265	33	5	12	2	300	324	31	4	2	3	152	167	40
13	7	2	195	236	52	6	12	2	293	305	43	5	2	3	171	236	73
14	7	2	117	164	71	7	12	2	255	267	32	6	2	3	1899	1947	77
15	7	2	114	196	69	8	12	2	561	534	23	7	2	3	807	811	41
0	8	2	2340	2207	69	9	12	2	241	250	37	8	2	3	1025	1046	33
1	8	2	831	769	26	10	12	2	255	275	33	9	2	3	163	133	43
2	8	2	1245	1204	37	11	12	2	104	175	56	10	2	3	326	310	34
3	8	2	126	97	67	0	13	2	833	837	28	11	2	3	62	76	41
4	8	2	947	932	29	1	13	2	853	842	28	12	2	3	774	759	26

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
13	2	3	558	561	27	15	6	3	510	482	25	6	11	3	716	725	25
14	2	3	1129	1120	36	0	7	3	2651	2624	119	7	11	3	686	702	27
15	2	3	100	167	67	1	7	3	1960	1879	78	8	11	3	539	540	23
0	3	3	1649	1690	138	2	7	3	2182	2096	101	9	11	3	165	189	52
1	3	3	1518	1515	102	3	7	3	1199	1137	45	10	11	3	140	67	84
2	3	3	614	620	28	4	7	3	1043	1001	51	11	11	3	123	173	66
3	3	3	182	187	30	5	7	3	1479	1446	68	12	11	3	312	369	48
4	3	3	359	377	17	6	7	3	2471	2473	111	0	12	3	579	567	22
5	3	3	948	943	29	7	7	3	1608	1609	50	1	12	3	1373	1359	48
6	3	3	1177	1222	35	8	7	3	1719	1737	74	2	12	3	413	376	22
7	3	3	1428	1449	56	9	7	3	1029	1033	43	3	12	3	841	846	27
8	3	3	728	751	24	10	7	3	734	727	41	4	12	3	122	102	59
9	3	3	493	491	23	11	7	3	642	619	24	5	12	3	935	914	38
10	3	3	369	367	28	12	7	3	1388	1335	42	6	12	3	605	606	34
11	3	3	301	276	27	13	7	3	1151	1185	36	7	12	3	1404	1438	50
12	3	3	505	517	23	14	7	3	1231	1246	38	8	12	3	302	290	28
13	3	3	1234	1206	38	15	7	3	622	641	28	9	12	3	596	620	47
14	3	3	725	731	26	0	8	3	1797	1739	81	10	12	3	94	166	52
15	3	3	427	405	27	1	8	3	1082	1055	42	11	12	3	542	559	24
0	4	3	972	974	106	2	8	3	1097	1048	46	0	13	3	284	299	28
1	4	3	1229	1225	94	3	8	3	800	762	40	1	13	3	1347	1345	41
2	4	3	424	412	17	4	8	3	513	500	20	2	13	3	43	69	31
3	4	3	124	81	39	5	8	3	1072	1041	49	3	13	3	658	650	49
4	4	3	557	569	28	6	8	3	1654	1626	60	4	13	3	147	81	82
5	4	3	1064	1060	32	7	8	3	662	639	24	5	13	3	1079	1071	34
6	4	3	490	487	19	8	8	3	947	967	30	6	13	3	217	183	37
7	4	3	762	782	24	9	8	3	734	754	34	7	13	3	1123	1166	35
8	4	3	322	341	22	10	8	3	449	466	25	8	13	3	203	168	87
9	4	3	346	364	22	11	8	3	492	474	23	9	13	3	724	754	26
10	4	3	141	184	76	12	8	3	839	827	28	10	13	3	99	38	64
11	4	3	434	437	23	13	8	3	503	479	25	0	14	3	776	794	40
12	4	3	196	268	95	14	8	3	886	902	35	1	14	3	658	690	24
13	4	3	514	554	24	0	9	3	1051	1053	32	2	14	3	772	743	62
14	4	3	66	62	45	1	9	3	219	229	32	3	14	3	537	536	23
15	4	3	399	389	31	2	9	3	1028	1002	37	4	14	3	599	604	24
0	5	3	1499	1446	111	3	9	3	306	275	22	5	14	3	508	524	23
1	5	3	473	466	18	4	9	3	493	481	21	6	14	3	727	747	26
2	5	3	764	773	33	5	9	3	119	19	77	7	14	3	624	656	25
3	5	3	393	369	17	6	9	3	1010	1003	35	8	14	3	525	528	25
4	5	3	1361	1337	48	7	9	3	439	478	44	0	15	3	312	290	68
5	5	3	718	686	26	8	9	3	915	900	29	1	15	3	391	396	24
6	5	3	570	589	20	9	9	3	94	75	52	2	15	3	177	116	47
7	5	3	70	60	42	10	9	3	298	307	28	3	15	3	410	402	43
8	5	3	910	895	28	11	9	3	137	155	76	4	15	3	186	198	49
9	5	3	141	146	53	12	9	3	534	550	24	5	15	3	283	280	31
10	5	3	505	465	43	13	9	3	96	124	62	6	15	3	170	165	54
11	5	3	197	211	84	0	10	3	645	623	22	0	16	3	494	507	24
12	5	3	509	520	43	1	10	3	214	198	80	1	16	3	596	623	24
13	5	3	70	56	47	2	10	3	718	697	33	2	16	3	251	263	66
14	5	3	399	375	26	3	10	3	244	268	28	0	0	4	1309	1376	39
15	5	3	144	125	62	4	10	3	573	588	22	2	0	4	917	974	39
0	6	3	1250	1209	62	5	10	3	206	227	34	4	0	4	231	254	21
1	6	3	995	969	72	6	10	3	585	573	30	6	0	4	1266	1282	75
2	6	3	1009	991	49	7	10	3	58	85	40	8	0	4	1018	1013	41
3	6	3	560	535	19	8	10	3	560	560	23	10	0	4	188	214	50
4	6	3	770	757	28	9	10	3	149	209	55	12	0	4	738	748	25
5	6	3	566	550	22	10	10	3	366	374	32	14	0	4	712	684	26
6	6	3	934	938	44	11	10	3	104	110	62	16	0	4	386	394	37
7	6	3	1195	1200	36	12	10	3	372	352	51	0	1	4	2734	2853	108
8	6	3	792	789	29	13	10	3	92	40	62	1	1	4	1680	1727	53
9	6	3	409	439	22	0	11	3	533	520	24	2	1	4	178	205	26
10	6	3	392	406	55	1	11	3	640	627	23	3	1	4	725	728	29
11	6	3	295	295	78	2	11	3	654	636	39	4	1	4	90	168	48
12	6	3	646	640	24	3	11	3	134	128	81	5	1	4	1265	1306	60
13	6	3	808	808	28	4	11	3	60	37	41	6	1	4	1605	1666	77
14	6	3	403	373	60	5	11	3	398	367	23	7	1	4	1228	1270	54

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
8	1	4	1193	1192	65	10	5	4	91	53	61	0	10	4	1202	1190	73
9	1	4	683	698	23	11	5	4	1465	1462	44	1	10	4	135	63	66
10	1	4	60	74	40	12	5	4	348	324	26	2	10	4	552	570	68
11	1	4	616	634	44	13	5	4	2129	2130	64	3	10	4	329	341	23
12	1	4	952	933	55	14	5	4	157	191	76	4	10	4	347	359	23
13	1	4	683	683	25	15	5	4	1392	1349	43	5	10	4	79	21	53
14	1	4	1046	1058	40	0	6	4	1451	1445	129	6	10	4	929	892	44
15	1	4	625	609	39	1	6	4	1156	1151	85	7	10	4	165	133	52
0	2	4	295	299	18	2	6	4	982	973	59	8	10	4	711	698	25
1	2	4	285	273	18	3	6	4	597	598	20	9	10	4	59	17	40
2	2	4	49	56	33	4	6	4	690	640	48	10	10	4	101	136	54
3	2	4	601	592	20	5	6	4	776	800	25	11	10	4	102	125	57
4	2	4	91	135	44	6	6	4	1112	1153	35	12	10	4	545	550	25
5	2	4	145	200	38	7	6	4	988	1026	38	0	11	4	1258	1283	57
6	2	4	165	176	36	8	6	4	894	911	29	1	11	4	735	752	32
7	2	4	57	87	39	9	6	4	433	448	23	2	11	4	708	716	43
8	2	4	69	7	47	10	6	4	420	408	23	3	11	4	404	402	40
9	2	4	121	91	52	11	6	4	363	383	25	4	11	4	525	523	22
10	2	4	136	8	76	12	6	4	623	624	33	5	11	4	398	404	59
11	2	4	252	251	30	13	6	4	639	643	40	6	11	4	1026	1037	51
12	2	4	63	68	43	14	6	4	600	577	25	7	11	4	915	922	33
13	2	4	143	197	79	15	6	4	281	282	41	8	11	4	754	768	26
14	2	4	131	5	79	0	7	4	694	660	48	9	11	4	184	222	49
15	2	4	84	55	50	1	7	4	342	342	25	10	11	4	389	368	25
0	3	4	801	801	83	2	7	4	106	142	57	11	11	4	270	341	33
1	3	4	1697	1698	109	3	7	4	586	551	20	0	12	4	344	319	24
2	3	4	1182	1173	58	4	7	4	157	166	42	1	12	4	482	455	27
3	3	4	1267	1275	38	5	7	4	446	420	27	2	12	4	282	264	27
4	3	4	539	556	19	6	7	4	261	244	39	3	12	4	519	491	24
5	3	4	906	947	28	7	7	4	66	41	43	4	12	4	127	101	54
6	3	4	1023	1049	31	8	7	4	127	149	68	5	12	4	460	429	23
7	3	4	1587	1598	47	9	7	4	57	14	40	6	12	4	324	348	50
8	3	4	252	255	26	10	7	4	77	48	50	7	12	4	373	355	32
9	3	4	769	756	55	11	7	4	76	18	49	8	12	4	257	264	32
10	3	4	528	540	37	12	7	4	121	205	59	9	12	4	350	345	27
11	3	4	579	569	40	13	7	4	74	115	48	10	12	4	70	85	46
12	3	4	349	381	26	14	7	4	178	126	76	0	13	4	808	802	29
13	3	4	927	933	49	0	8	4	96	97	47	1	13	4	1023	1054	32
14	3	4	139	90	77	1	8	4	721	703	66	2	13	4	461	467	27
15	3	4	482	457	25	2	8	4	303	303	21	3	13	4	605	613	36
0	4	4	672	674	50	3	8	4	395	355	33	4	13	4	503	535	23
1	4	4	1090	1097	54	4	8	4	503	507	20	5	13	4	780	804	46
2	4	4	201	234	23	5	8	4	574	586	61	6	13	4	595	606	28
3	4	4	448	457	33	6	8	4	85	17	51	7	13	4	939	989	47
4	4	4	71	64	46	7	8	4	500	508	22	8	13	4	423	455	40
5	4	4	868	868	36	8	8	4	132	137	79	9	13	4	515	545	44
6	4	4	423	416	19	9	8	4	372	379	25	0	14	4	134	219	72
7	4	4	841	883	29	10	8	4	251	258	32	1	14	4	680	696	25
8	4	4	335	289	49	11	8	4	204	285	64	2	14	4	216	202	35
9	4	4	575	571	22	12	8	4	118	19	77	3	14	4	219	275	93
10	4	4	176	94	85	13	8	4	378	390	27	4	14	4	295	275	28
11	4	4	294	321	28	14	8	4	117	43	76	5	14	4	570	583	26
12	4	4	263	287	70	0	9	4	2508	2472	146	6	14	4	61	102	42
13	4	4	712	700	26	1	9	4	530	516	20	7	14	4	612	575	29
14	4	4	143	123	79	2	9	4	1158	1135	51	0	15	4	905	937	32
15	4	4	367	369	48	3	9	4	470	485	33	1	15	4	818	855	53
0	5	4	933	903	69	4	9	4	907	895	44	2	15	4	572	582	24
1	5	4	4051	4013	286	5	9	4	414	405	26	3	15	4	394	413	25
2	5	4	169	192	27	6	9	4	1870	1871	69	4	15	4	478	507	34
3	5	4	1755	1708	95	7	9	4	397	401	25	5	15	4	523	522	42
4	5	4	179	104	28	8	9	4	1474	1458	44	1	0	5	778	781	24
5	5	4	2809	2845	90	9	9	4	352	353	25	3	0	5	631	653	51
6	5	4	626	633	22	10	9	4	424	429	61	5	0	5	486	486	25
7	5	4	3485	3542	105	11	9	4	308	250	31	7	0	5	986	1047	70
8	5	4	325	309	24	12	9	4	1126	1117	35	9	0	5	85	135	47
9	5	4	1515	1547	47	13	9	4	220	251	69	11	0	5	511	499	22

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
13	0	5	422	335	30	0	5	5	410	375	66	6	9	5	780	791	25
15	0	5	339	327	29	1	5	5	540	556	58	7	9	5	79	127	47
0	1	5	2730	2849	107	2	5	5	252	236	21	8	9	5	579	582	23
1	1	5	91	90	44	3	5	5	297	257	30	9	9	5	91	105	51
2	1	5	2016	2061	79	4	5	5	214	232	80	10	9	5	91	158	50
3	1	5	537	596	20	5	5	5	487	494	20	11	9	5	81	113	49
4	1	5	1294	1353	62	6	5	5	194	169	32	12	9	5	478	449	34
5	1	5	94	29	45	7	5	5	319	349	24	13	9	5	107	42	59
6	1	5	2398	2433	109	8	5	5	299	306	27	0	10	5	59	44	42
7	1	5	96	107	58	9	5	5	68	9	46	1	10	5	496	493	24
8	1	5	1535	1679	92	10	5	5	131	75	70	2	10	5	453	489	39
9	1	5	141	178	52	11	5	5	153	220	57	3	10	5	392	419	22
10	1	5	801	782	25	12	5	5	64	129	43	4	10	5	206	224	88
11	1	5	100	124	54	13	5	5	127	186	82	5	10	5	333	353	25
12	1	5	1254	1241	46	14	5	5	76	150	50	6	10	5	131	192	71
13	1	5	93	133	56	15	5	5	87	111	52	7	10	5	485	483	23
14	1	5	1196	1197	43	0	6	5	310	331	38	8	10	5	138	196	59
15	1	5	173	87	54	1	6	5	419	405	18	9	10	5	233	291	30
0	2	5	1560	1578	76	2	6	5	500	499	45	10	10	5	102	177	55
1	2	5	1164	1174	63	3	6	5	123	168	66	11	10	5	211	239	46
2	2	5	1580	1629	50	4	6	5	221	184	26	12	10	5	167	149	71
3	2	5	851	869	26	5	6	5	208	208	29	0	11	5	1237	1276	91
4	2	5	1198	1221	36	6	6	5	370	348	29	1	11	5	1343	1357	86
5	2	5	1046	1078	32	7	6	5	533	556	22	2	11	5	847	837	32
6	2	5	1139	1163	50	8	6	5	287	290	27	3	11	5	618	646	39
7	2	5	638	620	27	9	6	5	63	41	42	4	11	5	572	573	23
8	2	5	1143	1181	43	10	6	5	140	151	75	5	11	5	1079	1050	34
9	2	5	656	637	23	11	6	5	134	223	72	6	11	5	1081	1090	49
10	2	5	651	638	37	12	6	5	155	195	75	7	11	5	1151	1202	68
11	2	5	543	534	27	13	6	5	251	265	36	8	11	5	824	830	33
12	2	5	723	731	26	14	6	5	126	124	61	9	11	5	610	599	24
13	2	5	355	346	27	0	7	5	2564	2606	216	10	11	5	373	402	57
14	2	5	654	659	25	1	7	5	2088	2104	143	11	11	5	551	571	25
15	2	5	179	274	96	2	7	5	1735	1718	111	0	12	5	78	146	47
0	3	5	2536	2579	203	3	7	5	744	706	53	1	12	5	290	288	91
1	3	5	3082	3176	193	4	7	5	1288	1287	73	2	12	5	122	104	66
2	3	5	1318	1354	65	5	7	5	1381	1377	75	3	12	5	124	182	75
3	3	5	1450	1480	45	6	7	5	2017	2050	99	4	12	5	98	72	59
4	3	5	810	856	26	7	7	5	1980	1945	63	5	12	5	212	205	56
5	3	5	1916	1970	57	8	7	5	1691	1717	59	6	12	5	92	110	51
6	3	5	1993	2034	70	9	7	5	706	747	32	7	12	5	276	294	32
7	3	5	2867	2961	84	10	7	5	803	798	28	8	12	5	167	123	53
8	3	5	1280	1285	40	11	7	5	745	758	26	9	12	5	107	107	57
9	3	5	1252	1272	46	12	7	5	1147	1118	56	10	12	5	82	41	56
10	3	5	551	543	23	13	7	5	1259	1253	66	0	13	5	79	130	48
11	3	5	944	930	49	14	7	5	1337	1339	41	1	13	5	1888	1943	69
12	3	5	1019	1038	34	0	8	5	785	785	51	2	13	5	58	13	40
13	3	5	1840	1811	84	1	8	5	451	438	64	3	13	5	872	874	58
14	3	5	931	920	31	2	8	5	403	410	20	4	13	5	58	15	40
15	3	5	1015	1017	37	3	8	5	367	361	21	5	13	5	1515	1532	62
0	4	5	488	469	44	4	8	5	556	568	43	6	13	5	116	119	76
1	4	5	394	399	17	5	8	5	418	459	56	7	13	5	1715	1737	90
2	4	5	89	50	53	6	8	5	533	502	40	8	13	5	82	74	49
3	4	5	253	244	21	7	8	5	309	297	26	0	14	5	278	273	87
4	4	5	148	196	39	8	8	5	355	404	33	1	14	5	188	204	59
5	4	5	388	395	50	9	8	5	238	235	32	2	14	5	70	62	45
6	4	5	191	195	31	10	8	5	395	415	47	3	14	5	164	170	70
7	4	5	63	61	41	11	8	5	256	261	32	4	14	5	166	131	52
8	4	5	96	206	52	12	8	5	212	226	46	5	14	5	147	200	71
9	4	5	289	325	33	13	8	5	144	151	61	6	14	5	194	174	72
10	4	5	115	95	56	0	9	5	884	886	62	7	14	5	138	132	59
11	4	5	140	121	68	1	9	5	262	258	25	0	15	5	232	256	62
12	4	5	187	111	50	2	9	5	482	459	21	1	15	5	473	472	26
13	4	5	55	163	40	3	9	5	141	11	85	2	15	5	143	32	79
14	4	5	253	262	80	4	9	5	253	234	28	3	15	5	287	296	30
15	4	5	211	57	56	5	9	5	271	267	28	4	15	5	71	39	46

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	0	6	172	90	23	10	4	6	346	341	25	2	9	6	1014	1043	79
2	0	6	953	926	57	11	4	6	60	52	41	3	9	6	84	68	47
4	0	6	173	226	74	12	4	6	136	169	58	4	9	6	636	647	25
6	0	6	151	211	43	13	4	6	197	222	73	5	9	6	57	33	39
8	0	6	800	803	44	14	4	6	232	316	89	6	9	6	1754	1830	73
10	0	6	113	15	55	15	4	6	46	120	34	7	9	6	53	40	38
12	0	6	250	283	34	0	5	6	946	987	77	8	9	6	1197	1195	59
14	0	6	440	442	26	1	5	6	3415	3593	102	9	9	6	133	7	80
0	1	6	3050	3201	96	2	5	6	270	229	21	10	9	6	421	442	45
1	1	6	1968	2034	58	3	5	6	1631	1638	90	11	9	6	54	4	39
2	1	6	2266	2332	73	4	5	6	102	136	55	12	9	6	992	963	33
3	1	6	806	873	28	5	5	6	2562	2617	100	0	10	6	874	899	93
4	1	6	1409	1434	52	6	5	6	675	661	23	1	10	6	218	237	34
5	1	6	1494	1559	65	7	5	6	3080	3083	93	2	10	6	257	251	29
6	1	6	2515	2636	114	8	5	6	245	254	31	3	10	6	112	124	55
7	1	6	1380	1429	66	9	5	6	1547	1580	47	4	10	6	301	285	36
8	1	6	2082	2128	83	10	5	6	150	172	56	5	10	6	267	232	30
9	1	6	859	860	28	11	5	6	1240	1237	39	6	10	6	661	666	35
10	1	6	817	811	47	12	5	6	192	250	51	7	10	6	194	137	83
11	1	6	725	723	25	13	5	6	2043	2040	61	8	10	6	221	239	37
12	1	6	1482	1484	61	14	5	6	147	254	79	9	10	6	115	83	75
13	1	6	910	895	34	0	6	6	212	202	27	10	10	6	309	325	29
14	1	6	1478	1441	67	1	6	6	676	663	86	11	10	6	100	112	60
15	1	6	552	540	52	2	6	6	105	101	63	0	11	6	1627	1529	123
0	2	6	361	357	18	3	6	6	160	176	42	1	11	6	871	862	57
1	2	6	563	567	49	4	6	6	127	117	83	2	11	6	1075	1082	86
2	2	6	412	413	19	5	6	6	510	546	21	3	11	6	545	541	23
3	2	6	73	92	41	6	6	6	124	18	75	4	11	6	916	919	71
4	2	6	191	208	28	7	6	6	614	586	23	5	11	6	675	646	40
5	2	6	305	312	21	8	6	6	110	7	71	6	11	6	1315	1346	71
6	2	6	332	369	22	9	6	6	219	195	37	7	11	6	798	815	34
7	2	6	279	312	74	10	6	6	101	94	55	8	11	6	1067	1042	56
8	2	6	346	360	23	11	6	6	285	291	76	9	11	6	552	550	24
9	2	6	309	322	27	12	6	6	204	145	110	10	11	6	579	596	25
10	2	6	116	159	56	13	6	6	347	332	29	0	12	6	557	589	37
11	2	6	80	69	48	14	6	6	127	112	62	1	12	6	79	64	47
12	2	6	259	219	33	0	7	6	1178	1166	119	2	12	6	622	647	39
13	2	6	235	254	38	1	7	6	771	759	42	3	12	6	131	175	56
14	2	6	226	229	109	2	7	6	1275	1260	91	4	12	6	459	424	23
15	2	6	143	143	61	3	7	6	1101	1097	59	5	12	6	99	77	66
0	3	6	484	487	25	4	7	6	995	973	71	6	12	6	590	564	67
1	3	6	1387	1434	108	5	7	6	721	757	56	7	12	6	88	55	61
2	3	6	793	786	33	6	7	6	1055	1054	36	8	12	6	587	548	25
3	3	6	1043	1047	36	7	7	6	465	508	29	9	12	6	95	91	53
4	3	6	261	286	43	8	7	6	934	957	47	0	13	6	475	463	23
5	3	6	981	1027	32	9	7	6	736	755	32	1	13	6	1137	1176	48
6	3	6	633	671	22	10	7	6	618	619	24	2	13	6	166	171	81
7	3	6	1242	1270	53	11	7	6	360	384	26	3	13	6	691	719	51
8	3	6	535	542	44	12	7	6	676	643	32	4	13	6	231	176	73
9	3	6	751	762	25	13	7	6	409	390	26	5	13	6	949	952	76
10	3	6	98	116	59	0	8	6	1012	1007	99	6	13	6	349	368	41
11	3	6	484	487	23	1	8	6	53	97	37	7	13	6	1057	1065	47
12	3	6	395	369	25	2	8	6	473	439	41	8	13	6	194	197	51
13	3	6	812	827	53	3	8	6	256	196	27	0	14	6	513	540	24
14	3	6	269	289	35	4	8	6	607	641	33	1	14	6	159	171	86
15	3	6	446	436	26	5	8	6	96	38	52	2	14	6	485	514	24
0	4	6	707	638	70	6	8	6	639	676	41	3	14	6	99	28	64
1	4	6	94	109	46	7	8	6	196	68	43	4	14	6	461	480	56
2	4	6	342	361	19	8	8	6	473	491	34	5	14	6	104	177	56
3	4	6	467	442	23	9	8	6	50	63	35	0	15	6	509	550	40
4	4	6	620	633	25	10	8	6	376	383	25	1	15	6	915	942	73
5	4	6	118	28	77	11	8	6	125	126	67	2	15	6	380	388	26
6	4	6	430	428	21	12	8	6	368	372	62	1	0	7	750	749	25
7	4	6	360	372	23	13	8	6	98	138	54	3	0	7	112	172	54
8	4	6	379	376	23	0	9	6	2226	2228	172	5	0	7	540	537	37
9	4	6	63	114	42	1	9	6	73	8	44	7	0	7	609	591	30

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
9	0	7	343	345	41	0	5	7	1024	1056	87	10	9	7	159	259	86
11	0	7	122	150	55	1	5	7	683	717	50	11	9	7	327	319	32
13	0	7	527	486	40	2	5	7	347	366	39	0	10	7	352	360	42
15	0	7	292	271	40	3	5	7	442	424	41	1	10	7	524	550	34
0	1	7	2954	3020	116	4	5	7	585	575	27	2	10	7	130	177	67
1	1	7	477	480	20	5	5	7	578	584	33	3	10	7	358	386	26
2	1	7	912	861	29	6	5	7	526	525	26	4	10	7	131	140	48
3	1	7	393	370	24	7	5	7	526	516	22	5	10	7	455	436	60
4	1	7	1028	1034	46	8	5	7	493	482	23	6	10	7	272	271	86
5	1	7	336	367	32	9	5	7	348	348	29	7	10	7	525	540	31
6	1	7	1313	1354	81	10	5	7	368	374	25	8	10	7	168	154	52
7	1	7	268	256	43	11	5	7	384	422	25	9	10	7	265	271	34
8	1	7	1161	1135	41	12	5	7	227	249	38	10	10	7	121	100	79
9	1	7	122	14	65	13	5	7	207	196	89	11	10	7	323	315	30
10	1	7	696	698	27	14	5	7	352	358	29	0	11	7	1114	1122	96
11	1	7	102	109	55	0	6	7	133	120	50	1	11	7	1154	1180	51
12	1	7	848	846	28	1	6	7	152	184	82	2	11	7	853	892	97
13	1	7	178	183	56	2	6	7	292	277	24	3	11	7	823	833	55
14	1	7	1029	990	39	3	6	7	186	182	49	4	11	7	540	570	23
15	1	7	76	52	49	4	6	7	521	522	21	5	11	7	901	860	58
0	2	7	2061	2075	100	5	6	7	111	157	54	6	11	7	979	972	42
1	2	7	1531	1580	63	6	6	7	89	54	49	7	11	7	1129	1129	65
2	2	7	461	484	19	7	6	7	131	146	56	8	11	7	943	986	102
3	2	7	342	367	26	8	6	7	167	150	90	9	11	7	638	628	35
4	2	7	668	681	23	9	6	7	48	42	34	10	11	7	325	259	39
5	2	7	1194	1215	45	10	6	7	189	241	50	0	12	7	676	686	41
6	2	7	1240	1261	66	11	6	7	100	13	54	1	12	7	813	854	91
7	2	7	1208	1187	50	12	6	7	122	19	59	2	12	7	656	636	40
8	2	7	722	719	45	13	6	7	141	150	68	3	12	7	592	576	24
9	2	7	545	574	32	0	7	7	1484	1487	128	4	12	7	593	591	44
10	2	7	392	405	24	1	7	7	1364	1357	104	5	12	7	632	608	25
11	2	7	669	647	64	2	7	7	843	824	67	6	12	7	515	528	54
12	2	7	659	644	25	3	7	7	771	778	25	7	12	7	819	845	45
13	2	7	777	743	36	4	7	7	384	392	48	8	12	7	619	631	25
14	2	7	496	531	26	5	7	7	970	985	56	0	13	7	134	160	57
15	2	7	502	473	25	6	7	7	1231	1239	85	1	13	7	1279	1317	83
0	3	7	1958	1976	120	7	7	7	1340	1368	53	2	13	7	283	318	89
1	3	7	2497	2563	122	8	7	7	1030	1040	32	3	13	7	817	795	51
2	3	7	553	575	20	9	7	7	635	636	24	4	13	7	168	158	53
3	3	7	1371	1392	41	10	7	7	80	75	48	5	13	7	961	986	42
4	3	7	644	658	23	11	7	7	516	546	24	6	13	7	125	216	61
5	3	7	1829	1875	54	12	7	7	855	823	30	0	14	7	103	125	57
6	3	7	1305	1319	39	13	7	7	910	913	30	1	14	7	467	491	25
7	3	7	2373	2414	76	0	8	7	608	599	62	2	14	7	111	7	72
8	3	7	725	718	25	1	8	7	124	135	53	3	14	7	204	218	45
9	3	7	1014	1017	34	2	8	7	400	396	22	4	14	7	152	85	57
10	3	7	525	519	23	3	8	7	259	224	28	0	0	8	1768	1927	57
11	3	7	1121	1104	45	4	8	7	231	238	39	2	0	8	1778	1813	67
12	3	7	546	569	30	5	8	7	127	26	54	4	0	8	1102	1109	35
13	3	7	1484	1423	58	6	8	7	437	458	45	6	0	8	1922	1940	74
14	3	7	709	709	32	7	8	7	284	252	29	8	0	8	1391	1398	91
0	4	7	1153	1172	88	8	8	7	584	586	28	10	0	8	861	867	48
1	4	7	939	952	56	9	8	7	171	121	73	12	0	8	1035	1011	62
2	4	7	963	1007	30	10	8	7	59	22	41	14	0	8	1251	1218	64
3	4	7	884	887	29	11	8	7	72	21	47	0	1	8	1262	1327	47
4	4	7	728	737	24	12	8	7	421	416	25	1	1	8	1061	1060	34
5	4	7	628	633	22	0	9	7	1017	1033	88	2	1	8	1533	1569	49
6	4	7	951	985	52	1	9	7	360	374	23	3	1	8	615	638	22
7	4	7	931	950	34	2	9	7	580	596	65	4	1	8	696	721	28
8	4	7	782	799	26	3	9	7	232	197	32	5	1	8	890	917	32
9	4	7	501	523	23	4	9	7	395	400	26	6	1	8	1373	1384	50
10	4	7	477	482	24	5	9	7	282	303	105	7	1	8	790	805	49
11	4	7	413	433	25	6	9	7	834	826	28	8	1	8	1372	1400	48
12	4	7	473	446	24	7	9	7	354	349	26	9	1	8	734	711	30
13	4	7	567	540	25	8	9	7	681	667	25	10	1	8	315	296	27
14	4	7	623	616	27	9	9	7	100	90	60	11	1	8	335	368	28

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
12	1	8	975	954	34	5	6	8	1190	1242	44	0	12	8	779	832	60
13	1	8	664	649	26	6	6	8	543	549	23	1	12	8	360	404	25
14	1	8	834	871	40	7	6	8	1304	1314	44	2	12	8	575	595	24
0	2	8	1002	999	31	8	6	8	258	234	68	3	12	8	245	310	35
1	2	8	717	746	28	9	6	8	637	637	25	4	12	8	651	663	56
2	2	8	88	103	53	10	6	8	251	257	32	5	12	8	278	350	33
3	2	8	961	993	31	11	6	8	558	550	36	6	12	8	527	560	38
4	2	8	136	144	51	12	6	8	179	227	56	7	12	8	301	330	32
5	2	8	652	636	43	13	6	8	830	899	30	0	13	8	661	697	85
6	2	8	676	646	26	0	7	8	239	313	76	1	13	8	929	982	76
7	2	8	707	709	30	1	7	8	434	463	34	2	13	8	390	394	30
8	2	8	340	324	25	2	7	8	207	174	34	3	13	8	429	421	29
9	2	8	395	393	34	3	7	8	570	548	31	4	13	8	433	458	45
10	2	8	101	29	65	4	7	8	86	78	52	5	13	8	858	894	63
11	2	8	637	603	24	5	7	8	192	260	72	1	0	9	580	580	23
12	2	8	315	361	84	6	7	8	311	316	37	3	0	9	584	591	22
13	2	8	271	238	35	7	7	8	500	535	24	5	0	9	471	458	51
14	2	8	131	237	70	8	7	8	186	192	49	7	0	9	360	428	95
0	3	8	265	253	25	9	7	8	357	364	29	9	0	9	591	590	24
1	3	8	45	10	32	10	7	8	137	103	66	11	0	9	51	30	36
2	3	8	80	23	44	11	7	8	121	143	59	13	0	9	445	428	29
3	3	8	117	45	76	12	7	8	246	195	37	0	1	9	152	196	48
4	3	8	526	530	21	0	8	8	562	558	74	1	1	9	105	83	68
5	3	8	230	275	32	1	8	8	149	149	80	2	1	9	583	588	22
6	3	8	119	62	80	2	8	8	483	463	39	3	1	9	80	54	55
7	3	8	307	346	43	3	8	8	77	147	46	4	1	9	345	379	24
8	3	8	64	77	43	4	8	8	183	204	48	5	1	9	240	165	31
9	3	8	71	117	46	5	8	8	113	120	68	6	1	9	99	88	53
10	3	8	383	390	33	6	8	8	535	500	57	7	1	9	358	397	29
11	3	8	186	160	90	7	8	8	119	141	58	8	1	9	344	327	38
12	3	8	126	124	58	8	8	8	545	550	25	9	1	9	167	101	53
13	3	8	208	271	89	9	8	8	171	121	92	10	1	9	136	79	82
14	3	8	87	93	52	10	8	8	104	114	56	11	1	9	119	35	66
0	4	8	109	125	53	11	8	8	52	71	37	12	1	9	66	52	44
1	4	8	1065	1089	86	0	9	8	1584	1623	148	13	1	9	145	195	62
2	4	8	439	438	20	1	9	8	146	186	55	0	2	9	1361	1389	50
3	4	8	285	317	25	2	9	8	651	689	54	1	2	9	1200	1230	51
4	4	8	334	322	24	3	9	8	147	51	55	2	2	9	614	609	24
5	4	8	635	672	23	4	9	8	566	595	64	3	2	9	607	592	22
6	4	8	302	312	27	5	9	8	132	121	79	4	2	9	554	533	22
7	4	8	1125	1142	35	6	9	8	1254	1303	83	5	2	9	825	810	48
8	4	8	129	83	62	7	9	8	137	223	59	6	2	9	586	906	315
9	4	8	450	440	24	8	9	8	716	717	26	7	2	9	1293	1276	75
10	4	8	335	368	45	9	9	8	140	18	84	8	2	9	1069	1089	50
11	4	8	231	253	36	10	9	8	529	528	24	9	2	9	526	517	49
12	4	8	151	95	91	11	9	8	123	155	60	10	2	9	82	58	56
13	4	8	847	853	38	0	10	8	1500	1552	160	11	2	9	485	463	46
0	5	8	495	469	35	1	10	8	159	138	88	12	2	9	783	789	27
1	5	8	1438	1469	107	2	10	8	1139	1147	67	13	2	9	834	820	29
2	5	8	302	281	24	3	10	8	99	35	53	0	3	9	93	63	56
3	5	8	426	434	28	4	10	8	718	712	34	1	3	9	1343	1384	52
4	5	8	407	441	45	5	10	8	71	96	46	2	3	9	359	329	43
5	5	8	1041	1054	40	6	10	8	1431	1476	97	3	3	9	503	469	44
6	5	8	314	321	27	7	10	8	275	194	44	4	3	9	178	155	47
7	5	8	1325	1349	42	8	10	8	980	942	31	5	3	9	872	896	28
8	5	8	173	250	55	9	10	8	110	18	66	6	3	9	93	105	56
9	5	8	650	646	24	10	10	8	585	597	61	7	3	9	1370	1377	42
10	5	8	401	389	32	0	11	8	625	636	40	8	3	9	186	207	69
11	5	8	444	438	24	1	11	8	587	596	32	9	3	9	463	435	24
12	5	8	65	32	45	2	11	8	79	101	47	10	3	9	101	21	65
13	5	8	1009	1021	33	3	11	8	233	239	35	11	3	9	615	589	24
0	6	8	346	317	31	4	11	8	151	165	56	12	3	9	176	154	98
1	6	8	1583	1617	110	5	11	8	328	409	87	13	3	9	869	829	30
2	6	8	525	511	54	6	11	8	457	459	57	0	4	9	616	598	26
3	6	8	465	448	35	7	11	8	612	590	26	1	4	9	778	763	26
4	6	8	175	175	47	8	11	8	269	200	33	2	4	9	951	965	39

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	4	9	355	327	42	6	9	9	226	263	97	1	3	10	633	634	23
4	4	9	464	423	32	7	9	9	176	173	98	2	3	10	115	202	55
5	4	9	452	453	23	8	9	9	336	395	73	3	3	10	329	320	25
6	4	9	757	796	34	9	9	9	237	215	37	4	3	10	234	215	34
7	4	9	857	839	29	10	9	9	127	153	71	5	3	10	693	694	27
8	4	9	602	539	24	0	10	9	156	225	52	6	3	10	223	166	36
9	4	9	227	270	71	1	10	9	572	567	59	7	3	10	254	283	114
10	4	9	384	372	25	2	10	9	132	159	56	8	3	10	524	501	29
11	4	9	309	313	30	3	10	9	108	182	73	9	3	10	408	400	24
12	4	9	383	369	27	4	10	9	42	23	31	10	3	10	104	19	67
13	4	9	519	485	26	5	10	9	497	516	24	11	3	10	379	364	35
0	5	9	305	278	30	6	10	9	82	40	49	12	3	10	249	184	36
1	5	9	650	654	43	7	10	9	416	405	52	0	4	10	255	220	30
2	5	9	242	214	32	8	10	9	105	16	56	1	4	10	1469	1522	92
3	5	9	159	110	50	9	10	9	149	261	72	2	4	10	115	21	56
4	5	9	164	200	52	0	11	9	781	843	83	3	4	10	473	456	29
5	5	9	784	794	26	1	11	9	231	207	36	4	4	10	133	147	56
6	5	9	282	276	30	2	11	9	784	827	95	5	4	10	1192	1223	41
7	5	9	229	252	37	3	11	9	194	212	49	6	4	10	324	331	28
8	5	9	121	196	59	4	11	9	507	553	53	7	4	10	1278	1279	39
9	5	9	314	333	32	5	11	9	100	124	55	8	4	10	109	78	65
10	5	9	135	206	58	6	11	9	755	776	66	9	4	10	686	701	25
11	5	9	468	419	24	7	11	9	326	295	36	10	4	10	136	107	58
12	5	9	125	151	70	0	12	9	921	931	58	11	4	10	545	531	60
0	6	9	1113	1137	81	1	12	9	958	969	89	12	4	10	100	10	67
1	6	9	717	726	59	2	12	9	345	363	27	0	5	10	46	41	33
2	6	9	557	543	22	3	12	9	461	449	38	1	5	10	365	330	50
3	6	9	256	236	31	4	12	9	451	463	31	2	5	10	137	125	66
4	6	9	401	417	24	5	12	9	740	715	51	3	5	10	100	64	54
5	6	9	445	439	23	0	13	9	114	86	74	4	5	10	70	46	45
6	6	9	949	951	30	1	13	9	453	473	29	5	5	10	279	275	31
7	6	9	846	842	31	2	13	9	85	25	57	6	5	10	137	76	66
8	6	9	504	503	45	0	0	10	2431	2521	72	7	5	10	348	297	41
9	6	9	80	164	52	2	0	10	1102	1091	48	8	5	10	61	40	42
10	6	9	413	391	57	4	0	10	465	451	23	9	5	10	89	107	53
11	6	9	340	348	29	6	0	10	2228	2245	98	10	5	10	127	13	76
12	6	9	436	421	36	8	0	10	1049	1038	91	11	5	10	98	176	54
0	7	9	459	449	54	10	0	10	634	613	53	0	6	10	379	320	40
1	7	9	1061	1024	66	12	0	10	1004	974	65	1	6	10	1488	1463	85
2	7	9	259	260	30	0	1	10	472	484	22	2	6	10	555	539	67
3	7	9	688	669	26	1	1	10	473	510	22	3	6	10	1042	1051	59
4	7	9	63	37	42	2	1	10	285	293	30	4	6	10	102	26	55
5	7	9	736	745	43	3	1	10	382	370	23	5	6	10	1090	1090	61
6	7	9	433	438	52	4	1	10	273	278	29	6	6	10	609	602	29
7	7	9	993	987	45	5	1	10	421	443	24	7.	6	10	1458	1436	45
8	7	9	355	357	28	6	1	10	386	357	25	8	6	10	363	325	51
9	7	9	573	573	24	7	1	10	373	391	26	9	6	10	801	823	53
10	7	9	135	104	66	8	1	10	381	376	26	10	6	10	157	118	76
11	7	9	382	380	51	9	1	10	429	421	31	11	6	10	684	648	26
0	8	9	1851	1846	136	10	1	10	119	67	57	0	7	10	654	653	45
1	8	9	643	638	30	11	1	10	140	221	60	1	7	10	318	280	47
2	8	9	768	803	57	12	1	10	292	291	32	2	7	10	158	82	59
3	8	9	100	188	54	0	2	10	582	567	30	3	7	10	424	420	27
4	8	9	905	927	61	1	2	10	77	61	47	4	7	10	206	244	100
5	8	9	447	454	26	2	2	10	122	70	68	5	7	10	112	41	73
6	8	9	1196	1209	79	3	2	10	271	292	36	6	7	10	447	409	30
7	8	9	600	615	55	4	2	10	69	55	45	7	7	10	496	534	24
8	8	9	1089	1147	52	5	2	10	53	39	38	8	7	10	122	220	66
9	8	9	160	177	77	6	2	10	210	280	46	9	7	10	237	208	37
10	8	9	505	487	24	7	2	10	152	9	57	10	7	10	90	131	61
0	9	9	231	199	34	8	2	10	187	182	50	0	8	10	1280	1259	71
1	9	9	318	324	69	9	2	10	152	155	57	1	8	10	177	251	95
2	9	9	486	495	30	10	2	10	82	60	49	2	8	10	1226	1208	59
3	9	9	75	42	51	11	2	10	154	23	57	3	8	10	388	402	25
4	9	9	308	286	28	12	2	10	201	173	86	4	8	10	973	974	75
5	9	9	321	337	28	0	3	10	397	392	46	5	8	10	126	78	68

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	8	10	1119	1127	38	6	3	11	134	71	75	1	10	11	139	143	60
7	8	10	402	375	26	7	3	11	83	93	50	2	10	11	246	248	77
8	8	10	1007	1027	32	8	3	11	100	85	63	3	10	11	302	320	31
9	8	10	163	89	91	9	3	11	148	131	82	4	10	11	268	229	32
0	9	10	353	367	27	10	3	11	124	116	80	5	10	11	102	74	55
1	9	10	636	644	24	11	3	11	122	14	70	0	11	11	106	88	57
2	9	10	77	19	53	0	4	11	222	197	35	1	11	11	83	103	50
3	9	10	468	463	24	1	4	11	949	971	30	2	11	11	264	251	33
4	9	10	134	109	49	2	4	11	53	66	38	0	0	12	2191	2197	74
5	9	10	546	542	24	3	4	11	135	122	81	2	0	12	1582	1539	63
6	9	10	174	199	84	4	4	11	340	327	56	4	0	12	1324	1314	46
7	9	10	562	552	51	5	4	11	810	836	27	6	0	12	1906	1920	86
8	9	10	134	153	80	6	4	11	119	37	58	8	0	12	1415	1409	72
0	10	10	1126	1126	125	7	4	11	757	777	27	10	0	12	979	936	52
1	10	10	533	553	83	8	4	11	130	132	72	0	1	12	655	665	28
2	10	10	963	997	88	9	4	11	337	342	29	1	1	12	85	7	51
3	10	10	136	212	58	10	4	11	107	148	72	2	1	12	517	530	44
4	10	10	428	435	51	0	5	11	806	801	34	3	1	12	107	91	69
5	10	10	431	439	25	1	5	11	523	535	77	4	1	12	229	219	50
6	10	10	1171	1185	78	2	5	11	698	706	45	5	1	12	345	124	207
7	10	10	505	489	25	3	5	11	81	115	49	6	1	12	633	713	25
0	11	10	60	17	41	4	5	11	207	270	88	7	1	12	106	164	57
1	11	10	469	458	71	5	5	11	515	506	24	8	1	12	467	427	25
2	11	10	65	113	44	6	5	11	897	879	33	9	1	12	145	150	81
3	11	10	270	290	33	7	5	11	420	394	26	10	1	12	76	212	49
4	11	10	96	5	53	8	5	11	524	514	29	0	2	12	83	136	50
5	11	10	318	316	29	9	5	11	242	199	36	1	2	12	555	566	24
0	12	10	83	134	54	10	5	11	348	326	33	2	2	12	241	220	31
1	12	10	287	279	32	0	6	11	1061	1059	94	3	2	12	445	448	24
2	12	10	398	406	33	1	6	11	1245	1249	87	4	2	12	172	217	54
1	0	11	352	331	25	2	6	11	746	722	41	5	2	12	276	321	87
3	0	11	166	117	52	3	6	11	996	972	56	6	2	12	74	179	48
5	0	11	389	380	25	4	6	11	522	542	31	7	2	12	677	636	25
7	0	11	73	118	47	5	6	11	832	837	70	8	2	12	141	60	60
9	0	11	263	245	32	6	6	11	938	939	44	9	2	12	284	243	32
11	0	11	179	160	67	7	6	11	1356	1314	63	10	2	12	111	177	62
0	1	11	71	54	48	8	6	11	616	628	25	0	3	12	828	836	29
1	1	11	811	805	27	9	6	11	653	635	34	1	3	12	331	306	28
2	1	11	101	90	54	0	7	11	777	773	76	2	3	12	505	492	24
3	1	11	536	539	32	1	7	11	119	112	58	3	3	12	102	58	55
4	1	11	240	239	34	2	7	11	550	542	53	4	3	12	711	702	26
5	1	11	663	576	26	3	7	11	176	176	85	5	3	12	140	146	60
6	1	11	203	271	98	4	7	11	595	623	68	6	3	12	436	458	25
7	1	11	677	695	25	5	7	11	122	121	80	7	3	12	378	422	28
8	1	11	62	68	42	6	7	11	537	523	45	8	3	12	645	649	25
9	1	11	525	468	24	7	7	11	87	68	52	9	3	12	88	22	59
10	1	11	79	15	54	8	7	11	587	550	25	0	4	12	884	877	29
11	1	11	419	384	58	9	7	11	172	149	84	1	4	12	1500	1516	45
0	2	11	1560	1556	79	0	8	11	2093	2047	154	2	4	12	696	720	39
1	2	11	1089	1129	34	1	8	11	598	589	55	3	4	12	721	713	44
2	2	11	1032	1070	32	2	8	11	1047	1023	67	4	4	12	651	647	25
3	2	11	591	608	37	3	8	11	157	111	102	5	4	12	1156	1192	36
4	2	11	951	943	38	4	8	11	1069	1083	86	6	4	12	771	802	27
5	2	11	772	762	28	5	8	11	546	520	25	7	4	12	1363	1343	42
6	2	11	1103	1132	34	6	8	11	1513	1505	66	8	4	12	551	514	25
7	2	11	1189	1166	37	7	8	11	461	461	26	9	4	12	707	696	33
8	2	11	1261	1251	54	8	8	11	1166	1157	46	0	5	12	135	46	58
9	2	11	466	462	25	0	9	11	125	222	61	1	5	12	571	583	25
10	2	11	414	425	39	1	9	11	518	499	51	2	5	12	101	64	66
11	2	11	429	433	30	2	9	11	454	479	59	3	5	12	309	306	29
0	3	11	103	53	62	3	9	11	347	280	38	4	5	12	105	5	69
1	3	11	83	51	54	4	9	11	350	333	28	5	5	12	521	496	29
2	3	11	258	206	31	5	9	11	426	428	43	6	5	12	135	39	75
3	3	11	132	139	64	6	9	11	247	276	39	7	5	12	476	453	28
4	3	11	192	154	82	7	9	11	344	399	91	8	5	12	126	22	61
5	3	11	120	40	58	0	10	11	434	418	25	0	6	12	659	667	26

Table A-11 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	6	12	553	856	84	1	2	13	479	479	24	3	7	13	262	331	28
2	6	12	783	769	43	2	2	13	1224	1139	49	4	7	13	297	267	41
3	6	12	619	614	42	3	2	13	101	124	55	0	8	13	1023	992	71
4	6	12	594	546	34	4	2	13	961	920	31	1	8	13	74	85	48
5	6	12	540	540	24	5	2	13	322	346	30	2	8	13	620	629	72
6	6	12	653	667	26	6	2	13	1350	1336	54	0	0	14	760	723	47
7	6	12	967	935	48	7	2	13	427	442	32	2	0	14	241	254	75
8	6	12	653	616	29	8	2	13	1127	1100	43	4	0	14	224	273	84
0	7	12	527	499	32	0	3	13	562	540	25	6	0	14	553	537	29
1	7	12	483	475	24	1	3	13	611	592	24	0	1	14	1202	1156	37
2	7	12	257	293	68	2	3	13	315	337	29	1	1	14	56	52	40
3	7	12	302	284	30	3	3	13	458	479	25	2	1	14	807	803	28
4	7	12	423	415	34	4	3	13	251	256	35	3	1	14	137	119	67
5	7	12	326	374	30	5	3	13	467	403	24	4	1	14	599	597	25
6	7	12	275	280	34	6	3	13	433	422	26	5	1	14	89	34	58
7	7	12	462	427	25	7	3	13	727	671	31	6	1	14	1055	1044	34
0	8	12	651	656	60	8	3	13	410	394	28	0	2	14	179	208	56
1	8	12	386	362	29	0	4	13	466	418	24	1	2	14	250	237	36
2	8	12	293	297	31	1	4	13	495	496	24	2	2	14	115	152	69
3	8	12	86	85	56	2	4	13	441	428	51	3	2	14	97	103	54
4	8	12	237	228	38	3	4	13	173	212	84	4	2	14	108	156	58
5	8	12	202	314	53	4	4	13	376	376	27	5	2	14	180	182	57
6	8	12	517	529	25	5	4	13	409	413	34	0	3	14	430	434	45
0	9	12	396	381	51	6	4	13	403	360	40	1	3	14	432	378	33
1	9	12	283	297	75	7	4	13	434	430	30	2	3	14	144	151	87
2	9	12	486	503	26	0	5	13	205	218	65	3	3	14	166	165	71
3	9	12	128	102	74	1	5	13	211	267	46	4	3	14	283	215	32
4	9	12	206	231	34	2	5	13	226	228	38	5	3	14	330	274	42
1	0	13	317	284	29	3	5	13	273	291	86	0	4	14	312	323	83
3	0	13	241	299	117	4	5	13	95	18	53	1	4	14	429	474	27
5	0	13	267	273	42	5	5	13	109	163	71	2	4	14	100	126	65
7	0	13	165	182	61	6	5	13	320	345	31	3	4	14	327	294	30
0	1	13	568	521	37	0	6	13	145	115	78	4	4	14	144	167	61
1	1	13	962	971	31	1	6	13	622	611	51	5	4	14	266	344	58
2	1	13	213	170	46	2	6	13	53	49	37	0	5	14	113	140	68
3	1	13	663	645	25	3	6	13	259	336	69	1	5	14	754	749	42
4	1	13	257	277	56	4	6	13	106	50	57	2	5	14	195	199	52
5	1	13	449	818	269	5	6	13	500	471	25	3	5	14	241	232	38
6	1	13	280	270	34	0	7	13	667	651	26	0	6	14	736	732	29
7	1	13	801	768	40	1	7	13	583	563	25	1	0	15	362	333	41
8	1	13	372	362	29	2	7	13	224	247	84	0	1	15	396	405	32
0	2	13	1588	1549	55												

Table A-12. Observed and Calculated Structure Factors for 5[illegible]

F_0, F_c and SIG (σ) values have been multiplied by 10.

H	K L	FO	FC	SIG	H	K L	FO	FC	SIG	H	K L	FO	FC	SIG
4	0-16	155	167	13	0	8-14	252	252	10	1	2-12	259	242	9
1	1-16	79	87	22	1	8-14	137	141	15	2	2-12	78	197	11
3	1-16	144	153	15	0	9-14	179	157	12	3	2-12	259	262	9
0	2-16	182	155	11	1	9-14	119	120	18	4	2-12	644	653	14
1	2-16	86	67	21	2	0-13	667	676	15	5	2-12	59	24	21
0	3-16	85	78	21	4	0-13	122	143	15	6	2-12	40	69	18
1	3-16	115	121	17	6	0-13	348	338	10	8	2-12	302	324	11
0	4-16	165	171	13	1	1-13	594	577	13	0	3-12	334	344	9
1	4-16	106	59	18	2	1-13	121	82	15	1	3-12	457	459	11
2	4-16	81	64	22	3	1-13	522	536	12	2	3-12	96	89	18
0	5-16	158	147	13	4	1-13	50	63	20	3	3-12	483	484	11
1	5-16	134	142	16	5	1-13	256	265	10	4	3-12	221	227	10
2	0-15	262	261	10	7	1-13	267	278	10	5	3-12	401	421	10
4	0-15	38	38	17	1	2-13	63	50	21	6	3-12	44	24	19
1	1-15	137	132	14	2	2-13	661	667	15	7	3-12	217	224	11
2	1-15	55	76	21	3	2-13	160	174	12	8	3-12	129	95	16
3	1-15	187	192	11	4	2-13	84	75	21	0	4-12	664	655	14
5	1-15	109	98	19	5	2-13	150	155	13	1	4-12	183	175	10
1	2-15	71	85	22	6	2-13	388	386	10	2	4-12	123	110	14
2	2-15	202	197	11	1	3-13	406	409	10	3	4-12	245	245	10
1	3-15	167	177	12	2	3-13	214	211	10	4	4-12	583	584	13
2	3-15	118	117	16	3	3-13	417	426	10	5	4-12	176	174	12
3	3-15	152	154	13	4	3-13	107	101	18	6	4-12	61	49	22
5	3-15	183	178	12	6	3-13	95	100	20	0	5-12	405	414	10
1	4-15	49	56	20	7	3-13	205	203	12	1	5-12	482	480	11
2	4-15	153	164	13	1	4-13	148	155	13	2	5-12	95	81	18
1	5-15	173	155	12	2	4-13	513	507	12	3	5-12	269	272	9
2	5-15	111	97	17	3	4-13	97	96	18	4	5-12	245	257	10
1	6-15	89	133	22	4	4-13	66	95	22	5	5-12	310	315	10
2	6-15	171	172	12	5	4-13	176	167	12	6	5-12	34	25	16
1	7-15	91	128	22	6	4-13	351	347	10	7	5-12	171	169	13
2	7-15	134	139	15	1	5-13	356	348	10	0	6-12	571	566	13
2	0-14	180	154	11	2	5-13	202	205	10	1	6-12	242	236	10
4	0-14	278	283	10	3	5-13	276	270	10	2	6-12	64	91	22
0	1-14	70	75	21	4	5-13	50	58	20	3	6-12	214	219	10
1	1-14	361	359	10	5	5-13	227	233	11	4	6-12	397	378	10
2	1-14	65	73	22	6	5-13	209	208	11	5	6-12	186	179	12
3	1-14	296	299	10	1	6-13	334	312	10	6	6-12	61	73	22
4	1-14	134	138	14	2	6-13	369	354	10	7	6-12	148	149	15
5	1-14	217	207	11	3	6-13	65	69	22	0	7-12	347	352	10
0	2-14	314	293	9	4	6-13	126	67	15	1	7-12	376	373	10
1	2-14	123	124	15	5	6-13	160	171	14	2	7-12	113	115	16
4	2-14	312	319	10	6	6-13	264	270	11	3	7-12	168	164	12
0	3-14	77	73	21	1	7-13	192	197	11	4	7-12	219	223	10
1	3-14	258	246	9	2	7-13	212	209	11	5	7-12	263	246	10
3	3-14	263	234	10	3	7-13	182	176	12	0	8-12	296	277	9
4	3-14	176	154	12	4	7-13	61	27	22	1	8-12	224	215	10
0	4-14	418	418	10	1	8-13	222	208	10	2	8-12	83	49	20
1	4-14	224	208	10	2	8-13	234	239	10	3	8-12	206	184	11
3	4-14	120	144	16	3	8-13	170	157	12	4	8-12	244	242	10
4	4-14	312	327	10	1	9-13	119	101	16	5	8-12	145	119	14
0	5-14	321	312	10	2	9-13	254	231	10	0	9-12	230	208	10
1	5-14	262	239	10	3	9-13	177	170	13	1	9-12	274	262	10
2	5-14	46	36	19	1	10-13	131	116	15	2	9-12	51	30	20
3	5-14	146	138	13	2	0-12	76	94	21	3	9-12	155	151	13
4	5-14	168	165	13	4	0-12	599	588	13	4	9-12	293	280	10
5	5-14	192	192	12	6	0-12	241	255	10	5	9-12	212	180	11
0	6-14	420	408	10	8	0-12	418	424	11	0	10-12	124	102	15
1	6-14	155	166	13	0	1-12	244	251	9	1	10-12	129	129	15
2	6-14	107	102	10	1	1-12	561	565	13	2	10-12	88	63	22
4	6-14	240	222	11	2	1-12	141	153	13	3	10-12	205	201	11
5	6-14	159	156	14	3	1-12	604	615	13	0	11-12	134	132	15
0	7-14	321	304	10	4	1-12	48	43	19	1	11-12	126	120	16
1	7-14	163	187	13	5	1-12	351	357	10	2	11-12	64	65	23
3	7-14	160	150	13	7	1-12	316	326	10	2	0-11	1012	1005	22
4	7-14	180	183	12	0	2-12	863	851	18	4	0-11	119	137	14

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	0	-11	521	527	12	2	10	-11	209	211	11	3	7	-10	343	345	9
8	0	-11	62	86	22	3	10	-11	258	255	10	4	7	-10	222	221	10
1	1	-11	499	497	11	5	10	-11	142	154	16	5	7	-10	221	221	10
2	1	-11	74	102	20	1	11	-11	66	45	22	6	7	-10	47	72	19
3	1	-11	409	408	10	2	11	-11	331	314	10	7	7	-10	244	233	10
4	1	-11	89	94	19	3	11	-11	122	124	17	8	7	-10	166	173	14
5	1	-11	374	351	9	1	12	-11	184	181	12	0	8	-10	445	425	10
6	1	-11	91	101	20	2	0	-10	167	157	10	1	8	-10	323	317	9
7	1	-11	391	389	10	4	0	-10	441	452	10	2	8	-10	45	23	18
1	2	-11	252	254	9	6	0	-10	421	439	10	3	8	-10	191	166	10
2	2	-11	786	770	17	8	0	-10	494	503	11	4	8	-10	260	260	10
3	2	-11	203	211	10	0	1	-10	388	391	9	5	8	-10	295	285	10
4	2	-11	143	139	12	1	1	-10	375	375	9	6	8	-10	52	85	21
5	2	-11	70	86	21	2	1	-10	109	111	14	7	8	-10	161	149	14
6	2	-11	451	455	11	3	1	-10	211	209	9	0	9	-10	319	319	9
8	2	-11	67	92	23	4	1	-10	232	232	9	1	9	-10	145	135	13
1	3	-11	497	488	11	5	1	-10	220	216	9	2	9	-10	156	164	12
2	3	-11	127	142	13	6	1	-10	63	77	21	3	9	-10	337	341	10
3	3	-11	510	512	12	7	1	-10	335	345	10	4	9	-10	356	353	10
4	3	-11	153	169	12	0	2	-10	314	317	8	5	9	-10	183	176	12
5	3	-11	441	422	9	1	2	-10	316	321	8	6	9	-10	51	15	21
6	3	-11	198	197	11	2	2	-10	162	157	10	0	10	-10	298	284	9
7	3	-11	260	255	10	3	2	-10	159	136	10	1	10	-10	252	234	10
8	3	-11	66	11	22	4	2	-10	585	595	13	2	10	-10	107	122	18
1	4	-11	238	246	9	5	2	-10	141	138	12	3	10	-10	275	276	10
2	4	-11	577	551	13	6	2	-10	184	169	10	4	10	-10	243	247	10
3	4	-11	146	153	12	8	2	-10	371	351	10	5	10	-10	232	238	11
4	4	-11	248	247	9	0	3	-10	395	392	10	0	11	-10	348	333	10
5	4	-11	159	173	12	1	3	-10	351	354	9	1	11	-10	146	125	13
6	4	-11	427	432	10	2	3	-10	185	175	9	2	11	-10	131	124	15
7	4	-11	124	129	15	3	3	-10	471	473	11	3	11	-10	103	122	19
8	4	-11	95	126	20	4	3	-10	212	213	9	4	11	-10	340	328	10
1	5	-11	411	411	10	5	3	-10	347	349	9	0	12	-10	125	121	16
2	5	-11	258	271	9	6	3	-10	74	82	20	1	12	-10	199	199	12
3	5	-11	429	430	10	7	3	-10	284	281	9	2	12	-10	33	22	16
4	5	-11	123	118	14	8	3	-10	79	88	21	3	12	-10	191	193	12
5	5	-11	320	322	9	0	4	-10	375	366	9	2	0	-9	507	507	11
6	5	-11	261	247	10	1	4	-10	238	227	9	4	0	-9	377	377	9
7	5	-11	210	222	11	2	4	-10	101	116	16	6	0	-9	430	435	10
1	6	-11	332	322	9	3	4	-10	180	172	10	8	0	-9	84	75	21
2	6	-11	410	398	10	4	4	-10	543	539	12	1	1	-9	443	441	10
3	6	-11	250	246	9	5	4	-10	307	315	9	2	1	-9	262	244	8
4	6	-11	180	184	11	6	4	-10	142	137	13	3	1	-9	481	479	11
5	6	-11	135	131	14	7	4	-10	55	63	21	4	1	-9	138	148	11
6	6	-11	320	318	10	8	4	-10	264	263	10	5	1	-9	166	179	11
7	6	-11	96	136	21	0	5	-10	293	301	9	6	1	-9	61	26	20
1	7	-11	353	361	10	1	5	-10	368	367	9	7	1	-9	400	414	10
2	7	-11	333	343	9	2	5	-10	112	92	14	1	2	-9	281	282	8
3	7	-11	247	235	9	3	5	-10	324	308	9	2	2	-9	548	531	12
4	7	-11	120	109	15	4	5	-10	307	306	9	3	2	-9	361	369	9
5	7	-11	211	227	11	5	5	-10	365	356	10	4	2	-9	124	128	13
6	7	-11	248	227	10	6	5	-10	207	213	10	5	2	-9	250	258	9
7	7	-11	256	232	10	7	5	-10	254	233	10	6	2	-9	510	523	11
1	8	-11	257	241	9	8	5	-10	129	115	15	7	2	-9	81	71	20
2	8	-11	327	322	9	0	6	-10	621	603	14	8	2	-9	98	50	19
3	8	-11	258	267	10	1	6	-10	299	307	9	1	3	-9	233	232	8
4	8	-11	73	67	22	2	6	-10	149	144	12	2	3	-9	340	337	8
5	8	-11	197	192	11	3	6	-10	180	173	10	3	3	-9	455	441	10
6	8	-11	221	216	11	4	6	-10	317	298	9	4	3	-9	110	127	14
1	9	-11	184	178	11	5	6	-10	284	297	9	5	3	-9	373	386	9
2	9	-11	369	366	10	6	6	-10	79	80	21	6	3	-9	61	49	21
3	9	-11	175	157	12	7	6	-10	93	76	20	7	3	-9	240	258	9
4	9	-11	56	51	21	8	6	-10	260	252	10	8	3	-9	90	89	19
5	9	-11	167	173	13	0	7	-10	569	575	13	1	4	-9	157	165	10
6	9	-11	215	199	12	1	7	-10	351	334	9	2	4	-9	559	542	12
1	10	-11	202	203	11	2	7	-10	75	86	20	3	4	-9	267	259	8

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	4	-9	80	96	20	2	1	-8	442	445	10	6	8	-8	59	101	21
5	4	-9	174	158	10	3	1	-8	602	611	13	7	8	-8	203	192	11
6	4	-9	415	404	10	4	1	-8	142	150	10	8	8	-8	261	258	10
7	4	-9	244	235	10	5	1	-8	603	608	13	0	9	-8	413	396	10
8	4	-9	46	20	19	6	1	-8	113	132	14	1	9	-8	280	272	9
1	5	-9	305	293	8	7	1	-8	343	352	9	2	9	-8	104	103	16
2	5	-9	207	213	9	0	2	-8	1071	1046	23	3	9	-8	220	225	10
3	5	-9	360	349	9	1	2	-8	191	159	8	4	9	-9	546	540	12
4	5	-9	127	135	13	2	2	-8	109	122	12	5	9	-8	308	298	9
5	5	-9	368	364	9	3	2	-8	476	465	11	6	9	-8	92	48	20
6	5	-9	150	184	12	4	2	-8	697	708	15	7	9	-8	112	117	17
7	5	-9	199	206	11	5	2	-8	46	69	18	8	9	-8	192	195	12
8	5	-9	78	78	21	6	2	-8	140	121	12	0	10	-8	220	230	10
1	6	-9	379	372	9	7	2	-8	139	153	12	1	10	-8	353	344	9
2	6	-9	480	460	11	8	2	-8	405	425	10	2	10	-8	84	95	21
3	6	-9	138	138	12	0	3	-8	407	427	9	3	10	-8	285	284	9
4	6	-9	135	127	13	1	3	-8	232	220	8	4	10	-8	352	330	10
5	6	-9	69	62	21	2	3	-8	132	136	10	5	10	-8	288	293	10
6	6	-9	372	369	10	3	3	-8	641	628	14	6	10	-8	34	34	16
7	6	-9	288	292	10	4	3	-8	328	329	9	7	10	-8	129	115	16
8	6	-9	56	29	21	5	3	-8	568	576	13	0	11	-8	313	315	9
1	7	-9	411	402	10	6	3	-8	111	118	15	1	11	-8	240	244	10
2	7	-9	441	446	10	7	3	-8	236	259	9	2	11	-8	161	163	12
3	7	-9	126	109	13	8	3	-8	155	180	12	3	11	-8	146	156	13
4	7	-9	141	134	12	0	4	-8	657	641	14	4	11	-8	391	405	10
5	7	-9	306	313	9	1	4	-8	271	274	8	5	11	-8	124	105	16
6	7	-9	276	284	10	2	4	-8	121	135	12	0	12	-8	213	224	11
7	7	-9	205	206	11	3	4	-8	363	361	9	1	12	-8	326	301	10
8	7	-9	51	53	21	4	4	-8	864	864	18	2	12	-8	74	111	23
1	8	-9	216	201	9	5	4	-8	319	319	9	3	12	-8	229	221	10
2	8	-9	335	330	9	6	4	-8	358	362	9	4	12	-8	125	108	16
3	8	-9	323	322	9	7	4	-8	190	181	10	5	12	-8	200	211	12
4	8	-9	82	88	20	8	4	-8	293	301	9	0	13	-8	376	358	10
5	8	-9	192	194	11	0	5	-8	703	709	15	1	13	-8	94	79	20
6	8	-9	291	294	10	1	5	-8	687	681	15	2	13	-8	45	45	19
7	8	-9	230	224	11	2	5	-8	200	214	9	3	13	-8	81	72	22
8	8	-9	69	38	23	3	5	-8	426	416	10	4	13	-8	212	216	11
1	9	-9	254	257	9	4	5	-8	295	294	9	0	14	-8	125	89	16
2	9	-9	419	411	10	5	5	-8	263	249	9	2	0	-7	1349	1344	27
3	9	-9	109	108	16	6	5	-8	241	251	9	4	0	-7	555	545	12
4	9	-9	64	40	21	7	5	-8	408	399	10	6	0	-7	856	863	18
5	9	-9	254	261	10	8	5	-8	203	210	11	8	0	-7	198	206	10
6	9	-9	283	279	10	0	6	-8	758	747	16	1	1	-7	1411	1401	28
7	9	-9	156	137	13	1	6	-8	323	334	9	2	1	-7	234	245	7
1	10	-9	246	232	9	2	6	-8	308	313	8	3	1	-7	923	907	19
2	10	-9	244	247	10	3	6	-8	250	248	9	4	1	-7	146	121	10
3	10	-9	403	400	10	4	6	-8	415	418	10	5	1	-7	661	664	14
4	10	-9	81	92	22	5	6	-8	375	369	9	6	1	-7	178	179	10
5	10	-9	224	217	11	6	6	-8	154	141	12	7	1	-7	576	597	13
6	10	-9	202	188	11	7	6	-8	179	164	11	1	2	-7	174	182	8
1	11	-9	163	159	12	8	6	-8	357	352	10	2	2	-7	1445	1437	29
2	11	-9	458	452	11	0	7	-8	737	717	16	3	2	-7	666	661	14
3	11	-9	152	156	13	1	7	-8	504	500	11	4	2	-7	321	328	8
4	11	-9	94	86	20	2	7	-8	257	265	9	5	2	-7	376	380	9
5	11	-9	240	209	10	3	7	-8	294	287	9	6	2	-7	701	723	15
1	12	-9	294	300	10	4	7	-8	376	375	9	7	2	-7	180	169	10
2	12	-9	102	123	19	5	7	-8	248	250	9	8	2	-7	175	172	11
3	12	-9	286	277	10	6	7	-8	42	75	18	1	3	-7	616	612	13
1	13	-9	83	86	23	7	7	-8	269	249	10	2	3	-7	545	540	12
2	13	-9	348	331	10	8	7	-8	292	283	10	3	3	-7	1059	1055	23
2	0	-8	150	142	9	0	8	-8	676	690	15	4	3	-7	69	89	19
4	0	-8	365	364	9	1	8	-8	499	504	11	5	3	-7	681	678	15
6	0	-8	129	116	13	2	8	-8	234	232	9	6	3	-7	298	288	9
8	0	-8	500	524	11	3	8	-8	99	116	17	7	3	-7	467	450	11
0	1	-8	401	398	9	4	8	-8	453	454	11	8	3	-7	110	96	15
1	1	-8	718	712	15	5	8	-8	300	289	9	1	4	-7	380	381	9

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	4	-7	1371	1312	28	1	13	-7	61	39	22	2	7	-6	224	224	8
3	4	-7	391	379	9	2	13	-7	300	293	10	3	7	-6	381	385	9
4	4	-7	138	120	11	3	13	-7	145	124	13	4	7	-6	270	278	9
5	4	-7	221	221	9	4	13	-7	74	48	23	5	7	-6	428	430	10
6	4	-7	616	619	14	1	14	-7	221	225	11	7	7	-6	248	250	10
7	4	-7	206	225	10	2	14	-7	63	80	22	8	7	-6	368	355	10
8	4	-7	52	58	20	2	0	-6	120	132	9	0	8	-6	721	708	16
1	5	-7	615	620	13	4	0	-6	1220	1234	25	1	8	-6	563	549	13
2	5	-7	702	699	15	6	0	-6	573	597	13	2	8	-6	148	129	11
3	5	-7	776	763	17	8	0	-6	692	702	15	3	8	-6	476	462	11
4	5	-7	137	130	11	0	1	-6	688	676	15	4	8	-6	340	350	9
5	5	-7	441	432	10	1	1	-6	1774	1744	35	5	8	-6	244	245	9
6	5	-7	365	380	9	2	1	-6	128	124	8	6	8	-6	137	137	13
7	5	-7	394	383	10	3	1	-6	775	762	17	7	8	-6	341	318	10
8	5	-7	59	61	21	4	1	-6	191	191	8	8	8	-6	311	293	10
1	6	-7	738	719	16	5	1	-6	744	745	16	0	9	-6	485	479	11
2	6	-7	860	854	18	6	1	-6	329	340	9	1	9	-6	200	185	9
3	6	-7	180	193	9	7	1	-6	602	615	13	2	9	-6	244	248	9
4	6	-7	218	203	9	8	1	-6	68	79	21	3	9	-6	337	328	9
5	6	-7	212	205	9	0	2	-6	1627	1590	32	4	9	-6	491	489	11
6	6	-7	441	432	10	1	2	-6	549	554	12	5	9	-6	453	465	11
7	6	-7	255	244	9	2	2	-6	167	171	7	6	9	-6	79	95	21
8	6	-7	61	71	22	3	2	-6	577	553	12	7	9	-6	98	74	19
1	7	-7	563	545	12	4	2	-6	1574	1564	31	8	9	-6	187	181	12
2	7	-7	451	428	10	5	2	-6	158	149	10	0	10	-6	507	478	11
3	7	-7	331	328	9	6	2	-6	216	228	9	1	10	-6	195	178	10
4	7	-7	155	169	11	7	2	-6	220	219	9	2	10	-6	144	136	12
5	7	-7	274	256	9	8	2	-6	491	484	11	3	10	-6	446	428	10
6	7	-7	410	408	10	0	3	-6	760	739	16	4	10	-6	369	368	10
7	7	-7	361	348	10	1	3	-6	1263	1244	26	5	10	-6	337	310	10
8	7	-7	66	31	22	2	3	-6	146	122	8	6	10	-6	84	50	21
1	8	-7	323	319	9	3	3	-6	1298	1275	26	7	10	-6	173	183	12
2	8	-7	503	492	11	4	3	-6	639	631	14	0	11	-6	386	392	10
3	8	-7	343	330	9	5	3	-6	881	892	19	1	11	-6	182	172	10
4	8	-7	123	108	13	6	3	-6	289	304	9	2	11	-6	230	221	10
5	8	-7	339	338	9	7	3	-6	419	420	10	3	11	-6	112	87	15
6	8	-7	426	413	10	8	3	-6	207	218	10	4	11	-6	456	449	11
7	8	-7	189	186	11	0	4	-6	856	848	18	5	11	-6	87	115	21
8	8	-7	61	44	22	1	4	-6	231	202	7	6	11	-6	92	27	20
1	9	-7	355	344	9	2	4	-6	178	179	8	0	12	-6	203	195	10
2	9	-7	521	529	12	3	4	-6	536	547	12	1	12	-6	166	178	12
3	9	-7	290	286	9	4	4	-6	1269	1231	26	2	12	-6	179	180	11
4	9	-7	147	116	12	5	4	-6	324	323	8	3	12	-6	257	254	10
5	9	-7	225	218	10	6	4	-6	148	140	11	4	12	-6	158	174	13
6	9	-7	395	390	10	7	4	-6	250	246	9	5	12	-6	199	214	11
7	9	-7	210	209	11	8	4	-6	443	447	10	6	12	-6	68	42	23
8	9	-7	86	32	21	0	5	-6	507	518	11	0	13	-6	459	460	11
1	10	-7	211	221	10	1	5	-6	936	939	20	1	13	-6	153	145	13
2	10	-7	229	229	10	2	5	-6	503	489	11	2	13	-6	55	67	21
3	10	-7	344	328	9	3	5	-6	741	747	16	3	13	-6	78	62	21
4	10	-7	84	110	21	4	5	-6	544	551	12	4	13	-6	102	150	19
5	10	-7	324	340	10	5	5	-6	545	529	12	0	14	-6	55	79	21
6	10	-7	167	168	12	6	5	-6	176	175	10	1	14	-6	168	176	13
7	10	-7	181	159	12	7	5	-6	333	334	9	2	14	-6	60	23	21
1	11	-7	156	161	12	8	5	-6	346	332	9	3	14	-6	171	142	12
2	11	-7	364	351	10	0	6	-6	1276	1270	26	2	0	-5	1462	1529	29
3	11	-7	212	217	11	1	6	-6	539	544	12	4	0	-5	294	292	7
4	11	-7	93	107	20	2	6	-6	320	313	8	6	0	-5	1098	1109	23
5	11	-7	171	163	12	3	6	-6	529	516	12	8	0	-5	110	97	15
6	11	-7	250	241	10	4	6	-6	559	537	12	1	1	-5	1564	1524	31
1	12	-7	353	336	10	5	6	-6	222	220	9	2	1	-5	138	140	7
2	12	-7	178	180	11	6	6	-6	61	39	20	3	1	-5	589	593	13
3	12	-7	228	202	10	7	6	-6	296	297	9	4	1	-5	85	101	13
4	12	-7	50	25	20	8	6	-6	540	520	12	5	1	-5	882	901	19
5	12	-7	151	172	14	0	7	-6	841	831	18	6	1	-5	161	164	10
6	12	-7	112	110	19	1	7	-6	641	638	14	7	1	-5	608	614	13

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
8	1	-5	51	53	19	2	10	-5	494	474	11	6	4	-4	115	103	12
1	2	-5	624	593	13	3	10	-5	362	358	9	7	4	-4	120	113	13
2	2	-5	1260	1247	25	4	10	-5	95	89	18	8	4	-4	532	528	12
3	2	-5	676	658	14	5	10	-5	456	437	11	0	5	-4	471	457	10
4	2	-5	66	60	16	6	10	-5	295	293	9	1	5	-4	780	768	17
5	2	-5	428	438	10	7	10	-5	113	129	17	2	5	-4	293	293	7
6	2	-5	964	971	21	1	11	-5	44	39	18	3	5	-4	782	742	16
7	2	-5	174	168	10	2	11	-5	454	449	10	4	5	-4	656	623	14
8	2	-5	202	199	10	3	11	-5	240	248	10	5	5	-4	413	408	10
1	3	-5	1104	1106	22	4	11	-5	163	168	12	6	5	-4	397	387	9
2	3	-5	551	575	12	5	11	-5	214	213	11	7	5	-4	542	519	12
3	3	-5	1270	1249	26	6	11	-5	360	359	10	8	5	-4	351	351	9
4	3	-5	289	281	8	1	12	-5	359	359	10	0	6	-4	713	723	15
5	3	-5	869	863	19	2	12	-5	167	175	11	1	6	-4	580	569	13
6	3	-5	320	325	8	3	12	-5	263	271	10	2	6	-4	170	173	8
7	3	-5	406	409	10	4	12	-5	83	53	20	3	6	-4	619	609	13
8	3	-5	157	166	11	5	12	-5	172	181	12	4	6	-4	518	501	11
1	4	-5	807	790	17	6	12	-5	94	113	20	5	6	-4	277	264	8
2	4	-5	1265	1254	26	7	12	-5	186	157	12	6	6	-4	138	162	12
3	4	-5	305	302	8	1	13	-5	49	71	20	7	6	-4	153	155	12
4	4	-5	443	440	10	2	13	-5	342	332	10	8	6	-4	612	607	14
5	4	-5	441	442	10	3	13	-5	43	57	18	0	7	-4	817	800	18
6	4	-5	621	596	13	4	13	-5	132	94	14	1	7	-4	580	544	12
7	4	-5	142	128	12	5	13	-5	132	119	15	2	7	-4	348	346	9
8	4	-5	74	118	20	1	14	-5	287	299	10	3	7	-4	376	362	9
1	5	-5	545	531	12	2	14	-5	56	68	21	4	7	-4	250	241	8
2	5	-5	720	694	15	3	14	-5	161	181	13	5	7	-4	196	184	9
3	5	-5	1195	1173	25	4	14	-5	95	62	20	6	7	-4	221	230	9
4	5	-5	159	156	9	1	15	-5	58	75	22	7	7	-4	550	523	12
5	5	-5	385	380	9	2	0	-4	688	681	15	8	7	-4	437	424	10
6	5	-5	319	309	9	4	0	-4	230	230	7	0	8	-4	821	783	17
7	5	-5	447	441	10	6	0	-4	494	497	11	1	8	-4	903	895	19
8	5	-5	163	147	11	8	0	-4	656	667	14	2	8	-4	492	471	11
1	6	-5	565	539	12	0	1	-4	842	828	17	3	8	-4	263	271	8
2	6	-5	1160	1149	24	1	1	-4	968	968	20	4	8	-4	549	530	12
3	6	-5	334	341	8	2	1	-4	473	489	11	5	8	-4	249	255	9
4	6	-5	383	387	9	3	1	-4	579	589	13	6	8	-4	122	149	14
5	6	-5	247	237	8	4	1	-4	364	362	8	7	8	-4	261	257	9
6	6	-5	617	602	14	5	1	-4	895	911	19	8	8	-4	397	372	10
7	6	-5	401	389	10	6	1	-4	379	389	9	0	9	-4	487	478	11
8	6	-5	104	112	18	7	1	-4	523	549	12	1	9	-4	125	134	12
1	7	-5	863	826	19	8	1	-4	67	78	20	2	9	-4	230	240	9
2	7	-5	814	791	17	0	2	-4	804	809	17	3	9	-4	321	314	9
3	7	-5	504	487	11	1	2	-4	617	600	13	4	9	-4	720	700	16
4	7	-5	172	156	10	2	2	-4	397	397	9	5	9	-4	376	373	10
5	7	-5	176	169	10	3	2	-4	398	375	9	6	9	-4	141	127	13
6	7	-5	398	377	10	4	2	-4	914	914	20	7	9	-4	239	230	10
7	7	-5	435	426	10	5	2	-4	270	274	7	0	10	-4	446	424	10
8	7	-5	132	117	14	6	2	-4	412	418	9	1	10	-4	583	574	13
1	8	-5	362	343	9	7	2	-4	212	209	9	2	10	-4	252	249	9
2	8	-5	655	668	14	8	2	-4	490	501	11	3	10	-4	379	372	9
3	8	-5	390	380	9	0	3	-4	765	756	16	4	10	-4	535	514	12
4	8	-5	220	208	9	1	3	-4	594	569	13	5	10	-4	512	496	12
5	8	-5	477	466	11	2	3	-4	261	260	7	6	10	-4	111	119	16
6	8	-5	422	418	10	3	3	-4	1370	1320	27	7	10	-4	112	122	17
7	8	-5	334	319	9	4	3	-4	363	366	8	0	11	-4	512	509	12
8	8	-5	73	67	22	5	3	-4	738	711	16	1	11	-4	324	301	9
1	9	-5	472	469	11	6	3	-4	236	239	8	2	11	-4	95	114	18
2	9	-5	494	490	11	7	3	-4	321	313	9	3	11	-4	112	91	15
3	9	-5	192	188	10	8	3	-4	228	232	9	4	11	-4	619	618	14
4	9	-5	152	128	12	0	4	-4	191	206	6	5	11	-4	100	101	19
5	9	-5	256	254	9	1	4	-4	508	497	11	6	11	-4	91	83	20
6	9	-5	403	392	10	2	4	-4	358	343	8	7	11	-4	151	134	13
7	9	-5	249	233	10	3	4	-4	532	514	12	0	12	-4	239	234	9
8	9	-5	50	48	20	4	4	-4	1211	1203	25	1	12	-4	408	410	10
1	10	-5	397	388	9	5	4	-4	512	527	11	2	12	-4	210	212	10

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	12	-4	259	235	9	4	6	-3	71	95	17	0	1	-2	295	286	7
4	12	-4	226	221	10	5	6	-3	170	163	9	1	1	-2	2171	2190	42
5	12	-4	352	350	10	6	6	-3	446	435	10	2	1	-2	921	903	19
6	12	-4	155	128	13	7	6	-3	534	517	12	3	1	-2	663	661	14
7	12	-4	139	147	15	8	6	-3	57	54	20	4	1	-2	64	62	14
0	13	-4	652	629	14	1	7	-3	767	752	16	5	1	-2	937	943	19
1	13	-4	199	199	11	2	7	-3	701	685	15	6	1	-2	467	500	11
2	13	-4	78	68	21	3	7	-3	229	228	8	7	1	-2	487	491	11
3	13	-4	150	130	13	4	7	-3	120	115	12	8	1	-2	55	50	20
4	13	-4	326	318	10	5	7	-3	340	326	9	0	2	-2	1886	1832	36
5	13	-4	87	83	21	6	7	-3	445	440	10	1	2	-2	220	214	6
0	14	-4	103	117	19	7	7	-3	382	375	10	2	2	-2	330	315	8
1	14	-4	356	358	10	8	7	-3	166	141	11	3	2	-2	909	833	19
2	14	-4	86	50	21	1	8	-3	260	246	8	4	2	-2	1523	1490	30
3	14	-4	214	194	11	2	8	-3	604	706	13	5	2	-2	59	30	16
4	14	-4	56	34	21	3	8	-3	513	501	11	6	2	-2	277	267	8
0	15	-4	312	324	10	4	8	-3	42	29	17	7	2	-2	433	441	10
1	15	-4	76	53	23	5	8	-3	265	259	9	8	2	-2	515	523	11
2	15	-4	58	91	22	6	8	-3	619	601	14	0	3	-2	152	140	6
2	0	-3	717	753	15	7	8	-3	390	367	10	1	3	-2	448	442	10
4	0	-3	301	326	7	8	8	-3	99	98	19	2	3	-2	383	371	9
6	0	-3	877	900	18	1	9	-3	600	594	13	3	3	-2	1125	1084	23
8	0	-3	137	131	12	2	9	-3	631	619	14	4	3	-2	752	733	16
1	1	-3	1544	1542	30	3	9	-3	231	207	9	5	3	-2	798	780	17
2	1	-3	713	709	15	4	9	-3	78	64	19	6	3	-2	323	334	8
3	1	-3	365	369	8	5	9	-3	345	346	9	7	3	-2	285	288	8
4	1	-3	567	552	12	6	9	-3	592	585	13	8	3	-2	114	133	14
5	1	-3	707	728	15	7	9	-3	116	143	16	0	4	-2	323	294	8
6	1	-3	45	67	17	1	10	-3	333	323	9	1	4	-2	427	401	10
7	1	-3	570	572	13	2	10	-3	259	264	9	2	4	-2	169	171	7
8	1	-3	162	153	10	3	10	-3	566	553	13	3	4	-2	312	320	7
1	2	-3	361	372	8	4	10	-3	48	69	19	4	4	-2	1489	1430	30
2	2	-3	577	542	13	5	10	-3	471	471	11	5	4	-2	403	375	9
3	2	-3	558	552	12	6	10	-3	266	277	10	6	4	-2	247	229	8
4	2	-3	163	152	7	7	10	-3	265	245	9	7	4	-2	210	220	9
5	2	-3	383	374	9	1	11	-3	236	234	9	8	4	-2	532	532	12
6	2	-3	767	792	16	2	11	-3	448	436	10	0	5	-2	649	611	14
7	2	-3	191	177	9	3	11	-3	291	288	9	1	5	-2	918	881	19
8	2	-3	78	71	19	4	11	-3	186	191	11	2	5	-2	609	586	13
1	3	-3	418	386	9	5	11	-3	414	404	10	3	5	-2	1049	993	22
2	3	-3	426	414	10	6	11	-3	394	376	10	4	5	-2	473	445	10
3	3	-3	795	783	17	7	11	-3	38	33	17	5	5	-2	261	252	8
4	3	-3	689	665	15	1	12	-3	612	605	14	6	5	-2	334	334	9
5	3	-3	732	706	16	2	12	-3	150	165	12	7	5	-2	676	670	15
6	3	-3	198	198	8	3	12	-3	370	363	10	8	5	-2	400	396	10
7	3	-3	402	408	9	4	12	-3	199	175	10	0	6	-2	1191	1150	24
8	3	-3	242	250	9	5	12	-3	257	260	10	1	6	-2	516	508	11
1	4	-3	327	335	8	6	12	-3	94	124	20	2	6	-2	583	548	13
2	4	-3	1358	1311	27	7	12	-3	211	204	11	3	6	-2	699	669	15
3	4	-3	599	573	13	1	13	-3	55	39	21	4	6	-2	415	390	9
4	4	-3	145	148	8	2	13	-3	503	477	12	5	6	-2	324	300	8
5	4	-3	40	68	16	3	13	-3	65	73	22	6	6	-2	181	163	9
6	4	-3	603	597	13	4	13	-3	61	100	22	7	6	-2	218	206	9
7	4	-3	266	269	9	5	13	-3	181	172	12	8	6	-2	752	724	16
8	4	-3	68	41	21	6	13	-3	294	292	10	0	7	-2	877	882	18
1	5	-3	392	370	9	1	14	-3	381	363	10	1	7	-2	480	472	11
2	5	-3	770	768	16	2	14	-3	139	124	14	2	7	-2	417	410	9
3	5	-3	701	702	15	3	14	-3	280	286	10	3	7	-2	598	578	13
4	5	-3	569	540	12	4	14	-3	142	161	15	4	7	-2	324	326	8
5	5	-3	533	496	12	5	14	-3	127	155	16	5	7	-2	338	330	9
6	5	-3	260	267	8	2	15	-3	400	389	11	6	7	-2	239	226	9
7	5	-3	337	335	9	3	15	-3	91	92	22	7	7	-2	562	533	13
8	5	-3	196	190	10	2	0	-2	672	658	14	8	7	-2	548	547	12
1	6	-3	663	631	14	4	0	-2	569	581	12	0	8	-2	1075	1045	23
2	6	-3	1081	1025	23	6	0	-2	175	179	8	1	8	-2	937	915	20
3	6	-3	330	322	8	8	0	-2	564	598	12	2	8	-2	527	530	12

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	8	-2	296	303	8	1	2	-1	624	592	13	4	10	-1	188	199	10
4	8	-2	358	355	9	2	2	-1	2013	1939	39	5	10	-1	542	540	12
5	8	-2	309	294	9	3	2	-1	1280	1218	25	6	10	-1	284	292	9
6	8	-2	163	155	11	4	2	-1	423	410	9	7	10	-1	166	153	11
7	8	-2	235	224	9	5	2	-1	477	496	11	1	11	-1	86	104	19
8	8	-2	378	367	10	6	2	-1	1149	1172	24	2	11	-1	458	463	11
0	9	-2	851	850	18	7	2	-1	227	239	8	3	11	-1	316	324	9
1	9	-2	44	52	18	8	2	-1	148	155	11	4	11	-1	131	115	13
2	9	-2	368	366	9	1	3	-1	869	859	18	5	11	-1	276	285	9
3	9	-2	424	416	10	2	3	-1	867	838	18	6	11	-1	415	428	10
4	9	-2	673	666	15	3	3	-1	1680	1621	33	7	11	-1	54	19	20
5	9	-2	515	502	12	4	3	-1	481	479	11	1	12	-1	435	430	10
6	9	-2	57	53	20	5	3	-1	1001	984	21	2	12	-1	194	206	10
7	9	-2	215	217	10	6	3	-1	343	346	8	3	12	-1	226	222	10
0	10	-2	530	521	12	7	3	-1	528	546	12	4	12	-1	82	80	20
1	10	-2	315	319	9	8	3	-1	101	116	15	5	12	-1	261	268	10
2	10	-2	31	44	14	1	4	-1	1102	1075	22	6	12	-1	99	108	19
3	10	-2	498	499	11	2	4	-1	2037	1964	39	7	12	-1	167	147	12
4	10	-2	496	482	11	3	4	-1	762	758	16	1	13	-1	47	77	19
5	10	-2	639	640	14	4	4	-1	143	147	8	2	13	-1	360	355	10
6	10	-2	123	119	14	5	4	-1	279	283	7	3	13	-1	128	96	14
7	10	-2	58	75	21	6	4	-1	664	642	14	4	13	-1	78	80	21
0	11	-2	728	718	16	7	4	-1	218	198	9	5	13	-1	124	134	15
1	11	-2	269	288	9	8	4	-1	123	110	13	6	13	-1	268	260	10
2	11	-2	198	193	10	1	5	-1	557	550	12	1	14	-1	311	315	10
3	11	-2	205	212	10	2	5	-1	1013	992	21	2	14	-1	77	72	21
4	11	-2	655	624	14	3	5	-1	1616	1557	32	3	14	-1	173	174	12
5	11	-2	134	149	14	4	5	-1	284	266	7	4	14	-1	108	117	19
6	11	-2	85	103	21	5	5	-1	435	436	10	5	14	-1	156	152	13
7	11	-2	143	141	13	6	5	-1	398	388	9	1	15	-1	51	52	21
0	12	-2	177	186	11	7	5	-1	568	564	13	2	15	-1	334	321	10
1	12	-2	385	382	10	8	5	-1	48	17	19	3	15	-1	69	78	23
2	12	-2	294	278	9	1	6	-1	904	867	19	2	0	0	688	703	14
3	12	-2	344	341	9	2	6	-1	1457	1439	29	4	0	0	1565	1539	31
4	12	-2	168	160	11	3	6	-1	568	549	12	6	0	0	40	34	16
5	12	-2	429	432	10	4	6	-1	166	157	8	8	0	0	826	778	18
6	12	-2	160	155	13	5	6	-1	139	130	10	0	1	0	279	372	6
7	12	-2	156	165	13	6	6	-1	600	569	13	1	1	0	1352	1330	26
0	13	-2	718	706	15	7	6	-1	576	557	13	2	1	0	260	263	6
1	13	-2	236	234	10	8	6	-1	53	58	20	3	1	0	811	842	17
2	13	-2	54	5	20	1	7	-1	1149	1119	24	4	1	0	300	306	7
3	13	-2	134	128	14	2	7	-1	973	946	21	5	1	0	1427	1415	29
4	13	-2	285	282	10	3	7	-1	649	637	14	6	1	0	705	680	15
5	13	-2	79	52	22	4	7	-1	316	307	8	7	1	0	506	510	11
6	13	-2	131	109	15	5	7	-1	141	129	11	8	1	0	78	88	19
0	14	-2	125	114	15	6	7	-1	493	485	11	1	2	0	579	592	12
1	14	-2	344	339	10	7	7	-1	523	513	12	2	2	0	165	172	6
2	14	-2	98	52	19	8	7	-1	126	107	15	3	2	0	408	389	9
3	14	-2	198	198	11	1	8	-1	358	339	9	4	2	0	1990	2031	39
4	14	-2	81	88	22	2	8	-1	684	586	15	5	2	0	64	40	16
5	14	-2	204	195	11	3	8	-1	427	428	10	6	2	0	258	254	8
0	15	-2	360	350	10	4	8	-1	332	332	9	7	2	0	381	386	9
2	15	-2	67	12	23	5	8	-1	482	484	11	8	2	0	505	487	11
3	15	-2	130	109	16	6	8	-1	535	522	12	0	3	0	276	265	7
2	0	-1	2059	2109	39	7	8	-1	422	416	10	1	3	0	1503	1507	29
4	0	-1	386	401	9	8	8	-1	127	132	14	2	3	0	211	215	6
6	0	-1	1473	1488	30	1	9	-1	773	752	16	3	3	0	2115	2067	41
8	0	-1	137	134	12	2	9	-1	622	605	13	4	3	0	466	471	10
1	1	-1	1820	1782	35	3	9	-1	338	330	9	5	3	0	1235	1260	25
2	1	-1	558	549	12	4	9	-1	194	202	9	7	3	0	440	442	10
3	1	-1	437	456	10	5	9	-1	278	279	9	8	3	0	242	229	9
4	1	-1	283	287	7	6	9	-1	545	543	12	0	4	0	1011	1019	20
5	1	-1	1055	1089	22	7	9	-1	231	216	9	1	4	0	359	344	8
6	1	-1	142	152	9	1	10	-1	265	260	8	2	4	0	688	679	15
7	1	-1	665	699	14	2	10	-1	369	366	9	3	4	0	979	977	20
8	1	-1	65	34	20	3	10	-1	340	327	9	4	4	0	1765	1757	35

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
5	4	0	526	513	11	2	12	0	335	338	9	7	5	1	567	575	13
6	4	0	50	59	18	3	12	0	156	132	11	8	5	1	41	19	17
7	4	0	308	320	8	4	12	0	247	247	9	1	6	1	846	845	18
8	4	0	599	619	13	5	12	0	291	282	9	2	6	1	1390	1436	28
0	5	0	313	325	8	6	12	0	50	23	20	3	6	1	510	531	11
1	5	0	1348	1387	27	7	12	0	115	129	17	4	6	1	151	152	9
2	5	0	984	967	20	0	13	0	622	622	14	5	6	1	106	114	13
3	5	0	1057	1013	22	1	13	0	230	246	10	6	6	1	564	566	12
4	5	0	703	702	15	2	13	0	60	89	21	7	6	1	545	564	12
5	5	0	551	551	12	3	13	0	70	99	21	8	6	1	48	60	19
6	5	0	31	47	14	4	13	0	251	253	10	1	7	1	1151	1125	24
7	5	0	439	448	10	5	13	0	59	16	21	2	7	1	942	946	20
8	5	0	460	468	11	6	13	0	50	16	20	3	7	1	655	649	14
0	6	0	866	908	19	0	14	0	43	34	18	4	7	1	307	308	8
1	6	0	723	720	16	1	14	0	282	268	10	5	7	1	160	145	10
2	6	0	202	190	7	2	14	0	58	45	21	6	7	1	466	466	11
3	6	0	674	676	15	3	14	0	173	174	12	7	7	1	511	510	12
4	6	0	559	582	12	4	14	0	49	19	20	8	7	1	96	106	18
5	6	0	184	174	8	5	14	0	89	113	22	1	8	1	331	316	8
6	6	0	109	115	13	0	15	0	178	177	12	2	8	1	588	598	13
7	6	0	382	390	9	1	15	0	50	15	20	3	8	1	418	418	10
8	6	0	712	709	15	2	15	0	92	41	20	4	8	1	343	334	9
0	7	0	1056	1075	22	3	15	0	104	127	20	5	8	1	484	482	11
1	7	0	1183	1131	24	4	15	0	210	213	12	6	8	1	535	536	12
2	7	0	62	86	17	2	0	1	2215	2139	42	7	8	1	413	421	10
3	7	0	304	276	8	4	0	1	430	403	10	8	8	1	141	134	13
4	7	0	182	167	8	6	0	1	1530	1485	31	1	9	1	754	754	16
5	7	0	378	389	9	8	0	1	150	138	11	2	9	1	581	590	13
6	7	0	59	41	20	1	1	1	1737	1768	33	3	9	1	337	331	9
7	7	0	546	536	12	2	1	1	575	560	13	4	9	1	182	201	10
8	7	0	434	425	10	3	1	1	486	470	11	5	9	1	285	286	9
0	8	0	557	601	12	4	1	1	292	286	7	6	9	1	533	539	12
1	8	0	905	887	19	5	1	1	1087	1073	23	7	9	1	205	210	10
2	8	0	467	450	10	6	1	1	169	156	8	1	10	1	269	261	8
3	8	0	460	460	10	7	1	1	742	712	16	2	10	1	382	383	9
4	8	0	462	462	10	8	1	1	45	35	18	3	10	1	339	330	9
5	8	0	203	202	9	1	2	1	578	583	12	4	10	1	204	200	10
6	8	0	208	214	10	2	2	1	1897	1940	37	5	10	1	524	538	12
7	8	0	398	411	10	3	2	1	1181	1209	24	6	10	1	287	292	9
8	8	0	336	330	9	4	2	1	437	412	10	7	10	1	114	144	16
0	9	0	506	487	11	5	2	1	507	489	11	1	11	1	87	117	19
1	9	0	174	171	9	6	2	1	1195	1167	25	2	11	1	439	448	10
2	9	0	222	223	8	7	2	1	251	238	8	3	11	1	319	322	9
3	9	0	283	283	8	8	2	1	161	156	10	4	11	1	95	112	18
4	9	0	738	747	16	1	3	1	817	848	17	5	11	1	284	285	9
5	9	0	555	567	13	2	3	1	808	817	17	6	11	1	425	431	10
6	9	0	44	29	18	3	3	1	1601	1639	31	7	11	1	58	27	21
7	9	0	154	153	12	4	3	1	458	482	10	1	12	1	433	428	10
0	10	0	350	359	9	5	3	1	967	978	20	2	12	1	208	213	10
1	10	0	418	426	10	6	3	1	328	336	8	3	12	1	228	217	9
2	10	0	106	117	14	7	3	1	565	550	12	4	12	1	58	80	21
3	10	0	315	306	9	8	3	1	125	113	12	5	12	1	240	257	10
4	10	0	482	478	11	1	4	1	1058	1067	21	6	12	1	94	110	20
5	10	0	429	430	10	2	4	1	1940	1967	38	7	12	1	120	138	16
6	10	0	52	8	20	3	4	1	712	750	15	1	13	1	55	82	21
7	10	0	172	187	11	4	4	1	150	151	8	2	13	1	358	359	10
0	11	0	516	516	11	5	4	1	297	300	8	3	13	1	77	102	21
1	11	0	288	304	9	6	4	1	622	649	13	4	13	1	84	79	21
2	11	0	238	235	9	7	4	1	196	200	9	5	13	1	139	138	13
3	11	0	81	73	20	8	4	1	117	112	14	6	13	1	275	265	10
4	11	0	688	705	15	1	5	1	597	572	13	1	14	1	319	312	10
5	11	0	116	90	14	2	5	1	978	988	20	2	14	1	98	73	19
6	11	0	46	27	19	3	5	1	1562	1567	31	3	14	1	152	172	13
7	11	0	53	6	20	4	5	1	260	270	7	4	14	1	107	115	18
0	12	0	230	243	9	5	5	1	416	414	10	5	14	1	163	155	13
1	12	0	248	242	9	6	5	1	357	370	9	2	15	1	315	313	10

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	15	1	83	78	23	6	7	2	216	224	9	2	1	3	672	703	15
0	0	2	1629	1595	39	7	7	2	526	538	12	3	1	3	427	414	9
2	0	2	686	662	15	8	7	2	536	544	12	4	1	3	557	551	12
4	0	2	600	586	13	0	8	2	1040	1055	22	5	1	3	710	718	15
6	0	2	181	174	8	1	8	2	897	904	19	6	1	3	108	75	12
8	0	2	607	595	13	2	8	2	527	530	12	7	1	3	578	564	13
0	1	2	276	294	7	3	8	2	293	290	8	8	1	3	144	153	12
1	1	2	2109	2178	40	4	8	2	377	372	9	1	2	3	366	380	9
2	1	2	901	902	18	5	8	2	280	289	9	2	2	3	599	599	13
3	1	2	620	606	13	6	8	2	157	155	11	3	2	3	551	552	12
4	1	2	73	65	13	7	8	2	232	223	9	4	2	3	168	157	7
5	1	2	1000	958	21	8	8	2	341	361	10	5	2	3	377	377	9
6	1	2	532	502	12	0	9	2	816	840	17	6	2	3	814	797	17
7	1	2	490	478	11	1	9	2	81	77	17	7	2	3	163	174	10
8	1	2	45	45	18	2	9	2	366	366	9	8	2	3	73	75	20
0	2	2	1817	1854	35	3	9	2	419	423	10	1	3	3	381	369	9
1	2	2	196	202	6	4	9	2	636	649	14	2	3	3	378	397	9
2	2	2	317	318	8	5	9	2	497	504	11	3	3	3	766	777	16
3	2	2	859	829	18	6	9	2	93	48	18	4	3	3	662	662	14
4	2	2	1495	1495	30	7	9	2	223	218	9	5	3	3	699	690	15
5	2	2	64	39	16	0	10	2	515	539	12	6	3	3	202	212	8
6	2	2	271	270	8	1	10	2	312	311	9	7	3	3	411	419	9
7	2	2	450	439	10	2	10	2	77	40	19	8	3	3	292	252	9
8	2	2	529	523	12	3	10	2	497	496	11	1	4	3	320	333	8
0	3	2	172	164	6	4	10	2	494	492	11	2	4	3	1329	1320	26
1	3	2	449	464	10	5	10	2	638	639	14	3	4	3	577	577	12
2	3	2	379	372	9	6	10	2	106	119	17	4	4	3	149	147	8
3	3	2	1037	1078	21	7	10	2	58	83	21	5	4	3	58	58	18
4	3	2	705	727	15	0	11	2	695	707	15	6	4	3	589	585	13
5	3	2	772	786	16	1	11	2	282	292	9	7	4	3	256	267	9
6	3	2	338	332	8	2	11	2	165	195	11	8	4	3	55	39	20
7	3	2	255	265	8	3	11	2	232	213	9	1	5	3	338	354	8
8	3	2	143	123	11	4	11	2	640	626	14	2	5	3	717	752	15
0	4	2	315	303	8	5	11	2	118	150	16	3	5	3	688	694	15
1	4	2	411	389	9	6	11	2	98	100	18	4	5	3	514	536	11
2	4	2	203	173	6	7	11	2	125	143	15	5	5	3	486	505	11
3	4	2	307	319	7	0	12	2	186	186	10	6	5	3	265	268	8
4	4	2	1375	1427	28	1	12	2	374	373	9	7	5	3	341	345	9
5	4	2	369	378	9	2	12	2	272	277	9	8	5	3	171	191	11
6	4	2	226	230	8	3	12	2	331	332	9	1	6	3	620	623	13
7	4	2	215	213	9	4	12	2	144	164	13	2	6	3	1015	1025	21
8	4	2	538	532	12	5	12	2	449	431	11	3	6	3	326	338	8
0	5	2	596	585	13	6	12	2	139	154	14	4	6	3	76	100	16
1	5	2	883	902	19	7	12	2	157	164	13	5	6	3	146	160	10
2	5	2	597	586	13	0	13	2	708	708	15	6	6	3	434	436	10
3	5	2	987	997	21	1	13	2	223	238	10	7	6	3	491	514	11
4	5	2	413	422	9	2	13	2	65	5	22	8	6	3	70	55	21
5	5	2	280	289	8	3	13	2	114	133	16	1	7	3	729	750	16
6	5	2	333	336	8	4	13	2	284	282	10	2	7	3	671	691	14
7	5	2	652	665	14	5	13	2	36	50	16	3	7	3	214	213	8
8	5	2	378	385	10	6	13	2	82	107	22	4	7	3	94	112	15
0	6	2	1116	1159	23	0	14	2	51	113	21	5	7	3	331	340	9
1	6	2	474	492	11	1	14	2	320	337	10	6	7	3	428	442	10
2	6	2	553	544	12	2	14	2	40	52	18	7	7	3	379	380	10
3	6	2	649	657	14	3	14	2	188	198	12	8	7	3	146	143	13
4	6	2	431	396	10	4	14	2	94	86	20	1	8	3	226	230	8
5	6	2	286	293	8	5	14	2	180	188	12	2	8	3	703	699	15
6	6	2	153	163	10	0	15	2	329	345	10	3	8	3	467	503	11
7	6	2	186	202	10	1	15	2	66	19	22	4	8	3	44	29	18
8	6	2	684	720	15	2	15	2	51	12	21	5	8	3	223	245	9
0	7	2	849	874	18	3	15	2	105	110	20	6	8	3	577	595	13
1	7	2	539	508	12	2	0	3	751	748	16	7	8	3	357	368	10
2	7	2	407	409	9	4	0	3	331	330	8	8	8	3	97	98	18
3	7	2	576	581	12	6	0	3	903	903	19	1	9	3	586	599	13
4	7	2	323	320	8	8	0	3	108	133	15	2	9	3	635	625	14
5	7	2	339	340	9	1	1	3	1493	1539	29	3	9	3	199	205	9

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	9	3	91	63	17	5	3	4	714	704	15	1	11	4	290	298	9
5	9	3	346	354	9	6	3	4	242	240	8	2	11	4	108	110	16
6	9	3	568	584	13	7	3	4	332	320	9	3	11	4	81	95	20
7	9	3	145	139	13	8	3	4	208	219	10	4	11	4	608	615	13
1	10	3	335	327	9	0	4	4	174	184	7	5	11	4	92	97	20
2	10	3	248	252	9	1	4	4	500	513	11	6	11	4	79	84	21
3	10	3	543	549	12	2	4	4	330	345	8	7	11	4	114	132	17
4	10	3	95	69	18	3	4	4	495	506	11	0	12	4	221	237	10
5	10	3	470	467	11	4	4	4	1184	1207	24	1	12	4	411	409	10
6	10	3	269	278	9	5	4	4	521	540	12	2	12	4	229	214	10
7	10	3	227	248	10	6	4	4	101	104	14	3	12	4	229	241	10
1	11	3	232	239	9	7	4	4	122	105	13	4	12	4	187	215	11
2	11	3	440	443	10	8	4	4	531	533	12	5	12	4	342	352	10
3	11	3	299	291	9	0	5	4	461	478	10	6	12	4	113	129	17
4	11	3	187	194	11	1	5	4	770	775	16	7	12	4	149	153	14
5	11	3	392	404	10	2	5	4	288	295	7	0	13	4	627	628	14
6	11	3	375	375	10	3	5	4	752	748	16	1	13	4	171	194	12
7	11	3	49	25	20	4	5	4	631	643	14	2	13	4	85	70	21
1	12	3	616	607	13	5	5	4	360	376	9	3	13	4	119	127	16
2	12	3	141	166	13	6	5	4	370	384	9	4	13	4	320	321	10
3	12	3	358	363	9	7	5	4	506	521	11	5	13	4	75	79	23
4	12	3	168	175	12	8	5	4	346	351	9	6	13	4	35	30	16
5	12	3	270	266	10	0	6	4	685	716	14	0	14	4	103	110	19
6	12	3	148	121	13	1	6	4	564	585	12	1	14	4	362	362	10
7	12	3	204	202	11	2	6	4	168	178	8	2	14	4	94	50	20
1	13	3	50	38	20	3	6	4	602	626	13	3	14	4	190	191	11
2	13	3	483	474	11	4	6	4	461	480	10	4	14	4	56	37	21
3	13	3	77	74	21	5	6	4	262	274	8	5	14	4	155	184	14
4	13	3	120	101	15	6	6	4	146	161	11	0	15	4	333	326	10
5	13	3	158	167	13	7	6	4	153	148	12	1	15	4	68	52	23
6	13	3	298	290	10	8	6	4	596	609	13	2	15	4	97	92	21
1	14	3	375	360	10	0	7	4	756	800	16	2	0	5	1518	1537	30
2	14	3	114	126	17	1	7	4	519	541	12	4	0	5	304	294	7
3	14	3	282	287	10	2	7	4	341	347	8	6	0	5	1118	1113	24
4	14	3	146	162	14	3	7	4	355	353	9	8	0	5	81	94	20
5	14	3	161	158	13	4	7	4	234	240	8	1	1	5	1541	1533	30
2	15	3	389	393	11	5	7	4	187	194	9	2	1	5	121	133	8
3	15	3	77	93	23	6	7	4	227	231	9	3	1	5	575	585	12
0	0	4	2730	2724	53	7	7	4	522	517	12	4	1	5	117	106	10
2	0	4	706	684	16	8	7	4	426	432	10	5	1	5	936	917	20
4	0	4	255	248	7	0	8	4	766	777	17	6	1	5	179	163	9
6	0	4	507	495	11	1	8	4	871	902	19	7	1	5	631	600	14
8	0	4	706	668	15	2	8	4	452	470	10	1	2	5	620	607	13
0	1	4	835	829	17	3	8	4	274	281	8	2	2	5	1224	1249	25
1	1	4	967	958	20	4	8	4	505	526	11	3	2	5	663	657	14
2	1	4	515	490	11	5	8	4	230	244	9	4	2	5	77	64	15
3	1	4	590	585	13	6	8	4	134	150	13	5	2	5	446	448	10
4	1	4	372	355	8	7	8	4	258	263	9	6	2	5	994	965	21
5	1	4	894	896	19	8	8	4	364	365	10	7	2	5	158	168	11
6	1	4	388	387	9	0	9	4	493	504	11	8	2	5	183	200	10
7	1	4	572	570	13	1	9	4	134	130	11	1	3	5	1080	1109	22
8	1	4	78	76	19	2	9	4	221	239	9	2	3	5	536	565	12
0	2	4	730	779	16	3	9	4	272	304	9	3	3	5	1221	1240	25
1	2	4	592	615	13	4	9	4	694	713	15	4	3	5	297	282	8
2	2	4	399	396	9	5	9	4	371	383	9	5	3	5	871	868	18
3	2	4	346	369	8	6	9	4	123	127	14	6	3	5	340	329	9
4	2	4	926	922	19	7	9	4	197	225	11	7	3	5	401	409	10
5	2	4	294	284	8	0	10	4	403	401	10	8	3	5	133	164	13
6	2	4	415	414	9	1	10	4	555	562	12	1	4	5	799	794	17
7	2	4	235	213	8	2	10	4	239	249	9	2	4	5	1197	1256	24
8	2	4	485	501	11	3	10	4	370	371	9	3	4	5	275	290	7
0	3	4	740	772	16	4	10	4	483	506	11	4	4	5	430	438	10
1	3	4	529	521	11	5	10	4	494	502	11	5	4	5	447	453	10
2	3	4	255	261	7	6	10	4	91	118	19	6	4	5	604	597	13
3	3	4	1291	1323	26	7	10	4	110	128	17	7	4	5	148	132	11
4	3	4	368	371	8	0	11	4	524	529	12	8	4	5	75	115	20

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	5	5	518	507	11	2	14	5	74	71	22	2	7	6	242	225	8
2	5	5	699	715	15	3	14	5	194	189	12	3	7	6	347	372	9
3	5	5	1106	1166	23	4	14	5	74	60	23	4	7	6	270	291	9
4	5	5	168	156	9	1	15	5	52	73	21	5	7	6	397	427	10
5	5	5	358	374	9	2	15	5	278	278	10	6	7	6	38	16	17
6	5	5	301	311	9	0	0	6	2981	2968	58	7	7	6	229	251	10
7	5	5	443	440	10	2	0	6	131	130	8	8	7	6	340	359	10
8	5	5	154	144	12	4	0	6	1227	1230	25	0	8	6	672	707	15
1	6	5	523	538	12	6	0	6	607	597	13	1	8	6	549	557	12
2	6	5	1120	1137	23	8	0	6	724	703	16	2	8	6	108	132	15
3	6	5	355	359	9	0	1	6	671	686	15	3	8	6	463	469	11
4	6	5	368	383	9	1	1	6	1705	1727	33	4	8	6	355	359	9
5	6	5	238	252	8	2	1	6	116	121	9	5	8	6	244	238	9
6	6	5	586	607	13	3	1	6	788	764	17	6	8	6	135	140	13
7	6	5	391	393	10	4	1	6	210	194	8	7	8	6	321	322	10
8	6	5	84	109	21	5	1	6	746	741	15	8	8	6	278	283	10
1	7	5	797	818	17	6	1	6	335	342	9	0	9	6	449	468	10
2	7	5	770	801	17	7	1	6	620	624	14	1	9	6	166	166	10
3	7	5	457	475	10	8	1	6	124	77	13	2	9	6	246	250	9
4	7	5	171	157	9	0	2	6	1563	1583	31	3	9	6	308	324	9
5	7	5	168	174	10	1	2	6	588	556	13	4	9	6	441	472	10
6	7	5	369	373	9	2	2	6	167	166	7	5	9	6	456	467	10
7	7	5	412	420	10	3	2	6	553	543	12	6	9	6	72	94	22
8	7	5	132	114	14	4	2	6	1552	1562	31	7	9	6	92	63	20
1	8	5	343	354	9	5	2	6	168	158	9	0	10	6	491	486	11
2	8	5	626	643	14	6	2	6	230	234	9	1	10	6	171	176	11
3	8	5	377	391	9	7	2	6	222	214	9	2	10	6	162	139	11
4	8	5	204	207	9	8	2	6	506	491	11	3	10	6	413	430	10
5	8	5	457	467	11	0	3	6	766	760	16	4	10	6	353	376	10
6	8	5	407	426	10	1	3	6	1241	1245	25	5	10	6	302	310	10
7	8	5	315	322	9	2	3	6	156	121	8	6	10	6	84	51	21
8	8	5	66	69	22	3	3	6	1247	1293	26	7	10	6	184	189	11
1	9	5	467	469	11	4	3	6	628	635	14	0	11	6	388	387	10
2	9	5	506	514	11	5	3	6	873	886	18	1	11	6	175	167	11
3	9	5	184	182	10	6	3	6	297	303	9	2	11	6	229	221	9
4	9	5	122	127	14	7	3	6	407	420	10	3	11	6	45	74	18
5	9	5	250	253	9	8	3	6	214	221	10	4	11	6	446	455	11
6	9	5	390	399	10	0	4	6	770	818	16	5	11	6	137	113	14
7	9	5	204	224	11	1	4	6	211	213	7	6	11	6	59	26	21
1	10	5	392	400	9	2	4	6	174	179	8	0	12	6	181	188	11
2	10	5	445	461	10	3	4	6	540	555	12	1	12	6	162	169	12
3	10	5	363	360	9	4	4	6	1220	1221	25	2	12	6	171	178	11
4	10	5	95	88	18	5	4	6	327	328	8	3	12	6	248	245	10
5	10	5	413	433	10	6	4	6	154	143	11	4	12	6	157	171	13
6	10	5	273	288	9	7	4	6	253	236	9	5	12	6	211	219	11
7	10	5	87	127	21	8	4	6	455	454	10	6	12	6	66	42	22
1	11	5	56	31	20	0	5	6	497	507	11	0	13	6	440	462	11
2	11	5	452	454	10	1	5	6	934	946	19	1	13	6	144	148	14
3	11	5	228	244	9	2	5	6	488	489	11	2	13	6	55	67	21
4	11	5	167	169	12	3	5	6	714	747	15	3	13	6	78	67	21
5	11	5	207	210	10	4	5	6	538	558	12	4	13	6	135	151	15
6	11	5	358	364	10	5	5	6	521	529	12	0	14	6	123	74	15
7	11	5	79	31	22	6	5	6	178	176	10	1	14	6	173	181	12
1	12	5	368	367	10	7	5	6	331	327	9	2	14	6	56	22	21
2	12	5	160	174	12	8	5	6	333	329	9	3	14	6	117	141	17
3	12	5	269	281	10	0	6	6	1218	1276	25	2	0	7	1372	1338	28
4	12	5	54	52	21	1	6	6	537	551	12	4	0	7	569	546	12
5	12	5	174	182	12	2	6	6	332	313	8	6	0	7	873	863	19
6	12	5	94	105	20	3	6	6	502	518	11	8	0	7	214	208	10
7	12	5	163	154	13	4	6	6	517	540	12	1	1	7	1417	1411	28
1	13	5	55	66	21	5	6	6	197	213	9	2	1	7	245	242	7
2	13	5	323	334	10	6	6	6	86	42	18	3	1	7	926	924	19
3	13	5	55	54	21	7	6	6	280	295	9	4	1	7	106	119	13
4	13	5	67	96	22	8	6	6	523	519	12	5	1	7	685	657	15
5	13	5	81	118	22	0	7	6	798	825	17	6	1	7	180	185	10
1	14	5	286	298	10	1	7	6	620	649	14	7	1	7	598	592	13

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	2	7	178	183	8	4	10	7	111	111	16	4	5	8	303	300	9
2	2	7	1402	1430	28	5	10	7	334	338	10	5	5	8	255	250	9
3	2	7	644	653	14	6	10	7	157	171	13	6	5	8	251	254	9
4	2	7	329	330	8	7	10	7	149	158	14	7	5	8	385	395	10
5	2	7	386	373	9	1	11	7	184	168	10	8	5	8	212	201	10
6	2	7	731	726	16	2	11	7	349	340	9	0	6	8	738	763	16
7	2	7	179	165	11	3	11	7	208	217	10	1	6	8	308	325	8
8	2	7	170	176	11	4	11	7	79	109	21	2	6	8	306	313	8
1	3	7	605	622	13	5	11	7	159	159	12	3	6	8	236	254	9
2	3	7	519	524	11	6	11	7	216	241	11	4	6	8	409	413	10
3	3	7	1039	1065	22	1	12	7	328	338	10	5	6	8	352	360	9
4	3	7	129	90	11	2	12	7	165	186	12	6	6	8	132	139	13
5	3	7	660	670	14	3	12	7	188	199	11	7	6	8	164	159	12
6	3	7	303	300	9	4	12	7	60	26	21	8	6	8	340	351	10
7	3	7	469	457	11	5	12	7	168	171	13	0	7	8	668	700	15
8	3	7	83	98	20	6	12	7	124	109	16	1	7	8	480	510	11
1	4	7	377	375	9	1	13	7	56	46	21	2	7	8	252	267	9
2	4	7	1311	1314	27	2	13	7	293	291	10	3	7	8	277	286	9
3	4	7	360	370	9	3	13	7	102	128	19	4	7	8	353	360	9
4	4	7	118	120	12	4	13	7	39	48	17	5	7	8	256	262	9
5	4	7	227	225	9	1	14	7	221	219	11	6	7	8	39	78	17
6	4	7	607	615	13	2	14	7	68	80	23	7	7	8	244	246	10
7	4	7	199	212	10	0	0	8	1142	1149	24	8	7	8	272	287	10
8	4	7	74	59	20	2	0	8	144	141	9	0	8	8	684	711	15
1	5	7	589	617	13	4	0	8	361	353	9	1	8	8	479	498	11
2	5	7	660	684	14	6	0	8	112	111	14	2	8	8	226	231	9
3	5	7	739	761	16	8	0	8	524	523	12	3	8	8	130	109	12
4	5	7	119	128	13	0	1	8	387	402	9	4	8	8	456	468	10
5	5	7	421	427	10	1	1	8	730	725	16	5	8	8	275	274	9
6	5	7	365	381	9	2	1	8	454	445	10	6	8	8	92	101	20
7	5	7	406	400	10	3	1	8	592	594	13	7	8	8	178	195	12
8	5	7	59	60	21	4	1	8	141	143	10	8	8	8	258	251	10
1	6	7	699	710	15	5	1	8	625	614	14	0	9	8	375	386	9
2	6	7	832	861	18	6	1	8	136	130	12	1	9	8	252	268	9
3	6	7	185	185	9	7	1	8	357	352	9	2	9	8	69	99	21
4	6	7	209	205	9	0	2	8	1045	1023	22	3	9	8	221	228	10
5	6	7	189	196	10	1	2	8	150	159	9	4	9	8	525	532	12
6	6	7	432	434	10	2	2	8	139	122	10	5	9	8	305	308	10
7	6	7	245	237	9	3	2	8	451	462	10	6	9	8	79	46	21
8	6	7	100	71	19	4	2	8	706	710	15	7	9	8	102	112	19
1	7	7	524	540	12	5	2	8	72	67	20	0	10	8	259	252	9
2	7	7	424	430	10	6	2	8	120	125	14	1	10	8	336	332	9
3	7	7	314	323	9	7	2	8	140	153	12	2	10	8	64	94	21
4	7	7	165	166	11	8	2	8	405	423	10	3	10	8	275	285	9
5	7	7	273	274	9	0	3	8	428	438	10	4	10	8	322	335	10
6	7	7	400	400	10	1	3	8	210	227	8	5	10	8	281	297	10
7	7	7	350	349	10	2	3	8	135	137	10	7	10	8	131	120	15
8	7	7	36	29	16	3	3	8	620	628	13	0	11	8	294	302	9
1	8	7	291	309	9	4	3	8	321	322	8	1	11	8	241	244	9
2	8	7	493	499	11	5	3	8	564	581	12	2	11	8	165	162	12
3	8	7	329	328	9	6	3	8	103	119	16	3	11	8	130	160	15
4	8	7	[illegible]	111	16	7	3	8	237	243	9	4	11	8	384	396	10
5	8	7	[illegible]	131	9	8	3	8	163	167	12	5	11	8	87	107	21
6	8	7	[illegible]	418	10	0	4	8	649	652	14	6	11	8	74	78	23
7	8	7	[illegible]	192	11	1	4	8	229	257	8	0	12	8	235	233	10
8	8	7	56	43	21	2	4	8	132	136	11	1	12	8	297	296	10
1	9	7	330	343	9	3	4	8	352	352	9	2	12	8	141	111	13
2	9	7	494	516	11	4	4	8	870	867	19	3	12	8	204	220	11
3	9	7	264	280	9	5	4	8	302	322	9	4	12	8	117	107	17
4	9	7	112	116	15	6	4	8	361	363	9	5	12	8	225	210	11
5	9	7	232	232	10	7	4	8	177	175	11	0	13	8	368	356	10
6	9	7	373	383	10	8	4	8	323	310	10	1	13	8	68	82	23
7	9	7	192	204	11	0	5	8	672	698	15	2	13	8	56	46	21
1	10	7	232	239	9	1	5	8	689	699	15	3	13	8	49	75	20
2	10	7	248	247	9	2	5	8	214	213	8	4	13	8	198	217	12
3	10	7	323	329	9	3	5	8	412	426	10	0	14	8	115	85	18

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	14	8	229	229	11	7	8	9	223	224	11	2	5	10	86	93	18
2	0	9	485	482	11	8	8	9	57	38	22	3	5	10	301	309	9
4	0	9	386	383	9	1	9	9	260	263	9	4	5	10	326	318	9
6	0	9	420	427	10	2	9	9	411	419	10	5	5	10	343	347	9
8	0	9	43	79	18	3	9	9	108	119	16	6	5	10	205	211	10
1	1	9	460	457	10	4	9	9	43	39	18	7	5	10	229	235	10
2	1	9	252	239	8	5	9	9	248	260	10	8	5	10	111	112	17
3	1	9	497	499	11	6	9	9	281	282	10	0	6	10	604	609	13
4	1	9	152	149	11	7	9	9	135	129	15	1	6	10	313	315	9
5	1	9	196	189	9	1	10	9	232	239	10	2	6	10	148	145	12
6	1	9	73	28	20	2	10	9	221	241	10	3	6	10	180	188	11
7	1	9	410	411	10	3	10	9	386	396	10	4	6	10	286	290	9
1	2	9	290	288	8	4	10	9	111	92	17	5	6	10	283	300	9
2	2	9	561	540	12	5	10	9	208	210	11	6	6	10	105	79	18
3	2	9	357	362	9	6	10	9	198	187	11	7	6	10	93	74	20
4	2	9	124	132	13	1	11	9	151	165	13	8	6	10	246	253	11
5	2	9	244	264	9	2	11	9	436	448	11	0	7	10	555	574	12
6	2	9	520	515	12	3	11	9	134	159	15	1	7	10	334	339	9
7	2	9	109	75	16	4	11	9	62	88	22	2	7	10	63	86	21
8	2	9	40	51	18	5	11	9	225	209	11	3	7	10	330	339	9
1	3	9	220	229	8	1	12	9	311	305	10	4	7	10	228	231	10
2	3	9	325	328	8	2	12	9	120	129	17	5	7	10	226	218	10
3	3	9	435	437	10	3	12	9	280	281	10	6	7	10	65	71	22
4	3	9	74	128	20	4	12	9	49	35	20	7	7	10	228	231	11
5	3	9	372	372	9	2	13	9	320	326	10	8	7	10	162	182	14
6	3	9	57	48	20	0	0	10	761	771	17	0	8	10	377	409	10
7	3	9	263	271	9	2	0	10	140	156	11	1	8	10	312	329	9
8	3		97	87	18	4	0	10	445	449	10	2	8	10	93	27	18
1	4	.	174	155	9	6	0	10	437	436	10	3	8	10	191	168	10
2	4	9	567	556	12	8	0	10	507	500	12	4	8	10	253	261	9
3	4	9	233	246	9	0	1	10	395	395	9	5	8	10	273	279	10
4	4	9	92	94	17	1	1	10	350	357	9	6	8	10	110	86	17
5	4	9	179	163	10	2	1	10	125	113	12	7	8	10	177	157	13
6	4	9	405	402	10	3	1	10	216	207	9	0	9	10	331	327	9
7	4	9	244	239	9	4	1	10	246	228	9	1	9	10	91	129	20
8	4	9	55	17	21	5	1	10	206	210	10	2	9	10	154	164	12
1	5	9	270	283	8	6	1	10	52	77	20	3	9	10	329	337	10
2	5	9	177	211	10	7	1	10	359	354	10	4	9	10	349	357	10
3	5	9	337	343	9	0	2	10	300	333	8	5	9	10	188	180	11
4	5	9	139	136	12	1	2	10	328	325	8	7	9	10	122	133	18
5	5	9	351	361	9	2	2	10	164	153	10	0	10	10	264	277	9
6	5	9	153	174	12	3	2	10	129	127	13	1	10	10	201	227	11
7	5	9	192	210	11	4	2	10	601	594	13	2	10	10	107	124	18
8	5	9	60	76	21	5	2	10	156	145	11	3	10	10	265	275	10
1	6	9	355	357	9	6	2	10	180	168	11	4	10	10	243	248	10
2	6	9	465	461	11	8	2	10	352	351	10	5	10	10	225	240	11
3	6	9	143	145	12	0	3	10	400	408	10	0	11	10	338	342	10
4	6	9	127	126	13	1	3	10	336	336	9	1	11	10	115	122	17
5	6	9	57	74	20	2	3	10	163	174	10	2	11	10	95	123	20
6	6	9	374	377	10	3	3	10	472	488	11	3	11	10	97	117	21
7	6	9	294	292	10	4	3	10	209	215	10	4	11	10	331	334	10
8	6	9	34	28	16	5	3	10	330	349	9	5	11	10	58	55	22
1	7	9	387	398	9	6	3	10	106	82	16	0	12	10	118	116	17
2	7	9	429	446	10	7	3	10	261	281	10	1	12	10	199	199	12
3	7	9	122	109	14	8	3	10	86	84	21	2	12	10	33	22	15
4	7	9	154	135	11	0	4	10	354	356	9	3	12	10	207	191	12
5	7	9	309	315	9	1	4	10	225	232	9	2	0	11	1018	1014	22
6	7	9	272	281	9	2	4	10	127	115	12	4	0	11	159	137	11
7	7	9	213	203	11	3	4	10	199	176	9	6	0	11	534	532	12
8	7	9	48	53	20	4	4	10	530	532	12	8	0	11	75	86	23
1	8	9	195	192	10	5	4	10	324	322	9	1	1	11	499	495	11
2	8	9	318	326	9	6	4	10	126	137	14	2	1	11	93	103	18
3	8	9	310	322	9	7	4	10	59	57	21	3	1	11	411	406	10
4	8	9	78	90	21	8	4	10	265	265	10	4	1	11	81	95	20
5	8	9	167	184	12	0	5	10	306	303	9	5	1	11	371	359	10
6	8	9	285	300	10	1	5	10	357	373	9	6	1	11	104	103	18

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
7	1	11	390	379	10	0	0	12	923	942	19	0	9	12	204	216	11
1	2	11	259	260	9	2	0	12	112	94	16	1	9	12	257	254	10
2	2	11	783	769	17	4	0	12	608	600	13	3	9	12	161	155	13
3	2	11	223	211	9	6	0	12	221	255	11	4	9	12	264	273	10
4	2	11	107	139	16	8	0	12	427	424	11	5	9	12	187	181	12
5	2	11	53	87	20	0	1	12	262	256	9	0	10	12	94	103	20
6	2	11	464	456	11	1	1	12	560	560	12	1	10	12	125	125	15
8	2	11	117	92	17	2	1	12	164	152	12	2	10	12	62	65	22
1	3	11	487	491	11	3	1	12	593	607	13	3	10	12	181	204	13
2	3	11	125	137	14	4	1	12	71	46	21	0	11	12	155	138	13
3	3	11	498	508	11	5	1	12	348	351	10	1	11	12	103	115	19
4	3	11	184	169	10	6	1	12	60	38	21	2	11	12	83	64	23
5	3	11	426	424	10	7	1	12	331	330	10	2	0	13	672	674	35
6	3	11	216	204	10	0	2	12	820	844	18	4	0	13	150	145	13
7	3	11	260	255	10	1	2	12	231	244	9	6	0	13	354	336	10
1	4	11	248	253	9	2	2	12	204	198	10	1	1	13	580	575	13
2	4	11	554	548	12	3	2	12	270	258	9	2	1	13	115	78	15
3	4	11	157	161	12	4	2	12	655	659	14	3	1	13	538	538	12
4	4	11	256	246	9	5	2	12	64	24	21	5	1	13	261	265	10
5	4	11	181	181	11	6	2	12	72	67	22	7	1	13	263	280	10
6	4	11	425	428	10	8	2	12	327	323	10	1	2	13	57	53	20
7	4	11	129	124	15	0	3	12	344	353	9	2	2	13	667	671	15
8	4	11	110	125	19	1	3	12	443	459	10	3	2	13	162	169	12
1	5	11	401	404	10	2	3	12	90	89	19	4	2	13	36	76	16
2	5	11	263	282	9	3	3	12	492	487	11	5	2	13	168	155	12
3	5	11	430	422	10	4	3	12	224	227	10	6	2	13	393	386	10
4	5	11	140	116	13	5	3	12	412	420	10	1	3	13	415	407	10
5	5	11	331	319	9	6	3	12	40	23	18	2	3	13	197	209	10
6	5	11	252	253	10	7	3	12	217	224	11	3	3	13	430	424	10
7	5	11	256	229	10	0	4	12	643	651	14	4	3	13	85	100	21
8	5	11	69	26	23	1	4	12	193	[illegible]	10	5	3	13	281	287	10
1	6	11	311	320	9	2	4	12	96	109	18	6	3	13	51	99	21
2	6	11	403	389	10	3	4	12	275	248	9	7	3	13	208	210	12
3	6	11	263	258	9	4	4	12	563	580	12	1	4	13	164	149	12
4	6	11	176	183	11	5	4	12	184	178	11	2	4	13	509	510	12
5	6	11	134	134	14	6	4	12	86	50	21	3	4	13	99	88	19
6	6	11	299	315	10	8	4	12	223	217	11	5	4	13	168	167	13
7	6	11	122	138	17	0	5	12	410	414	10	6	4	13	341	347	10
8	6	11	85	98	23	1	5	12	494	483	11	1	5	13	355	350	10
1	7	11	343	354	9	2	5	12	100	81	17	2	5	13	208	204	10
2	7	11	351	361	9	3	5	12	268	274	9	3	5	13	282	270	9
3	7	11	232	228	10	4	5	12	257	266	10	5	5	13	239	230	10
4	7	11	127	107	14	5	5	12	317	316	10	6	5	13	197	203	12
5	7	11	213	234	11	6	5	12	38	27	17	1	6	13	297	307	10
6	7	11	231	225	11	7	5	12	189	169	11	2	6	13	370	355	10
7	7	11	232	230	11	0	6	12	550	561	13	3	6	13	104	71	18
1	8	11	240	245	10	1	6	12	246	237	10	4	6	13	55	67	21
2	8	11	303	307	9	2	6	12	77	92	21	5	6	13	180	171	12
3	8	11	261	274	10	3	6	12	217	222	10	6	6	13	261	273	11
4	8	11	99	65	19	4	6	12	353	371	10	1	7	13	189	196	11
5	8	11	200	192	11	5	6	12	190	178	11	2	7	13	213	209	11
6	8	11	248	215	10	6	6	12	102	73	19	3	7	13	163	181	13
1	9	11	172	174	11	7	6	12	153	150	14	4	7	13	72	28	22
2	9	11	364	376	10	0	7	12	355	355	10	5	7	13	99	129	21
3	9	11	152	151	13	1	7	12	373	374	10	1	8	13	209	204	11
4	9	11	67	53	23	2	7	12	110	115	16	2	8	13	249	241	10
5	9	11	163	177	13	3	7	12	172	162	12	3	8	13	157	156	13
6	9	11	182	201	13	4	7	12	241	223	10	1	9	13	102	106	19
1	10	11	214	212	10	5	7	12	254	246	10	2	9	13	231	226	11
2	10	11	195	204	11	6	7	12	104	71	20	1	10	13	129	121	16
3	10	11	255	255	10	0	8	12	274	275	9	2	10	13	137	133	16
5	10	11	152	153	15	1	8	12	243	216	10	0	0	14	281	276	8
1	11	11	43	47	16	2	8	12	50	50	20	2	0	14	156	155	13
2	11	11	314	321	10	3	8	12	192	188	11	4	0	14	250	275	10
3	11	11	147	119	14	4	8	12	269	244	10	0	1	14	63	78	21
1	12	11	197	183	12	5	8	12	127	120	16	1	1	14	370	361	10

Table A-12 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	1	14	91	74	20	0	6	14	415	414	10	5	3	15	187	173	12
3	1	14	287	295	10	1	6	14	142	161	14	1	4	15	65	55	22
5	1	14	210	215	11	2	6	14	93	101	20	2	4	15	175	173	12
0	2	14	286	300	9	3	6	14	73	77	22	1	5	15	186	156	11
1	2	14	131	123	14	4	6	14	221	223	11	2	5	15	81	91	22
2	2	14	72	61	22	5	6	14	166	152	14	3	5	15	125	111	16
3	2	14	85	123	21	0	7	14	297	293	10	1	6	15	148	129	14
4	2	14	323	320	10	1	7	14	224	195	10	2	6	15	177	178	12
0	3	14	107	69	16	2	7	14	107	46	18	1	7	15	110	127	19
1	3	14	246	240	10	3	7	14	138	150	15	2	7	15	156	135	13
2	3	14	89	70	19	4	7	14	189	177	12	0	0	16	160	160	11
3	3	14	242	234	10	0	8	14	241	253	11	2	0	16	55	32	21
4	3	14	145	149	14	1	8	14	118	140	17	0	1	16	59	71	21
5	3	14	250	243	10	2	8	14	62	32	22	1	1	16	118	95	15
0	4	14	424	424	10	0	9	14	155	147	14	2	1	16	67	43	22
1	4	14	207	203	10	1	9	14	96	124	21	3	1	16	153	152	14
2	4	14	78	30	21	2	0	15	235	254	10	0	2	16	102	147	19
3	4	14	140	140	14	1	1	15	136	134	14	1	2	16	85	70	21
4	4	14	310	328	10	2	1	15	60	75	21	2	2	16	66	41	22
5	4	14	90	85	22	3	1	15	192	201	12	0	3	16	78	81	21
6	4	14	120	127	18	5	1	15	103	95	19	1	3	16	127	122	16
0	5	14	311	301	10	1	2	15	91	88	20	2	3	16	124	76	16
1	5	14	243	248	10	2	2	15	199	193	11	0	4	16	149	170	14
2	5	14	54	36	20	3	2	15	72	63	22	1	4	16	67	61	22
3	5	14	172	141	12	1	3	15	194	182	11	2	4	16	114	63	17
4	5	14	162	163	13	2	3	15	129	110	15	0	5	16	159	145	14
5	5	14	193	192	12	3	3	15	134	152	15	1	5	16	129	142	16

Table A-13. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 57b

H(21)-C(2)	0.98	H(31)-C(3)	0.98
H(32)-C(3)	0.88	H(41)-C(4)	0.98
H(42)-C(4)	0.88	H(51)-C(5)	0.99
H(O)-O	0.83		

H(21)-C(2)-C(1)	84	H(21)-C(2)-C(4)	142
H(31)-C(3)-C(2)	112	H(32)-C(3)-C(2)	138
H(41)-C(4)-C(2)	112	H(42)-C(4)-C(2)	138
H(41)-C(4)-H(42)	95	H(51)-C(5)-C(1)	112
H(O)-O-C(1)	107		

Table A-14. Atomic Positional Parameters (x10^3) and Isotropic Atomic Displacement Factors (Å^2) (x10^4) for Hydrogen Atoms in 57b

Atom	x	y	z	U_{iso}
H(21)	250	60	505	9
H(41)	381	135	278	5
H(42)	405	1	285	8
H(51)	162	202	631	6
H(O)	250	376	426	5

Table A-15. Temperature Factors (Å^2)(x10^3) for Non-Hydrogen Atoms in 57b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	43.6(3)	43.5(3)	49.2(3)	0	0	-1.0(2)
F(1)	82(3)	137(4)	119(3)	1(3)	46(2)	26(3)
F(2)	106(3)	170(4)	114(3)	56(3)	-26(3)	36(3)
F(3)	254(11)	78(4)	68(3)	80(11)	-16(13)	-10(3)
F(4)	104(19)	54(4)	95(4)	-49(24)	34(31)	-24(3)
C(1)	42(3)	45(4)	48(3)	0	0	-1(3)
C(2)	102(6)	48(4)	55(4)	0	0	8(3)
C(4)	80(4)	69(3)	83(3)	18(3)	3(3)	-34(3)
C(5)	60(4)	97(6)	40(3)	0	0	1(4)
O(1)	113(5)	40(3)	44(2)	0	0	0(2)

Table A-16. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 58b

H(31)-C(3)	1.02	H(32)-C(3)	0.83
H(41)-C(4)	0.92	H(42)-C(4)	0.90
H(51)-C(5)	0.83	H(52)-C(5)	1.08
H(53)-C(5)	0.92	H(61)-C(6)	0.88
H(62)-C(6)	0.93	H(63)-C(6)	1.09
H(O)-O	1.14		

H(31)-C(3)-C(2)	120	H(31)-C(3)-C(4)	119
H(32)-C(3)-C(2)	113	H(32)-C(3)-C(4)	116
H(41)-C(4)-C(2)	122	H(41)-C(4)-C(3)	121
H(42)-C(4)-C(2)	111	H(42)-C(4)-C(3)	114
H(51)-C(5)-C(1)	117	H(52)-C(5)-C(1)	122
H(53)-C(5)-C(1)	120	H(61)-C(6)-C(2)	112
H(62)-C(6)-C(2)	116	H(63)-C(6)-C(2)	108
H(51)-C(5)-H(52)	85	H(51)-C(5)-H(53)	99
H(52)-C(5)-H(53)	107	H(31)-C(3)-H(32)	116
H(41)-C(4)-H(42)	117	H(61)-C(6)-H(62)	93
H(61)-C(6)-H(63)	115	H(62)-C(6)-H(63)	114
H(O)-O-C(1)	113		

Table A-17. Atomic Positional Parameters ($x10^3$) and Isotropic Atomic Displacement Factors (Å^2) ($x10^4$) for Hydrogen Atoms in 58b

Atom	x	y	z	U_{iso}
H(31)	-9	906	-704	4
H(32)	-59	872	-612	3
H(41)	17	613	-697	2
H(42)	-36	609	-606	3
H(51)	278	874	-675	4
H(52)	281	721	-699	9
H(53)	151	828	-739	8
H(61)	202	682	-366	7
H(62)	196	840	-357	6
H(63)	47	745	-414	5
H(O)	434	806	-470	5

Table A-18. Temperature Factors (Å^2)(x10^3) for Non-Hydrogen Atoms in 58b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	29.6(4)	21.3(4)	31.3(4)	-0.5(1)	13.1(3)	-0.5(1)
F(1)	37(2)	52(2)	57(3)	-2(2)	22(2)	17(2)
F(2)	58(2)	44(2)	40(2)	-7(2)	10(2)	-9(2)
F(3)	42(2)	49(2)	58(2)	17(2)	8(2)	18(2)
F(4)	42(2)	37(2)	95(4)	19(2)	25(2)	21(2)
F(5)	78(3)	66(3)	78(3)	1(3)	58(3)	13(3)
F(6)	96(4)	45(2)	55(3)	-12(3)	22(3)	-20(2)
C(1)	30(3)	20(3)	27(3)	2(2)	7(3)	1(2)
C(2)	28(3)	19(3)	32(3)	-2(2)	7(3)	1(2)
C(3)	41(4)	55(4)	34(4)	8(3)	16(3)	6(3)
C(4)	23(3)	47(4)	42(3)	5(3)	8(3)	-3(3)
C(5)	32(3)	37(3)	42(3)	-10(3)	10(3)	-10(3)
C(6)	45(4)	49(3)	33(4)	1(3)	19(3)	2(3)
O(1)	27(3)	43(4)	32(3)	5(1)	8(3)	-1(1)

Table A-19. Bond Lengths (Å) and Angles (°) Involving Hydrogen Atoms in 59b

H(21)-C(2)	0.90	H(31)-C(3)	1.02
H(41)-C(4)	0.94	H(42)-C(4)	1.36
H(51)-C(5)	1.37	H(52)-C(5)	0.68
H(61)-C(6)	1.08	H(62)-C(6)	1.14
H(71)-C(7)	1.12	H(72)-C(7)	0.92
H(O)-O	1.31		

H(21)-C(2)-C(1)	112	H(21)-(C2)-C(3)	113
H(21)-C(2)-C(4)	127	H(31)-C(3)-C(2)	115
H(31)-C(3)-C(7)	117	H(31)-C(3)-C(4)	114
H(41)-C(4)-C(2)	105	H(41)-C(4)-C(3)	118
H(41)-C(4)-H(42)	116	H(42)-C(4)-C(2)	119
H(42)-C(4)-C(3)	123	H(51)-C(5)-C(1)	117
H(51)-C(5)-C(6)	100	H(51)-C(5)-H(52)	74
H(52)-C(5)-C(1)	122	H(52)-C(5)-C(6)	118
H(61)-C(6)-C(7)	114	H(61)-C(6)-C(5)	102
H(61)-C(6)-H(62)	104	H(62)-C(6)-C(7)	117
H(62)-C(6)-C(5)	108	H(71)-C(7)-C(3)	110
H(71)-C(7)-C(6)	100	H(71)-C(7)-H(72)	118
H(72)-C(7)-C(3)	105	H(72)-C(7)-C(6)	112
H(O)-O-C(1)	113		

Table A-20. Atomic Positional Parameters (x10^3) and Isotropic Atomic Displacement Factors (Å^2) (x10^2) for Hydrogen Atoms in 59b

Atom	x	y	z	U_{iso}
H(21)	-575	658	1119	1
H(31)	-261	699	1075	2
H(41)	-399	554	1023	9
H(42)	-501	604	915	7
H(51)	-842	747	889	7
H(52)	-813	817	949	7
H(61)	-564	876	886	3
H(62)	-530	751	857	2
H(71)	-243	799	933	5
H(72)	-378	851	1018	2
H(O)	-889	662	1144	2

Table A-21. Temperature Factors (Å^2)(x10^3) for Non-Hydrogen Atoms in 59b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	20.0(3)	16.6(3)	15.6(2)	0.6(1)	−0.6(1)	1.1(2)
Cl(1)	47(1)	39(1)	17.3(7)	2.7(9)	−3.8(7)	−0.9(7)
Cl(2)	31.5(8)	20(1)	30.2(8)	8.2(8)	2.3(6)	0.2(6)
Cl(3)	76(1)	37(2)	18.8(8)	18(1)	−11.4(8)	−6.1(8)
Cl(4)	22.9(8)	29(1)	70(1)	−5.3(7)	−2.7(8)	5(1)
Cl(5)	24.9(7)	27.6(9)	55(1)	−4.2(7)	7.7(9)	10.7(9)
Cl(6)	29.8(8)	21(1)	37.7(9)	6.5(8)	3.5(6)	3.9(6)
O	31(2)	37(3)	38(3)	2(2)	8(2)	4(2)
C(1)	12(3)	29(4)	32(4)	−4(3)	−3(2)	−7(3)
C(2)	28(4)	48(5)	27(4)	5(4)	0(3)	6(4)
C(3)	23(4)	47(5)	46(5)	−6(4)	−10(3)	9(4)
C(4)	42(5)	37(4)	66(5)	12(4)	14(5)	1(4)
C(5)	47(5)	35(5)	27(4)	−2(4)	4(3)	8(4)
C(6)	53(4)	44(5)	21(4)	−12(4)	5(3)	4(4)
C(7)	40(5)	59(6)	32(4)	−24(5)	−3(3)	−2(4)

Table A-22. Observed and Calculated Structure Factors for 57b

F_o, F_c and SIG (σ) values have been multiplied by 10.

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	0	0	1159	1127	7	3	2	1	453	454	3	3	9	1	369	377	3
6	0	0	1195	1198	7	4	2	1	146	144	1	4	9	1	115	123	2
8	0	0	582	615	4	5	2	1	244	255	2	5	9	1	291	290	2
10	0	0	277	300	3	6	2	1	315	300	2	6	9	1	106	96	2
2	2	0	1183	1168	7	7	2	1	114	110	2	0	10	1	78	75	3
3	2	0	568	581	4	8	2	1	139	135	2	1	10	1	120	112	2
4	2	0	937	929	6	9	2	1	102	91	2	2	10	1	91	89	2
5	2	0	638	593	4	0	3	1	1169	1119	7	3	10	1	79	71	3
6	2	0	865	846	6	1	3	1	438	455	3	4	10	1	93	88	3
7	2	0	471	468	3	2	3	1	1003	1003	6	5	10	1	61	41	3
8	2	0	419	428	3	3	3	1	153	152	1	0	11	1	296	284	2
9	2	0	247	256	2	4	3	1	877	872	5	1	11	1	157	153	2
10	2	0	181	207	3	5	3	1	262	267	2	2	11	1	264	253	2
0	4	0	267	270	2	6	3	1	633	610	4	3	11	1	134	131	2
1	4	0	559	609	4	7	3	1	219	216	2	4	11	1	211	216	2
2	4	0	204	192	2	8	3	1	354	355	2	0	12	1	140	138	2
3	4	0	979	970	6	9	3	1	107	100	2	4	0	2	1074	1075	6
4	4	0	97	103	2	0	4	1	736	801	4	6	0	2	805	811	5
5	4	0	915	871	6	1	4	1	257	255	2	8	0	2	403	416	3
6	4	0	73	78	3	2	4	1	582	586	4	10	0	2	196	207	2
7	4	0	546	531	4	3	4	1	179	196	1	1	1	2	708	680	4
8	4	0	45	51	6	4	4	1	402	377	3	2	1	2	1291	1277	7
9	4	0	317	322	3	5	4	1	40	24	4	3	1	2	35	14	3
0	6	0	486	486	3	6	4	1	244	226	2	4	1	2	894	904	5
1	6	0	873	923	6	7	4	1	27	22	4	5	1	2	173	166	1
2	6	0	602	609	4	8	4	1	138	133	2	6	1	2	588	576	4
3	6	0	921	897	6	9	4	1	43	25	4	7	1	2	185	183	2
4	6	0	586	586	4	0	5	1	976	994	6	8	1	2	294	297	2
5	6	0	488	481	3	1	5	1	336	350	2	9	1	2	92	89	2
6	6	0	320	316	3	2	5	1	1118	1106	7	10	1	2	173	179	2
7	6	0	275	284	2	3	5	1	455	464	3	1	2	2	778	755	5
8	6	0	165	173	2	4	5	1	897	892	6	2	2	2	754	731	5
0	8	0	774	774	5	5	5	1	279	276	2	3	2	2	982	992	6
1	8	0	110	112	3	6	5	1	494	497	3	4	2	2	444	429	3
2	8	0	776	785	5	7	5	1	140	130	2	5	2	2	599	585	4
3	8	0	172	154	2	8	5	1	312	315	2	6	2	2	523	509	3
4	8	0	573	589	4	9	5	1	110	102	2	7	2	2	303	300	2
5	8	0	117	99	3	0	6	1	205	198	2	8	2	2	287	284	2
6	8	0	337	340	3	1	6	1	336	330	2	9	2	2	194	190	2
7	8	0	95	79	3	2	6	1	304	315	2	0	3	2	313	313	2
0	10	0	346	336	3	3	6	1	207	212	2	1	3	2	594	597	4
1	10	0	241	227	2	4	6	1	305	299	2	2	3	2	325	338	2
2	10	0	335	345	3	5	6	1	147	152	2	3	3	2	415	397	3
3	10	0	192	194	2	6	6	1	176	164	2	4	3	2	509	536	3
4	10	0	290	309	3	7	6	1	90	86	2	5	3	2	542	541	3
5	10	0	150	149	3	8	6	1	104	106	2	6	3	2	152	158	2
0	12	0	98	87	4	0	7	1	281	296	2	7	3	2	373	380	2
1	12	0	260	240	3	1	7	1	701	704	4	8	3	2	99	91	2
1	0	1	543	506	3	2	7	1	378	367	2	9	3	2	192	197	2
3	0	1	330	328	2	3	7	1	703	720	4	0	4	2	644	643	4
5	0	1	472	455	3	4	7	1	289	296	2	1	4	2	882	883	5
7	0	1	306	287	2	5	7	1	460	479	3	2	4	2	132	109	1
9	0	1	126	127	2	6	7	1	155	163	2	3	4	2	849	839	5
0	1	1	780	727	5	7	7	1	282	288	2	4	4	2	69	60	2
2	1	1	469	456	3	8	7	1	113	113	2	5	4	2	535	517	3
3	1	1	364	376	2	0	8	1	118	118	2	6	4	2	150	142	2
4	1	1	347	340	2	1	8	1	124	130	2	7	4	2	345	349	2
5	1	1	739	725	5	2	8	1	98	92	2	8	4	2	57	61	4
6	1	1	309	308	2	3	8	1	177	178	2	9	4	2	246	245	2
7	1	1	576	576	4	4	8	1	32	26	4	0	5	2	562	579	4
8	1	1	160	167	2	5	8	1	151	158	2	1	5	2	437	454	3
9	1	1	239	251	2	6	8	1	41	7	4	2	5	2	293	289	2
10	1	1	80	84	3	7	8	1	96	108	3	3	5	2	598	591	4
0	2	1	435	447	3	0	9	1	188	171	2	4	5	2	222	214	2
1	2	1	723	708	4	1	9	1	373	365	2	5	5	2	435	436	3
2	2	1	67	70	1	2	9	1	136	146	2	6	5	2	225	233	2

Table A-22 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
7	5	2	265	263	2	5	2	3	647	644	4	0	10	3	226	233	2
8	5	2	87	94	3	6	2	3	448	441	3	1	10	3	239	243	2
9	5	2	178	179	2	7	2	3	333	328	2	2	10	3	215	219	2
0	6	2	319	290	2	8	2	3	265	253	2	3	10	3	209	201	2
1	6	2	620	635	4	9	2	3	230	228	2	4	10	3	174	170	2
2	6	2	420	417	3	0	3	3	56	50	2	5	10	3	175	172	2
3	6	2	554	544	4	1	3	3	346	367	2	0	11	3	81	79	3
4	6	2	317	317	2	2	3	3	478	503	3	1	11	3	103	87	2
5	6	2	388	397	3	3	3	3	133	133	1	2	11	3	75	76	3
6	6	2	150	150	2	4	3	3	480	459	3	3	11	3	83	90	3
7	6	2	259	273	2	5	3	3	194	188	2	0	0	4	238	205	2
8	6	2	150	136	2	6	3	3	192	181	2	2	0	4	178	181	1
0	7	2	581	596	4	7	3	3	202	191	2	4	0	4	74	61	2
1	7	2	353	335	2	8	3	3	158	157	2	6	0	4	34	28	4
2	7	2	536	553	3	9	3	3	26	30	4	8	0	4	36	8	4
3	7	2	288	288	2	0	4	3	1260	1293	7	0	1	4	712	727	4
4	7	2	411	425	3	1	4	3	74	63	2	1	1	4	206	199	1
5	7	2	157	156	2	2	4	3	1207	1176	7	2	1	4	1311	1332	8
6	7	2	260	265	2	3	4	3	217	221	2	3	1	4	611	601	4
7	7	2	131	122	2	4	4	3	940	903	6	4	1	4	1251	1266	7
8	7	2	166	169	2	5	4	3	76	76	2	5	1	4	459	429	3
0	8	2	469	477	3	6	4	3	603	598	4	6	1	4	599	606	4
1	8	2	62	42	3	7	4	3	32	5	4	7	1	4	229	224	2
2	8	2	463	475	3	8	4	3	363	361	2	8	1	4	388	381	3
3	8	2	113	91	2	9	4	3	36	27	4	9	1	4	136	128	2
4	8	2	392	404	3	0	5	3	450	469	3	0	2	4	77	67	1
5	8	2	88	75	2	1	5	3	249	262	2	1	2	4	257	255	2
6	8	2	287	287	2	2	5	3	388	373	3	2	2	4	276	267	2
7	8	2	41	39	5	3	5	3	207	202	2	3	2	4	409	421	3
0	9	2	456	444	3	4	5	3	231	236	2	4	2	4	137	143	1
1	9	2	52	58	4	5	5	3	86	77	2	5	2	4	79	66	2
2	9	2	403	411	3	6	5	3	181	193	2	6	2	4	90	74	2
3	9	2	76	62	3	7	5	3	64	51	3	7	2	4	35	6	4
4	9	2	302	316	2	8	5	3	126	130	2	8	2	4	42	17	4
5	9	2	57	32	4	0	6	3	694	696	4	9	2	4	37	34	4
6	9	2	213	229	2	1	6	3	557	559	3	0	3	4	597	646	4
0	10	2	296	279	2	2	6	3	648	653	4	1	3	4	1262	1277	7
1	10	2	161	152	2	3	6	3	431	423	3	2	3	4	586	592	4
2	10	2	259	268	2	4	6	3	471	477	3	3	3	4	1125	1087	7
3	10	2	124	133	2	5	6	3	329	347	2	4	3	4	370	362	2
4	10	2	208	217	2	6	6	3	331	321	2	5	3	4	665	666	4
5	10	2	122	121	2	7	6	3	228	240	2	6	3	4	186	180	2
0	11	2	138	141	2	8	6	3	214	215	2	7	3	4	412	429	3
1	11	2	193	188	2	0	7	3	80	79	2	8	3	4	155	148	2
2	11	2	128	128	2	1	7	3	398	402	3	9	3	4	286	281	2
3	11	2	184	178	2	2	7	3	70	56	3	0	4	4	413	391	3
1	0	3	1159	1137	7	3	7	3	291	280	2	1	4	4	248	223	2
3	0	3	1067	1076	6	4	7	3	48	45	4	2	4	4	69	13	2
5	0	3	771	786	5	5	7	3	161	152	2	3	4	4	218	213	2
7	0	3	451	449	3	6	7	3	33	38	4	4	4	4	41	36	4
9	0	3	307	303	2	7	7	3	121	117	2	5	4	4	87	95	2
0	1	3	471	447	3	0	8	3	126	114	2	6	4	4	99	102	2
1	1	3	589	598	4	1	8	3	482	489	3	7	4	4	59	72	3
2	1	3	567	562	4	2	8	3	76	71	3	8	4	4	53	5	4
3	1	3	348	346	2	3	8	3	391	406	3	9	4	4	40	40	5
4	1	3	280	275	2	4	8	3	32	25	4	0	5	4	486	494	3
5	1	3	311	300	2	5	8	3	310	310	2	1	5	4	965	965	6
6	1	3	39	8	4	6	8	3	29	31	4	2	5	4	372	359	2
7	1	3	223	221	2	7	8	3	235	234	2	3	5	4	714	701	4
8	1	3	48	37	4	0	9	3	207	191	2	4	5	4	168	157	2
9	1	3	108	112	2	1	9	3	199	194	2	5	5	4	515	533	3
0	2	3	990	1032	6	2	9	3	113	120	2	6	5	4	102	111	2
1	2	3	840	820	5	3	9	3	180	182	2	7	5	4	405	421	3
2	2	3	719	740	4	4	9	3	35	43	4	8	5	4	104	101	2
3	2	3	1055	1053	6	5	9	3	164	151	2	0	6	4	70	69	2
4	2	3	578	550	4	6	9	3	28	39	4	1	6	4	181	161	2

Table A-22 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	6	4	33	11	4	3	3	5	192	184	2	6	0	6	364	372	2
3	6	4	127	117	2	4	3	5	347	339	2	8	0	6	271	275	2
4	6	4	40	15	4	5	3	5	67	61	3	0	1	6	482	481	3
5	6	4	77	94	3	6	3	5	217	219	2	1	1	6	422	419	3
6	6	4	28	3	4	7	3	5	66	64	3	2	1	6	774	767	5
7	6	4	27	44	4	8	3	5	114	118	2	3	1	6	345	331	2
8	6	4	30	27	4	9	3	5	51	53	4	4	1	6	665	669	4
0	7	4	624	613	4	0	4	5	1095	1113	6	5	1	6	184	187	2
1	7	4	333	338	2	1	4	5	161	149	1	6	1	6	337	336	2
2	7	4	538	527	2	2	4	5	1004	971	6	7	1	6	126	120	2
3	7	4	265	275	2	3	4	5	102	91	2	8	1	6	267	260	2
4	7	4	416	429	3	4	4	5	688	679	4	9	1	6	91	87	3
5	7	4	281	277	2	5	4	5	64	65	3	0	2	6	641	643	4
6	7	4	379	374	3	6	4	5	477	498	3	1	2	6	373	387	2
7	7	4	206	198	2	7	4	5	47	10	4	2	2	6	633	641	4
0	8	4	41	12	4	8	4	5	319	324	2	3	2	6	531	526	3
1	8	4	69	47	3	0	5	5	415	406	3	4	2	6	375	367	2
2	8	4	35	13	4	1	5	5	105	111	2	5	2	6	351	335	2
3	8	4	42	16	4	2	5	5	342	347	2	6	2	6	193	209	2
4	8	4	35	16	4	3	5	5	117	123	2	7	2	6	185	179	2
5	8	4	31	8	4	4	5	5	269	264	2	8	2	6	193	193	2
6	8	4	30	15	4	5	5	5	129	146	2	0	3	6	233	252	2
7	8	4	30	5	4	6	5	5	202	195	2	1	3	6	902	950	5
0	9	4	598	588	4	7	5	5	67	65	3	2	3	6	361	352	2
1	9	4	50	55	4	8	5	5	110	112	2	3	3	6	724	723	4
2	9	4	498	513	3	0	6	5	559	545	4	4	3	6	358	359	2
3	9	4	91	86	3	1	6	5	503	511	3	5	3	6	485	470	3
4	9	4	395	404	3	2	6	5	406	394	3	6	3	6	190	195	2
5	9	4	89	85	3	3	6	5	348	340	2	7	3	6	324	338	2
6	9	4	304	303	2	4	6	5	290	302	2	8	3	6	118	113	2
0	10	4	41	2	4	5	6	5	270	273	2	0	4	6	111	123	2
1	10	4	41	2	4	6	6	5	285	292	2	1	4	6	604	614	4
2	10	4	28	10	4	7	6	5	231	233	2	2	4	6	54	41	3
3	10	4	33	14	4	8	6	5	183	182	2	3	4	6	433	425	3
4	10	4	42	20	4	0	7	5	234	227	2	4	4	6	28	13	4
0	11	4	216	209	2	1	7	5	165	168	2	5	4	6	282	286	2
1	11	4	279	285	2	2	7	5	120	135	2	6	4	6	62	48	3
2	11	4	178	182	2	3	7	5	134	144	2	7	4	6	223	224	2
1	0	5	456	462	3	4	7	5	38	54	4	8	4	6	41	43	5
3	0	5	1179	1234	7	5	7	5	105	109	2	0	5	6	184	190	2
5	0	5	668	681	4	6	7	5	75	59	3	1	5	6	697	697	4
7	0	5	348	341	2	7	7	5	94	77	3	2	5	6	98	89	2
9	0	5	293	288	2	0	8	5	40	14	4	3	5	6	544	515	3
0	1	5	227	234	2	1	8	5	506	516	3	4	5	6	40	43	4
1	1	5	61	82	2	2	8	5	27	19	4	5	5	6	418	439	3
2	1	5	109	111	1	3	8	5	396	384	3	6	5	6	121	116	2
3	1	5	274	275	2	4	8	5	40	12	4	7	5	6	289	305	2
4	1	5	70	60	2	5	8	5	337	331	2	8	5	6	70	75	3
5	1	5	96	92	2	6	8	5	36	23	5	0	6	6	190	191	2
6	1	5	43	49	4	0	9	5	48	45	4	1	6	6	251	247	2
7	1	5	79	80	2	1	9	5	106	113	2	2	6	6	184	183	2
8	1	5	39	28	4	2	9	5	47	47	4	3	6	6	169	178	2
9	1	5	110	97	2	3	9	5	68	79	3	4	6	6	156	153	2
0	2	5	479	528	3	4	9	5	27	10	4	5	6	6	220	223	2
1	2	5	675	694	4	5	9	5	72	73	3	6	6	6	131	126	2
2	2	5	775	791	4	0	10	5	193	203	2	7	6	6	169	172	2
3	2	5	880	865	5	1	10	5	280	283	2	0	7	6	362	353	2
4	2	5	657	639	4	2	10	5	177	189	2	1	7	6	275	287	2
5	2	5	533	529	3	3	10	5	258	247	2	2	7	6	286	271	2
6	2	5	318	318	2	4	10	5	160	164	2	3	7	6	217	217	2
7	2	5	292	293	2	0	11	5	80	75	3	4	7	6	231	226	2
8	2	5	233	231	2	1	11	5	31	15	4	5	7	6	167	162	2
9	2	5	204	202	2	2	11	5	81	75	3	6	7	6	220	214	2
0	3	5	416	436	3	0	0	6	428	426	3	7	7	6	114	109	3
1	3	5	18	15	3	2	0	6	789	810	5	0	8	6	314	324	2
2	3	5	405	403	3	4	0	6	736	721	5	1	8	6	74	65	3

Table A-22 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	8	6	286	291	2	3	6	7	136	138	2	1	5	8	150	152	2
3	8	6	36	21	4	4	6	7	130	130	2	2	5	8	29	3	4
4	8	6	245	252	2	5	6	7	155	146	2	3	5	8	149	138	2
5	8	6	30	25	4	6	6	7	107	110	2	4	5	8	44	19	4
6	8	6	203	198	2	7	6	7	107	110	2	5	5	8	90	88	3
0	9	6	338	333	2	0	7	7	168	161	2	6	5	8	36	27	4
1	9	6	48	51	4	1	7	7	397	405	3	7	5	8	40	47	4
2	9	6	297	286	2	2	7	7	130	124	2	0	6	8	227	229	2
3	9	6	48	42	4	3	7	7	340	331	2	1	6	8	423	434	3
4	9	6	222	225	2	4	7	7	137	143	2	2	6	8	229	225	2
5	9	6	37	28	4	5	7	7	291	279	2	3	6	8	349	350	2
0	10	6	209	213	2	6	7	7	135	134	2	4	6	8	228	231	2
1	10	6	163	161	2	0	8	7	55	49	4	5	6	8	271	277	2
2	10	6	179	186	2	1	8	7	207	213	2	6	6	8	186	185	2
3	10	6	126	132	2	2	8	7	33	30	4	0	7	8	38	7	4
1	0	7	256	267	2	3	8	7	221	206	2	1	7	8	79	75	3
3	0	7	414	416	3	4	8	7	33	8	4	2	7	8	32	3	4
5	0	7	267	283	2	5	8	7	185	179	2	3	7	8	62	65	4
7	0	7	164	160	2	0	9	7	97	91	2	4	7	8	22	8	4
0	1	7	144	137	1	1	9	7	287	295	2	5	7	8	60	44	4
1	1	7	541	561	3	2	9	7	75	83	3	0	8	8	370	379	3
2	1	7	273	289	2	3	9	7	280	271	2	1	8	8	30	55	4
3	1	7	618	634	4	4	9	7	74	68	3	2	8	8	353	342	2
4	1	7	281	278	2	0	10	7	96	84	3	3	8	8	60	57	4
5	1	7	402	389	3	1	10	7	177	167	2	4	8	8	285	275	2
6	1	7	153	142	2	2	10	7	95	90	3	0	9	8	27	4	4
7	1	7	311	307	2	0	0	8	871	847	5	1	9	8	65	56	4
8	1	7	95	97	2	2	0	8	769	775	5	2	9	8	30	2	4
0	2	7	209	215	2	4	0	8	520	522	3	3	9	8	30	27	4
1	2	7	347	334	2	6	0	8	401	389	3	1	0	9	155	151	2
2	2	7	136	134	2	8	0	8	303	302	2	3	0	9	137	148	2
3	2	7	359	356	2	0	1	8	111	114	2	5	0	9	175	166	2
4	2	7	108	114	2	1	1	8	39	16	4	7	0	9	138	131	2
5	2	7	150	156	2	2	1	8	166	154	2	0	1	9	240	231	2
6	2	7	150	160	2	3	1	8	60	65	3	1	1	9	739	734	5
7	2	7	56	56	4	4	1	8	135	146	2	2	1	9	175	166	2
8	2	7	97	101	2	5	1	8	30	11	4	3	1	9	489	510	3
0	3	7	769	783	5	6	1	8	79	65	3	4	1	9	136	133	2
1	3	7	466	481	3	7	1	8	33	35	4	5	1	9	391	383	3
2	3	7	729	739	4	8	1	8	49	53	4	6	1	9	133	133	2
3	3	7	245	237	2	0	2	8	485	500	3	7	1	9	295	301	2
4	3	7	532	539	3	1	2	8	671	672	4	0	2	9	118	100	2
5	3	7	155	153	2	2	2	8	464	465	3	1	2	9	211	218	2
6	3	7	355	353	2	3	2	8	482	511	3	2	2	9	162	168	2
7	3	7	139	153	2	4	2	8	383	371	3	3	2	9	84	89	2
8	3	7	235	231	2	5	2	8	343	339	2	4	2	9	149	142	2
0	4	7	379	394	3	6	2	8	310	314	2	5	2	9	125	118	2
1	4	7	164	167	2	7	2	8	246	237	2	6	2	9	75	65	3
2	4	7	269	258	2	8	2	8	220	218	2	7	2	9	107	101	2
3	4	7	78	67	3	0	3	8	40	32	4	0	3	9	531	520	3
4	4	7	146	159	2	1	3	8	171	166	2	1	3	9	277	292	2
5	4	7	31	3	4	2	3	8	185	180	2	2	3	9	408	419	3
6	4	7	140	152	2	3	3	8	63	53	3	3	3	9	241	247	2
7	4	7	54	46	4	4	3	8	159	170	2	4	3	9	307	335	2
8	4	7	101	98	2	5	3	8	99	100	2	5	3	9	166	171	2
0	5	7	685	696	4	6	3	8	43	16	4	6	3	9	285	280	2
1	5	7	191	180	2	7	3	8	69	73	3	7	3	9	114	124	2
2	5	7	548	548	3	0	4	8	73	68	3	0	4	9	240	246	2
3	5	7	186	192	2	1	4	8	641	655	4	1	4	9	129	143	2
4	5	7	395	405	3	2	4	8	68	40	3	2	4	9	207	216	2
5	5	7	120	124	2	3	4	8	554	563	4	3	4	9	47	29	4
6	5	7	333	336	2	4	4	8	37	18	4	4	4	9	147	139	2
7	5	7	85	78	3	5	4	8	464	483	3	5	4	9	55	71	4
0	6	7	38	26	4	6	4	8	35	21	4	6	4	9	88	90	3
1	6	7	263	269	2	7	4	8	321	322	2	0	5	9	350	364	2
2	6	7	88	70	2	0	5	8	125	124	2	1	5	9	173	166	2

Table A-22 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	5	9	383	357	3	4	4	10	57	13	4	1	5	11	32	8	4
3	5	9	119	120	2	5	4	10	256	267	2	2	5	11	151	135	2
4	5	9	339	344	2	6	4	10	29	6	4	3	5	11	78	52	3
5	5	9	111	107	2	0	5	10	54	33	4	4	5	11	113	118	2
6	5	9	258	254	2	1	5	10	203	212	2	0	6	11	188	184	2
0	6	9	89	93	2	2	5	10	73	60	3	1	6	11	177	180	2
1	6	9	60	69	3	3	5	10	191	194	2	2	6	11	216	195	2
2	6	9	93	92	2	4	5	10	58	68	4	3	6	11	177	170	2
3	6	9	64	48	3	5	5	10	140	146	2	0	7	11	95	95	3
4	6	9	104	104	2	0	6	10	189	195	2	1	7	11	123	123	2
5	6	9	40	15	5	1	6	10	250	250	2	0	0	12	55	71	4
0	7	9	149	149	2	2	6	10	188	190	2	2	0	12	45	56	4
1	7	9	310	313	2	3	6	10	248	239	2	4	0	12	35	37	5
2	7	9	162	152	2	4	6	10	155	163	2	0	1	12	331	334	2
3	7	9	326	311	2	0	7	10	181	187	2	1	1	12	129	129	2
4	7	9	131	129	2	1	7	10	70	80	3	2	1	12	299	297	2
0	8	9	41	35	4	2	7	10	173	165	2	3	1	12	120	113	2
1	8	9	59	47	4	3	7	10	91	83	3	4	1	12	247	249	2
2	8	9	33	8	4	0	8	10	181	175	2	0	2	12	63	67	3
3	8	9	67	63	4	1	8	10	70	61	3	1	2	12	38	24	5
0	9	9	47	61	5	2	8	10	203	187	3	2	2	12	56	52	4
1	9	9	270	269	2	1	0	11	502	493	3	3	2	12	43	34	5
0	0	10	469	479	3	3	0	11	327	337	2	4	2	12	44	28	4
2	0	10	369	371	2	5	0	11	286	286	2	0	3	12	126	112	2
4	0	10	285	280	2	0	1	11	106	107	2	1	3	12	291	284	2
6	0	10	271	262	2	1	1	11	285	292	2	2	3	12	109	105	2
0	1	10	324	296	2	2	1	11	84	80	3	3	3	12	255	252	2
1	1	10	217	212	2	3	1	11	192	209	2	4	3	12	84	91	3
2	1	10	209	208	2	4	1	11	63	57	3	0	4	12	37	19	4
3	1	10	130	145	2	5	1	11	163	158	2	1	4	12	59	56	4
4	1	10	166	158	2	6	1	11	42	42	5	2	4	12	31	1	4
5	1	10	74	74	3	0	2	11	257	246	2	3	4	12	62	60	4
6	1	10	178	161	2	1	2	11	301	306	2	0	5	12	107	100	2
0	2	10	328	328	2	2	2	11	201	201	2	1	5	12	265	256	2
1	2	10	301	286	2	3	2	11	247	254	2	2	5	12	103	86	3
2	2	10	261	273	2	4	2	11	151	156	2	0	6	12	37	23	5
3	2	10	226	222	2	5	2	11	242	227	2	1	0	13	286	291	2
4	2	10	182	192	2	0	3	11	114	116	2	3	0	13	248	247	2
5	2	10	225	221	2	1	3	11	88	78	2	0	1	13	31	14	4
6	2	10	149	158	2	2	3	11	121	123	2	1	1	13	86	61	3
0	3	10	37	36	4	3	3	11	70	76	3	2	1	13	27	1	4
1	3	10	255	248	2	4	3	11	132	140	2	3	1	13	85	69	3
2	3	10	37	7	4	5	3	11	76	63	3	0	2	13	155	159	2
3	3	10	218	226	2	0	4	11	265	261	2	1	2	13	183	178	2
4	3	10	40	39	4	1	4	11	42	33	4	2	2	13	161	156	2
5	3	10	183	183	2	2	4	11	271	266	2	3	2	13	163	165	2
6	3	10	64	63	4	3	4	11	59	45	4	0	3	13	42	31	5
0	4	10	33	24	4	4	4	11	256	255	2	1	3	13	24	31	4
1	4	10	406	400	3	5	4	11	49	42	4	2	3	13	32	26	4
2	4	10	29	2	4	0	5	11	139	128	2	0	4	13	207	205	2
3	4	10	319	344	2												

Table A-23. Observed and Calculated Structure Factors for 58b

F_0, F_c and SIG (σ) values have been multiplied by 10.

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	0	0	838	723	59	8	6	0	162	160	12	3	2	1	1060	967	75
4	0	0	312	265	22	9	6	0	463	433	33	4	2	1	682	652	48
6	0	0	884	830	63	1	7	0	584	592	42	5	2	1	612	591	44
8	0	0	523	515	37	2	7	0	140	136	11	6	2	1	342	334	25
10	0	0	644	611	46	3	7	0	677	615	48	7	2	1	794	763	56
1	1	0	338	303	24	4	7	0	106	92	9	8	2	1	178	167	13
3	1	0	445	428	32	5	7	0	36	3	13	9	2	1	371	370	27
4	1	0	483	455	34	6	7	0	140	133	11	10	2	1	119	115	10
5	1	0	506	485	36	7	7	0	528	513	38	11	2	1	307	317	22
6	1	0	527	519	38	8	7	0	76	75	11	−11	3	1	368	358	26
7	1	0	172	171	13	0	8	0	32	36	12	−10	3	1	291	287	21
8	1	0	662	637	47	1	8	0	748	752	53	−9	3	1	164	158	12
9	1	0	152	149	12	2	8	0	44	50	13	−8	3	1	67	82	10
10	1	0	92	85	10	3	8	0	178	180	13	−7	3	1	589	559	42
11	1	0	79	73	11	4	8	0	77	52	10	−6	3	1	698	655	50
1	2	0	995	868	70	5	8	0	557	540	40	−5	3	1	1149	1047	81
2	2	0	618	561	44	6	8	0	47	38	14	−4	3	1	498	469	35
3	2	0	541	496	38	1	9	0	318	339	23	−3	3	1	254	235	18
4	2	0	1404	1214	99	2	9	0	123	124	10	−2	3	1	360	337	26
5	2	0	626	575	45	3	9	0	537	507	38	−1	3	1	44	46	7
6	2	0	841	782	60	4	9	0	127	125	11	0	3	1	76	55	6
7	2	0	129	141	10	−11	0	1	188	175	14	1	3	1	98	93	8
8	2	0	270	258	20	−9	0	1	841	820	60	2	3	1	105	109	8
9	2	0	365	358	26	−7	0	1	665	645	47	3	3	1	967	898	68
10	2	0	618	602	44	−5	0	1	293	271	21	4	3	1	725	673	51
11	2	0	217	204	16	3	0	1	695	661	49	5	3	1	858	810	61
1	3	0	152	137	11	5	0	1	539	506	38	6	3	1	390	366	28
2	3	0	1298	1122	92	7	0	1	1014	945	72	7	3	1	113	107	10
3	3	0	1120	1023	79	9	0	1	362	362	26	8	3	1	310	309	22
4	3	0	626	587	45	11	0	1	336	357	24	9	3	1	361	371	26
5	3	0	229	215	17	−12	1	1	45	44	15	10	3	1	239	238	17
6	3	0	574	547	41	−11	1	1	458	456	33	−11	4	1	78	67	11
7	3	0	442	428	32	−10	1	1	120	122	10	−10	4	1	171	157	13
8	3	0	514	498	37	−9	1	1	232	221	17	−9	4	1	379	372	27
9	3	0	32	34	13	−8	1	1	125	127	10	−8	4	1	606	575	43
10	3	0	65	56	11	−7	1	1	599	555	43	−7	4	1	457	433	33
11	3	0	187	179	14	−6	1	1	300	289	22	−6	4	1	443	410	32
0	4	0	396	469	28	−5	1	1	746	735	53	−5	4	1	554	530	39
1	4	0	803	746	57	−4	1	1	147	152	11	−4	4	1	985	904	70
2	4	0	377	352	27	−3	1	1	133	124	10	−3	4	1	890	815	63
3	4	0	196	189	14	−2	1	1	173	161	13	−2	4	1	588	572	42
4	4	0	1191	1072	84	0	1	1	404	372	29	−1	4	1	313	339	22
5	4	0	1089	985	77	2	1	1	191	177	14	0	4	1	204	195	15
6	4	0	600	567	43	3	1	1	915	851	65	1	4	1	580	537	41
7	4	0	63	54	11	4	1	1	59	37	7	2	4	1	991	911	70
8	4	0	196	188	14	5	1	1	588	580	42	3	4	1	731	686	52
9	4	0	414	402	30	6	1	1	166	160	12	4	4	1	281	270	20
10	4	0	431	436	31	7	1	1	149	148	12	5	4	1	173	176	13
1	5	0	412	405	29	8	1	1	269	282	20	6	4	1	615	576	44
2	5	0	649	600	46	9	1	1	523	501	37	7	4	1	518	536	37
3	5	0	983	879	70	10	1	1	84	72	10	8	4	1	525	526	38
4	5	0	522	487	37	11	1	1	223	230	16	9	4	1	112	131	10
5	5	0	127	129	10	−12	2	1	108	109	11	10	4	1	94	89	10
6	5	0	235	232	17	−11	2	1	134	129	11	−10	5	1	307	298	22
7	5	0	574	560	41	−10	2	1	94	93	10	−9	5	1	224	215	16
8	5	0	237	242	17	−9	2	1	796	752	57	−8	5	1	78	69	10
9	5	0	254	238	18	−8	2	1	325	328	23	−7	5	1	384	374	28
10	5	0	109	108	11	−7	2	1	705	648	50	−6	5	1	762	706	54
0	6	0	348	409	25	−6	2	1	152	144	11	−5	5	1	398	368	29
1	6	0	1074	1010	76	−5	2	1	249	228	18	−4	5	1	766	720	54
2	6	0	284	253	20	−4	2	1	860	807	61	−3	5	1	94	91	8
3	6	0	244	256	18	−2	2	1	589	577	42	−2	5	1	496	468	35
4	6	0	293	267	21	−1	2	1	296	371	21	−1	5	1	339	335	24
5	6	0	743	699	53	0	2	1	190	169	14	0	5	1	483	479	34
6	6	0	185	187	14	1	2	1	1118	954	79	1	5	1	22	24	10
7	6	0	166	163	13	2	2	1	687	637	49	2	5	1	73	59	8

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	5	1	62	56	9	-10	0	2	755	729	54	3	3	2	860	800	61
4	5	1	781	727	56	-8	0	2	164	170	12	4	3	2	76	36	8
5	5	1	451	439	32	-6	0	2	978	946	69	5	3	2	155	147	12
6	5	1	458	427	33	-4	0	2	592	597	42	6	3	2	429	433	31
7	5	1	135	128	11	2	0	2	202	196	15	7	3	2	265	262	19
8	5	1	253	236	18	4	0	2	1481	1308	105	8	3	2	255	267	19
9	5	1	200	213	15	6	0	2	359	344	26	9	3	2	59	13	13
-9	6	1	43	65	14	8	0	2	526	531	38	10	3	2	253	246	18
-8	6	1	636	617	45	10	0	2	395	414	28	-11	4	2	445	420	32
-7	6	1	213	204	16	-12	1	2	280	249	20	-10	4	2	401	385	29
-6	6	1	282	274	20	-11	1	2	43	39	14	-9	4	2	264	249	19
-5	6	1	356	344	26	-10	1	2	224	221	16	-8	4	2	85	76	9
-4	6	1	753	686	54	-9	1	2	55	41	12	-7	4	2	331	298	24
-3	6	1	281	267	20	-8	1	2	1075	1023	76	-6	4	2	861	802	61
-2	6	1	1007	915	71	-7	1	2	70	71	9	-5	4	2	979	916	69
-1	6	1	130	138	10	-6	1	2	174	185	13	-4	4	2	462	439	33
0	6	1	251	262	18	-5	1	2	292	294	21	-3	4	2	450	451	32
1	6	1	293	272	21	-4	1	2	339	347	24	-2	4	2	312	390	22
2	6	1	696	645	50	-3	1	2	207	206	15	-1	4	2	891	821	63
3	6	1	166	159	12	-1	1	2	33	25	7	0	4	2	1000	908	71
4	6	1	138	122	11	1	1	2	431	403	31	1	4	2	174	337	27
5	6	1	107	100	10	2	1	2	1228	1068	87	2	4	2	270	265	19
6	6	1	647	622	46	3	1	2	423	398	30	3	4	2	912	838	65
7	6	1	249	254	18	4	1	2	314	300	23	4	4	2	892	830	63
8	6	1	532	532	38	5	1	2	50	14	11	5	4	2	651	610	46
-8	7	1	39	41	14	6	1	2	943	905	67	6	4	2	179	173	13
-7	7	1	27	15	12	7	1	2	86	83	10	7	4	2	55	39	12
-6	7	1	620	601	44	8	1	2	230	222	17	8	4	2	376	386	27
-5	7	1	24	14	11	9	1	2	35	45	14	9	4	2	428	427	31
-4	7	1	403	403	29	10	1	2	193	195	14	-11	5	2	36	17	14
-3	7	1	138	117	11	-12	2	2	340	337	24	-10	5	2	35	22	14
-2	7	1	460	429	33	-11	2	2	224	215	16	-9	5	2	429	399	31
-1	7	1	158	187	12	-10	2	2	636	615	45	-8	5	2	202	206	15
0	7	1	778	805	55	-9	2	2	319	298	23	-7	5	2	595	554	43
1	7	1	30	23	12	-8	2	2	113	104	10	-6	5	2	46	40	13
2	7	1	27	22	12	-7	2	2	412	391	30	-5	5	2	299	259	22
3	7	1	119	117	10	-6	2	2	1101	1025	78	-4	5	2	679	654	48
4	7	1	488	470	35	-5	2	2	403	380	29	-3	5	2	850	858	60
5	7	1	80	74	10	-4	2	2	587	576	42	-2	5	2	392	500	28
6	7	1	357	359	26	-3	2	2	68	58	7	-1	5	2	170	164	13
7	7	1	40	37	14	-2	2	2	854	1039	61	0	5	2	68	61	7
-7	8	1	33	7	13	-1	2	2	749	688	53	1	5	2	859	797	61
-6	8	1	174	173	13	1	2	2	81	63	7	2	5	2	670	628	48
-5	8	1	79	64	10	2	2	2	436	424	31	3	5	2	503	459	36
-4	8	1	512	494	37	3	2	2	388	370	28	4	5	2	50	29	12
-3	8	1	118	104	10	4	2	2	1569	1381	111	5	5	2	272	275	20
-2	8	1	633	610	45	5	2	2	513	479	37	6	5	2	269	283	19
-1	8	1	155	182	12	6	2	2	341	332	25	7	5	2	497	508	36
0	8	1	198	201	14	7	2	2	212	228	16	8	5	2	159	155	12
1	8	1	40	54	13	8	2	2	412	411	29	9	5	2	40	21	15
2	8	1	599	571	43	9	2	2	260	260	19	-10	6	2	137	135	11
3	8	1	41	61	14	10	2	2	359	377	26	-9	6	2	230	220	17
4	8	1	182	169	14	-12	3	2	266	268	19	-8	6	2	29	43	13
5	8	1	46	47	14	-11	3	2	39	19	14	-7	6	2	444	410	32
6	8	1	473	455	34	-10	3	2	209	204	15	-6	6	2	287	290	21
-5	9	1	146	149	12	-9	3	2	240	218	17	-5	6	2	739	714	53
-4	9	1	296	293	21	-8	3	2	579	556	41	-4	6	2	161	167	12
-3	9	1	100	105	10	-7	3	2	513	489	37	-3	6	2	359	350	26
-2	9	1	242	238	18	-6	3	2	258	249	19	-2	6	2	246	299	18
-1	9	1	102	116	10	-5	3	2	364	346	26	-1	6	2	1341	1219	95
0	9	1	381	417	27	-4	3	2	870	851	62	0	6	2	400	371	28
1	9	1	90	95	10	-3	3	2	392	406	28	1	6	2	380	338	27
2	9	1	35	13	13	-2	3	2	294	393	21	2	6	2	38	10	13
3	9	1	93	109	10	-1	3	2	377	358	27	3	6	2	522	490	37
4	9	1	489	475	35	0	3	2	258	240	18	4	6	2	216	207	16
-12	0	2	343	334	25	1	3	2	1024	925	73	5	6	2	614	600	44

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	6	2	69	57	11	1	1	3	345	307	25	0	4	3	922	857	65
7	6	2	149	150	12	2	1	3	208	205	15	1	4	3	1003	931	71
8	6	2	213	217	16	3	1	3	1074	1009	76	2	4	3	871	830	62
−9	7	2	403	392	29	4	1	3	210	209	15	3	4	3	366	344	26
−8	7	2	32	25	13	5	1	3	589	590	42	4	4	3	123	109	10
−7	7	2	382	373	27	6	1	3	31	59	13	5	4	3	448	425	32
−6	7	2	160	153	12	7	1	3	367	359	26	6	4	3	485	469	35
−5	7	2	285	260	21	8	1	3	155	148	12	7	4	3	318	338	23
−4	7	2	172	171	13	9	1	3	414	423	30	8	4	3	202	219	15
−3	7	2	839	838	60	10	1	3	91	93	11	9	4	3	40	47	15
−2	7	2	26	47	12	−12	2	3	112	107	10	−11	5	3	180	193	14
−1	7	2	70	56	10	−11	2	3	181	165	14	−10	5	3	240	231	17
0	7	2	68	70	8	−10	2	3	174	186	13	−9	5	3	19	7	9
1	7	2	644	623	46	−9	2	3	852	800	60	−8	5	3	221	206	16
2	7	2	119	109	10	−8	2	3	225	228	16	−7	5	3	532	509	38
3	7	2	351	313	25	−7	2	3	427	393	31	−6	5	3	674	662	48
4	7	2	28	13	12	−6	2	3	223	220	16	−5	5	3	303	291	22
5	7	2	292	304	21	−5	2	3	1250	1213	88	−4	5	3	19	27	9
6	7	2	50	67	14	−4	2	3	537	578	38	−3	5	3	21	19	10
7	7	2	501	482	36	−3	2	3	709	918	50	−2	5	3	994	967	70
−7	8	2	358	358	26	−2	2	3	463	511	33	−1	5	3	617	570	44
−6	8	2	78	57	10	−1	2	3	188	186	14	0	5	3	572	541	41
−5	8	2	499	479	36	0	2	3	900	843	64	1	5	3	185	175	14
−4	8	2	47	14	13	-2	2	3	441	411	32	2	5	3	320	312	23
−3	8	2	201	196	15	3	2	3	429	417	31	3	5	3	257	235	19
−2	8	2	71	72	9	4	2	3	50	23	11	4	5	3	473	460	34
−1	8	2	902	864	64	5	2	3	739	699	53	5	5	3	208	211	15
0	8	2	42	40	10	6	2	3	407	398	29	6	5	3	93	113	10
1	8	2	304	265	22	7	2	3	617	616	44	7	5	3	229	245	17
2	8	2	44	39	13	8	2	3	93	75	10	8	5	3	408	403	29
3	8	2	472	459	34	9	2	3	134	128	11	−10	6	3	381	354	27
4	8	2	38	41	14	10	2	3	100	99	11	−9	6	3	243	236	18
5	8	2	500	489	36	−12	3	3	258	250	19	−8	6	3	502	485	36
−5	9	2	180	180	14	−11	3	3	465	454	33	−7	6	3	59	55	10
−4	9	2	128	116	11	−10	3	3	223	205	16	−6	6	3	216	205	16
−3	9	2	467	454	33	−9	3	3	27	21	12	−5	6	3	205	207	15
−2	9	2	80	96	10	−8	3	3	227	205	17	−4	6	3	975	1045	69
−1	9	2	22	14	10	−7	3	3	742	695	53	−3	6	3	402	494	29
0	9	2	78	70	8	−6	3	3	608	585	43	−2	6	3	503	475	36
1	9	2	552	554	40	−5	3	3	509	511	36	−1	6	3	252	231	18
2	9	2	170	166	13	−4	3	3	262	272	19	0	6	3	616	586	44
3	9	2	368	363	26	−3	3	3	430	382	31	1	6	3	139	126	11
−13	0	3	413	394	30	−2	3	3	549	563	39	2	6	3	451	435	32
−11	0	3	189	191	14	−1	3	3	895	828	63	3	6	3	122	131	10
−9	0	3	1097	1067	78	0	3	3	289	281	21	4	6	3	189	184	14
−7	0	3	450	479	32	1	3	3	262	250	19	5	6	3	254	242	18
−5	0	3	1354	1294	96	2	3	3	529	502	38	6	6	3	672	664	48
−3	0	3	1114	1255	79	3	3	3	975	927	69	7	6	3	164	160	13
−1	0	3	168	146	12	4	3	3	437	419	31	−9	7	3	50	20	14
3	0	3	207	222	15	5	3	3	277	279	20	−8	7	3	324	309	23
5	0	3	1104	1036	78	6	3	3	73	64	10	−7	7	3	85	94	10
7	0	3	836	836	59	7	3	3	235	218	17	−6	7	3	593	582	42
9	0	3	127	118	11	8	3	3	323	330	23	−5	7	3	72	65	10
−13	1	3	124	111	11	9	3	3	381	385	27	−4	7	3	57	59	11
−12	1	3	59	62	13	−12	4	3	146	145	12	−3	7	3	56	73	11
−11	1	3	545	531	39	−11	4	3	46	38	14	−2	7	3	823	796	59
−10	1	3	112	98	10	−10	4	3	387	360	28	−1	7	3	114	97	10
−9	1	3	26	10	11	−9	4	3	505	472	36	0	7	3	410	400	29
−8	1	3	256	240	19	−8	4	3	415	398	30	1	7	3	148	124	11
−7	1	3	1039	997	74	−7	4	3	52	28	11	2	7	3	220	216	16
−6	1	3	223	224	16	−6	4	3	69	54	9	3	7	3	27	5	12
−5	1	3	571	608	41	−5	4	3	773	777	55	4	7	3	553	545	40
−4	1	3	436	483	31	−4	4	3	1001	1064	71	5	7	3	111	102	10
−3	1	3	845	1052	60	−3	4	3	684	886	49	6	7	3	66	27	12
−2	1	3	153	157	11	−2	4	3	177	182	13	−7	8	3	77	70	11
0	1	3	112	111	8	−1	4	3	159	159	12	−6	8	3	195	191	14

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	8	3	84	75	10	2	2	4	997	901	71	4	5	4	90	99	9
-4	8	3	610	659	44	3	2	4	568	550	40	5	5	4	373	387	27
-3	8	3	81	100	9	4	2	4	968	913	69	6	5	4	255	262	19
-2	8	3	321	315	23	5	2	4	123	115	10	7	5	4	286	293	21
-1	8	3	156	136	12	6	2	4	219	220	16	-10	6	4	36	23	14
0	8	3	464	443	33	7	2	4	173	173	13	-9	6	4	92	76	10
1	8	3	70	80	10	8	2	4	472	484	34	-8	6	4	109	106	10
2	8	3	470	451	34	9	2	4	246	246	18	-7	6	4	598	594	43
3	8	3	25	10	12	-12	3	4	92	76	10	-6	6	4	265	282	19
4	8	3	181	172	14	-11	3	4	150	152	12	-5	6	4	272	319	20
5	8	3	69	54	12	-10	3	4	336	319	24	-4	6	4	56	63	11
-5	9	3	55	78	13	-9	3	4	324	299	23	-3	6	4	757	813	54
-4	9	3	20	22	10	-8	3	4	423	407	30	-2	6	4	346	321	25
-3	9	3	37	32	14	-7	3	4	79	80	9	-1	6	4	962	884	68
-2	9	3	394	382	28	-6	3	4	376	387	27	0	6	4	62	54	8
-1	9	3	163	158	13	-5	3	4	325	382	23	1	6	4	119	116	10
0	9	3	296	301	21	-4	3	4	581	733	41	2	6	4	265	245	19
1	9	3	29	15	13	-3	3	4	563	629	40	3	6	4	644	640	46
2	9	3	280	280	20	-2	3	4	58	50	7	4	6	4	147	132	12
-12	0	4	355	342	25	-1	3	4	648	585	46	5	6	4	270	273	20
-10	0	4	440	455	31	0	3	4	1155	1054	82	6	6	4	33	19	13
-8	0	4	1021	1025	72	1	3	4	846	794	60	7	6	4	376	381	27
-6	0	4	1041	1082	74	2	3	4	870	784	62	-9	7	4	492	473	35
-4	0	4	21	14	9	3	3	4	38	26	13	-8	7	4	49	62	13
0	0	4	48	33	6	4	3	4	235	233	17	-7	7	4	110	115	10
2	0	4	782	731	55	5	3	4	220	228	16	-6	7	4	43	41	13
4	0	4	1625	1493	115	6	3	4	333	341	24	-5	7	4	487	535	35
6	0	4	402	410	29	7	3	4	247	246	18	-4	7	4	57	92	11
8	0	4	414	429	30	8	3	4	60	62	13	-3	7	4	514	544	37
-13	1	4	40	23	15	9	3	4	144	133	12	-2	7	4	25	18	11
-12	1	4	46	49	14	-12	4	4	356	345	26	-1	7	4	362	346	26
-11	1	4	41	27	14	-11	4	4	343	323	25	0	7	4	129	127	10
-10	1	4	616	604	44	-10	4	4	172	158	13	1	7	4	523	520	37
-9	1	4	188	184	14	-9	4	4	27	34	12	2	7	4	20	14	10
-8	1	4	786	799	56	-8	4	4	300	302	22	3	7	4	70	64	10
-7	1	4	120	120	10	-7	4	4	576	583	41	4	7	4	39	22	14
-6	1	4	398	403	28	-6	4	4	584	603	42	5	7	4	516	530	37
-5	1	4	50	51	8	-5	4	4	335	390	24	-7	8	4	508	498	36
-4	1	4	853	1038	60	-4	4	4	163	185	12	-6	8	4	41	26	14
-3	1	4	585	646	41	-3	4	4	670	718	48	-5	8	4	240	265	17
-2	1	4	32	13	10	-2	4	4	924	850	65	-4	8	4	79	77	10
-1	1	4	363	343	26	-1	4	4	1098	1002	78	-3	8	4	476	509	34
0	1	4	497	484	35	0	4	4	666	605	47	-2	8	4	27	22	12
1	1	4	57	49	7	1	4	4	282	259	20	-1	8	4	632	589	45
2	1	4	815	750	58	2	4	4	735	684	52	0	8	4	24	15	8
3	1	4	54	52	9	3	4	4	661	643	47	1	8	4	118	122	10
4	1	4	742	718	53	4	4	4	331	301	24	2	8	4	23	21	11
5	1	4	222	226	16	5	4	4	187	175	14	3	8	4	615	618	44
6	1	4	706	734	50	6	4	4	102	99	10	4	8	4	52	50	14
7	1	4	100	94	10	7	4	4	286	286	21	-5	9	4	330	362	24
8	1	4	46	12	14	8	4	4	399	418	29	-4	9	4	87	123	10
9	1	4	29	12	13	-11	5	4	226	217	17	-3	9	4	269	290	19
-13	2	4	179	170	14	-10	5	4	161	159	12	-2	9	4	42	29	14
-12	2	4	442	420	32	-9	5	4	435	407	31	-1	9	4	272	253	20
-11	2	4	175	162	13	-8	5	4	131	132	10	0	9	4	127	136	10
-10	2	4	360	350	26	-7	5	4	187	201	14	1	9	4	555	544	40
-9	2	4	200	196	15	-6	5	4	174	178	13	-13	0	5	160	160	12
-8	2	4	585	600	42	-5	5	4	597	681	43	-11	0	5	508	503	36
-7	2	4	576	571	41	-4	5	4	397	489	28	-9	0	5	1035	1051	73
-6	2	4	883	916	63	-3	5	4	488	523	35	-7	0	5	168	188	12
-5	2	4	685	765	49	-2	5	4	195	176	14	-5	0	5	1261	1424	89
-4	2	4	399	495	29	-1	5	4	498	457	36	-3	0	5	526	571	37
-3	2	4	184	222	13	0	5	4	644	632	46	-1	0	5	370	373	27
-1	2	4	394	392	28	1	5	4	829	792	59	1	0	5	894	828	63
0	2	4	834	754	59	2	5	4	216	203	16	3	0	5	221	232	16
1	2	4	726	695	51	3	5	4	43	34	13	5	0	5	1161	1171	82

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
7	0	5	316	343	23	8	3	5	230	257	17	0	7	5	37	57	10
9	0	5	226	227	17	-12	4	5	80	64	11	1	7	5	28	33	12
-13	1	5	308	303	22	-11	4	5	243	238	18	2	7	5	500	509	36
-12	1	5	106	98	10	-10	4	5	449	437	32	3	7	5	95	87	10
-11	1	5	359	347	26	-9	4	5	348	340	25	4	7	5	386	394	28
-10	1	5	111	104	10	-8	4	5	181	183	13	5	7	5	29	8	13
-9	1	5	298	288	21	-7	4	5	153	158	12	-7	8	5	38	6	14
-8	1	5	321	320	23	-6	4	5	433	490	31	-6	8	5	371	435	27
-7	1	5	1140	1207	81	-5	4	5	588	714	42	-5	8	5	60	33	12
-6	1	5	342	398	24	-4	4	5	650	727	46	-4	8	5	472	536	34
-5	1	5	21	36	9	-3	4	5	431	437	31	-3	8	5	58	14	11
-4	1	5	502	594	36	-2	4	5	132	124	10	-2	8	5	75	66	10
-3	1	5	585	650	42	-1	4	5	850	781	60	-1	8	5	99	106	10
-2	1	5	127	122	10	0	4	5	1112	1035	79	0	8	5	520	502	37
-1	1	5	545	518	39	1	4	5	743	708	53	1	8	5	42	41	14
0	1	5	563	556	40	2	4	5	247	233	18	2	8	5	235	225	17
1	1	5	371	401	27	3	4	5	40	14	13	3	8	5	22	7	11
2	1	5	248	248	18	4	4	5	285	291	21	-4	9	5	189	203	14
3	1	5	1009	1005	72	5	4	5	390	382	28	-3	9	5	109	115	10
4	1	5	177	193	13	6	4	5	372	395	27	-2	9	5	432	404	31
5	1	5	243	265	18	7	4	5	187	207	14	-1	9	5	28	22	12
6	1	5	73	71	10	-11	5	5	208	214	15	0	9	5	78	75	9
7	1	5	465	481	33	-10	5	5	70	56	11	-12	0	6	444	454	32
8	1	5	74	62	11	-9	5	5	250	245	18	-10	0	6	80	86	10
-13	2	5	214	206	16	-8	5	5	354	366	25	-8	0	6	950	1053	67
-12	2	5	32	30	13	-7	5	5	253	262	18	-6	0	6	562	645	40
-11	2	5	403	400	29	-6	5	5	300	358	22	-4	0	6	1198	1201	85
-10	2	5	338	329	24	-5	5	5	294	354	21	-2	0	6	1164	1058	82
-9	2	5	706	707	50	-4	5	5	439	506	31	0	0	6	102	120	14
-8	2	5	45	21	12	-3	5	5	442	449	32	2	0	6	1441	1324	102
-7	2	5	144	153	11	-2	5	5	875	841	62	4	0	6	485	515	35
-6	2	5	99	92	8	-1	5	5	177	171	13	6	0	6	465	485	33
-5	2	5	1109	1312	79	0	5	5	237	242	17	8	0	6	336	354	24
-4	2	5	661	758	47	1	5	5	183	182	14	-13	1	6	39	28	14
-3	2	5	339	368	24	2	5	5	523	517	37	-12	1	6	150	139	12
-2	2	5	156	130	11	3	5	5	351	333	25	-11	1	6	117	105	10
-1	2	5	669	619	47	4	5	5	288	283	21	-10	1	6	700	710	50
0	2	5	696	653	49	5	5	5	46	8	14	-9	1	6	50	37	12
1	2	5	1277	1148	90	6	5	5	151	157	12	-8	1	6	179	203	13
2	2	5	30	13	12	7	5	5	152	154	12	-7	1	6	49	48	11
3	2	5	130	133	10	-10	6	5	554	533	40	-6	1	6	774	892	55
4	2	5	261	274	19	-9	6	5	162	166	12	-5	1	6	209	226	15
5	2	5	705	696	50	-8	6	5	260	258	19	-4	1	6	870	911	62
6	2	5	252	264	18	-7	6	5	109	110	10	-3	1	6	159	157	12
7	2	5	273	302	20	-6	6	5	430	501	31	-2	1	6	708	691	50
8	2	5	40	56	15	-5	6	5	171	191	13	-1	1	6	394	380	28
-12	3	5	332	316	24	-4	6	5	648	703	46	0	1	6	794	734	56
-11	3	5	329	318	24	-3	6	5	311	293	22	1	1	6	49	44	10
-10	3	5	84	83	9	-2	6	5	123	119	10	2	1	6	348	335	25
-9	3	5	138	133	11	-1	6	5	340	328	24	3	1	6	73	78	10
-8	3	5	369	377	27	0	6	5	710	690	50	4	1	6	826	860	59
-7	3	5	624	667	44	1	6	5	90	97	9	5	1	6	110	125	10
-6	3	5	465	541	33	2	6	5	281	267	20	6	1	6	239	259	17
-5	3	5	86	85	8	3	6	5	27	15	12	7	1	6	33	43	14
-4	3	5	99	80	8	4	6	5	489	490	35	8	1	6	220	225	16
-3	3	5	795	813	56	5	6	5	241	239	18	-13	2	6	172	159	13
-2	3	5	644	620	46	6	6	5	432	454	31	-12	2	6	430	420	31
-1	3	5	923	850	65	-9	7	5	73	86	11	-11	2	6	105	110	10
0	3	5	151	155	11	-8	7	5	497	487	36	-10	2	6	26	13	11
1	3	5	284	280	20	-7	7	5	33	28	13	-9	2	6	419	433	30
2	3	5	528	517	38	-6	7	5	301	346	22	-8	2	6	722	809	51
3	3	5	506	483	36	-5	7	5	97	105	9	-7	2	6	332	379	24
4	3	5	179	174	13	-4	7	5	243	291	18	-6	2	6	382	452	27
5	3	5	94	95	9	-3	7	5	122	110	10	-5	2	6	410	465	29
6	3	5	101	102	10	-2	7	5	672	623	48	-4	2	6	1129	1146	80
7	3	5	371	386	27	-1	7	5	33	5	13	-3	2	6	591	575	42

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-2	2	6	1336	1195	95	3	5	6	246	245	18	-2	1	7	26	18	11
-1	2	6	22	18	10	4	5	6	221	210	16	-1	1	7	147	136	11
0	2	6	39	28	7	5	5	6	353	369	25	0	1	7	134	125	10
1	2	6	443	435	32	6	5	6	178	183	13	1	1	7	563	576	40
2	2	6	1041	981	74	-10	6	6	51	57	14	2	1	7	188	190	14
3	2	6	317	324	23	-9	6	6	315	327	23	3	1	7	449	464	32
4	2	6	294	297	21	-8	6	6	219	244	16	4	1	7	34	25	13
5	2	6	81	73	10	-7	6	6	412	483	29	5	1	7	187	188	14
6	2	6	434	450	31	-6	6	6	164	186	12	6	1	7	68	63	11
7	2	6	183	191	14	-5	6	6	156	189	12	7	1	7	339	374	24
8	2	6	353	377	25	-4	6	6	64	57	10	-13	2	7	99	89	10
-13	3	6	76	63	11	-3	6	6	818	791	58	-12	2	7	128	120	11
-12	3	6	153	140	12	-2	6	6	283	274	20	-11	2	7	436	448	31
-11	3	6	221	216	16	-1	6	6	484	452	35	-10	2	7	176	180	13
-10	3	6	372	381	27	0	6	6	219	204	16	-9	2	7	309	340	22
-9	3	6	165	174	12	1	6	6	535	529	38	-8	2	7	163	187	12
-8	3	6	191	201	14	2	6	6	294	285	21	-7	2	7	695	775	49
-7	3	6	231	264	17	3	6	6	597	619	43	-6	2	7	382	444	27
-6	3	6	618	703	44	4	6	6	151	135	12	-5	2	7	893	953	63
-5	3	6	486	542	35	5	6	6	91	86	10	-4	2	7	383	382	27
-4	3	6	484	525	35	-9	7	6	391	386	28	-3	2	7	56	45	9
-3	3	6	282	271	20	-8	7	6	38	29	14	-2	2	7	428	415	31
-2	3	6	554	539	40	-7	7	6	139	154	11	-1	2	7	886	834	63
-1	3	6	763	726	54	-6	7	6	79	84	10	0	2	7	315	301	22
0	3	6	1148	1066	81	-5	7	6	432	501	31	1	2	7	187	186	14
1	3	6	411	393	29	-4	7	6	81	56	9	2	2	7	28	9	12
2	3	6	121	110	10	-3	7	6	91	78	9	3	2	7	402	410	29
3	3	6	190	195	14	-2	7	6	30	33	12	4	2	7	301	326	22
4	3	6	320	312	23	-1	7	6	597	555	43	5	2	7	533	567	38
5	3	6	207	211	15	0	7	6	154	152	11	6	2	7	56	82	13
6	3	6	258	259	19	1	7	6	473	464	34	7	2	7	53	29	14
7	3	6	45	54	15	2	7	6	47	60	14	-13	3	7	307	299	22
-12	4	6	320	307	23	3	7	6	242	235	18	-12	3	7	189	188	14
-11	4	6	220	211	16	4	7	6	100	92	11	-11	3	7	37	17	14
-10	4	6	34	31	13	-7	8	6	398	449	28	-10	3	7	222	229	16
-9	4	6	287	319	21	-6	8	6	54	59	13	-9	3	7	375	399	27
-8	4	6	435	491	31	-5	8	6	77	75	10	-8	3	7	410	461	29
-7	4	6	412	487	30	-4	8	6	31	26	13	-7	3	7	471	547	34
-6	4	6	308	368	22	-3	8	6	600	584	43	-6	3	7	140	153	11
-5	4	6	179	208	13	-2	8	6	35	29	13	-5	3	7	315	341	23
-4	4	6	508	526	36	-1	8	6	294	266	21	-4	3	7	373	388	27
-3	4	6	912	872	65	0	8	6	57	51	9	-3	3	7	675	654	48
-2	4	6	884	827	63	1	8	6	419	423	30	-2	3	7	426	413	30
-1	4	6	726	690	52	2	8	6	37	10	14	-1	3	7	132	119	10
0	4	6	296	289	21	-13	0	7	122	113	11	0	3	7	157	153	12
1	4	6	558	529	40	-11	0	7	542	563	39	1	3	7	393	386	28
2	4	6	584	552	42	-9	0	7	372	402	27	2	3	7	300	297	22
3	4	6	351	340	25	-7	0	7	751	833	53	3	3	7	191	186	14
4	4	6	237	228	17	-5	0	7	1099	1151	78	4	3	7	38	33	14
5	4	6	95	98	10	-3	0	7	57	33	8	5	3	7	151	147	12
6	4	6	331	325	24	-1	0	7	822	801	58	6	3	7	235	256	17
7	4	6	370	387	27	1	0	7	270	257	20	-12	4	7	237	232	17
-11	5	6	339	331	24	3	0	7	548	581	39	-11	4	7	346	359	25
-10	5	6	243	239	18	5	0	7	638	683	46	-10	4	7	313	342	22
-9	5	6	353	370	25	7	0	7	56	31	14	-9	4	7	130	151	10
-8	5	6	103	113	9	-13	1	7	337	339	24	-8	4	7	155	176	12
-7	5	6	217	259	16	-12	1	7	86	84	10	-7	4	7	276	319	20
-6	5	6	184	218	14	-11	1	7	62	54	11	-6	4	7	681	763	48
-5	5	6	473	546	34	-10	1	7	157	150	12	-5	4	7	526	558	38
-4	5	6	292	293	21	-9	1	7	499	549	36	-4	4	7	377	372	27
-3	5	6	169	152	13	-8	1	7	139	165	11	-3	4	7	225	234	16
-2	5	6	419	387	30	-7	1	7	551	612	39	-2	4	7	258	251	19
-1	5	6	744	692	53	-6	1	7	226	233	16	-1	4	7	640	608	46
0	5	6	602	600	43	-5	1	7	440	493	32	0	4	7	618	612	44
1	5	6	554	547	39	-4	1	7	152	160	11	1	4	7	237	244	17
2	5	6	44	28	13	-3	1	7	867	867	61	2	4	7	196	210	15

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
3	4	7	234	223	17	6	0	8	307	338	22	-6	4	8	99	103	9
4	4	7	441	453	32	-13	1	8	47	30	14	-5	4	8	342	345	25
5	4	7	307	311	22	-12	1	8	396	410	28	-4	4	8	504	487	36
6	4	7	168	197	13	-11	1	8	140	132	11	-3	4	8	559	540	40
-11	5	7	35	36	14	-10	1	8	468	474	33	-2	4	8	312	298	22
-10	5	7	190	201	14	-9	1	8	47	19	13	-1	4	8	44	25	13
-9	5	7	262	287	19	-8	1	8	32	39	12	0	4	8	495	480	35
-8	5	7	466	520	33	-7	1	8	72	52	9	1	4	8	629	608	45
-7	5	7	179	221	13	-6	1	8	766	836	54	2	4	8	471	477	34
-6	5	7	49	12	12	-5	1	8	120	124	10	3	4	8	235	232	17
-5	5	7	35	11	13	-4	1	8	288	305	21	4	4	8	44	47	15
-4	5	7	466	467	33	-3	1	8	345	330	25	5	4	8	222	236	16
-3	5	7	358	340	26	-2	1	8	917	873	65	-11	5	8	407	415	29
-2	5	7	572	540	41	-1	1	8	209	198	15	-10	5	8	225	255	16
-1	5	7	112	114	10	0	1	8	795	759	56	-9	5	8	191	202	14
0	5	7	199	193	14	1	1	8	263	254	19	-8	5	8	44	45	13
1	5	7	171	171	13	2	1	8	266	272	19	-7	5	8	375	403	27
2	5	7	460	461	33	3	1	8	98	92	10	-6	5	8	238	256	17
3	5	7	223	224	16	4	1	8	443	482	32	-5	5	8	293	299	21
4	5	7	20	8	10	5	1	8	51	14	14	-4	5	8	66	69	10
5	5	7	83	96	11	6	1	8	88	107	11	-3	5	8	138	142	11
-10	6	7	464	479	33	-13	2	8	172	172	13	-2	5	8	462	431	33
-9	6	7	25	17	12	-12	2	8	230	251	17	-1	5	8	673	633	48
-8	6	7	92	108	9	-11	2	8	37	36	14	0	5	8	326	335	23
-7	6	7	62	60	10	-10	2	8	309	348	22	1	5	8	113	104	10
-6	6	7	506	600	36	-9	2	8	297	325	21	2	5	8	42	17	14
-5	6	7	207	209	15	-8	2	8	683	739	49	3	5	8	384	399	28
-4	6	7	334	319	24	-7	2	8	166	168	12	4	5	8	299	311	22
-3	6	7	181	174	13	-6	2	8	92	87	9	-10	6	8	80	87	11
-2	6	7	394	370	28	-5	2	8	288	296	21	-9	6	8	454	490	32
-1	6	7	149	139	11	-4	2	8	1027	980	73	-8	6	8	193	218	14
0	6	7	549	563	39	-3	2	8	369	358	26	-7	6	8	261	281	19
1	6	7	221	211	16	-2	2	8	593	553	42	-6	6	8	31	0	13
2	6	7	142	143	11	-1	2	8	20	4	10	-5	6	8	336	338	24
3	6	7	150	150	12	0	2	8	706	679	50	-4	6	8	191	187	14
4	6	7	511	513	37	1	2	8	348	337	25	-3	6	8	585	565	42
-9	7	7	69	84	11	2	2	8	739	744	53	-2	6	8	212	197	16
-8	7	7	410	454	29	3	2	8	199	196	15	-1	6	8	79	92	10
-7	7	7	26	48	12	4	2	8	50	13	14	0	6	8	146	146	11
-6	7	7	55	68	12	5	2	8	136	141	11	1	6	8	682	672	49
-5	7	7	33	35	13	6	2	8	396	429	28	2	6	8	251	245	18
-4	7	7	450	461	32	-13	3	8	33	18	14	3	6	8	323	341	23
-3	7	7	41	47	14	-12	3	8	276	287	20	-9	7	8	174	177	13
-2	7	7	382	361	27	-11	3	8	292	301	21	-8	7	8	65	67	11
-1	7	7	102	81	10	-10	3	8	356	403	26	-7	7	8	280	303	20
0	7	7	210	210	15	-9	3	8	84	80	9	-6	7	8	72	64	10
1	7	7	50	11	14	-8	3	8	62	57	10	-5	7	8	338	350	24
2	7	7	495	507	35	-7	3	8	344	364	25	-4	7	8	117	110	10
3	7	7	37	10	14	-6	3	8	601	657	43	-3	7	8	253	240	18
-7	8	7	50	28	14	-5	3	8	255	256	18	-2	7	8	48	24	13
-6	8	7	450	512	32	-4	3	8	219	209	16	-1	7	8	583	550	42
-5	8	7	78	77	10	-3	3	8	248	242	18	0	7	8	124	113	10
-4	8	7	286	286	21	-2	3	8	660	625	47	1	7	8	164	165	13
-3	8	7	79	70	10	-1	3	8	536	510	38	-6	8	8	58	52	12
-2	8	7	340	320	24	0	3	8	508	503	36	-5	8	8	315	311	23
-1	8	7	103	107	10	1	3	8	226	210	17	-4	8	8	50	51	14
0	8	7	408	404	29	2	3	8	195	205	14	-3	8	8	476	460	34
-12	0	8	367	375	26	3	3	8	258	278	19	-2	8	8	131	128	11
-10	0	8	359	396	26	4	3	8	428	454	31	-1	8	8	71	65	11
-8	0	8	550	587	39	5	3	8	155	177	12	-13	0	9	317	313	23
-6	0	8	102	94	9	-12	4	8	145	140	12	-11	0	9	496	484	35
-4	0	8	1434	1368	102	-11	4	8	38	28	14	-9	0	9	202	209	15
-2	0	8	585	563	42	-10	4	8	213	242	16	-7	0	9	753	804	54
0	0	8	677	663	50	-9	4	8	504	549	36	-5	0	9	584	596	42
2	0	8	1065	1050	76	-8	4	8	542	599	39	-3	0	9	869	820	62
4	0	8	32	29	13	-7	4	8	253	271	18	-1	0	9	912	877	65

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	0	9	84	88	10	-4	4	9	24	8	11	-2	1	10	688	663	49
3	0	9	441	450	32	-3	4	9	399	381	29	-1	1	10	177	182	13
5	0	9	128	149	11	-2	4	9	437	432	31	0	1	10	177	195	13
-13	1	9	333	315	24	-1	4	9	375	364	27	1	1	10	64	64	11
-12	1	9	79	70	10	0	4	9	237	240	17	2	1	10	437	449	31
-11	1	9	152	150	12	1	4	9	35	27	14	3	1	10	79	90	11
-10	1	9	67	56	10	2	4	9	303	315	22	4	1	10	258	270	19
-9	1	9	443	458	32	3	4	9	335	344	24	-13	2	10	142	130	12
-8	1	9	30	38	12	4	4	9	312	340	22	-12	2	10	94	59	10
-7	1	9	65	67	10	-11	5	9	136	149	11	-11	2	10	111	107	10
-6	1	9	179	202	13	-10	5	9	314	322	23	-10	2	10	512	510	37
-5	1	9	850	836	60	-9	5	9	259	267	19	-9	2	10	250	243	18
-4	1	9	279	281	20	-8	5	9	360	381	26	-8	2	10	438	455	31
-3	1	9	917	868	65	-7	5	9	93	94	9	-7	2	10	47	44	13
-2	1	9	61	63	11	-6	5	9	258	273	19	-6	2	10	243	244	18
-1	1	9	350	352	25	-5	5	9	343	344	25	-5	2	10	377	381	27
0	1	9	49	55	9	-4	5	9	470	468	34	-4	2	10	633	597	45
1	1	9	392	399	28	-3	5	9	83	78	9	-3	2	10	98	100	9
2	1	9	130	134	11	-2	5	9	208	190	15	-2	2	10	41	31	14
3	1	9	46	44	14	-1	5	9	48	20	13	-1	2	10	34	21	13
4	1	9	83	109	11	0	5	9	363	371	26	0	2	10	725	718	51
5	1	9	301	338	22	1	5	9	282	277	20	1	2	10	311	312	22
-13	2	9	285	282	21	2	5	9	231	233	17	2	2	10	300	320	22
-12	2	9	144	139	11	3	5	9	29	24	13	3	2	10	40	39	15
-11	2	9	408	420	29	-10	6	9	201	214	15	4	2	10	177	187	14
-10	2	9	103	114	10	-9	6	9	71	78	11	-12	3	10	286	282	21
-9	2	9	147	153	11	-8	6	9	355	370	25	-11	3	10	273	258	20
-8	2	9	248	261	18	-7	6	9	186	190	14	-10	3	10	164	162	12
-7	2	9	792	832	56	-6	6	9	518	546	37	-9	3	10	80	72	10
-6	2	9	299	320	22	-5	6	9	22	18	11	-8	3	10	341	359	24
-5	2	9	490	485	35	-4	6	9	44	16	13	-7	3	10	335	347	24
-4	2	9	262	271	19	-3	6	9	197	190	15	-6	3	10	396	399	28
-3	2	9	537	531	38	-2	6	9	539	510	38	-5	3	10	21	7	10
-2	2	9	344	334	25	-1	6	9	177	161	13	-4	3	10	36	11	13
-1	2	9	683	657	49	0	6	9	251	243	18	-3	3	10	255	257	18
0	2	9	369	371	26	1	6	9	64	47	13	-2	3	10	483	464	35
1	2	9	192	196	14	2	6	9	290	296	21	-1	3	10	298	289	21
2	2	9	92	93	10	-8	7	9	237	261	17	0	3	10	52	68	9
3	2	9	435	443	31	-7	7	9	32	33	[illegible]	1	3	10	78	92	10
4	2	9	146	152	12	-6	7	9	207	216	15	2	3	10	320	339	23
5	2	9	191	221	14	-5	7	9	100	113	10	3	3	10	279	296	20
-12	3	9	91	90	10	-4	7	9	572	544	41	-12	4	10	28	25	13
-11	3	9	208	207	15	-3	7	9	39	13	14	-11	4	10	216	217	16
-10	3	9	218	223	16	-2	7	9	109	116	10	-10	4	10	393	401	28
-9	3	9	559	559	40	-1	7	9	47	49	14	-9	4	10	535	518	38
-8	3	9	300	304	22	0	7	9	300	313	21	-8	4	10	318	323	23
-7	3	9	143	135	11	-12	0	10	32	26	13	-7	4	10	61	50	11
-6	3	9	340	354	24	-10	0	10	425	428	30	-6	4	10	144	139	11
-5	3	9	442	443	32	-8	0	10	345	355	25	-5	4	10	339	343	24
-4	3	9	402	403	29	-6	0	10	414	416	30	-4	4	10	361	334	26
-3	3	9	416	395	30	-4	0	10	963	917	68	-3	4	10	220	198	16
-2	3	9	232	213	17	-2	0	10	31	21	13	-2	4	10	23	3	11
-1	3	9	298	294	21	0	0	10	817	780	59	-1	4	10	344	339	25
0	3	9	165	160	12	2	0	10	312	325	23	0	4	10	388	386	28
1	3	9	325	343	23	4	0	10	180	191	14	1	4	10	424	430	30
2	3	9	186	193	14	-13	1	10	40	28	15	2	4	10	266	279	19
3	3	9	36	34	14	-12	1	10	462	451	33	-11	5	10	306	285	22
4	3	9	190	193	14	-11	1	10	95	100	10	-10	5	10	90	104	10
-12	4	9	256	261	18	-10	1	10	131	122	11	-9	5	10	94	102	10
-11	4	7	296	306	21	-9	1	10	20	17	10	-8	5	10	201	207	15
-10	4	9	216	230	16	-8	1	10	243	254	18	-7	5	10	432	450	31
-9	4	9	118	100	10	-7	1	10	117	111	10	-6	5	10	176	174	13
-8	4	9	443	457	32	-6	1	10	600	617	43	-5	5	10	187	190	14
-7	4	9	512	548	37	-5	1	10	95	94	9	-4	5	10	42	50	14
-6	4	9	495	521	35	-4	1	10	190	186	14	-3	5	10	328	317	24
-5	4	9	238	214	17	-3	1	10	175	173	13	-2	5	10	288	268	21

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-1	5	10	266	263	19	-7	3	11	170	173	13	-8	2	12	27	3	12
0	5	10	166	163	12	-6	3	11	289	306	21	-7	2	12	102	115	10
1	5	10	171	177	13	-5	3	11	432	419	31	-6	2	12	463	448	33
2	5	10	149	154	12	-4	3	11	209	203	15	-5	2	12	227	223	17
-9	6	10	430	433	31	-3	3	11	157	142	12	-4	2	12	322	300	23
-8	6	10	46	58	14	-2	3	11	72	74	11	-3	2	12	38	26	14
-7	6	10	68	65	11	-1	3	11	366	378	26	-2	2	12	304	307	22
-6	6	10	114	101	10	0	3	11	263	270	19	-1	2	12	165	169	13
-5	6	10	476	464	34	1	3	11	266	285	19	0	2	12	465	468	33
-4	6	10	212	207	16	2	3	11	73	69	12	1	2	12	46	82	15
-3	6	10	269	252	19	-11	4	11	159	161	12	-11	3	12	88	76	10
-2	6	10	81	69	10	-10	4	11	84	80	10	-10	3	12	123	124	11
-1	6	10	345	335	25	-9	4	11	293	272	21	-9	3	12	168	159	13
0	6	10	100	92	9	-8	4	11	426	419	30	-8	3	12	364	361	26
-7	7	10	385	401	28	-7	4	11	434	434	31	-7	3	12	239	236	17
-6	7	10	39	12	14	-6	4	11	185	180	14	-6	3	12	120	122	10
-5	7	10	167	174	13	-5	4	11	67	56	10	-5	3	12	106	99	10
-4	7	10	40	24	15	-4	4	11	288	289	21	-4	3	12	281	260	20
-3	7	10	370	348	27	-3	4	11	373	357	27	-3	3	12	276	270	20
-2	7	10	84	72	11	-2	4	11	431	421	31	-2	3	12	336	324	24
-13	0	11	508	438	36	-1	4	11	275	268	20	-1	3	12	60	71	13
-11	0	11	375	368	27	0	4	11	31	18	8	0	3	12	106	107	9
-9	0	11	378	379	27	1	4	11	201	209	15	-10	4	12	322	296	23
-7	0	11	571	577	41	-10	5	11	344	318	25	-9	4	12	263	237	19
-5	0	11	26	1	12	-9	5	11	189	199	14	-8	4	12	24	28	11
-3	0	11	877	876	62	-8	5	11	131	126	11	-7	4	12	170	173	13
-1	0	11	390	388	28	-7	5	11	135	141	11	-6	4	12	291	284	21
1	0	11	256	250	19	-6	5	11	373	364	27	-5	4	12	381	369	27
3	0	11	334	359	24	-5	5	11	317	306	23	-4	4	12	254	237	18
-13	1	11	211	190	16	-4	5	11	352	345	25	-3	4	12	24	32	12
-12	1	11	30	8	13	-3	5	11	100	105	10	-2	4	12	192	186	14
-11	1	11	355	335	25	-2	5	11	173	167	13	-1	4	12	340	336	24
-10	1	11	86	70	10	-1	5	11	105	101	10	-9	5	12	257	245	19
-9	1	11	353	332	25	0	5	11	301	310	22	-8	5	12	191	185	14
-8	1	11	24	21	11	-8	6	11	423	423	30	-7	5	12	340	339	24
-7	1	11	218	228	16	-7	6	11	223	227	16	-6	5	12	105	98	10
-6	1	11	186	192	14	-6	6	11	320	305	23	-5	5	12	79	75	11
-5	1	11	726	714	52	-5	6	11	77	84	11	-4	5	12	188	170	14
-4	1	11	86	84	10	-4	6	11	338	314	24	-3	5	12	363	346	26
-3	1	11	230	223	17	-3	6	11	113	107	10	-2	5	12	161	142	13
-2	1	11	64	56	11	-2	6	11	404	398	29	-11	0	13	47	44	14
-1	1	11	463	472	33	-12	0	12	322	289	23	-9	0	13	508	472	36
0	1	11	87	83	8	-10	0	12	454	416	32	-7	0	13	373	367	27
1	1	11	310	324	22	-8	0	12	41	46	14	-5	0	13	265	270	19
2	1	11	33	2	14	-6	0	12	641	618	46	-3	0	13	382	390	27
3	1	11	132	126	11	-4	0	12	335	324	24	-1	0	13	29	38	13
-12	2	11	176	165	13	-2	0	12	268	255	19	-11	1	13	457	408	33
-11	2	11	346	319	25	0	0	12	528	527	38	-10	1	13	119	98	10
-10	2	11	64	81	11	-12	1	12	322	271	23	-9	1	13	165	154	13
-9	2	11	391	382	28	-11	1	12	54	20	13	-8	1	13	49	20	13
-8	2	11	225	228	16	-10	1	12	117	118	10	-7	1	13	321	300	23
-7	2	11	532	531	38	-9	1	12	49	41	13	-6	1	13	87	83	10
-6	2	11	47	37	13	-8	1	12	471	483	34	-5	1	13	361	359	26
-5	2	11	31	13	13	-7	1	12	120	108	10	-4	1	13	38	25	14
-4	2	11	278	276	20	-6	1	12	168	170	13	-3	1	13	119	121	10
-3	2	11	715	693	51	-5	1	12	71	68	10	-2	1	13	60	49	13
-2	2	11	284	280	21	-4	1	12	340	328	24	-1	1	13	308	319	22
-1	2	11	314	316	23	-3	1	12	79	69	10	0	1	13	39	50	11
0	2	11	116	127	9	-2	1	12	409	396	29	-11	2	13	57	50	14
1	2	11	273	271	20	-1	1	12	60	68	13	-10	2	13	92	71	10
2	2	11	170	184	13	0	1	12	182	173	13	-9	2	13	443	412	32
-12	3	11	36	13	14	1	1	12	82	88	11	-8	2	13	218	198	16
-11	3	11	337	306	24	-12	2	12	262	231	19	-7	2	13	261	256	19
-10	3	11	297	269	21	-11	2	12	201	180	15	-6	2	13	58	29	12
-9	3	11	407	385	29	-10	2	12	460	424	33	-5	2	13	249	253	18
-8	3	11	113	104	10	-9	2	12	172	161	13	-4	2	13	168	171	13

Table A-23 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-3	2	13	438	433	31	-6	4	13	44	21	15	-4	1	14	319	307	23
-2	2	13	97	100	10	-5	4	13	195	177	15	-3	1	14	37	44	14
-1	2	13	48	50	15	-4	4	13	371	357	27	-9	2	14	92	84	11
-10	3	13	247	215	18	-3	4	13	318	310	23	-8	2	14	228	223	17
-9	3	13	105	100	10	-10	0	14	386	352	28	-7	2	14	140	128	11
-8	3	13	35	21	14	-8	0	14	236	244	17	-6	2	14	376	372	27
-7	3	13	283	273	20	-6	0	14	384	374	28	-5	2	14	102	105	10
-6	3	13	215	218	16	-4	0	14	51	32	14	-4	2	14	40	44	15
-5	3	13	304	295	22	-2	0	14	410	415	29	-3	2	14	115	104	11
-4	3	13	80	84	11	-10	1	14	283	257	20	-8	3	14	228	223	17
-3	3	13	37	59	14	-9	1	14	82	70	10	-7	3	14	121	114	11
-2	3	13	224	212	16	-8	1	14	398	378	29	-6	3	14	68	69	12
-9	4	13	282	265	20	-7	1	14	82	73	10	-5	3	14	179	169	14
-8	4	13	293	289	21	-6	1	14	88	94	10	-4	3	14	359	347	26
-7	4	13	172	166	13	-5	1	14	51	37	14	-7	0	15	29	34	13

Table A-24. Observed and Calculated Structure Factors for 59b

F_o, F_c and SIG (σ) values have been multiplied by 10.

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	12	0	1287	1357	71	5	7	1	233	242	14	1	3	2	585	558	30
1	12	0	966	968	50	6	7	1	145	120	14	2	3	2	895	936	45
2	12	0	531	545	28	7	7	1	137	161	17	3	3	2	696	691	35
3	12	0	825	812	43	1	8	1	989	991	50	4	3	2	493	467	25
4	12	0	763	755	40	2	8	1	30	24	15	5	3	2	264	264	15
5	12	0	461	474	25	3	8	1	535	576	30	6	3	2	141	139	13
0	14	0	1067	1031	55	4	8	1	229	228	14	7	3	2	294	285	16
1	14	0	817	812	42	5	8	1	287	289	16	0	4	2	255	259	14
2	14	0	441	445	24	6	8	1	206	236	14	1	4	2	911	900	46
3	14	0	531	523	29	7	8	1	282	288	17	2	4	2	2138	2101	107
1	0	1	28	37	12	1	9	1	141	128	11	3	4	2	1114	1188	56
2	0	1	207	208	11	2	9	1	255	260	14	4	4	2	912	856	46
3	0	1	216	196	12	3	9	1	175	166	12	5	4	2	927	902	47
4	0	1	53	47	18	4	9	1	240	243	14	6	4	2	505	504	26
5	0	1	106	106	13	5	9	1	31	32	18	7	4	2	483	468	25
6	0	1	123	115	14	6	9	1	136	154	16	0	5	2	425	431	22
7	0	1	90	81	21	1	10	1	194	189	12	1	5	2	746	741	38
8	0	1	26	24	16	2	10	1	342	328	18	2	5	2	717	741	37
1	1	1	288	301	15	3	10	1	354	346	19	3	5	2	311	314	16
2	1	1	647	529	33	4	10	1	177	167	13	4	5	2	330	330	17
3	1	1	523	490	27	5	10	1	53	25	19	5	5	2	592	566	30
4	1	1	395	382	20	6	10	1	252	236	16	6	5	2	354	349	19
7	5	2	154	160	14	5	0	3	26	20	15	1	10	3	168	163	12
0	6	2	1193	1167	60	6	0	3	168	167	13	2	10	3	134	132	12
1	6	2	1725	1674	87	7	0	3	80	65	22	3	10	3	82	107	20
2	6	2	1193	1157	60	8	0	3	89	35	17	4	10	3	321	328	17
3	6	2	259	237	14	1	1	3	235	228	12	5	10	3	192	198	14
4	6	2	616	621	32	2	1	3	838	815	42	6	10	3	89	66	17
5	6	2	1302	1304	66	3	1	3	435	416	22	1	11	3	201	200	13
6	6	2	875	871	45	4	1	3	338	337	18	2	11	3	68	71	22
7	6	2	330	334	18	5	1	3	105	91	15	3	11	3	119	117	14
0	7	2	937	893	48	6	1	3	238	234	14	4	11	3	359	349	19
1	7	2	743	735	38	7	1	3	83	80	21	5	11	3	202	197	14
2	7	2	413	404	21	8	1	3	50	70	23	1	12	3	262	267	15
3	7	2	196	199	12	1	2	3	32	33	14	2	12	3	119	125	14
4	7	2	276	282	15	2	2	3	963	986	49	3	12	3	289	299	16
5	7	2	458	479	24	3	2	3	312	302	16	4	12	3	334	336	18
6	7	2	297	302	17	4	2	3	643	642	33	5	12	3	201	209	13
7	7	2	123	126	15	5	2	3	365	359	19	1	13	3	162	169	13
0	8	2	1107	1101	56	6	2	3	544	525	28	2	13	3	148	135	13
1	8	2	1034	1010	52	7	2	3	218	199	14	3	13	3	246	250	15
2	8	2	981	952	50	1	3	[illegible]	[illegible]	411	20	4	13	3	49	59	21
3	8	2	809	786	41	2	3	[illegible]	[illegible]	387	20	1	14	3	29	14	17
4	8	2	761	776	39	3	3	[illegible]	[illegible]	407	21	2	14	3	386	378	20

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
5	8	2	862	870	44	4	3	3	303	298	16	3	14	3	205	211	14
6	8	2	546	598	28	5	3	3	199	185	12	1	15	3	123	125	15
0	9	2	465	457	24	6	3	3	377	357	20	2	15	3	233	225	15
1	9	2	391	372	20	7	3	3	40	10	20	0	0	4	2067	2104	104
2	9	2	474	463	24	1	4	3	648	661	33	1	0	4	441	448	23
3	9	2	558	556	29	2	4	3	251	235	13	2	0	4	399	377	21
4	9	2	377	374	20	3	4	3	548	585	28	3	0	4	681	687	35
5	9	2	250	269	15	4	4	3	87	89	15	4	0	4	742	719	38
6	9	2	163	171	14	5	4	3	396	379	20	5	0	4	732	705	37
0	10	2	672	651	34	6	4	3	109	111	14	6	0	4	791	757	40
1	10	2	726	720	37	7	4	3	201	192	13	7	0	4	664	643	34
2	10	2	875	858	45	1	5	3	471	450	24	0	1	4	1745	1786	88
3	10	2	1340	1322	68	2	5	3	154	128	10	1	1	4	546	580	28
4	10	2	908	909	46	3	5	3	232	247	13	2	1	4	251	252	13
5	10	2	165	160	13	4	5	3	421	437	22	3	1	4	739	729	38
6	10	2	291	302	16	5	5	3	281	274	16	4	1	4	822	807	42
0	11	2	603	600	31	6	5	3	35	25	18	5	1	4	617	611	32
1	11	2	349	350	18	7	5	3	209	205	14	6	1	4	777	737	40
2	11	2	267	277	15	1	6	3	308	298	16	7	1	4	702	685	36
3	11	2	462	457	24	2	6	3	264	267	14	0	2	4	740	756	38
4	11	2	307	304	17	3	6	3	203	195	12	1	2	4	508	537	26
5	11	2	37	29	20	4	6	3	432	459	22	2	2	4	801	823	41
0	12	2	1441	1395	73	5	6	3	160	164	13	3	2	4	746	762	38
1	12	2	752	741	38	6	6	3	115	129	15	4	2	4	785	767	40
2	12	2	398	406	21	7	6	3	45	27	22	5	2	4	412	413	21
3	12	2	725	724	37	1	7	3	491	476	25	6	2	4	488	476	25
4	12	2	626	610	32	2	7	3	132	133	11	7	2	4	572	566	29
5	12	2	355	386	19	3	7	3	96	85	14	0	3	4	1010	973	51
0	13	2	518	507	27	4	7	3	226	219	13	1	3	4	638	638	32
1	13	2	383	377	20	5	7	3	100	143	17	2	3	4	990	1069	50
2	13	2	226	221	14	6	7	3	127	105	14	3	3	4	1118	1159	57
3	13	2	170	174	13	7	7	3	178	174	14	4	3	4	813	799	41
4	13	2	203	204	14	1	8	3	1058	1041	54	5	3	4	527	498	27
0	14	2	805	802	41	2	8	3	490	490	25	6	3	4	484	472	25
1	14	2	698	687	36	3	8	3	179	181	12	7	3	4	464	467	24
2	14	2	563	563	29	4	8	3	166	169	12	0	4	4	548	506	28
3	14	2	369	374	20	5	8	3	42	63	21	1	4	4	468	477	24
0	15	2	159	164	14	6	8	3	63	93	22	2	4	4	904	955	46
1	15	2	282	284	16	1	9	3	544	535	28	3	4	4	906	945	46
2	15	2	311	300	17	2	9	3	95	73	15	4	4	4	620	619	32
1	0	3	305	302	16	3	9	3	153	150	12	5	4	4	593	568	30
2	0	3	30	43	15	4	9	3	121	133	14	6	4	4	359	356	19
3	0	3	121	91	10	5	9	3	29	46	16	7	4	4	315	320	17
4	0	3	124	124	11	6	9	3	42	46	21	0	5	4	980	940	50

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	5	4	665	671	34	1	15	4	439	432	23	4	9	5	51	25	21
2	5	4	970	963	49	2	15	4	536	514	28	5	9	5	105	84	18
3	5	4	449	467	23	1	0	5	622	646	32	6	9	5	41	52	21
4	5	4	513	524	26	2	0	5	47	30	16	1	10	5	288	295	16
5	5	4	807	810	41	3	0	5	29	31	15	2	10	5	46	37	20
6	5	4	475	468	25	4	0	5	733	721	37	3	10	5	121	126	14
7	5	4	345	365	19	5	0	5	364	357	19	4	10	5	211	218	13
0	6	4	659	631	34	6	0	5	87	79	19	5	10	5	155	142	14
1	6	4	942	934	48	7	0	5	232	219	14	1	11	5	269	277	15
2	6	4	645	658	33	1	1	5	665	671	34	2	11	5	316	317	17
3	6	4	58	44	20	2	1	5	416	431	21	3	11	5	199	197	13
4	6	4	300	305	16	3	1	5	496	479	25	4	11	5	245	250	15
5	6	4	877	922	45	4	1	5	697	681	36	5	11	5	150	140	13
6	6	4	664	672	34	5	1	5	300	294	16	1	12	5	361	356	19
7	6	4	264	258	16	6	1	5	236	226	14	2	12	5	102	112	16
0	7	4	493	480	25	7	1	5	154	150	14	3	12	5	156	161	13
1	7	4	971	951	49	1	2	5	563	563	29	4	12	5	227	240	14
2	7	4	762	756	39	2	2	5	586	609	30	1	13	5	202	194	14
3	7	4	151	143	11	3	2	5	390	390	20	2	13	5	69	71	23
4	7	4	493	497	25	4	2	5	692	703	35	3	13	5	107	105	17
5	7	4	962	992	49	5	2	5	348	343	18	4	13	5	90	106	21
6	7	4	677	686	35	6	2	5	147	137	13	1	14	5	87	83	21
7	7	4	333	345	18	7	2	5	208	193	14	2	14	5	149	160	14
0	8	4	596	587	30	1	3	5	336	344	17	3	14	5	48	70	23
1	8	4	655	645	34	2	3	5	272	274	14	1	15	5	116	114	18
2	8	4	629	612	32	3	3	5	109	100	11	0	0	6	1395	1429	70
3	8	4	426	432	22	4	3	5	445	450	23	1	0	6	940	966	48
4	8	4	592	599	30	5	3	5	149	146	12	2	0	6	456	433	23
5	8	4	540	551	28	6	3	5	283	285	16	3	0	6	171	177	11
6	8	4	377	391	20	7	3	5	36	67	19	4	0	6	432	437	22
0	9	4	632	630	32	1	4	5	586	588	30	5	0	6	263	264	15
1	9	4	663	662	34	2	4	5	384	379	20	6	0	6	325	305	18
2	9	4	648	647	33	3	4	5	503	519	26	7	0	6	275	271	16
3	9	4	896	874	46	4	4	5	102	100	14	0	1	6	2560	2629	129
4	9	4	660	663	34	5	4	5	236	234	14	1	1	6	1993	2087	100
5	9	4	328	331	18	6	4	5	366	368	19	2	1	6	1250	1286	63
6	9	4	249	260	15	7	4	5	179	188	13	3	1	6	1261	1298	64
0	10	4	503	495	26	1	5	5	681	692	35	4	1	6	1190	1198	60
1	10	4	294	275	16	2	5	5	458	458	24	5	1	6	868	861	44
2	10	4	572	552	29	3	5	5	315	320	17	6	1	6	944	912	48
3	10	4	935	929	48	4	5	5	358	377	19	7	1	6	680	657	35
4	10	4	551	553	28	5	5	5	164	168	13	0	2	6	816	830	41
5	10	4	149	130	16	6	5	5	190	189	13	1	2	6	559	562	29
6	10	4	203	201	14	7	5	5	223	238	14	2	2	6	597	624	30

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	11	4	641	621	33	1	6	5	270	253	14	3	2	6	832	846	42
1	11	4	441	435	23	2	6	5	431	425	22	4	2	6	486	481	25
2	11	4	615	606	31	3	6	5	426	441	22	5	2	6	424	403	22
3	11	4	788	786	40	4	6	5	199	208	13	6	2	6	241	233	14
4	11	4	533	537	27	5	6	5	222	239	14	7	2	6	231	230	14
5	11	4	262	256	15	6	6	5	401	406	21	0	3	6	1518	1507	76
0	12	4	787	771	40	7	6	5	155	131	15	1	3	6	1391	1456	70
1	12	4	552	546	28	1	7	5	460	462	24	2	3	6	1832	1933	92
2	12	4	279	274	16	2	7	5	40	26	19	3	3	6	1829	1907	92
3	12	4	367	358	19	3	7	5	217	229	13	4	3	6	1148	1177	58
4	12	4	398	403	21	4	7	5	60	68	21	5	3	6	651	656	33
5	12	4	242	273	15	5	7	5	73	94	23	6	3	6	366	364	19
0	13	4	995	964	51	6	7	5	123	113	16	7	3	6	529	514	27
1	13	4	669	666	34	1	8	5	398	392	21	0	4	6	634	627	32
2	13	4	255	256	15	2	8	5	186	177	12	1	4	6	585	614	30
3	13	4	349	365	19	3	8	5	216	208	13	2	4	6	803	849	41
4	13	4	396	412	21	4	8	5	197	195	13	3	4	6	555	592	28
0	14	4	619	604	32	5	8	5	240	240	14	4	4	6	392	411	20
1	14	4	497	488	26	6	8	5	147	156	14	5	4	6	331	342	18
2	14	4	280	284	16	1	9	5	493	508	25	6	4	6	130	118	13
3	14	4	280	281	16	2	9	5	164	168	12	7	4	6	175	166	13
0	15	4	412	417	22	3	9	5	277	276	15	0	5	6	1043	1060	53
1	5	6	1835	1836	92	6	0	7	410	393	21	2	11	7	420	418	22
2	5	6	1732	1787	87	7	0	7	35	45	18	3	11	7	171	176	13
3	5	6	876	926	45	1	1	7	128	129	10	4	11	7	74	79	23
4	5	6	856	890	44	2	1	7	496	527	25	5	11	7	38	37	20
5	5	6	1000	1012	51	3	1	7	388	358	20	1	12	7	228	225	14
6	5	6	692	716	35	4	1	7	467	467	24	2	12	7	165	165	13
7	5	6	395	424	21	5	1	7	307	320	17	3	12	7	132	136	14
0	6	6	694	700	35	6	1	7	251	251	15	4	12	7	182	178	13
1	6	6	587	577	30	7	1	7	212	209	14	1	13	7	216	194	14
2	6	6	561	552	29	1	2	7	245	253	13	2	13	7	58	75	22
3	6	6	143	154	12	2	2	7	108	115	11	3	13	7	104	80	17
4	6	6	303	316	16	3	2	7	234	236	13	1	14	7	45	28	22
5	6	6	431	461	22	4	2	7	162	168	12	2	14	7	106	96	18
6	6	6	286	308	16	5	2	7	179	182	12	0	0	8	276	273	15
7	6	6	169	176	13	6	2	7	165	160	13	1	0	8	223	208	12
0	7	6	1955	1926	98	7	2	7	50	60	22	2	0	8	119	119	11
1	7	6	1574	1574	79	1	3	7	79	92	14	3	0	8	80	79	18
2	7	6	973	992	50	2	3	7	235	246	13	4	0	8	129	121	13
3	7	6	640	654	33	3	3	7	31	30	16	5	0	8	44	22	20
4	7	6	797	818	41	4	3	7	381	379	20	6	0	8	33	8	18
5	7	6	1044	1093	53	5	3	7	195	207	13	7	0	8	44	33	22
6	7	6	712	735	36	6	3	7	153	139	13	0	1	8	2093	2147	105

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	8	6	411	402	21	7	3	7	118	105	15	1	1	8	1511	1649	81
1	8	6	526	526	27	1	4	7	296	311	16	2	1	8	952	1015	48
2	8	6	519	515	27	2	4	7	134	128	11	3	1	8	1029	1058	52
3	8	6	417	422	22	3	4	7	171	170	12	4	1	8	955	974	49
4	8	6	248	250	14	4	4	7	284	281	16	5	1	8	915	906	47
5	8	6	356	368	19	5	4	7	166	157	12	6	1	8	858	826	44
6	8	6	220	221	14	6	4	7	162	159	13	7	1	8	595	583	31
0	9	6	813	787	41	7	4	7	57	49	22	0	2	8	405	423	21
1	9	6	939	937	48	1	5	7	737	733	38	1	2	8	268	271	14
2	9	6	1273	1256	65	2	5	7	702	724	36	2	2	8	542	570	28
3	9	6	1180	11[illegible]	60	3	5	7	37	46	18	3	2	8	216	214	13
4	9	6	861	879	44	4	5	7	197	214	13	4	2	8	193	192	12
5	9	6	514	526	27	5	5	7	142	138	13	5	2	8	262	275	15
6	9	6	402	416	21	6	5	7	178	194	13	6	2	8	159	149	13
0	10	6	231	236	14	7	5	7	280	292	16	7	2	8	192	193	14
1	10	6	409	407	21	1	6	7	493	497	25	0	3	8	763	782	39
2	10	6	442	440	23	2	6	7	204	199	12	1	3	8	1228	1241	62
3	10	6	438	435	23	3	6	7	306	314	16	2	3	8	1773	1821	89
4	10	6	347	356	19	4	6	7	303	316	16	3	3	8	1418	1483	72
5	10	6	71	66	22	5	6	7	106	107	16	4	3	8	1050	1071	54
0	11	6	1028	986	52	6	6	7	179	193	13	5	3	8	503	512	26
1	11	6	812	804	41	1	7	7	262	264	14	6	3	8	393	397	21
2	11	6	749	748	38	2	7	7	136	135	12	7	3	8	523	515	27
3	11	6	1060	1038	54	3	7	7	358	354	19	0	4	8	359	348	19
4	11	6	766	777	39	4	7	7	216	217	13	1	4	8	407	425	21
5	11	6	288	310	15	5	7	7	282	300	16	2	4	8	400	414	21
0	12	6	454	437	24	6	7	7	209	220	14	3	4	8	181	188	12
1	12	6	270	264	15	1	8	7	219	214	13	4	4	8	65	92	22
2	12	6	127	137	14	2	8	7	85	87	16	5	4	8	252	262	15
3	12	6	251	264	15	3	8	7	232	228	14	6	4	8	37	31	18
4	12	6	186	190	13	4	8	7	61	93	20	7	4	8	224	219	14
0	13	6	1082	1074	55	5	8	7	34	54	18	0	5	8	1373	1362	69
1	13	6	820	809	42	6	8	7	83	79	21	1	5	8	1293	1321	65
2	13	6	465	459	24	1	9	7	365	370	19	2	5	8	1114	1163	57
3	13	6	456	438	24	2	9	7	152	143	13	3	5	8	1014	1056	52
0	14	6	459	461	24	3	9	7	360	366	19	4	5	8	806	828	41
1	14	6	241	238	15	4	9	7	343	362	18	5	5	8	875	900	45
2	14	6	215	203	14	5	9	7	253	260	15	6	5	8	581	612	30
0	15	6	469	461	24	1	10	7	283	279	16	0	6	8	530	544	27
1	0	7	427	446	22	2	10	7	105	95	14	1	6	8	317	317	17
2	0	7	491	490	25	3	10	7	175	179	13	2	6	8	216	222	13
3	0	7	377	376	20	4	10	7	81	95	22	3	6	8	175	160	12
4	0	7	294	296	16	5	10	7	45	65	20	4	6	8	114	114	15
5	0	7	106	126	15	1	11	7	461	455	24	5	6	8	73	82	23

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
6	6	8	50	57	22	3	3	9	137	137	12	1	2	10	271	272	15
0	7	8	1461	1464	74	4	3	9	212	207	13	2	2	10	414	432	21
1	7	8	1446	1433	73	5	3	9	57	22	19	3	2	10	467	461	24
2	7	8	959	988	49	6	3	9	132	135	14	4	2	10	441	443	23
3	7	8	401	419	21	1	4	9	316	300	17	5	2	10	364	366	19
4	7	8	683	711	35	2	4	9	79	73	19	6	2	10	257	248	15
5	7	8	885	925	45	3	4	9	182	202	12	0	3	10	122	127	12
6	7	8	720	786	37	4	4	9	443	454	23	1	3	10	337	336	18
0	8	8	669	655	34	5	4	9	278	292	16	2	3	10	709	741	36
1	8	8	168	168	12	6	4	9	44	51	20	3	3	10	1015	1060	52
2	8	8	29	30	17	1	5	9	410	421	21	4	3	10	655	679	34
3	8	8	402	418	21	2	5	9	252	271	14	5	3	10	437	442	23
4	8	8	252	269	15	3	5	9	72	91	21	6	3	10	355	358	19
5	8	8	217	231	14	4	5	9	498	513	26	0	4	10	170	168	12
6	8	8	73	81	23	5	5	9	263	270	15	1	4	10	279	296	15
0	9	8	825	803	42	6	5	9	54	93	24	2	4	10	507	526	26
1	9	8	752	751	38	1	6	9	508	529	26	3	4	10	477	496	25
2	9	8	894	907	46	2	6	9	88	74	15	4	4	10	339	346	18
3	9	8	1206	1201	61	3	6	9	259	262	15	5	4	10	329	337	18
4	9	8	868	887	44	4	6	9	394	396	21	6	4	10	265	270	15
5	9	8	438	459	23	5	6	9	186	198	13	0	5	10	517	515	27
0	10	8	509	504	26	6	6	9	90	89	21	1	5	10	613	620	31
1	10	8	307	311	17	1	7	9	281	300	15	2	5	10	660	665	34
2	10	8	94	76	17	2	7	9	202	198	13	3	5	10	392	389	20
3	10	8	284	298	16	3	7	9	50	52	22	4	5	10	540	552	28
4	10	8	83	108	22	4	7	9	28	28	17	5	5	10	530	546	27
5	10	8	171	170	13	5	7	9	51	45	23	6	5	10	499	526	26
0	11	8	726	715	37	6	7	9	44	57	22	0	6	10	433	444	22
1	11	8	757	756	39	1	8	9	169	176	12	1	6	10	402	404	21
2	11	8	829	844	42	2	8	9	89	80	19	2	6	10	252	238	14
3	11	8	881	869	45	3	8	9	146	130	13	3	6	10	232	248	14
4	11	8	560	573	29	4	8	9	196	195	13	4	6	10	336	351	18
0	12	8	180	183	13	5	8	9	74	98	23	5	6	10	365	357	19
1	12	8	300	292	17	1	9	9	332	331	18	6	6	10	324	333	18
2	12	8	218	218	14	2	9	9	250	241	14	0	7	10	974	975	50
3	12	8	57	88	23	3	9	9	33	30	18	1	7	10	603	599	31
4	12	8	50	39	22	4	9	9	86	100	21	2	7	10	217	219	13
0	13	8	1011	988	51	5	9	9	37	32	19	3	7	10	387	388	20
1	13	8	751	750	38	1	10	9	231	228	14	4	7	10	497	515	26
2	13	8	439	434	23	2	10	9	107	103	17	5	7	10	716	734	37
3	13	8	322	321	18	3	10	9	261	255	15	0	8	10	431	423	22
0	14	8	122	103	16	4	10	9	82	68	21	1	8	10	320	334	17
1	14	8	218	224	14	1	11	9	264	259	15	2	8	10	351	343	19
1	0	9	264	264	14	2	11	9	157	156	13	3	8	10	350	353	19

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	0	9	458	454	24	3	11	9	134	132	14	4	8	10	290	295	16
3	0	9	472	475	24	4	11	9	312	311	17	5	8	10	391	403	21
4	0	9	142	131	13	1	12	9	204	195	14	0	9	10	338	336	18
5	0	9	217	217	14	2	12	9	180	181	14	1	9	10	472	476	24
6	0	9	453	443	24	3	12	9	135	148	14	2	9	10	685	686	35
7	0	9	115	112	18	1	13	9	84	71	23	3	9	10	738	728	38
1	1	9	528	539	27	2	13	9	64	65	25	4	9	10	523	546	27
2	1	9	348	362	18	0	0	10	422	416	22	5	9	10	250	280	15
3	1	9	178	195	12	1	0	10	353	352	19	0	10	10	283	296	16
4	1	9	373	370	20	2	0	10	363	365	19	1	10	10	220	217	14
5	1	9	129	120	14	3	0	10	136	143	13	2	10	10	473	469	24
6	1	9	116	103	15	4	0	10	268	266	15	3	10	10	349	361	19
7	1	9	153	150	14	5	0	10	465	453	24	4	10	10	263	262	15
1	2	9	144	142	11	6	0	10	464	469	24	0	11	10	462	449	24
2	2	9	447	460	23	0	1	10	780	811	40	1	11	10	419	420	22
3	2	9	503	515	26	1	1	10	614	622	31	2	11	10	552	549	28
4	2	9	222	216	13	2	1	10	420	417	22	3	11	10	596	595	31
5	2	9	167	165	13	3	1	10	322	323	17	0	12	10	332	318	18
6	2	9	266	268	15	4	1	10	580	585	30	1	12	10	352	345	19
7	2	9	31	27	17	5	1	10	740	730	38	2	12	10	213	215	14
1	3	9	37	32	18	6	1	10	709	700	36	3	12	10	268	259	16
2	3	9	135	149	12	0	2	10	538	546	28	0	13	10	737	720	38
1	13	10	634	629	33	1	0	12	991	1025	51	1	11	12	398	398	21
1	0	11	272	274	15	2	0	12	552	559	28	2	11	12	453	462	24
2	0	11	92	92	16	3	0	12	556	556	29	0	12	12	554	548	29
3	0	11	85	82	20	4	0	12	651	633	33	1	12	12	567	561	29
4	0	11	440	432	23	5	0	12	799	801	41	1	0	13	76	84	22
5	0	11	222	223	14	6	0	12	630	600	32	2	0	13	64	75	22
6	0	11	72	104	25	0	1	12	875	848	45	3	0	13	39	41	20
1	1	11	363	353	19	1	1	12	786	784	40	4	0	13	98	80	18
2	1	11	330	319	17	2	1	12	570	585	29	5	0	13	38	43	20
3	1	11	125	132	14	3	1	12	455	461	24	1	1	13	281	283	16
4	1	11	366	357	19	4	1	12	463	467	24	2	1	13	103	107	15
5	1	11	276	282	16	5	1	12	567	560	29	3	1	13	224	228	14
6	1	11	68	73	25	6	1	12	501	472	26	4	1	13	360	354	19
1	2	11	325	325	17	0	2	12	776	794	40	5	1	13	143	136	14
2	2	11	268	274	15	1	2	12	866	875	44	1	2	13	382	390	20
3	2	11	221	211	13	2	2	12	1008	1038	51	2	2	13	63	79	23
4	2	11	239	251	14	3	2	12	718	718	37	3	2	13	153	155	13
5	2	11	147	145	14	4	2	12	587	595	30	4	2	13	211	220	14
6	2	11	51	50	22	5	2	12	505	510	26	5	2	13	154	146	14
1	3	11	197	199	13	6	2	12	451	452	24	1	3	13	115	100	14
2	3	11	262	270	15	0	3	12	5[illegible]0	506	26	2	3	13	158	157	13
3	3	11	208	205	13	1	3	12	5[illegible]6	554	28	3	3	13	135	135	14

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
4	3	11	162	153	13	2	3	12	847	851	43	4	3	13	80	92	22
5	3	11	56	51	23	3	3	12	782	777	40	5	3	13	110	126	18
6	3	11	166	155	14	4	3	12	565	581	29	1	4	13	192	186	13
1	4	11	29	25	17	5	3	12	317	324	17	2	4	13	235	229	14
2	4	11	225	201	13	6	3	12	191	173	14	3	4	13	163	174	13
3	4	11	266	278	15	0	4	12	763	764	39	4	4	13	126	134	15
4	4	11	173	171	13	1	4	12	655	662	34	5	4	13	51	57	22
5	4	11	145	136	14	2	4	12	782	799	40	1	5	13	183	174	13
6	4	11	220	224	14	3	4	12	960	955	49	2	5	13	321	307	17
1	5	11	300	309	16	4	4	12	716	731	37	3	5	13	276	283	16
2	5	11	275	271	15	5	4	12	427	433	22	4	5	13	106	114	18
3	5	11	285	288	16	0	5	12	753	762	38	5	5	13	103	106	19
4	5	11	330	342	18	1	5	12	573	561	29	1	6	13	181	189	13
5	5	11	241	237	14	2	5	12	502	527	26	2	6	13	232	242	14
6	5	11	211	198	14	3	5	12	581	580	30	3	6	13	151	150	13
1	6	11	279	278	15	4	5	12	440	445	23	4	6	13	72	73	23
2	6	11	225	225	14	5	5	12	405	408	21	1	7	13	158	163	14
3	6	11	275	285	15	0	6	12	1061	1070	54	2	7	13	57	91	24
4	6	11	182	174	13	1	6	12	885	892	45	3	7	13	130	141	14
5	6	11	163	150	13	2	6	12	555	577	29	4	7	13	88	92	22
1	7	11	224	219	14	3	6	12	504	508	26	1	8	13	58	95	24
2	7	11	195	189	13	4	6	12	503	524	26	2	8	13	114	108	16
3	7	11	205	210	13	5	6	12	544	548	28	3	8	13	106	97	18
4	7	11	64	60	15	0	7	12	780	757	40	4	8	13	398	402	21
5	7	11	105	96	18	1	7	12	746	746	38	1	9	13	162	141	13
1	8	11	171	164	13	2	7	12	405	401	21	2	9	13	41	86	21
2	8	11	258	260	15	3	7	12	257	266	15	3	9	13	27	28	16
3	8	11	168	173	13	4	7	12	414	421	22	1	10	13	180	178	14
4	8	11	53	60	22	5	7	12	416	420	22	2	10	13	109	97	19
5	8	11	113	115	16	0	8	12	748	759	38	1	11	13	225	212	15
1	9	11	223	215	14	1	8	12	689	690	35	0	0	14	1413	1417	72
2	9	11	280	274	16	2	8	12	645	642	33	1	0	14	1354	1371	69
3	9	11	50	29	22	3	8	12	543	546	28	2	0	14	1135	1130	58
4	9	11	71	87	23	4	8	12	555	567	29	3	0	14	472	480	24
1	10	11	228	210	14	0	9	12	385	388	20	4	0	14	586	582	30
2	10	11	44	34	21	1	9	12	393	383	21	5	0	14	818	812	42
3	10	11	97	98	20	2	9	12	552	543	28	0	1	14	432	427	23
4	10	11	71	71	24	3	9	12	586	601	30	1	1	14	366	367	19
1	11	11	289	282	16	4	9	12	399	415	21	2	1	14	261	260	15
2	11	11	109	94	18	0	10	12	384	376	20	3	1	14	162	150	13
3	11	11	181	194	14	1	10	12	588	587	30	4	1	14	188	172	13
1	12	11	146	166	16	2	10	12	687	685	35	5	1	14	216	208	14
2	12	11	38	30	20	3	10	12	712	707	37	0	2	14	1087	1069	55
0	0	12	1087	1085	55	0	11	12	317	313	17	1	2	14	1093	1090	55

Table A-24 (Con't).

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	2	14	1068	1070	54	3	1	15	329	319	18	2	3	16	187	188	14
3	2	14	987	1000	50	4	1	15	93	117	22	3	3	16	80	90	23
4	2	14	773	757	40	1	2	15	342	343	19	0	4	16	413	396	22
5	2	14	598	590	31	2	2	15	174	185	13	1	4	16	303	305	17
0	3	14	254	243	15	3	2	15	127	138	15	2	4	16	515	510	27
1	3	14	235	230	14	4	2	15	162	164	14	3	4	16	683	666	35
2	3	14	437	437	23	1	3	15	52	39	23	0	5	16	191	179	14
3	3	14	360	354	19	2	3	15	143	133	14	1	5	16	196	184	14
4	3	14	198	193	14	3	3	15	194	185	14	2	5	16	55	70	23
5	3	14	173	161	14	4	3	15	300	308	17	3	5	16	140	148	15
0	4	14	879	886	45	1	4	15	69	56	24	0	6	16	761	742	39
1	4	14	1037	1019	53	2	4	15	277	267	15	1	6	16	527	523	27
2	4	14	1080	1096	55	3	4	15	106	108	16	2	6	16	265	253	16
3	4	14	1030	1042	52	4	4	15	214	197	14	0	7	16	290	274	16
4	4	14	721	724	37	1	5	15	250	235	15	1	7	16	149	137	14
0	5	14	311	310	17	2	5	15	57	66	24	2	7	16	170	160	14
1	5	14	351	361	19	3	5	15	167	170	14	0	8	16	479	485	25
2	5	14	198	193	13	4	5	15	248	243	15	1	0	17	41	39	21
3	5	14	185	208	14	1	6	15	210	190	14	2	0	17	39	30	20
4	5	14	224	218	14	2	6	15	86	88	18	3	0	17	69	56	23
0	6	14	1355	1354	69	3	6	15	98	61	19	1	1	17	36	41	20
1	6	14	1005	1006	51	1	7	15	199	197	14	2	1	17	59	73	25
2	6	14	626	624	32	2	7	15	122	103	17	3	1	17	59	26	25
3	6	14	630	632	32	3	7	15	38	48	21	1	2	17	333	329	18
4	6	14	654	662	34	1	8	15	95	109	22	2	2	17	159	156	14
0	7	14	497	492	26	2	8	15	169	166	14	3	2	17	106	91	19
1	7	14	268	257	15	1	9	15	102	70	17	1	3	17	71	97	22
2	7	14	178	181	13	0	0	16	659	653	34	2	3	17	110	107	18
3	7	14	204	215	14	1	0	16	600	581	31	1	4	17	38	68	20
4	7	14	171	155	14	2	0	16	337	343	18	2	4	17	80	76	23
0	8	14	940	928	48	3	0	16	188	190	14	1	5	17	69	61	24
1	8	14	810	800	41	4	0	16	387	377	21	2	5	17	38	19	21
2	8	14	692	672	35	0	1	16	132	112	15	1	6	17	33	29	18
3	8	14	672	685	34	1	1	16	123	121	16	0	0	18	445	429	23
0	9	14	264	258	16	2	1	16	204	198	14	1	0	18	538	522	28
1	9	14	171	173	14	3	1	16	95	105	17	2	0	18	391	376	21
2	9	14	227	211	15	4	1	16	139	130	15	0	1	18	263	272	16
0	10	14	369	370	20	0	2	16	211	200	14	1	1	18	314	300	18
1	10	14	594	588	31	1	2	16	459	454	24	2	1	18	318	303	18
1	0	15	67	77	19	2	2	16	605	589	31	0	2	18	392	388	21
2	0	15	32	25	18	3	2	16	489	486	25	1	2	18	353	353	19
3	0	15	53	51	23	4	2	16	467	459	24	0	3	18	272	260	16
4	0	15	42	26	21	0	3	16	164	161	14	1	3	18	261	262	16
1	1	15	70	68	21	1	3	16	193	185	14	0	4	18	222	220	15
2	1	15	305	290	17												

References

1. A. Baeyer, V. Villiger, Chem. Ber. 35, 1189, 3013 (1902); H. Meerwein, K. van Emster, Ber. 55, 2500 (1922); F. C. Whitmore, J. Am. Chem. Soc. 54, 3274 (1932); D. Bethell, V. Gold, in "Carbonium Ions An Introduction", Academic Press: London (1967).
2. G. Olah and P. v. R. Schleyer, Eds., "Carbonium Ions", Vol. I-V, Wiley-Interscience: New York (1968-1976); P. Vogel, in "Carbocation Chemistry", Elsevier Publishers: New York (1985).
3. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans 2, S1-S19 (1987).
4. J. P. Glusker, K. N. Trueblood, in "Crystal Structure Analysis; A Primer", 2nd Ed., Oxford University Press: New York (1985).
5. G. A. Olah, G. K. S. Prakash, J. Sommer, in "Superacids", J. Wiley and Sons Inc.: New York (1985), p. 69, 177.
6. F. H. Allen, O. Kennard, R. Taylor, Accounts Chem. Res. 16, 146 (1983).
7. H. B. Bürgi, J. D. Dunitz, Accounts Chem. Res. 16,

153 (1983).

8. J. D. Dunitz in "X-Ray Analysis and the Structure of Organic Molecules", Cornell University Press: Ithaca, NY (1979).

9. H. B. Bürgi, J. D. Dunitz, E. Shefler, J. Am. Chem. Soc. 95, 5065 (1973).

10. J. A. Wunderlich, Acta Cryst. B23, 846 (1967); A. Tulinsky, J. H. van der Hende, J. Am. Chem. Soc. 89, 2905 (1967); S. R. Hall, F. R. Ahmed, Acta Cryst. B24, 346 (1968); S. R. Hall, F. R. Ahmed, Acta Cryst. B24, 337 (1968); K. B. Birnbaum, Acta Cryst. B28, 2825 (1972).

11. H. B. Bürgi, J. D. Dunitz, J. M. Lehn, G. Wipff, Tetrahedron 30, 1563 (1974); J. E. Baldwin, J. Chem. Soc. Chem. Commun., 738 (1976); N. T. Anh, O. Eisenstein, Nouv. J. Chim. 1, 61 (1977); R. E. Rosenfield, J. D. Dunitz, Helv. Chim. Acta. 61, 2176 (1978); M. M. Kayser, P. Morand, Tetrahedron Lett., 695 (1979)

12. E. L. Muetterties, L. J. Guggenberger, J. Am. Chem. Soc. 96, 1748 (1974); R. R. Holmes, Acc. Chem. Res. 12, 257 (1979).

13. H. B. Bürgi, I. E. Shefter, J. D. Dunitz, Tetrahedron 31, 3089 (1975); D. J. Chadwick, J. D. Dunitz, J. Chem. Soc. Perkin Trans 2, 276 (1979).

14. P. G. Jones, A. J. Kirby, J. Chem. Soc. Chem. Commun., 288 (1979).

15. M. Sundaralingham, A. K. Chwang, Carbonium Ions 5, 2427 (1976).

16. A. H. Gomes de Mesquita, C. H. MacGillavry, K. Eriks, Acta Cryst. 18, 437 (1965); P. M. Cook, L. F. Dahl, D. W. Dickerhoof, J. Am. Chem. Soc. 94, 5511 (1972).

17. N. C. Baenziger, R. E. Buckles, T. D. Simpson, J. Am. Chem. Soc. 89, 3405 (1967).

18. L. L. Koh, K. Eriks, Acta Cryst. B27, 1405 (1971); J. S. McKechnie, I. C. Paul, J. Chem. Soc. (B), 918 (1971).

19. R. Breslow, J. Am. Chem. Soc. 79, 5318 (1957); M. Sundaralingam, L. H. Jensen, J. Am. Chem. Soc. 88, 198 (1966); A. T. Ku, M. Sundaralingam, J. Am. Chem. Soc. 94, 1688 (1972); M. Sundaralingam, L. H. Jensen, J. Am. Chem. Soc. 85 3303 (1973); J. C. Thibeault, R. F. Ziolo, H. B. Gray, Cryst. Struct. Commun. 3, 473 (1974).

20. R. F. Childs, M. Mahendran, S. D. Zweep, G. Shaw, S. Chadda, N. Burke, B. George, R. Faggiani, C. J. L. Lock, Pure and Appld. Chem. 58, 111 (1986).

21. E. S. Gould, Acta Cryst. 8, 657 (1955); A. I. Kitaigorodskii, Y. T. Struchkou, T. L. Khotsyanova, M.

E. Volpin, D. N. Kursanow, Izv. Akad. Nauk, SSR, Ord. Khim. Nauk, 39 (1960); P. J. Stang, G. Maas, J. Org. Chem. 48, 3038 (1983).

22. C. Kbuto, M. Oda, Y. Kitahara, Tetrahedron Lett. 48, 4851 (1972).

23. A. S. Wingrove, R. L. Caret, in "Organic Chemistry", Harper and Row: New York, pp. 271, 409, 733, 786, 818, 939.

24. H. Perst in "Oxonium Ions in Organic Chemistry", Academic Press: New York, NY (1971); H. Perst, Carbonium Ions 5, 1961 (1976); H. G Richey, J. M. Richey, Carbonium Ions 2, 899 (1970); R. C. Fort, Jr., Carbonium Ions 4, 1783 (1973); R. E. Leone, J. C. Barborak, P. v. R. Schleyer, Carbonium Ions 4, 1837 (1973).

25. F. P. Boer, J. Am. Chem. Soc. 88, 1572 (1966); F. P. Boer, J. Am. Chem. Soc. 90, 6706 (1968).

26. J. -M. LeCarpentier, R. Weiss, Compt. Rend. 265, 797 (1967); J. -M. LeCarpentier, Acta Cryst. B28, 1421 (1972).

27. J. -M. LeCarpentier, Acta Cryst. B28, 1430 (1972).

28. B. Chevrier, J. -M. LeCarpentier, R. Weiss, J. Am. Chem. Soc. 94, 5718 (1972).

29. B. Chevrier, J. -M. LeCarpentier, R. Weiss, Acta Cryst. B28, 2673 (1972).

30. B. Rees, A. Veillard, R. Weiss, Theor. Chim. Acta. 23, 266 (1971).

31. R. H. Nobes, W. J. Bouma, L. Radom, J. Am. Chem. Soc. 105, 309 (1983).

32. M. Brookhart, G. C. Levy, S. Winstein, J. Am. Chem. Soc. 89, 1735 (1967); G. A. Olah, M. Calin, D. H. O'Brien, J. Am. Chem. Soc. 89, 3586 (1967); G. A. Olah, D. H. O'Brien, M. Calin, J. Am. Chem. Soc. 89, 3582 (1967).

33. J. L. Franklin, Carbonium Ions 1, 77 (1968).

34. D. Cremer, J. Gauss, R. F. Childs, C. Blackburn, J. Am. Chem. Soc. 107, 2535 (1985); K. B. Wiberg, K. E. Laidig, J. Am. Chem. Soc. 109, 5935 (1987); C. F. Rodriquez, A. C. Hopkinson, Theochem. 37, 69 (1987); R. J. Loncharich, T. R. Schwartz, K. N. Houk, J. Am. Chem. Soc. 109, 14 (1987); T. J. LePage, K. B. Wiberg, J. Am. Chem. Soc. 110, 6642 (1988).

35. E. M. Arnett, R. P. Quirk, J. W. Larsen, J. Am. Chem. Soc. 92, 3977 (1970); J. W. Larsen, J. Am. Chem. Soc. 100, 330 (1978); G. Scorrano, V. Lucchini, J. Org. Chem. 44, 1726 (1979); J. W. Larsen, P. A. Bouis, C. A. Riddle, J. Org. Chem. 45, 4969 (1980); R. F. Childs, D. L. Mulholland, A. Varadarajan, S. Yeroushalmi, J. Org. Chem. 48, 1431 (1983).

36. G. A. Olah, A. M. White, D. H. O'Brien, Carbonium

Ions 4, 1697 (1973).

37. R. F. Childs, Reviews Chem. Intermediates 3, 285 (1980).

38. P. -G. Jönnson, I. Olovsson, Acta Cryst. B24, 559 (1968); A. Kvick, P. -G. Jönnson, I. Olovsson, Inorg. Chem. 8, 2775 (1969).

39. R. V. G. Sunders-Rao, J. W. Turley, R. Pepinsky, Acta Cryst. 10, 435 (1957).

40. R. F. Childs, R. Faggiani, C. J. L. Lock, M. Mahendran, S. D. Zweep, J. Am. Chem. Soc. 108, 1692 (1986).

41. S. K. Chadda, R. F. Childs, R. Faggiani, C. J. L. Lock, J. Am. Chem. Soc. 108, 1694 (1986).

42. R. F. Childs, R. Faggiani, C. J. L. Lock, A. Varadarajan, Acta Cryst. C40, 1291 (1984).

43. R. F. Childs, A. Varadarajan, C. J. L. Lock, R. Faggiani, C. A. Fyfe, R. E. Wasylishen, J. Am. Chem. Soc. 104, 2452 (1982).

44. R. F. Childs, R. Faggiani, C. J. L. Lock, C. V. Rogerson, J. Org. Chem. 48, 3043 (1983); L. K. Montgomery, M. P. Grendze, J. C. Huffman, J. Am. Chem. Soc. 109, 4749 (1987).

45. H. Paulsen, R. Dammeyer, Chem. Ber. 109, 1837 (1976).

46. H. Paulsen, R. Dammeyer, Chem. Ber. 106, 2324 (1973).

47. H. Paulsen, E. Schüttpelz, Chem. Ber. 112, 3214

(1979).

48. H. Paulsen, R. Dammeyer, Chem. Ber. 109, 605 (1976).
49. M. R. Caira, J. E. de Wet, Acta Cryst. B37, 709 (1981).
50. R. M. Orgias, PhD. Thesis, McMaster University, Hamilton, Ontario (1989).
51. R. F. Childs, R. Faggiani, C. J. L. Lock, M. Mahendran, J. Am. Chem. Soc. 108, 3613 (1986).
52. L. Brun, Acta Cryst. 20, 739 (1966); F. D. Lewis, J. D. Oxman, J. C. Huffman, J. Am. Chem. Soc. 106, 466 (1984); T. Poll, J. O. Metter, G. Helmchen, Angew. Chem. Int. Ed. Engl. 24, 112 (1985); M. T. Reetz, M. Hüllmann, W. Massa, S. Berger, P. Rademacher, P. Heymanns, J. Am. Chem. Soc. 108, 2405 (1986); T. Laube, H. U. Stilz, J. Am. Chem. Soc. 109, 5876 (1987); H. van Koningsveld, J. J. Scheele, J. C. Jansen, Acta Cryst. C43, 294 (1987).
53. U. Pindur, J. Müller, C. Flo, H. Witzel, Chem. Soc. Rev. 16, 75 (1987).
54. H. Paulsen, Pure and Appl. Chem. 41, 69 (1975).
55. R. A. McClelland and M. Ahmad, J. Am. Chem. Soc. 99, 5356 (1977); M. Ahmad, R. G. Bergstrom, M. J. Cashen, Y. Chiang, A. J. Kresge, R. A. McClelland, M. F. Powell, J. Am. Chem. Soc. 101, 2669 (1979).
56. B. G. Ramsey, R. W. Taft, J. Am. Chem. Soc. 88, 3058

(1966); R. F. Borch, J. Am. Chem. Soc. 90, 5303 (1968).

57. Ch. H. V. Dusseau, S. E. Schaafsma, H. Steinberg, Th. J. de Boer, Tetrahedron Lett., 467 (1969).

58. R. F. Childs, R. Orgias, C. J. L. Lock, M. Mahendran, Can. J. Chem., manuscript submitted, 1990.

59. M. Sundaralingham, A. K. Chwang, Carbonium Ions 5, 2427 (1976).

60. G. A. Olah, A. M. White, J. Am. Chem. Soc. 89, 3591 (1967).

61. G. A. Olah, A. T. Ku, A. M. White, J. Org. Chem. 34, 1327 (1969).

62. C. U. Pittman, Jr., T. B. Patterson, L. D. Kispert, J. Org. Chem. 38, 471 (1973).

63. H. Hart, D. A. Tomalia, Tetrahedron Lett., 3383 (1966); H. Hart, D. A. Tomalia, Tetrahedron Lett., 1347 (1967); D. A. Tomalia, H. Hart, Tetrahedron Lett., 3389 (1966).

64. J. W. Larsen, S. Ewing, M. Wynn, Tetrahedron Lett., 539 (1970); J. W. Larsen, S. Ewing, J. Am. Chem. Soc. 93, 5107 (1971); J. W. Larsen, P. A. Bouis, C. A. Riddle, J. Org. Chem. 45, 4969 (1980).

65. P. Deslongchamps, in "Stereoelectronic Effects in Organic Chemistry", Pergamon Press: New York, NY (1983), Chapter 3; P. Deslongchamps, Tetrahedron 31,

2463 (1975).

66. P. Deslongchamps, P. Atlani, D. Fréhel, A. Malaval, Can. J. Chem. 50, 3405 (1972); P. Deslonchamps, D. Guay, R. Chênevert, Can. J. Chem. 63, 2493 (1985).

67. N. Beaulieu, P. Deslongchamps, Can. J. Chem. 58, 164 (1980).

68. P. Deslongchamps, R. Chênevert, R. J. Taillefer, C. Moreau, J. K. Saunders, Can. J. Chem. 53, 1601 (1975).

69. P. Deslongchamps, J. Lessard, Y. Nadeau, Can. J. Chem. 63, 2485 (1985).

70. C. L. Perrin, G. M. L. Arrhenius, J. Am. Chem. Soc. 104, 2839 (1982); A. J. Kirby, Accounts Chem. Res. 17, 305 (1984).

71. E. L. Eliel, F. W. Nader, J. Am. Chem. Soc. 92, 584 (1970); E. L. Eliel, F. W. Nader, J. Am. Chem. Soc. 91, 536 (1969).

72. F. F. Khouri, M. K. Kaloustian, J. Am. Chem. Soc. 108, 6683 (1986).

73. R. Breslow, in "Molecular Rearrangements", Vol. 1, P. de Mayo, Ed., Interscience Publishers: New York (1963), Chapter 4.

74. J. D. Roberts, R. H. Mazur, J. Am. Chem. Soc. 73, 2509 (1951); H. Hart, J. M. Sandri, J. Am. Chem. Soc. 81, 320 (1959); H. Hart, P. A. Law, J. Am. Chem. Soc.

84, 2462 (1962); R. Breslow, J. Lockhart, A. Small, J. Am. Chem. Soc 84, 2793 (1962); H. Hart, P. A. Law, J. Am. Chem. Soc. 86, 1957 (1964); D. D. Roberts, J. Org. Chem. 29, 294 (1964); D. D. Roberts, J. Org. Chem. 30, 23 (1965); K. B. Wiberg, A. J. Ashe III, Tetrahedron Lett. 21, 1553 (1965); K. B. Wiberg, A. J. Ashe III, Tetrahedron Lett. 47, 4245 (1965); M. Vogel, J. D. Roberts, J. Am. Chem. Soc. 88, 2262 (1966); H. G. Richey, Jr., J. M. Richey, J. Am. Chem. Soc. 88, 4971 (1966); K. B. Wiberg, T. Nakahira, Tetrahedron Lett. 3759 (1970); K. B. Wiberg, T. Nakahira, J. Am. Chem. Soc. 93, 5193 (1971); P. Gassman, E. A. Williams, F. J. Williams, J. Am. Chem. Soc. 93, 5199 (1971).

75. H. G. Richey, Jr., Carbonium Ions 3, 1201 (1972).

76. K. B. Wiberg, B. A. Hess, Jr., A. J. Ashe III, Carbonium Ions 3, 1295 (1972).

77. H. C. Brown (with comments by P. v. R. Schleyer), in "The Nonclassical Ion Problem", Plenum: New York (1977), Chapter 5.

78. P. D. Bartlett, in "Nonclassical Ions", W. A. Benjamin Inc.: New York (1965), p. 52.

79. D. Bethell, V. Gold, in "Carbonium Ions, An Introduction", Academic Press: London (1967), p. 266.

80. T. Tidwell in "The Chemistry of the Cyclopropyl Group", Z. Rappoport, Ed., Wiley-Interscience: New York (1987), Chapter 10; E. C. Friedrich in "The Chemistry of the Cyclopropyl Group", Z. Rappoport, Ed., Wiley-Interscience: New York (1987), Chapter 11.

81. P. v. R. Schleyer, G. W. Van Dine, J. Am. Chem. Soc. 88, 2321 (1966).

82. S. Winstein, M. Shatavsky, C. Norton, R. B. Woodward, J. Am. Chem. Soc. 77, 4183 (1955); L. S. Bartell, B. L. Carroll, J. P. Guillory, Tetrahedron Lett., 705 (1964); L. S. Bartell, J. P. Guillory, J. Chem. Phys. 43, 647 (1965); G. L. Closs, H. B. Klinger, J. Am. Chem. Soc. 87, 3265 (1965); C. U. Pittman, Jr., G. A. Olah, J. Am. Chem. Soc. 87, 2998 (1965); G. A. Olah, J. Lukas, J. Am. Chem. Soc. 89, 4739 (1967).

83. R. H. Eastman, J. Am. Chem. Soc. 76, 4115 (1954); R. H. Eastman, J. Am. Chem. Soc. 76, 4118 (1954); R. H. Eastman, J. Am. Chem. Soc. 77, 6645 (1955); N. C. Deno, J. J. Jaruzeiski, A. Schriesheim, J. Am. Chem. Soc. 77, 3044 (1955); E. M. Kosower, M. Oto, Proc. Chem. Soc., 25 (1962); N. C. Deno, C. U. Pittman, Jr., M. J. Wisotsky, J. Am. Chem. Soc. 86, 4370 (1964); N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, J. D. Turner, J. Am. Chem. Soc. 87, 4533 (1965); N. C. Deno, C. U. Pittman, Jr., R. Waack, M.

Doran, J. Am. Chem. Soc. 88, 1488 (1966).

84. A. S. Walsh, Trans. Faraday Soc. 45, 179 (1949); C. A. Coulson, W. Moffitt, Phil. Mag. 40, 1 (1949); M. Simonetta, S. Winstein, J. Am. Chem. Soc. 76, 18 (1954); W. G. Woods, R. A. Carboni, J. D. Roberts, J. Am. Chem. Soc. 78, 5653 (1953); C. A. Coulson, T. H. Goodwin, J. Chem. Soc., 2851 (1962); C. A. Coulson, T. H. Goodwin, J. Chem. Soc., 3161 (1963); M. E. H. Howden, J. D. Roberts, Tetrahedron 19, Suppl. 2, 403 (1963); R. J. Piccolini, S. Winstein, Tetrahedron 19, Suppl. 2, 423 (1963); D. Peters, Tetrahedron 19, 1539 (1963); R. Hoffmann, J. Chem. Phys. 40, 2480 (1964); M. Randic, A. Maskic, Theor. Chim. Acta 3, 59 (1965); K. B. Wiberg, Tetrahedron 24, 1083 (1968); H. S. Tremper, D. D. Shillady, J. Am. Chem. Soc. 91, 6341 (1969); L. Radom, J. A. Pople, V. Buss, P. v. R. Schleyer, J. Am. Chem. Soc. 92, 6380 (1970); W. J. Hehre, P. C. Hiberty, J. Am. Chem. Soc. 94, 5917 (1972); W. J. Hehre, P. C. Hiberty, J. Am. Chem. Soc. 96, 302 (1974).

85. M. Saunders, K. E. Laidig, K. B. Wiberg, P. v. R. Schleyer, J. Am. Chem. Soc. 110, 7652 (1988).

86. L. Radom, J. A. Pople, P. v. R. Schleyer, J. Am. Chem. Soc. 94, 5935 (1972).

87. L. R. Schmitz, T. S. Sorensen, J. Am. Chem. Soc. 104,

2600 (1982).

88. R. Radom, D. Poppinger, R. C. Hadon, Carbonium Ions 5, 2303 (1976).

89. C. D. Poulter, C. J. Spillner, J. Am. Chem. Soc. 96, 7591 (1974).

90. R. A. Moss, S. Shen, K. Krogh-Jespersen, J. A. Potenza, H. J. Schugar, R. C. Munjal, J. Am. Chem. Soc. 108, 134 (1986).

91. J. S. Staral, I. Yavari, J. D. Roberts, G. K. S. Prakash, D. J. Donovan, G. A. Olah, J. Am. Chem. Soc. 100, 8016 (1978); J. S. Staral, J. D. Roberts, J. Am. Chem. Soc. 100, 8018 (1978).

92. M. Saunders, H. -U. Siehl, J. Am. Chem. Soc. 102, 6868 (1980).

93. G. A. Olah, G. Liang, K. A. Babiale, T. K. Morgan, Jr., R. K. Murray, J. Am. Chem. Soc. 98, 576 (1976); G. A. Olah, G. Liang, K. A. Babiale, T. M. Ford, D. L. Goff, T. K. Morgan, Jr., R. K. Murray, J. Am. Chem. Soc. 100, 1494 (1978).

94. G. A. Olah, C. L. Jeuell, D. P. Kelly, R. D. Porter, J. Am. Chem. Soc. 92, 2544 (1970); G. A. Olah, C. L. Jeuell, D. P. Kelly, R. D. Porter, J. Am. Chem. Soc. 94, 146 (1972).

95. G. A. Olah, R. J. Spear, P. C. Hiberty, W. J. Hehre, J. Am. Chem. Soc. 98, 7470 (1976).

96. F. Cacace, M. Speranza, J. Am. Chem. Soc. 101, 1587 (1979).

97. M. L. McKee, J. Phys. Chem. 90, 4908 (1986).

98. B. A. Levi, E. S. Blurock, W. J. Hehre, J. Am. Chem. Soc. 101, 5537 (1979).

99. R. D. Bach, P. E. Blanchette, J. Am. Chem. Soc. 101, 46 (1979); M. J. S. Dewar, C. H. Reynolds, J. Am. Chem. Soc. 106, 6388 (1984).

100. W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople. in "*Ab Initio* Molecular Orbital Theory", Wiley-Interscience: New York (1986).

101. M. Yoshimine, A. D. McLean, B. Liu, J. Am. Chem. Soc. 105, 6185 (1983); K. Raghavachari, R. C. Haddon, P. v. R. Schleyer, H. F. Schaefer III, J. Am. Chem. Soc. 105, 5915 (1983); R. C. Haddon, K. Raghavachari, J. Am. Chem. Soc. 105, 118 (1983).

102. P. Lazzeretti, R. Zanasi, J. Am. Chem. Soc. 105, 12 (1983): P. Lanzzeretti, R. Zanasi, Chem. Phys. Lett. 80, 533 (1981).

103. W. J. Brittian, M. E. Squillacote, J. D. Roberts, J. Am. Chem. Soc. 106, 7280 (1984).

104. W. Koch, B. Liu, D. DeFrees, J. Am. Chem. Soc. 110, 7325 (1988).

105. D. Cremer, E. Kraka, T. S. Slee, R. F. W. Bader, C. D. H. Lau, T. T. Nguyen-Dang, P. J. MacDougall, J. Am. Chem. Soc. 105, 5069 (1983).

106. R. F. W. Bader, T. T. Nguyen-Dang, Y. Tal, Rep. Prog. Phys. 44, 893 (1981); R. F. W. Bader, T. T. Nguyen-Dang, Adv. Quantum Chem. 14, 63 (1981); R. F. W. Bader, Acc. Chem. Res. 18, 9 (1985).

107. C. Faulkenberg-Andersen, K. Ranajanayakulu, L. R. Schmitz, T. S. Sorensen, J. Am. Chem. Soc. 106, 178 (1984).

108. C. U. Pittman, Jr., G. A. Olah, J. Am. Chem. Soc. 87, 5123 (1965).

109. G. A. Olah, G. Liang, J. Am. Chem. Soc. 95, 3792 (1973).

110. O. Bastiansen, F. N. Fritsch, K. Hedberg, Acta Cryst. 17, 538 (1964); R. J. Butcher, W. J. Jones, J. Mol. Spectrosc. 47, 64 (1973); W. J. Jones, B. P. Stiocheff, Can. J. Phys. 42, 2259 (1964).

111. M. Schindler, J. Am. Chem. Soc. 109, 1020 (1987).

112. P. C. Myhre, G. C. Webb, C. S. Yannoni, J. Am. Chem. Soc. 112, 8992 (1990).

113. G. A. Olah, A. M. White, D. H. O'Brien, Chem. Rev. 70, 561 (1970); G. A. Olah, S. Prakash, J. Sommer, Science (Washington, DC) 206, 13 (1979).

114. G. A. Olah, P. W. Westerman, T. Nishimura, J. Am.

Chem. Soc. 96, 3548 (1974).

115. P. v. R. Schleyer, V. Buss, J. Am. Chem. Soc. 91, 5880 (1969).

116. J. C. Martin, B. R. Ree, J. Am. Chem. Soc. 91, 5882 (1969).

117. G. A. Olah, G. Liang, J. Am. Chem. Soc. 98, 7026 (1976).

118. G. A. Olah, G. K. S. Prakash, T. N. Rawdah, J. Org. Chem. 45, 965 (1980).

119. D. P. Kelly, D. R. Leslie, B. D. Smith, J. Am. Chem. Soc. 106, 687 (1984).

120. M. Saunders, J. Rosenfeld, J. Am. Chem. Soc. 92, 2548 (1970).

121. D. S. Kabakoff, E. Namanworth, J. Am. Chem. Soc. 92, 3234 (1970).

122. P. v. R. Schleyer, G. W. Van Dine, J. Am. Chem. Soc. 88, 2321 (1966).

123. E. F. Cox, M. C. Caserio, M. S. Silver, J. D. Roberts, J. Am. Chem. Soc. 83, 2719 (1961).

124. W. B. Kover, J. D. Roberts, J. Am. Chem. Soc. 91, 3687 (1969).

125. R. A. McClelland, W. F. Reynolds, Can. J. Chem. 54, 718 (1976).

126. A. R. Butler, J. Chem. Soc. Perkin Trans. 2, 959 (1976).

127. G. Bouchoux, Y. Hoppilliard, J. Phys. Chem. 92, 5869 (1988).

128. J. B. Stothers, in "^{13}C NMR Spectroscopy", Academic Press: New York (1972).

129. F. H. Allen, Acta Cryst. B36, 81 (1980); F. H. Allen, Acta Cryst. B37, 890 (1981).

130. R. C. Haddon, J. Org. Chem. 44, 3608 (1979).

131. R. C. Haddon, J. Am. Chem. Soc. 110, 1108 (1988).

132. J. Meinwald, E. Frauenglass, J. Am. Chem. Soc. 82, 5235 (1960).

133. C. S. Dean, J. R. Dixon, S. H. Graham, D. O. Lewis, J. Chem. Soc. (C), 1491 (1968).

134. H. O. House, H. Babad, R. B. Toothill, A. W. Noltes, J. Org. Chem. 27, 4141 (1962).

135. G. M. Sheldrick, SHELX Program for Crystal Structure Determination, University of Cambridge, England (1976).

136. W. B. Schweizer and J. D. Dunitz, Helv. Chim. Acta. 65, 1547 (1982).

137. F. H. Allen and A. J. Kirby, J. Am. Chem. Soc. 106, 6197 (1984).

138. P. G. Jones and A. J. Kirby, J. Am. Chem. Soc. 106, 6207 (1984).

139. P. G. Jones and A. J. Kirby, J. Chem. Soc. Chem. Commun., 444 (1986).

140. M. R. Edwards, P. G. Jones, A. J. Kirby, J. Am. Chem. Soc. 108, 7067 (1986).

141. L. Pauling in "The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry", 3rd Ed., Cornell University Press: Ithaca, NY (1960).

142. R. Kuhn, H. Trischmann, Ann. 611, 117 (1958).

143. G. A. Olah, P. W. Westerman, J. Nishimura, J. Am. Chem. Soc. 96, 3548 (1974); G. A. Olah, R. J. Spear, P. C. Hiberty, W. J. Hehre, J. Am. Chem. Soc. 98, 7470 (1976).

144. R. E. Long, H. Maddox, K. E. Trueblood, Acta Cryst. B25, 2083 (1969); A. L. Bednowitz, Acta Cryst. A25, S129 (1969); M. A. M. Meester, H. Schenk, C. H. MacGillavry, Acta Cryst. B27, 630 (1971); P. A. Luhan, A. T. McPhail, J. Chem. Soc. Perkin 2, 2372 (1972); R. J. Chandross, J. Bordner, Acta Cryst. B30, 1581 (1974); G. Bernardinelli, J. -J. Combremont, R. Gerdil, Helv. Chim. Acta 59, 1395 (1976); D. J. Brauer, C. Krüger, P. J. Roberts, J. Chem. Soc. Perkin 2, 532 (1976); R. Zelnik, D. Lavie, E. C. Levy, A. H. -J. Wang, I. C. Paul, Tetrahedron 33, 1457 (1977); D. G. Morris, P. Murray-Rust, J. Murray-Rust, J. Chem.

Soc. Perkin 2, 1577 (1977); C. Stålhandske, C. Svensson, C. Särnstrand, Acta Cryst. B33, 870 (1977).

145. J. Bordner, L. A. Jones, R. L. Johnson, Cryst. Struct. Commun. 1, 389 (1972).

146. R. P. Kirchen, T. S. Sorensen, J. Am. Chem. Soc. 99, 6687 (1977).

147. H. -U. Siehl, J. Am. Chem. Soc. 107, 3390 (1985).

148. R. Jost, J. Sommer, C. Engdahl, P. Ahlberg, J. Am. Chem. Soc. 102, 7663 (1980).

149. E. M. Arnett, T. C. Hofelich, J. Am. Chem. Soc. 105, 2889 (1983).

150. D. H. Aue, M. T. Bower, in "Gas Phase Ion Chemistry", Vol. II, Academic Press: New York (1979).

151. P. G. Gassman, A. F. Fentiman Jr., J. Am. Chem. Soc. 91, 1545 (1969).

152. R. D. Topsom, Progr. Phys. Org. Chem. 16, 85 (1987).

153. A. S. Kusher, PhD. Dissertation, The Pennsylvania State University, University Park, Pa (1966).

154. **AMPAC**; Austin Method 1 Package (QCPE 506), Dewar Research Group and J. J. P. Stewart, QCPE Bull. 6, 2 (1986).

155. **GAUSSIAN** 86, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Ragahavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A.

Whiteside, D. J. Fox, E. M. Flender, J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA, 1984.

156. F. W. Biegler-Konig, T. T. Nguyen-Dang, Y. Tal, R. F. W. Bader, A. J. Duke, J. Phys. B. 14, 2739 (1981); F. W. Biegler-Konig, R. F. W. Bader, T. -H. Tang, J. Comp. Chem. 13, 317 (1982).

157. R. F. W. Bader, Can. J. Chem. 64, 1036 (1986); R. F. W. Bader, Acc. Chem. Res. 18, 9 (1985).

158. R. F. W. Bader, T. S. Slee, D. Cremer, E. Kraka, J. Am. Chem. Soc. 105, 5061 (1983).

159. R. F. W. Bader, M. T. Carroll, J. R. Cheeseman, C. Chang, J. Am. Chem. Soc. 109, 7968 (1987).

160. W. L. Earl, D. L. Vander Hart, J. Magn. Res. 48, 35 (1982).

161. B. Lippert, C. J. L. Lock, B. Rosenberg, M. Zvagulis, Inorg. Chem. 16, 314 (1977).

162. R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, G. Turner, Inorg. Chem. 16, 1525 (1977).

163. J. M. Stewart, The **XRAY76** System, Tech. Rept. TR-446, Computer Science Center, University of Maryland, College Park, Maryland (1976).

164. J. M. Stewart, S. R. Hall, The **XTAL** System of Crystallographic Programs, Tech. Rept. TR-1364, University of Maryland, College Park, Maryland (1976).

165. D. T. Cromer, J. T. Waber in "International Tables for X-ray Crystallography", J. A. Ibers, W. C. Hamilton, Eds., Kynoch Press: Birmingham England (1974), p. 99.

166. J. Stephens, **MOLGEOM**, adapted from **CUDLS**, McMaster University, Canada (1973).

167. K. Davies, **CHEMX**, Chemical Design Ltd., Oxford, England (1986).

168. K. Davies, **SNOOPI**, **CHEMGRAF** suite, Chemical Design Ltd., Oxford, England (1983).

169. H. O. House, A. V. Prabhu, J. M. Wilkins, L. F. Lee, J. Org. Chem. 41, 3067 (1976).

170. S. D. Zweep, personal communication.

171. R. F. W. Bader, The AIMPAC Package, McMaster University, Canada (1990).