Phenylhydrides of the Groups 4B and 5B Elements and Their Monoanions

by

Raymond J. Batchelor (B.Sc.)

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University

PHENYLHYDRIDES OF THE GROUPS 4B AND 5B ELEMENTS

To

Meriel

DOCTOR OF PHILOSOPHY (1983) McMASTER UNIVERSITY
(Chemistry) Hamilton, Ontario

TITLE:	Phenylhydrides of the Groups <u>4B</u> and <u>5B</u> Elements and Their Monoanions
AUTHOR:	Raymond J. Batchelor, B.Sc. (University of British Columbia)
SUPERVISOR:	Professor T. Birchall
NUMBER OF PAGES:	xv; 200

ABSTRACT

^{1}H, ^{13}C and, where appropriate, ^{31}P NMR spectra for the series of compounds $(C_6H_5)_nXH_{3-n}$ and $(C_6H_5)_nXH_{2-n}Na$ (n = 1, 2; X = N, P or As), have been recorded and assigned. The results are consistent with the existence of a pπ-pπ interaction between substituent and phenyl ring in all cases when the atom is nitrogen but only in the anions when the substituent atom is phosphorus or arsenic. ^{13}C NMR spectra of the compounds $(C_6H_5)_nGeH_{4-n}$ and $(C_6H_5)_nGeH_{3-n}Na$ as well as $(p\text{-}CH_3C_6H_4)_3GeM$ (M = H, Na) have also been recorded and assigned. Comparison of the chemical shifts demonstrated that the extent of delocalization of the negative charge is significantly less in the phenylgermyl anions than in the analogous group <u>5B</u> species. This corroborates the observed differences in the effect of phenyl-substitution on the acidities of main group hydrides as rationalized in terms of hybridization at the anionic centre and subsequent degree of resonance delocalization.

The distribution of π-electrons in the mono-substituted benzenes, whose substituents are anionic centres, appears to be the result of the balance between mesomeric and electric field effects. The latter effect produces a polarization of the phenyl ring dependent upon the extent to which the negative charge is localized on the substituent atom. The magnitudes of these effects depend somewhat on the extent and nature of solute-solvent interaction, ion-pairing and association in the solutions of these salts which, in turn, are a function of the polarity of the solvent.

Adduct formation between cuprous iodide and both PH_3 and $C_6H_5PH_2$ was investigated. Comparison with literature results for complexes of $(C_6H_5)_2PH$, $P(C_6H_5)_3$ or other tertiary phosphines indicates that σ-donor strength alone, as opposed to π-acidity or steric bulk, is the dominant factor influencing the stability of the coordinative interactions of the smaller phosphines. The structure of the complex $[CuI(C_6H_5PH_2)_2]_2$ is reported. ^{127}I Mössbauer spectroscopy was found to be incapable of discriminating between different iodine environments in such complexes.

ACKNOWLEDGEMENTS

The author wishes to express gratitude to his supervisor, Professor T. Birchall, for his patience, encouragement and support throughout the course of this work.

Special thanks are due to Mr. B. Sayer who recorded some of the NMR spectra and who gave instruction and assistance in the use of the NMR instruments. Mr. I. Thompson is also thanked for his help in the use of these and other instruments.

The work of Mr. R. Faggiani, who collected the X-ray diffractometer data and who provided other practical help and instruction, is gratefully acknowledged. The instruction and advice of Professors C. J. L. Lock and I. D. Brown, on matters of crystallography, are greatly appreciated. Dr. J. Sawyer, Mr. J. Britten, Mr. P. Pilon and Dr. K. Franklin are also to be thanked for their help with this subject.

Dr. L. Soderholm, Dr. K. Ruebenbauer and Dr. G. Dénès are thanked for help with computing and programming.

Dr. R. D. Myers is specially thanked for his assistance in recording the ^{127}I Mössbauer spectra. Mr. J. P. Johnson was of much help in the earlier stages of the laboratory work. The encouragement and friendship of these individuals will be remembered.

The author is grateful to Mrs. E. Denham, Word Processing Centre, Faculty of Science, for the typing of this thesis.

The financial support of the Natural Sciences and Engineering Research Council and of McMaster University is gratefully acknowledged.

TABLE OF CONTENTS

Page

CHAPTER 1 -- INTRODUCTION 1

CHAPTER 2 -- EXPERIMENTAL SECTION 16

A. Preparative Techniques and Apparatus 16

(i) Vacuum System 16

(ii) Inert Atmosphere System 18

(iii) Reactions Vessels 18

B. Solvents and Reagents 21

(i) Purification of Solvents 21

(ii) Reagents for Synthesis 22

C. Preparations 22

(i) Hydrides and Precursors 22

(a) Compounds of Group 5B elements 23

(b) Compounds of Group 4B elements 24

(ii) Preparation of Sodium Salts of Hydrides 25

(a) Anions of Group 5B Hydrides 26

(b) Anions of Group 4B Hydrides 28

Page

(iii) Cuprous Iodide and its Complexes with Phosphines 30
- (a) CuI 30
- (b) $[CuI \cdot P(C_6H_5)_3]_4$ 31
- (c) $[CuI]_2[P(C_6H_5)_3]_3$ 31
- (d) $CuI[P(C_6H_5)_3]_3$ 31
- (e) $[CuI(C_6H_5PH_2)_2]_2$ 32
- (f) '$[CuI \cdot C_6H_5PH_2]_4$' 32
- (g) NMR Samples of $CuI \cdot nPH_3$ and $CuI \cdot nC_6H_5PH_2$ 32

D. Spectroscopic Methods 33

(i) NMR Spectroscopy 33
- (a) ^1H NMR 33
- (b) ^{13}C NMR 36
- (c) ^{31}P NMR 36

(ii) Mössbauer Spectroscopy 37

(iii) Infrared and Raman Spectroscopy 38
- (a) Raman 38
- (b) IR 39

(iv) X-Ray Crystallography 39

Page

CHAPTER 3 -- NMR OF PHENYL-SUBSTITUITED HYDRIDES AND ANIONS OF MAIN GROUP ELEMENTS 41

A. Introduction 41

(i) Substituent Chemical Shifts 43

B. ^{1}H NMR 51

(i) Monosubstituted Benzenes 53

(a) Ortho proton 53

(b) Meta proton 57

(c) Para proton 60

(ii) Results and Discussion 62

(a) Protons Directly Bonded to the Group <u>5B</u> Element 73

(b) Ring Protons 74

C. ^{13}C NMR 81

(i) Monosubstituted Benzenes 83

(a) Ipso Carbon 83

(b) Ortho Carbon 84

(c) Meta Carbon 85

(d) Para Carbon 86

(ii) Results 88

(a) Phenylhydrides of Group 5B and their Anions 88

(b) Arylgermanes and their Anions 97

Page

(iii) Discussion 103

(a) Ipso Carbon 103

(b) Ortho Carbon 109

(c) Meta Carbon 111

(d) Para Carbon 112

D. ^{31}P NMR 117

E. Relative Acidities 123

CHAPTER 4 -- COORDINATION CHEMISTRY OF PHOSPHINES WITH CUPROUS IODIDE 129

A. Introduction 129

B. ^{127}I Mössbauer Spectroscopy of $CuI \cdot nP(C_6H_5)_3$ Adducts 132

C. Coordination Chemistry of Phenylphosphine with Cuprous Iodide 140

(i) $CuI \cdot C_6H_5PH_2$ 140

(ii) $CuI \cdot 2C_6H_5PH_2$ 143

(a) Structure of Tetrakis(phenylphosphine)di-μ-iodo-dicopper(I) 147

D. Interaction of PH_3 with CuI 167

Page

CHAPTER 5 -- CONCLUSION 171

A. NMR of the Main Group Phenylhydrides and Their Anions 171

(i) Summary and Discussion 171

(ii) Future Work 182

B. Some Coordination Chemistry of PH_3 and $C_6H_5PH_2$ 188

LIST OF TABLES

Table		Page
1.1	Reported 'pKa' values for hydrides and organohydrides of some group 4B and group 5B elements.	7
3.1	^{1}H chemical shifts	69
3.2	^{13}C chemical shifts of group 5B phenylhydrides and anions	92
3.3	^{13}C chemical shifts of silanes, germanes and their anions	100
3.4	Relative ^{13}C chemical shifts, indicative of substituent resonance effects	115
3.5	^{31}P NMR parameters	118
4.1	^{127}I Mössbauer parameters	136
4.2	Crystal and diffraction-data-aquisition parameters for $[CuI(C_6H_5PH_2)_2]_2$.	148
4.3	Atomic positional coordinates for $[CuI(C_6H_5PH_2)_2]_2$	152
4.4	Anisotropic atomic temperature factors for $[CuI(C_6H_5PH_2)_2]_2$	154
4.5	Selected least squares planes and dihedral angles for $[CuI(C_6H_5PH_2)_2]_2$	157
4.6	Interatomic distances for $[CuI(C_6H_5PH_2)_2]_2$	161
4.7	Bond angles for $[CuI(C_6H_5PH_2)_2]_2$	162

LIST OF FIGURES

Figure		Page
2.1	Apparatus for trap to trap distillation of volatile hydrides	17
2.2	Vessel for the preparation of NMR samples	19
2.3	Vessel with break-seal attachment	20
2.4	Experimental and simulated ^1H NMR spectrum of C_6H_5NHNa	35
3.1	Classification of effects contributing to substituent chemical shifts	45
3.2	Position labels for a monosubstituted benzene	54
3.3	^1H NMR spectrum, aromatic region, of the solution resulting from the reaction of triphenylphosphine with sodium in THF	64
3.4	Observed and simulated ^1H NMR spectrum of $(C_6H_5)_2NNa$	67
3.5	Schematic diagram of phenyl-proton chemical shifts	71
3.6	Plot of para-^{13}C versus para-^1H substituent chemical shifts	76
3.7	Plot of meta-^{13}C versus meta-^1H substituent chemical shifts	80

Figure		Page
3.8	Plot of ortho-^{13}C versus ortho-^{1}H substituent chemical shifts	82
3.9	Schematic diagram of phenyl-^{13}C chemical shifts of group <u>5B</u> phenylhydrides and anions	90
3.10	^{13}C NMR spectrum of C_6H_5PHNa	91
3.11	Example of selective ^{1}H-decoupling of a ^{13}C NMR spectrum	94
3.12	Off-resonance ^{1}H-decoupled ^{13}C NMR spectrum of $C_6H_5PH_2$	95
3.13	Concentration dependence of ^{13}C chemical shifts of C_6H_5PHNa in THF	98
3.14	Schematic diagram of ^{13}C chemical shifts of arylgermanes and anions	102
3.15	Graph of ipso-^{13}C substituent chemical shifts of phenylhydrides versus the degree of phenyl-substitution	105
3.16	Graph of ortho-^{13}C substituent chemical shifts of phenylhydrides versus the degree of phenyl-substitution.	110
3.17	Concentration and temperature dependence of the ^{31}P chemical shift of C_6H_5PHNa in THF	120

Figure		Page
3.18	Plot of the change in pKa per phenyl-substituent versus $\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$ for the monoanions	128
4.1	Known geometries of cuprous halide:tertiary-phosphine adducts	134
4.2	^{127}I Mössbauer spectra	138
4.3	Experimental and simulated ^{31}P NMR spectrum of $[CuI(C_6H_5PH_2)_2]_2$ in THF at -97°C	144
4.4	Stereoscopic diagram of the packing of molecules of $[CuI(C_6H_5PH_2)_2]_2$	155
4.5	Molecular structure of $[CuI(C_6H_5PH_2)_2]_2$	160
5.1	Rough guide to ^{13}C substituent chemical shifts of monosubstituted benzenes with 'π-donor' substituents	176
5.2	Calculated π-electron distributions for some monosubstituted benzenes	178
5.3	Simplified perturbation molecular orbital diagrams for the interaction of filled π-orbitals on the substituent with those of the phenyl-ring	180

CHAPTER 1

INTRODUCTION

The term 'hydride' is formally used to indicate a compound of hydrogen in which the hydrogen atom has a partial negative charge. The same term however is also frequently used to refer to any member of the entire spectrum of hydrogen compounds regardless of the sign of polarization at the hydrogen atom. It is in this latter sense that the word 'hydride' is used in this thesis.

Compounds of hydrogen can be divided into four general classes of hydrides according to where the element, to which hydrogen is bonded, occurs in the periodic table (Shaw, 1967; Wiberg, 1971). First there are the compounds of hydrogen with the alkali metals or alkaline earths, groups 1A and 2A. These compounds are classed as 'ionic hydrides'. They are high-melting, salt-like solids, of M^+ or M^{2+} with H^-, possessing structures similar to the analogous halides. These hydrides are denser than the elemental metals from which they are made. The hydrides of beryllium, magnesium and aluminum are considered to be borderline between the ionic and covalent hydrides (see below) and display properties intermediate between the two. Second, many lanthanide, actinide or transition metals and their alloys absorb hydrogen under various conditions of temperature and pressure to form a class of compounds which may be referred to as 'metal hydrides'. Unlike the ionic hydrides these compounds generally have lower density than the elemental metals. These compounds are often non-stoichiometric and frequently retain metallic properties. Compounds of this type have recently been under investigation for use in hydrogen storage systems (Sandrock, 1980).

A third class of hydrides includes molecular transition metal complexes which contain hydrogen bonded to the metal atom. These are often volatile compounds and may possess properties reminiscent of the main-group-element covalent hydrides (see below). The current interest in transition metal cluster compounds, some of which contain encapsulated or interstitial hydrogen atoms (Bau, 1979) may provide a bridge of understanding between molecular hydrides and the 'metal hydrides' mentioned above.

The fourth general class of hydrides are those of the main group elements, <u>3B</u>, <u>4B</u>, <u>5B</u>, <u>6B</u> and <u>7B</u>. These are the 'covalent hydrides' and the monomers characteristically are molecular gases or liquids. This thesis deals with hydrides of this class. In these molecules the hydrogen atom may be either slightly negatively or slightly positively charged depending upon the electronegativity of the element to which it is bonded. The various covalent hydrides display considerable diversity as a consequence of differences in the valency, electronegativity and size of the central atoms, however they may show common features in their chemistry. For example, almost all of the covalent hydrides can be made to add across a multiple bond, e.g.,

The conditions, pathway and selectivity of such reactions however, are dependent upon the polarity of the bond to hydrogen in these compounds. A classic example of this is the 'Markovnikov' or 'anti-Markovnikov' additions of hydrobromination or hydroboration respectively.

Division of the covalent hydrides into two categories based on their hydridic or protonic nature may be qualitatively achieved by comparison of the electronegativities of the elements with that of hydrogen itself. Thus it can be seen that the hydrides of groups 3B, 4B and 5B are all, with the exceptions of methane and ammonia, genuinely 'hydridic', and are poor proton donors but are good reducing agents. Most of these hydrides are highly flammable and are susceptible to spontaneous oxidation in air. The electron deficient group 3B hydrides can show Lewis acid behaviour, forming dative bonds with donor bases. There is evidence that some substituted group 4B hydrides can also show Lewis acid behaviour by valence-shell expansion, cf.

$CH_2FCF_2SiH_3 \cdot N(CH_3)_3$ (Cook, 1966). However, this is not known to occur for the simple binary hydrides of this group.

The compounds of trivalent group <u>5B</u> elements all possess a formally 'non-bonding' pair of electrons and therefore have the potential to act as Lewis bases. For the binary hydrides of the heavier elements, P, As, Sb, however, simple basicity is weak, possibly because the non-bonding pair of electrons may be non-directional. Evidence for this is found in the fact that the H-M-H bond angles are close to 90° -- PH_3, 93.3°; AsH_3, 91.8°; SbH_3, 91.3° (Sutton, 1958) -- indicative of the predominant use of p-orbitals for M-H bonding thus leaving the 'lone-pair' orbital with a high degree of s-orbital character. In fact, all of the binary hydrides of both the groups <u>5B</u> and <u>6B</u> elements, with the exceptions of NH_3 and H_2O, have bond angles near 90° (Gillespie, 1960, and references therein).

For the hydrides of the elements which are more electronegative than hydrogen the H atoms are positively charged. These compounds are good proton donors and can display the feature of 'hydrogen bonding'. It is natural to consider as acids only those compounds which are capable of increasing measurably the concentration of oxonium ions in aqueous solutions. Normally, perhaps only the hydrides of the halogens and chalcogens would be considered as acids. However, in non-aqueous media, under strongly basic conditions even some of the more 'hydridic' compounds of groups 4B and 5B may act as proton donors. It has become increasingly important to know the relative acidities of very weak acids in solvents of low acidity. Such measurements have most frequently been made, usually by spectroscopic methods, by studying the equilibria established when two weak acids compete for a limited amount of strong base (1.1).

$$AH + A'^{-} \rightleftarrows A^{-} + A'H \qquad (1.1)$$

The relative equilibrium acidity of AH relative to A'H, ΔpKa, can then by given by (1.2)

$$\Delta pKa = -\log \left(\frac{[A^{-}][A'H]}{[AH][A'^{-}]}\right) \qquad (1.2)$$

A great deal of work of this general nature has been done to establish an acidity scale for carbon acids (Streitwieser, 1980 and references therein). This is largely because of the importance of the role of carbanions in organic reaction mechanisms. Much less work of this type has been done on the hydrides of the other elements of groups 4B and 5B.

The protonic acidities of the simple binary hydrides of the main group elements are primarily a function of the electronegativities of the elements. Consequently the acidities of the hydrides increase on proceeding across a period of the periodic table from left to right, towards the more electronegative elements. However, the acidities also generally increase upon descending a group of the periodic table. Thus, for example, the acidities of the group <u>6B</u> hydrides follow the order $TeH_2 > SeH_2 > SH_2 > OH_2$. This opposes the trend in electronegativities and is a consequence of the heavier atoms forming weaker bonds to hydrogen (Day, 1969). There have been a few investigations of trends in the acidities of hydrides and organo-hydrides of the heavier group <u>4B</u> and <u>5B</u> elements (Birchall, 1966; Birchall and Drummond, 1972; Issleib, 1965; Terekhova, 1982). Some of the reported pKa values are given in Table 1.1.

It has been determined by NMR spectroscopy (Birchall, 1966; Birchall and Drummond, 1972) that in NH_3 solutions the relative order of acidities for <u>alkyl</u>germanes is $GeH_4 > GeH_3R > GeH_2R_2 > GeHR_3$. Substitution of germane (GeH_4) with <u>aryl</u> groups also caused a decrease in acidity but to a lesser degree. This contrasts with the observation that phenyl-substitution of methane causes a considerable increase in acidity (Streitwieser, 1980). There do not appear to have been any relative acidity studies made on substituted silanes and stannanes, however NMR parameters for some substituted stannanes and their corresponding anions display similar trends to those observed for the germanes (Birchall, 1975).

Alkyl-substitution of arsine (AsH_3) or phosphine (PH_3) similarly was found to cause a reduction in their respective acidities (Birchall, 1966; Issleib, 1965). It has been reported however that in THF solution phenyl-substituted

Table 1.1. Reported 'pKa' values for hydrides and organohydrides of some group 4B and group 5B elements.[a]

Methanes (in DMSO)

CH_4	~ 55[b]
$C_6H_5CH_3$	42[c]
$(C_6H_5)_2CH_2$	32.2[d]
$(C_6H_5)_3CH$	30.6[d]

Amines (in DMSO)

NH_3	~ 41[b]
$C_6H_5NH_2$	30.7[d]
$(C_6H_5)_2NH$	25.1[e]

Phosphines (in THF[g]/HDO[h]/DMSO[i])

$(C_2H_5)_2PH$	33.7		
$C_6H_{11}PH_2$	32.3		
PH_3		~29	
$C_6H_5(C_2H_5)PH$			27.5
$C_6H_5PH_2$	24.5		22.4
$(C_6H_5)_2PH$	21.7		23.1

Germanes[f] (in NH_3)

$C_2H_5GeH_3$	23.9
$(C_6H_5)_3GeH$	23.2
$(C_6H_5)_2GeH_2$	21.4
$C_6H_5GeH_3$	19.8
GeH_4	17.7

Arsines[g] (in THF)

$(C_4H_9)_2AsH$	31.0
AsH_3	(~27?)[j]
$C_6H_5(C_2H_5)AsH$	23.5
$C_6H_5AsH_2$	22.2
$(C_6H_5)_2AsH$	20.3

[a] Direct comparison of 'pKa' values measured in different solvents may be meaningless since the equilibria may be influenced by ion pairing effects, particularly for the less polar solvent THF, and also because the standards used are different and have been assigned on the basis of different acidity scales.

[b] Algrim (1978) [c] Bordwell and Algrim (1977) [d] Bordwell (1977)

[e] Lebedeva (1977) [f] Birchall and Drummond (1972) [g] Issleib (1965)

[h] Weston (1954) [i] Terekhova (1982)

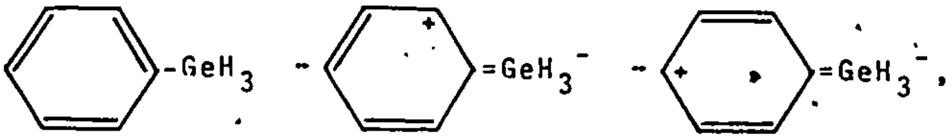
[j] assumed value; Issleib (1965).

arsines and phosphines are more acidic than AsH_3 and PH_3 respectively (Issleib, 1965). The question therefore arises as to what causes the difference between phenyl-substitution of germane (and perhaps other group 4B hydrides) and of those hydrides of the lower group 5B elements P and As, as well as of methane and ammonia.

Some of the conceivable means by which an organo-substituent could decrease the stability of a base (anion) relative to its conjugate acid (neutral hydride) and therefore decrease the acidity of the substituted acid relative to the unsubstituted acid are listed below:

(i) inductive effect of an electron donating substituent (e.g., alkyl groups).

(ii) pπ-dπ donation of electrons from the substituent (e.g. C_6H_5) into empty d-orbitals of the group 4B or 5B element in the neutral hydride, i.e.



etc.

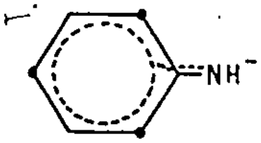
(iii) decreased solvation energy with increased size of anion.

(iv) greater steric crowding of bulky substituents in the anion as a consequence of the large stereochemical influence of the lone pair of electrons.

Conversely, two effects which could increase the stability of the anion relative to the acid thus causing an increased acidity upon substitution are:

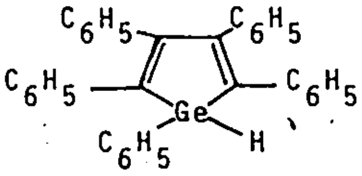
(i) inductive electron withdrawal of the organo-substituent (aryl).

(ii) pπ-dπ delocalization of negative charge of the anion into the π-system of the substituent, e.g.,



The decreased acidity of germane upon alkyl-substitution has been rationalized (Birchall and Drummond, 1972) in terms of inductive electron donation of the substituents, decreased solvation energy for the substituted anions and the stereochemical effect mentioned above. The decreased acidity of germane upon phenyl-substitution has also been attributed largely to the solvation and stereochemical effects. In this case however, the influence of these effects upon the acidity may be opposed by electron withdrawal of the phenyl-groups. This would explain why phenyl-substitution has a smaller effect upon the acidity of germane than does alkyl-substitution. The results of photoelectron spectroscopic studies of compounds of the group <u>4B</u> and <u>5B</u> elements have been interpreted as indicating some d-orbital involvement in the bonding for elements of the third, fourth and fifth periods (Debies, 1974 and references therein). This participation is thought to take the form of 'charge equalization' by back donation of electrons from the ligands into low-lying empty d-orbitals of the central atom. It is not clear, however, whether or not such interactions could lead to stabilizations of phenyl-substituted germanes relative to their corresponding anions of enough magnitude to significantly affect the observed acidities. As indicated above, however, the observed acidities can be rationalized without recourse to d-orbital involvement.

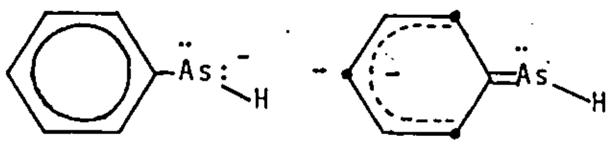
Jolly (1971) has suggested that delocalization of the negative charge of a phenylgermyl anion via pπ-pπ bonding between the ring and germanium will not occur because the formally non-bonding pair of electrons on germanium will occupy an orbital of predominantly s character as a consequence of the large $s^2p^3 \rightarrow sp^4$ promotion energy. This pair of electrons will therefore not have the correct symmetry for π-bonding. Jolly cited as further support for this rationale that no compounds having pπ-pπ double bonds between germanium and carbon were known. It has been noted however that the pentaphenyl-germole,



,

is about 10^6 times as acidic as triphenylgermane (Curtis, 1969). For such a compound the structural restrictions along with the potential added stability of a 6π-electron ring in the anion may make the necessary hybridization of the 'non-bonding' pair of electrons on Ge more favourable. Another observation relevant to Jolly's theory is that the bond angle in the GeH_3^- anion has been estimated to be ~ 93° (Drummond, 1970), which is consistent with the predominance of p-orbitals in the σ-bonding.

Alkyl substitution of phosphine and arsine causes a decrease in acidity for the same reasons as does alkyl substitution of germanes (Birchall, 1966; Issleib, 1965). However the evidence (Issleib, 1965) that phenyl-substitution <u>increases</u> the acidity of the remaining protons of phosphine and arsine may be attributed to resonance stabilization of the anions by delocalization of the negative charge into the phenyl rings. Jolly (1971) notes that, whereas the 'non-bonding' pair of electrons in the phenylgermyl anion may be essentially unavailable for π-bonding, there are two such 'non-bonding' electron pairs in a phenylarside anion at least one of which must have substantial p-orbital character. Therefore a pπ-pπ interaction with the phenyl ring is more feasible for the group <u>5B</u> anions, e.g.



This delocalization along with the inductive effect of the phenyl group would presumably be sufficient to overpower the other influences opposing increased acidity.

The above discussion shows how organo-substituents can affect the acidities of some hydrides of the groups 4B and 5B elements. The possible rationale for the observed trends have also been summarized. It is desirable to find corroborative evidence for such rationale so as to lend weight to predictions based upon these ideas. The bulk of this thesis consists of a nuclear magnetic resonance investigation of phenyl-substituted hydrides of groups 4B and 5B as well as of their mono-anions.

It should be pointed out that the labelling of a molecular fragment as a 'substituent' is somewhat arbitrary and is a question of point of view. The interpretation of the results of this study leans heavily upon discussions of the effects of 'substituents' on the parameters of the benzene ring whereas from the point of view of hydride chemistry it is the effect of the phenyl ring on the main group hydride which is of interest. It can be seen that a substituents-effect type of analysis is a two-way door in which the influences of two molecular fragments upon each other should be complementary. Thus the effect of a main group element hydride 'substituent' on the NMR parameters of the benzene ring, when correctly understood, should reflect the effect which the phenyl group has on observable properties of the hydride, such as its acidity. The NMR parameters of the C_6H_5 ring in the compounds studied will be discussed from the standpoint that these compounds are monosubstituted benzenes and therefore, in this context, the 'hydride' fragment of the molecule will frequently be referred to as the 'substituent'.

Theoretical justification for the observed trends could perhaps be found in molecular orbital calculations of energies and electron distributions of the species involved. It has been pointed out however (Libit, 1974) that, because of the complexity of such calculations, even when they yield the correct answer the rationale for this answer may be obscure. Libit and Hoffmann also point out that the concept of substituent effects, which is of vital importance to the practical chemist is not really approached well by these MO calculations since they treat the molecule as a whole and "no set of transferable properties associated with a functional group emerges". The work of Hoffmann and others (cf. Pross, 1981 and references therein) has been directed toward providing a means of understanding substituent effects by use of perturbation molecular orbital theory and may result in new sets of rules which the non-theoretician can apply to the prediction and interpretation of experimental results. Unfortunately, while numerous calculations of substituted benzenes have been made (Pross, 1981 and references therein), few of these have been ionic species and such treatments have not yet been extended to include those compounds having heavier-element substituents which are the subject of this thesis.

A secondary objective of this study was to examine the influence of the phenyl-substituent on the coordinative ability of phosphine. The basicity of phosphine, PH_3, is very low compared to that of ammonia (Henderson, 1960). This could be, as noted above, largely a consequence of the 'non-directionality' of the lone pair of electrons on phosphorus in PH_3. Molecular orbital calculations, which show agreement with observed binding energies for the 'non-bonding' orbitals of NH_3 and PH_3, indicate that the electron density of the PH_3 lone pair orbital in the z direction is lower than that for the analogous orbital of NH_3 over the entire range of radius in which overlap with orbitals of acceptor species may occur (Hamnett, 1977).

PH_3 is a much poorer coordinating ligand to metal ions than is NH_3 (Shaw, 1967). A great number of tertiary phosphine complexes with electron rich transition metals are known however. These ligands may display a greater degree of hybridization of the s and p orbitals of phosphorus than does PH_3 and therefore the 'non-bonding' pair of electrons would have more p-orbital character and therefore be more directed. By far the most commonly used phosphorus ligand is triphenylphosphine $(C_6H_5)_3P$. It has been suggested (Debies,

1974) that the higher basicity of phenyl substituted phosphines compared to PH_3 may arise from back donation of electrons from phenyl p-orbitals into empty d orbitals of phosphorus. It should be noted however that alkyl phosphines are even more basic than arylphosphines. In coordinative interactions phosphine ligands may compensate for their relatively low basicity by their high polarizability and low ionization potentials (Goldwhite, 1981). Also, in theory at least, they have the potential of accepting π-donated electrons from the electron-rich metal atom into empty d orbitals (Emsley, 1976; Malatesta, 1974).

Relatively little work has been reported on complexes of non-tertiary phosphines.

CHAPTER 2

EXPERIMENTAL SECTION

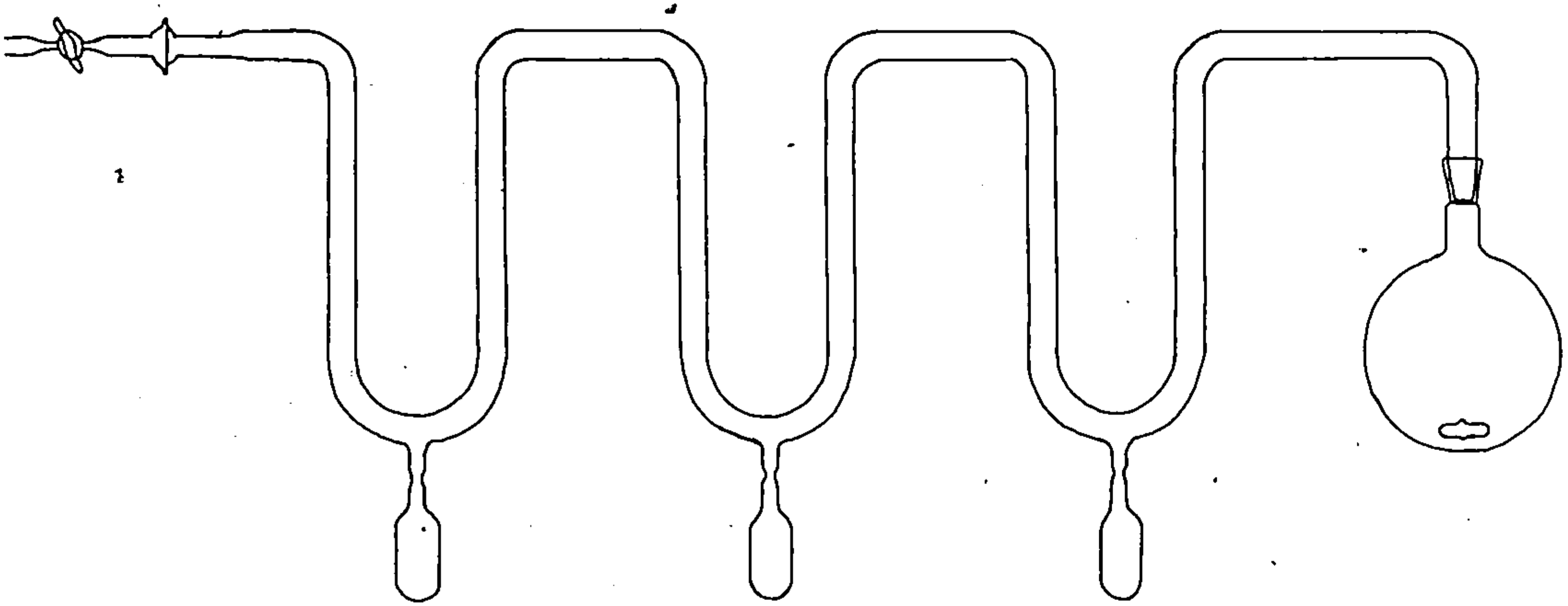
A. Preparative Techniques and Apparatus

(i) Vacuum System

Most preparative chemistry in this work was carried out using a Pyrex vacuum line with all ground-glass high-vacuum stopcocks. A Toepler pump was included in the vacuum system for the measurement of small amounts of gas produced in the reactions. Connections were made to the vacuum system with 9 mm i.d. ball-and-socket ground-glass joints. Joints and valves were sealed and lubricated with Apieson N high-vacuum grease. The vacuum was provided by a Welch Duo-Seal vacuum pump and was enhanced with a mercury-diffusion pump.

Trap-to-trap distillations of the volatile hydrides prepared were carried out in an all-Pyrex jointless section of the vacuum system consisting of "U" tubes with reservoirs (Figure 2.1).

Liquid hydrides, possessing sufficient volatility to be readily distilled under vacuum, were stored in Pyrex vessels equipped with Teflon Rotaflow valves. Less volatile hydrides were stored in glass-sealed Pyrex tubes until used.



7

Figure 2.1: Apparatus for trap-to-trap distillation of volatile hydrides

(ii) Inert Atmosphere System

Many of the hydrides used, particularly those of phosphorus and arsenic, and their derivatives are extremely susceptible to air oxidation. Substances which were insufficiently volatile to be easily transferred on the vacuum line were handled in a dry-nitrogen Labconco glove-box fitted with a constant circulation liquid nitrogen cooled drying system. Materials were transferred to the glove-box via an evacuable port. The atmosphere in the glove-box was supplied from the liquid nitrogen reservoir boil-off or from cylinders of "extra-dry nitrogen" provided by Specialty Gases.

(iii) Reaction Vessels

Preparations of hydrides were carried out in standard reaction apparatus consisting of a three-necked round-bottom flask equipped with magnetic stirrer, reflux condenser, addition funnel with a gas-bypass and a system for flushing dry nitrogen through the vessel and venting it, via the condenser, through a mercury gas-bubbler.

Solutions of anionic species were prepared in a vessel (Figure 2.2) styled on the Dean reaction vessel (Dean, 1974). Reactions involving more than one step were accomplished by making various attachments to the vessel, such as a tube containing the second reagent connected via a break-seal (Figure 2.3). Standard Dean reaction vessels were used for

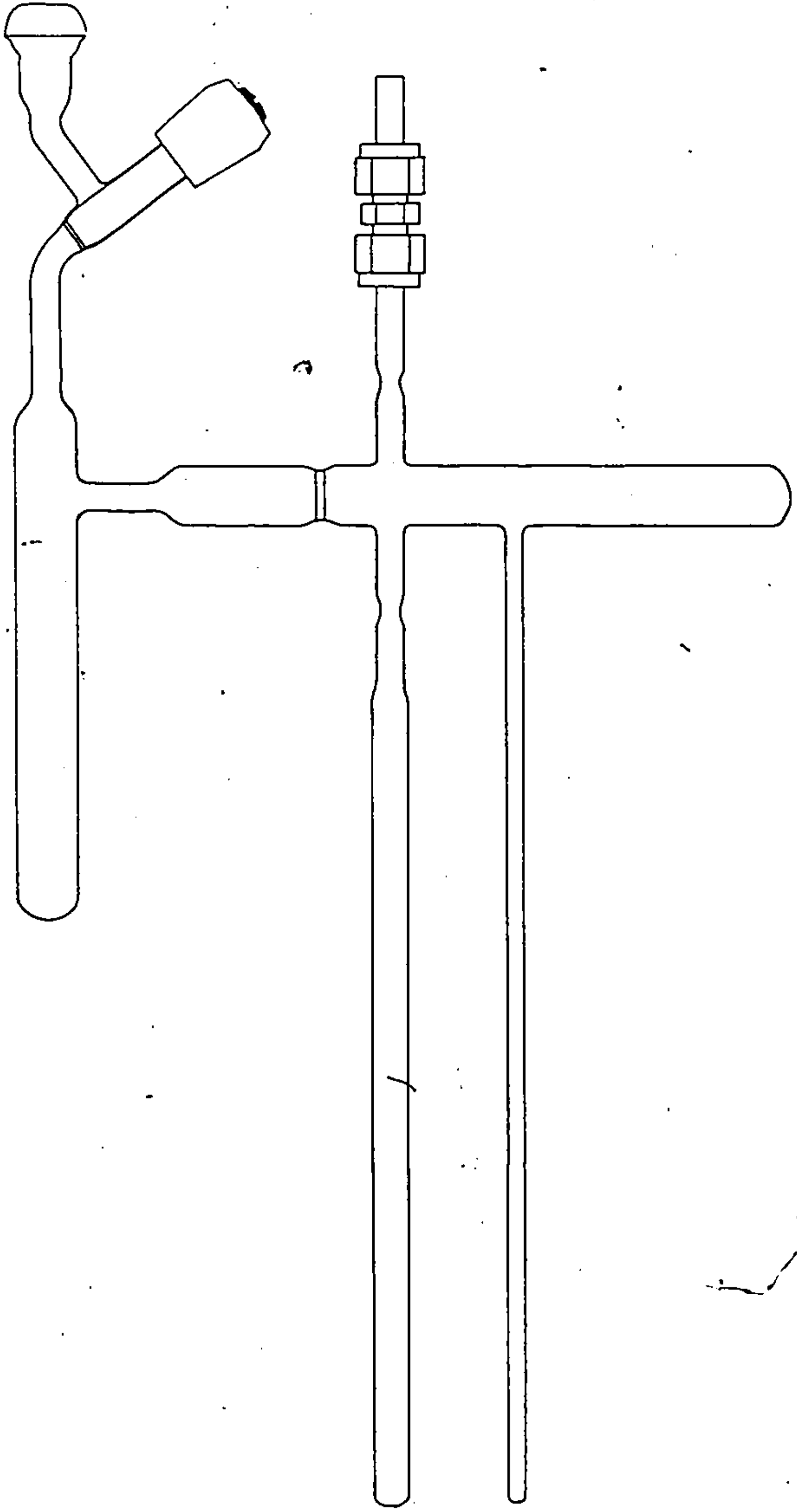


Figure 2.2: Vessel for the preparation of NMR samples

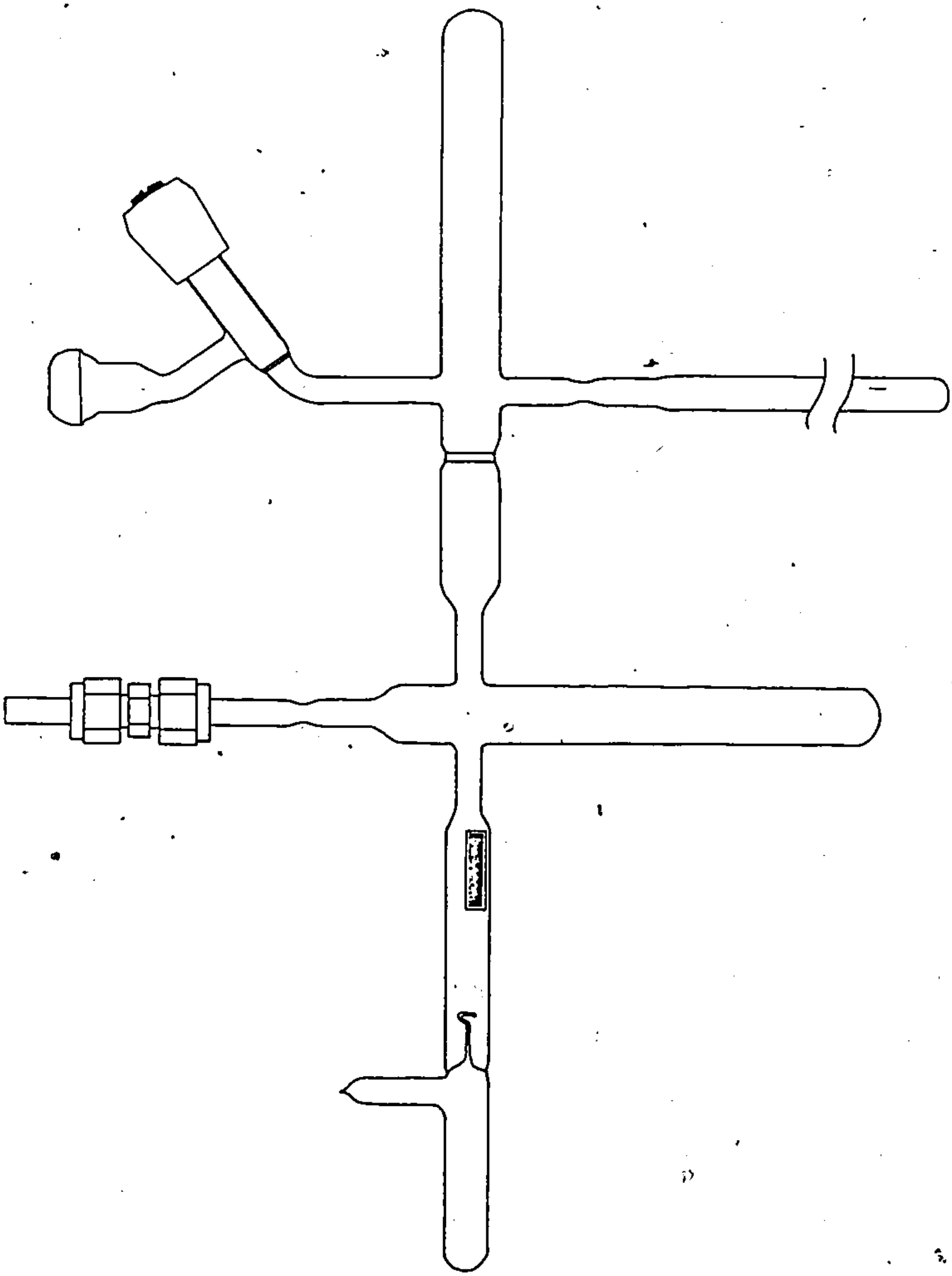


Figure 2.3: Vessel with break-seal attachment for the addition of non-volatile or premeasured amounts of hydrides

various other preparations requiring the exclusion of air. Vessels were dried by flaming with a Bunsen burner while they were under dynamic vacuum.

B. Solvents and Reagents

(i) Purification of Solvents

The two main solvents used in this work were tetrahydrofuran (THF) and liquid ammonia. Tetrahydrofuran (Fischer Scientific) was purified and dried, prior to use, by refluxing under an atmosphere of dry nitrogen for at least 24 h over sodium metal. The THF was then distilled. The pure THF was stirred over lithium aluminum hydride ($LiAlH_4$) for one day and stored over $LiAlH_4$ in a sealed vessel equipped with a Rotoflow stopcock and attached to the vacuum line. Other ether solvents (diethylether, 1,4-paradioxane and diglyme) were treated in an analogous fashion. Liquid ammonia was stored over sodium at -78.5°C until used. It also was transferred on a closed system by vacuum distillation.

Other solvents were used as provided by the supplier without further purification. Deuterated solvents, used in NMR spectroscopy, included D_2O, $DCCl_3$, D_2CCl_2, benzene-d_6 and acetone-d_6.

(ii) Reagents for Synthesis

The following reagents were used with no purification: $C_6H_5PCl_2$, $(C_6H_5)_2PCl$, $(C_6H_5)_3P$, $C_6H_5AsO_3H_2$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $GeCl_4$, $(C_6H_5)_2GeCl_2$, $(C_6H_5)_3GeCl$, $C_6H_5SiCl_3$, $LiAlH_4$, $AlCl_3$, NH_4Cl, $CuSO_4$, NaI, KI, Zn, Hg, Na and K. Aniline ($C_6H_5NH_2$) was purified by vacuum distillation. Diphenylamine ($(C_6H_5)_2NH$) was recrystallized from ethanol. Phosphine (PH_3) (prepared by I. Drummond) was purified by trap to trap distillation on the vacuum line. Germane (GeH_4) (also prepared by I. Drummond) was used without further purification other than routine transferal of this gas on the vacuum line. Tetraphenylgermane ($(C_6H_5)_4Ge$) was recrystallized from toluene.

C. Preparations

(i) Hydrides and Precursors

The purity of all hydrides prepared was confirmed by ^1H, ^{13}C and where applicable ^{31}P NMR spectroscopy. All of the hydrides were stored in sealed vessels under vacuum and appear to be stable at room temperature with the exception of diphenylgermane. This compound decomposes slowly over a period of weeks (Johnson and Harris, 1957) and therefore was generally used shortly after it was distilled or was stored at -78.5°C. Manipulations were carried out either by vacuum-line techniques or in a glove box under dry nitrogen atmosphere. Care was taken to exclude oxygen, especially in the cases of the hydrides of arsenic and phosphorus which are particularly susceptible to oxidation.

(a) Compounds of Group 5B Elements

Phenylphosphine ($C_6H_5PH_2$) was prepared by the lithium aluminum hydride reduction of dichlorophenylphosphine in diethylether (Wiberg and Nöth, 1957; Wiberg and Mödritzer, 1957). It was purified by trap to trap distillation under dynamic vacuum. The phenylphosphine was collected at -30°C.

Diphenylphosphine ($(C_6H_5)_2PH$) was prepared by the reaction of chlorodiphenylphosphine with sodium in liquid ammonia, followed by the addition of excess ammonium chloride. The solution was then filtered and the ammonia removed under vacuum at -78.5°C. The diphenylphosphine was distilled under dynamic vacuum at approximately 80°C and was collected at 0°C. The yield was 50% based on $(C_6H_5)_2PCl$.

Phosphine (PH_3) was available as a result of work performed in this laboratory by I. Drummond (1970). The purity of the phosphine was further ensured by a trap to trap distillation in which any less-volatile materials were condensed at -111°C while the pure phosphine was trapped at -196°C.

Phenylarsine ($C_6H_5AsH_2$) was prepared by the reduction of benzenearsonic acid ($C_6H_5AsO_3H_2$) with zinc-mercury amalgam and concentrated hydrochloric acid (Tzschach, 1964). The product was extracted with diethylether and dried over anhydrous calcium chloride. After evaporation of the ether, the phenylarsine was distilled under dynamic vacuum and was collected at -23°C.

Diphenylarsine ($(C_6H_5)_2AsH$) was prepared by the reaction of triphenylarsine with sodium in liquid ammonia (Mann, 1965) followed by addition of excess ammonium chloride. After evaporation of the ammonia the product was extracted with THF and this solution was filtered. The solvent was then evaporated under vacuum and the diphenylarsine was distilled at approximately 90°C under dynamic vacuum into an ice-water-cooled trap. The yield was 70% based on triphenylarsine.

(b) Compounds of Group 4B Elements

Phenyltrichlorogermane ($C_6H_5GeCl_3$) was prepared by an $AlCl_3$ catalyzed ligand exchange reaction between tetrachlorogermane and tetraphenylgermane in the ratio 3:1 (Rijkens, 1964). The crude product from this reaction was used in the preparation of phenylgermane without further purification.

Phenylgermane ($C_6H_5GeH_3$) was prepared by the reduction of phenyltrichlorogermane with lithium aluminum hydride in diethylether (Kühlein, 1967). The product was purified by trap to trap distillation under dynamic vacuum. The phenylgermane was collected at -30°C.

Diphenylgermane ($(C_6H_5)_2GeH_2$) was prepared by the lithium aluminum hydride reduction of dichlorodiphenylgerman in diethylether in a similar manner to that reported using the analogous dibromide (Johnson and Harris, 1957). The product was purified by distillation under dynamic vacuum. The diphenylgermane was collected at 0°C.

Triphenylgermane ($(C_6H_5)_3GeH$) was similarly prepared from chlorotriphenylgermane (Johnson and Nebergall, 1957). It was purified by recrystallization from methanol; m.p. 46-47°C, literature value (α phase) 47°C (Johnson, 1951).

Tri-para-tolylgermane $(CH_3C_6H_4)_3GeH$ was available as a result of the work of I. Drummond (1970) and was further recrystallized from methanol.

Phenylsilane ($C_6H_5SiH_3$) was prepared from trichlorophenylsilane by the lithium aluminum hydride reduction in diethylether (Benkeser, 1952). The phenylsilane was purified by trap-to-trap distillation under dynamic vacuum and was collected at -35°C.

Diphenylsilane ($(C_6H_5)_2SiH_2$) was earlier prepared by I. Drummond (Benkeser, 1952).

(ii) Preparation of Sodium Salts of Hydrides

All anionic species were prepared as solutions of the sodium salts in liquid ammonia or in ether solvents. These solutions were manipulated in sealed vessels under vacuum as they are very sensitive to oxidation and hydrolysis. All NMR samples of these anions were sealed under dynamic vacuum at -196°C.

(a) Anions of Group 5B Hydrides

Tetrahydrofuran solutions of the monosodium salts of the hydrides of phosphorus and arsenic were prepared by the reaction of each hydride with an approximately 50% excess of sodium metal in THF at, or slightly below, room temperature. The apparatus used to prepare these solutions as NMR samples has been shown in Figure 2.2. In these reactions hydrogen gas is evolved and brightly coloured solutions are formed. The colours of the solutions vary from yellow to orange in the order C_6H_5PHNa, $(C_6H_5)_2PNa$, C_6H_5AsHNa, $(C_6H_5)_2AsNa$. The reactions giving rise to these species are complete within 2 or 3 hours as evidenced by the cessation of hydrogen gas evolution. The reaction of PH_3 with sodium in THF proceeds at a much slower rate. In this case hydrogen was still being evolved after 24 h at which time the remaining PH_3 was removed under vacuum. The PH_2Na solution is lemon-yellow in colour.

The monosodium salts of aniline and diphenylamine were prepared by the reactions of these compounds with sodium in liquid ammonia at room temperature in sealed vessels. These reactions were found to be too slow in tetrahydrofuran. THF solutions of these salts were prepared by allowing the NH_3 solvent to evaporate to dryness under vacuum and then condensing dry THF solvent into the vessel containing the residual sodium salts. Solutions of these anions were only slightly coloured. The $(C_6H_5)_2NNa$ solution was pale-yellow and the C_6H_5NHNa solution was nearly colourless.

All of the above mentioned solutions were filtered and sealed in NMR tubes under vacuum at -196°C. The solutions of the group <u>5B</u> anions all appear to be relatively stable for long periods of time at room temperature. A trace of dark sediment was observed in some samples after a few days, but the amount of this sediment did not increase after storage for several months at room temperature and no changes in the NMR spectra were noted. The sediment is perhaps finely divided sodium or insoluble salts which eluded filtration. It has been noted previously that THF solutions of lithium diorganophosphides showed appreciable reaction with the solvent only after prolonged heating (Grim, 1974). The only solution to show appreciable change on long storage was that of C_6H_5AsHNa. After many months this solution darkens to a deep red colour and a crystalline substance precipitates. The nature of this decomposition was not investigated however it is likely that it involves breaking of the remaining As-H bond in this anion perhaps in a reaction with the THF solvent.

The reaction of triphenylstibine ($(C_6H_5)_3Sb$) with sodium in THF at -63.5°C yields a deep-red-coloured solution. When warmed to room temperature a black solid was deposited from the solution over a period of several hours. The red solution, it is thought, based upon its proton NMR spectrum, initially contains the diphenylstibide anion $(C_6H_5)_2Sb^-$.

In no case was there evidence for the formation of disodium salts in solution (see also Kosolapoff, 1972). The amount of hydrogen gas evolved in reactions of $C_6H_5PH_2$ with large excess of sodium was consistent with equation 2.1.

$$C_6H_5PH_2 + Na \rightarrow C_6H_5PHNa + \tfrac{1}{2}H_2 \qquad (2.1)$$

The NMR spectra for solutions of salts prepared from all species in which there was potentially more than one acidic hydrogen showed that only one hydrogen atom per molecule is displaced in these reactions.

(b) Anions of Group 4B Hydrides

Attempts to prepare sodium salts of the organogermanium hydrides in tetrahydrofuran were unsuccessful. The reactions are much too slow in THF and the tetrahydrofuran solutions of the sodium salts are not stable. Presumably the anionic species react with this solvent or with the neutral starting material. Solutions of the sodium salts in liquid ammonia, however, are relatively stable (Birchall, 1970). These solutions were prepared by adding the appropriate germane via a break-seal (Figure 2.3) to a slight excess of either sodium or sodium amide (generated in situ) in liquid ammonia. The reactions with sodium amide appeared to be cleaner and in both cases solutions of the desired monosodium salts were obtained. These solutions were all light yellow in colour once all of the sodium had been consumed. The ammonia solutions were filtered into the NMR tubes which were then sealed at -196°C.

Clean solutions of simple monoanions of either phenyl- or diphenylsilanes could not be obtained by direct metallation of these hydrides. Reaction of these hydrides with sodium metal in THF is slow at room temperature and initially yields radical anions (Wan, 1972) as evidenced by the formation of a transient green solution. After a period of several days these solutions acquire a reddish-brown colour. ^{1}H-decoupled ^{13}C NMR spectra of these solutions indicate that several species are present. It is known that in reactions of this kind exchange of phenyl-groups occurs and a variety of species may be formed (Wan, 1972). A somewhat cleaner spectrum was obtained from a sample prepared by allowing diphenylsilane to interact briefly with sodium in liquid ammonia at approximately -40°C. The ammonia was then removed on the vacuum line while maintaining the temperature below -25°C. The remaining residue was a resinous orange substance which faded to yellow with continued pumping overnight. When THF solvent was condensed onto this solid and allowed to warm to room temperature the solid in the vessel dissolved to give a bright green solution which quickly faded to an amber-yellow colour while gas was evolved. Slower gas evolution continued for several days. When all gas evolution had apparently ceased (six days) the THF solvent was removed by vacuum distillation and replaced by condensing in fresh THF solvent to ensure that there was no residual ammonia. The resulting solution was filtered and sealed in NMR tubes under vacuum at -196°C. The major peaks in the carbon-13 NMR spectrum of this solution can be assigned to a phenyl group as follows: δ_{C_1} = 146.2 ppm, δ_{C_2} = 136.4 ppm, δ_{C_3} = 127.5 ppm, δ_{C_4} = 126.9 ppm. These resonances most likely correspond to an anionic species as their chemical shifts are closely comparable with those found for $(C_6H_5)_3SiLi$ in tetrahydrofuran (Olah, 1980): δ_{C_1} = 145.0 ppm, δ_{C_2} = 136.1 ppm, δ_{C_3} = 127.5 ppm, δ_{C_4} = 128.4 ppm. Since it is known that direct metallation of diphenylsilane in ether solvents results in disproportionation and the formation of more highly phenylated species (Wan, 1972), it is quite possible that the predominant species in the present solution is $(C_6H_5)_3SiNa$. Attempts to prepare anionic species by the metallation of $C_6H_5SiH_3$ produced only mixtures of products - therefore further pursuit of this matter was discouraged.

(iii) Cuprous Iodide and Its Complexes With Phosphines

(a). CuI was prepared by the addition of sodium iodide solution to aqueous copper (II) sulfate. The insoluble CuI was filtered, washed and dried.

(b) $[CuI \cdot P(C_6H_5)_3]_4$

Equimolar amounts of cuprous iodide and triphenylphosphine were stirred at room temperature in dry, degassed THF in an evacuated Dean reaction vessel for several hours. After approximately 1 h all of the solid dissolved to give a clear solution. With continued stirring the product precipitated. $[CuI \cdot P(C_6H_5)_3]_4$ is almost completely insoluble and was washed several times with the solvent in the reaction vessel by successive filtration and recondensation of the solvent onto the solid product. Finally all of the solvent was removed and the product was dried under dynamic vacuum. M.P. 265°C; literature value 265-7°C (Costa, 1965).

(c) $[CuI]_2[P(C_6H_5)_3]_3$ was prepared by the reaction, in ethanol, of CuI with three equivalents of triphenylphosphine. A mixture of products results from this preparation (Costa, 1965) and the desired product was separated by fractional crystallization from ethanol. M.P. 223°C; literature value 223-6°C (Costa, 1965).

(d) $CuI[P(C_6H_5)_3]_3$ was prepared by the reaction of excess triphenylphosphine with CuI in chloroform (Costa, 1965). The product was recrystallized twice from ethanol/chloroform. M.P. 153-155°; literature value 150-151°C (Costa, 1965).

(e) $[CuI(C_6H_5PH_2)_2]_2$ was prepared by condensing, via the vacuum line, two equivalents of phenylphosphine into an evacuated Dean reaction vessel containing a suspension of cuprous iodide in ethanol. This mixture was stirred for four hours at room temperature by which time a floculent cream-coloured solid had formed. The product was recrystallized in the reaction vessel by the addition of approximately 5% THF to the ethanol solution, warming gently, filtering and allowing the filtrate to cool while slowly evaporating. M.P. 62-64°C; observed density 1.8 g cm^{-3} (flotation in aqueous $ZnBr_2$). The crystals slowly decompose in air and smell of phenylphosphine.

(f) "$[CuI \cdot C_6H_5PH_2]_4$"

Reaction of phenylphosphine with excess CuI in THF followed by filtration and evaporation of the solvent yielded an amorphous, viscous residue. This mass of residue crystallized slowly when immersed in diethylether solvent with needle-like crystals growing out of the mass. These crystals are also air sensitive but less so than $[CuI(C_6H_5PH_2)_2]_2$. Density 2.3 g cm^{-3}. M.P. not determined.

(g) NMR Samples of various stoichiometric ratios of phenylphosphine and CuI were prepared in THF solution and were sealed at -196°C under vacuum. Similar NMR samples of

PH_3 with CuI in THF solution were prepared. When cooled slowly to -76°C crystals of CuI precipitated from these latter solutions.

D. Spectroscopic Methods

(i) NMR Spectroscopy

(a) ^1H NMR. Samples for ^1H NMR were prepared by sealing solutions or neat liquids under vacuum at -196°C in 5-mm or 4-mm o.d. NMR tubes. When 4-mm tubes were used, these were inserted concentrically into 5-mm tubes containing the lock compound. When liquid ammonia was the solvent the sealed NMR tubes were warmed to at least 40°C in a water bath to ensure that the tube was capable of withstanding the internal pressure at the temperature of the NMR probe. The spectra were recorded at both 90 and 80 MHz using a Varian EM-390 spectrometer and a Bruker WP-80 Fourier transform spectrometer respectively. When the latter was used the spectra were ^2H-locked to acetone-d_6 contained in the outer concentric NMR tube. The spectra were accummulated in 8 K of memory at a spectral width of 1200 Hz (0.293 Hz/data point; pulse repetition time 3.408 s) and with a pulse width of 3.5 μs. Chemical shifts were measured relative to neat tetramethylsilane as an external reference.

Simulation of the proton spectra were made using the iterative program Numarit (Worvill, 1975). Initially estimates of the chemical shifts and coupling constants were made from the experimental spectrum and, where these were difficult to obtain, from known general values for monosubstituted benzenes. When a simulated spectrum, which closely resembled the experimental spectrum, was thus obtained it was then possible to assign many of the transitions. The program then adjusted the initial estimates for the coupling constants and chemical shifts by an iterative process until a criterion for convergence (or divergence) of the calculated and experimental line positions was satisfied. In all cases the default values for convergence criteria were used and these were: (i) a maximum fractional decrease of the rms (root mean square) deviation of line positions of 0.01, or (ii) a maximum rms deviation for line positions of 0.01 Hz. In general the first criterion applied. In several cases the degree of resolution of the experimental spectra and the small relative chemical shifts of the different proton resonances did not permit a reliable evaluation of all of the ^1H-^1H coupling constants. In these cases some of the smaller coupling constants were assigned reasonable values which were not allowed to vary in the iterative process thus allowing extraction of reliable chemical shift values. In general the rms deviation between calculated and assigned experimental line positions was 0.2 Hz or less. An example showing the calculated and experimental spectra for sodium anilide is shown in Figure 2.4.

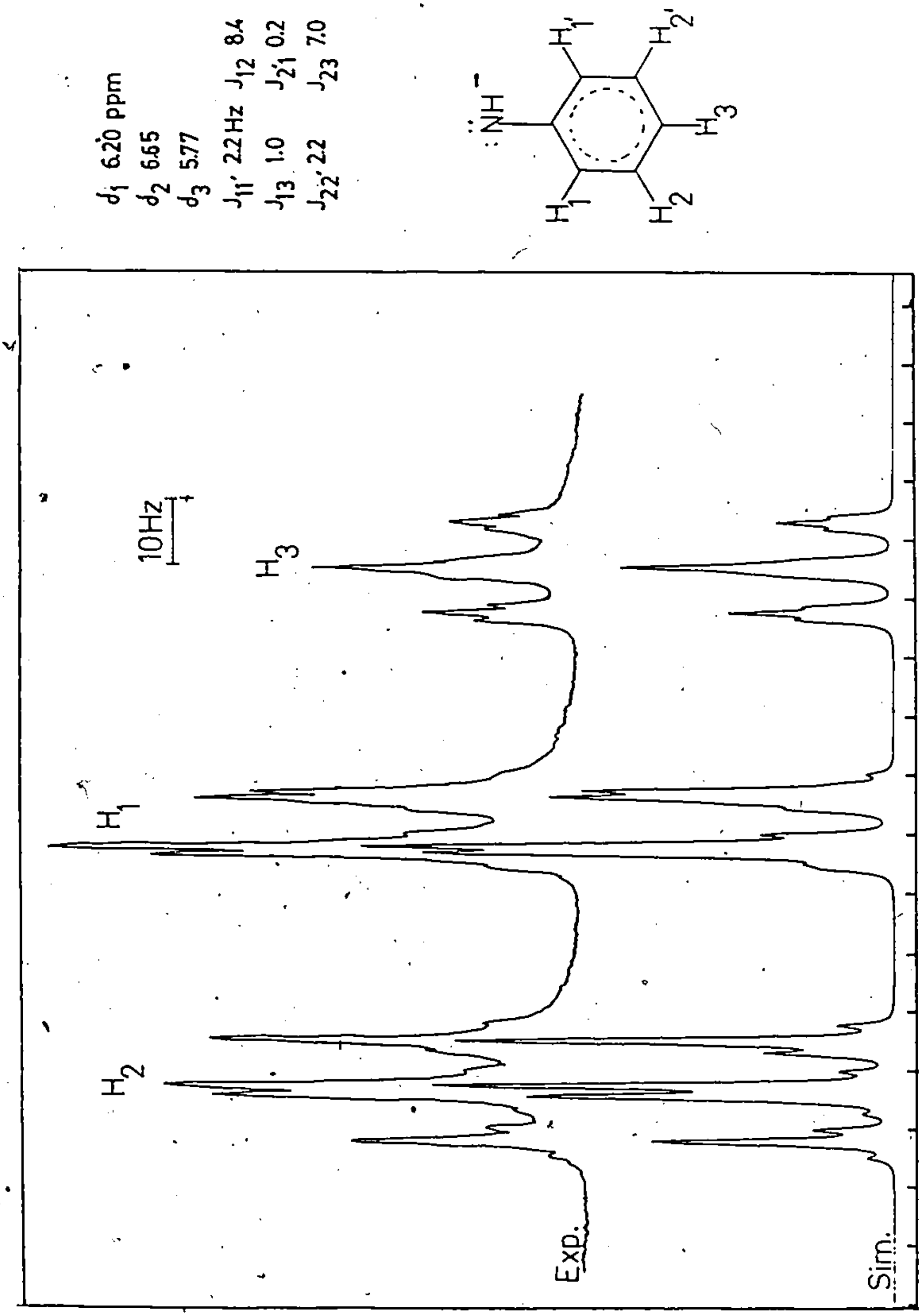


Figure 2.4: Experimental and simulated ^1H NMR spectrum of C_6H_5NHNA; 90 MHz; aromatic region

(b) ^{13}C NMR. Samples for ^{13}C NMR were prepared by sealing solutions or neat liquids in either 8-mm or 10-mm o.d. NMR tubes at -196°C under dynamic vacuum. Samples containing liquid ammonia solvent were warmed to at least 40°C to ensure that the tubes could withstand the internal pressure at the temperature of the NMR probe. When 10-mm o.d. tubes were used C_6D_6 was added as a lock compound. In most cases, however, samples were prepared in 8-mm o.d. tubes which were then inserted concentrically into a 10-mm o.d. tube containing D_2O or $(D_3C)_2CO$ as the lock compound.

The ^{13}C NMR spectra were recorded using a ^{2}H lock, at either 22.62 or 20.115 MHz using, respectively, a Bruker WH-90 or a Bruker WP-80 Fourier transform spectrometer. In either case the spectra were accumulated in 8 K of memory using a spectral width of 6000 Hz (1.47 Hz/data point; pulse repetition time 0.68 s) and pulse widths varying from 1.5 μs to 3.0 μs. Chemical shifts were measured relative to neat tetramethylsilane (TMS) as an external reference. In general the spectra were broad-band decoupled in the ^{1}H region. No systematic investigation of ^{13}C-^{1}H coupling constants was undertaken, however, undecoupled, off-resonance-^{1}H-decoupled and selectively ^{1}H-decoupled spectra were recorded to enable the unambiguous assignment of all ^{13}C resonances.

(c) ^{31}P NMR. Samples for ^{31}P NMR were prepared in the same manner as the ^{13}C NMR samples. The spectra were recorded at 36.43 MHz using the Bruker WH-90 Fourier transform multinuclear spectrometer. The spectra were ^{2}H-locked to acetone-d_6 or D_2O contained in the outer tube when concentric tubes were used or to C_6D_6 when a single 10-mm o.d. tube was used. The spectra were accumulated in 8 K of memory using spectral widths of from 8 to 25 kHz (1 to 6 Hz/data point; pulse repetition time 1.02 to 0.16 s) and a pulse width of 5 μs. Spectra were recorded both proton coupled and broadband decoupled. Variable temperature NMR spectra were obtained using a Bruker temperature controller and the temperature was monitored using a copper constantan thermocouple which was inserted directly into the sample chamber of the probe. Temperatures could be controlled to within ± 1°C. Chemical shifts were measured relative to 85% H_3PO_4 as an external reference.

(ii) Mössbauer Spectroscopy

The Mössbauer spectrometer and the technical details involved in obtaining ^{127}I gamma-resonance spectra have been previously described (Myers, 1982). Samples containing from 15 mg to 75 mg of ^{127}I per cm^2 were prepared. The air-stable compounds were finely ground and if necessary intimately mixed with Al_2O_3 or with Apieson grease. The air-sensitive samples were prepared under dry nitrogen atmosphere. These samples were placed in a 20-mm i.d. threaded Kel-F sample holder and further sealed with Teflon tape.

Spectra were recorded while both sample and source were maintained at liquid helium temperature. The source of gamma radiation was a 20 mCi $Zn^{127m}Te$ emitter prepared by the New England Nuclear Corporation. Count rates varied from 15-30 counts s^{-1} channel^{-1} depending upon the composition and size of the absorber and upon the activity of the source. Typical spectra were recorded in 24-54 h and generally displayed about 1% absorption.

The ^{127}I Mössbauer spectra were computer fitted using a program which incorporates full transmission integral procedures (Ruebenbauer, 1979). In all cases the source linewidth was fixed at 1.27 mm s^{-1}, the natural linewidth, during fitting. The dimensionless absorber thickness, (T_A), the absorber linewidth, isomer shift and where appropriate the quadrupole coupling constant and the asymmetry parameter, eta (η), were allowed to vary. The criteria for goodness of fit employed in the fitting procedure were χ^2 and the misfit value as defined by Ruby (1973). An optimally fitted spectrum has a value of χ^2/degree of freedom of one.

(iii) Infrared and Raman Spectroscopy

(a) The laser Raman spectrometer and auxiliary instrumentation has been fully described previously (Gillespie, 1976). Spectra were recorded at room temperature and at -196°C while spinning the sample tube. The tubes were mounted vertically with the angle between the incident beam and the sample at 45°. The Raman scattered radiation was observed at 45° to the incident beam or 90° to the sample tube direction.

(b) The infrared spectra were recorded using a Nicolet 7199 Fourier transform infrared spectrometer. Samples were prepared by pressing finely ground solid between silver chloride windows.

(iv) X-Ray Crystallography

Crystals of $[CuI(C_6H_5PH_2)_2]_2$ were grown by slow precipitation from ethanol/THF solution. The colourless parallelopipeds or needles are slightly air sensitive and may be unstable to loss of phenylphosphine. Crystals were mounted in dry Lindeman capillaries which were sealed under an atmosphere of dry nitrogen.

Alignment and zero layer precession X-ray photographs of the crystals were taken. Instrumentation and data acquisition technique for crystal structure determinations have been extensively described elsewhere (Turner, 1976). Diffractometer data collection was kindly performed by R. Faggiani, using a Syntex $P2_1$ automatic diffractometer.

The theory and practice of single crystal structure determination has been described in detail in various textbooks (Stout, 1968; Woolfson, 1970). The structure was solved using conventional heavy-atom, Patterson and Fourier synthesis methods with the program SHELX (Sheldrick, 1976).

Auxiliary programs used were from the XRAY package of crystallographic programs (Stewart, 1976). Scattering curves (Cromer and Waber, 1974) and anomalous dispersion corrections (Cromer, 1974) for Cu and I were taken from the 'International Tables for X-Ray Crystallography'. Scattering curves for the other atoms were included in the SHELX program. All calculations were performed on a CDC 6400 or Cyber 170/730 computer.

CHAPTER 3

NMR OF PHENYL-SUBSTITUTED HYDRIDES AND ANIONS OF MAIN GROUP ELEMENTS

A. Introduction

The initial objective of this work was to establish the nature of the electronic interactions between the aromatic rings and the main group substituents in phenyl hydrides of the elements of groups 4B and 5B and in their corresponding monoanions. Furthermore it was hoped that the importance of such interactions to the relative thermodynamic stabilities of these species might be inferred by comparison of the NMR parameters with the known relative acidities of the 'hydrides'. In particular, confirmation was sought of a relationship between mesomeric effects in the anions and the relative acidities of the corresponding neutral hydrides in order to determine whether or not differences in the effect of phenyl-substitution on the acidities of, for example, arsines as opposed to germanes, could be accounted for by differences in resonance stabilization of the anions. In order to do this an understanding is required of how changes in electron distribution in a molecule are reflected in its NMR parameters.

Traditionally the idea of a relationship between electron density and the NMR chemical shift has been a driving force in the interpretation of NMR spectra. This work is no exception. This idea is founded in the concept of electronic shielding, caused by induced cycling of the electrons giving rise to differing net magnetic fields at different nuclei in a molecule. Simplistically therefore, an increase in the electron density around a particular nucleus would cause an increase in the shielding of that nucleus from the external magnetic field thus causing it to resonate at a lower frequency. The formulation of chemical shift scales is well known (Becker, 1980) and will not be further discussed except to state that the convention used throughout this work is the commonly accepted one which defines a positive chemical shift (δ, ppm) as one to lower field strength (deshielded) or higher frequency.

In actual fact the picture of electronic shielding described above is a gross simplification since in general nuclei in molecules are not surrounded by perfectly spherical electron distributions and the magnetically induced cycling of these electrons is not necessarily isotropic with respect to different orientations of the molecule. A more sophisticated description of shielding is required in order to arrive at a better understanding of the chemical significance of the chemical shift. Conceptually changes in the shielding can be seen as arising from a number of different effects.

First the breakdown of the shielding of a nucleus in a real molecule into its component contributions will be considered and then the specific application of these concepts to ^1H and ^{13}C chemical shifts in monosubstituted benzenes.

(i) Substituent Chemical Shifts

The absolute chemical shift for a particular nucleus is seldom of chemical interest. Of more significance is the change in chemical shift when a change in the structure of a molecule is made. The chemical shift difference between a nucleus in a substituted molecule relative to the analogous nucleus in the 'unsubstituted' parent compound is referred to as the substituent chemical shift (SCS), denoted by the symbol S (ppm).

Raynes (1971) has pointed out that the often used concepts of local and non-local contributions to the shielding of a given nucleus are perhaps misleading because some of the so-called non-local contributions operate by indirectly affecting the local distribution of valence electrons about the nucleus. In a sense all substituent chemical shifts could be considered as arising from a sum of non-local effects. Raynes preferred to divide these into 'direct' contributions -- those which contribute directly to the shielding without affecting the local electron distributions -- and 'indirect' contributions -- those which cause a change in local electron distributions and thus in the shielding caused by the induced cycling of these electrons. A further subdivision of these classifications was suggested to distinguish between contributions from 'through-bond' or from 'through-space' effects (Figure 3.1); (Raynes, 1971). In this work it is of particular interest to identify the contributions to the substituent chemical shifts from resonance, inductive and electric field effects. In general intramolecular effects are of most importance but intermolecular effects can also contribute to the observed chemical shifts.

Ramsey (1950) derived a theoretical expression for the total shielding contribution arising from the local distribution of electrons about the nucleus. In practice rigorous calculations based on this expression are not generally feasible however an approximate statement of Ramsey's equation, first suggested by Saika and Slichter (Saika, 1954), more readily permits a 'physical understanding' of how changes in local electron distribution affect the shielding. Thus this expression may suggest or facilitate the explanation of correlations between experimental chemical shifts and other measurable or calculable parameters.

The total shielding, σ, may be given as the sum of three terms (Saika, 1954) (3.1).

$$\sigma = \sigma_D^{loc} + \sigma_P^{loc} + \sigma' \qquad (3.1)$$

	Through-bond:	Through-space:
Direct:	Contact shifts.	Neighbouring group magnetic anisotropies; ring currents.
Indirect:	Inductive effects; Resonance effects.	Electric field effects; Van der Waals and steric effects.

Figure 3.1: Classification of Effects Contributing to Substituent Chemical Shifts (Raynes, 1971) (slightly altered)

The diamagnetic contribution, σ_D^{loc}, depends upon the spherical electron density about the nucleus (Lamb, 1941) (3.2) (Karplus, 1963).

$$\sigma_D^{loc} = (e^2/3mc^2) \sum_i \langle r_i^{-1} \rangle \qquad (3.2)$$

$\langle r_i^{-1} \rangle$ is the mean inverse distance of the i^{th} electron from the nucleus. The paramagnetic term, σ_p^{loc}, arises from non-spherical electron distribution and as the name implies operates to enhance the external magnetic field at the nucleus (3.3) (Karplus, 1963; Pople, 1962).

$$\sigma_p^{loc} = -[e^2\hbar^2/2m^2c^2(\Delta E)] \langle r^{-3} \rangle_p \sum_B Q_{AB} \qquad (3.3)$$

ΔE is a mean value for the electronic excitation energies. $\langle r^{-3} \rangle_p$ is the mean of the cubed inverse of the distance of the valence p electrons from the nucleus -- the expression assumes the absence of valence d electrons. $\sum_B Q_{AB}$ may be referred to as the electron imbalance and depends upon the hybridization about the nucleus under consideration (A) and the bond orders to neighbouring atoms (B).

Unlike σ_D^{loc}, σ_p^{loc} is not simply related only to electron density. For nuclei in a series of compounds of similar structure, however, the ΔE and $\sum_B Q_{AB}$ terms may be nearly invariant (Karplus, 1963). For such series σ_p^{loc} may display a correlation with electron density based upon the $\langle r^{-3}\rangle_p$ term in the expression. An increase in electron density would result in expansion of the valence p orbitals thus reducing $\langle r^{-3}\rangle_p$. Consequently the dependence of σ_p^{loc} on electron density has the same sign as does that of σ_D^{loc}. Therefore for nuclei in a series of compounds of similar structure it is not unreasonable to expect a dependence of the chemical shifts on charge density provided the effects of neighbouring magnetic anisotropies are negligible or can be accounted for. These latter contributions are represented by σ' in equation (3.1).

The apparent dependence of certain chemical shifts in substituted benzenes on electron density has been demonstrated by various correlations between ^1H, ^{13}C or ^{19}F chemical shifts in these systems with calculated charge densities or with substituent parameters such as Hammett σ-values[*] (Ewing, 1978).

The question now arises of how substituents affect electron densities at remote sites in a given molecule. Of particular interest to the present study are substituent effects in monosubstituted benzenes. Even for these

---

[*] It is unfortunate that the letter 'σ' by common usage may refer to either the NMR shielding constant, Hammett substituent parameters or to sigma symmetry as in σ-bonds. It is used in all three of these meanings in this chapter however the use of subscripts or superscripts as well as the context should be sufficient to avoid confusion.

extensively studied systems the problem of parameterizing the effects of substituents is not a simple one. Topsom (1976) has described seven mechanisms by which a substituent's electronic effects can be transmitted throughout a molecule. These are as follows:

(a) σ-inductive effect -- a through σ-bond effect which rapidly diminishes with the number of bonds.

(b) field effect -- a through space electrostatic polarization of σ-bonds as a result of the polarity introduced by the substituent.

(c) σ-induced π effect -- a redistribution of π-electrons as a result of the changed σ-electron distribution.

(d) field-induced π effect -- a direct polarization of π electrons by the polar substituent.

(e) mesomeric or resonance effects (charge delocalization).

(f) π-induced σ effect -- a redistibution of σ-electrons as a result of large changes in the π-electron distribution.

(g) π-orbital effect -- a redistribution of π-electrons resulting from repulsions between the π-system and filled π-orbitals on the substituent.

In general, as pointed out by Vorpagel et al. (1981), these effects are not as yet completely separable and are usually divided into two broadly defined categories. The first four mechanisms are grouped together as effects which arise from the substituent's polarity and are called the 'field' effect or sometimes 'inductive' effect. The second category includes those effects which have their origin in the substituents charge-transfer ability as in the delocalization of electrons. This is generally called the 'resonance' effect. The π-orbital effect can be seen as contributing partially to each of these two general effects and is not usually considered separately.

The division of substituent effects into the field and resonance contributions has been the basis for a great deal of research and discussion in physical organic chemistry. This has led to 'dual substituent parameter' (DSP) analyses (Ewing, 1978 and references therein) of chemical shifts of nuclei in substituted aromatic molecules. In these treatments the substituent chemical shift of a particular nucleus is considered to be equal to a linear combination of the 'inductive' and 'resonance' substituent parameters as determined from linear free-energy relationships (3.4).

$$\delta = \rho_I \sigma_I + \rho_R \sigma_R + \text{constant} \qquad (3.4)$$

If substituent chemical shifts are used the constant in equation (3.4) should be close to zero since the substituent constants for the -H substituent are by definition equal to zero. Application of the results of such analyses to the molecules in the present study could, in principle, allow the determination of the magnitudes of resonance and field effects of the substitents. DSP analyses, however, are still the centre of controversy and the qualities of the correlations obtained are such that estimation of new σ_I and σ_R parameters by this method may involve large statistical errors. Also the relative and absolute values of the coefficients in equation (3.4) will be solvent dependent.

A more qualitative analysis may be achieved by consideration of the relative chemical shifts of the different nuclei within the same molecule. For instance, the substituent chemical shifts for nuclei in the meta position of the monosubstituted benzene will have relatively little contribution from resonance effects while those for nuclei in the para position will be dominated by resonance effects.

Contributions to chemical shifts arising from non-bonded interactions such as intramolecular van der Waals attractions (Schaefer, 1963) or steric repulsions (Grant, 1967) may also be considered as indirectly affecting the local electron distributions (Figure 3.1) although chemists do not usually think of these as 'electronic effects'. These influences may not be considered within the approximation of structural invariance at the nucleus in question, so that when variations in the extent of close non-bonded contacts are in effect the substituent chemical shifts will not show a simple dependence on electron density. Van der Waals interactions are thought to have in general a deshielding effect (Schaefer, 1963) but in practice this effect is not clearly separable from accompanying steric and magnetic anisotropic effects.

A brief summary of the state of understanding of substituent chemical shifts might be that for nuclei close to the substituents the origins of observed chemical shifts are not yet well understood although isolated comparisons for closely similar systems may be attributed to one effect or another. For nuclei more remote from the substituent the chemical shifts often display an apparent dependence upon local electron density provided nuclei in similar structural environments are being considered. The local electron densities will in turn depend predominantly upon resonance and electric field effects.

B. ^{1}H NMR

Variations in the local shielding for the ^{1}H nucleus depend predominantly on the diamagnetic term in equation (3.1). The paramagnetic term varies negligibly in general because of the relatively large values of the excitation energies (Raynes, 1974). Thus the local shielding of the ^{1}H nucleus is a function of the local electron density. Substituents in a molecule may indirectly affect σ_D^{loc} by causing an increase or decrease in the electron density at the proton in question either by 'field' or 'resonance' mechanisms which affect the electron balance in the C-H bond. For protons in contact with bulky substituents however, there may be contributions to the shielding resulting from changes in σ_p^{loc}.

Unfortunately the range of ^1H chemical shifts caused by changes in σ_D^{loc} is small so that direct contributions to the net shielding from the substituents' group magnetic anisotropies may be significant. Direct solvent effects may also play a significant role in ^1H NMR (Emsley, 1965). These effects are often minimized by measuring the chemical shifts of the substrate at various degrees of dilution in a 'non-interacting' solvent and extrapolating to infinite dilution (Hayamizu, 1969). When this is not practical the less satisfactory method of using relatively dilute solutions in a common solvent is often used when comparing ^1H chemical shifts for different species. This approach, employed in the present study, aims to systematize solvent effects to some extent and also eliminates the necessity of making corrections for solvent diamagnetic susceptibility when comparing chemical shifts of different molecules.

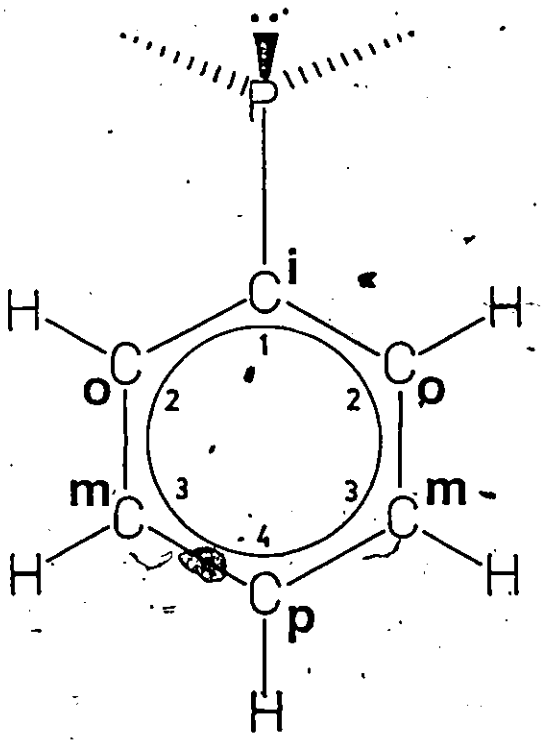
(i) Monosubstituted Benzenes

^{1}H chemical shifts have not been used as extensively as have ^{19}F and ^{13}C chemical shifts in the quantitative study of substituent effects in monosubstituted benzenes (Ewing, 1978). The reasons for this are the relative importances of magnetic anisotropies and direct solvent effects on ^{1}H chemical shifts mentioned above. Also, the proton spectra are complicated by second order homonuclear spin-spin couplings which make analyses of the spectra non-trivial.

The effects which are of major importance to the substituent chemical shifts of the different ring-hydrogen nuclei are summarized below. Figure 3.2 shows the common labels for the four positions of a phenyl ring.

(a) Ortho Proton

Substituent chemical shifts for ortho protons in monosubstituted benzenes are the least well understood of the phenyl proton chemical shifts. This is because not only are resonance and inductive effects important at this position but the group magnetic anisotropy of the substituent, electric field effects as well as steric and van der Waals influences may all make significant contributions. There do not appear to be any good single correlations between ortho ^{1}H SCS and either calculated electron densities or empirical substituent parameters. Dual substituent parameter analyses



i = ipso
o = ortho
m = meta
p = para

Figure 3.2: Position Labels for a Monosubstituted Benzene

appear to account reasonably well for the ortho proton chemical shifts in terms of only 'resonance' and 'field' contributions (Charton, 1971) (3.5).

$$\delta(H_o) = 0.64\,\sigma_I + 1.27\,\sigma_R + 0.186 \qquad (3.5)$$

However the quality of such correlations is much improved when bulky substituents are omitted (Hayamizu, 1969). It was concluded in the later study (Charton, 1971) that steric effects were not important in determining the ortho-^{1}H SCS because inclusion of a steric parameter (van der Waals radius of the substituent) in a triple parameter analysis of the chemical shift did not improve the correlation. Consequently it was decided that substituent magnetic anisotropies largely account for deviations from the correlation. It may be, however, that the simple van der Waals radius is not the best parameter with which to quantify steric effects on the chemical shift.

Another approach to the interpretation of ortho-^{1}H chemical shifts is based upon the observation of good correlations with the semi-empirical parameter Q (Hruska, 1965) (3.6), for the series of halogen-monosubstituted benzenes (C_6H_5X).

$$Q = P/Ir^3 \qquad (3.6)$$

P is the polarizability of the C-X bond; I is the first ionization potential of X; r is the C-X bond length. The significance of this parameter, Q, is uncertain although it was originally intended to be related to the paramagnetic shielding produced by the mixing of excited states of the substituent with the ground state electrons of the ortho C-H bond. It may also reflect to some extent the magnetic anisotropies of the substituents (Ewing, 1978).

Since 3.6 can only be evaluated for hydrogen or the halogen substituents, the parameter, Q, has been estimated from NMR data for most other substituents (Smith, 1967). Inclusion of this parameter along with 'field' and 'resonance' parameters in triple parameter linear analyses of ortho-^{1}H chemical shifts results in a significant improvement over correlations involving only the 'field' and 'resonance' parameter (Smith, 1970). It is not yet clear whether such treatments will be a genuine aid in the separation of polar and resonance effects at the ortho positions.

To summarize the dependencies of ortho-proton chemical shifts it seems that they depend comparably on 'resonance' and 'field' substituent effects but may also depend significantly on substituent magnetic anisotropies and contributions to the paramagnetic shielding as a consequence of the proximity of this proton to the substituent. Therefore great care must be taken in the interpretation of individual or relative ortho-^1H SCS. In general this shift is of doubtful use in determining the relative magnitudes of polar and resonance substituent effects.

(b) Meta Proton

The meta proton is sufficiently distant from the substituent that its chemical shift will not be influenced by steric effects or dispersion forces associated with the size of the substituent. Genuine inductive effects should be negligible (Topsom, 1976) as these diminish rapidly with increasing number of bonds separating the site in question from the substituent. Also, the effect of the magnetic anisotropy of the substituent should be considerably reduced at the meta position. Contributions to the substituent chemical shift of the meta proton from changes in the paramagnetic shielding term (3.3) appear not to be significant since there is no observed dependence of these chemical shifts on the semi-empirical parameter Q (Hruska, 1965) (3.6).

If all of the above effects are negligible then a dual substituent parameter analysis of the meta-^1H substituent chemical shifts may reveal the relative contributions of 'field' and 'resonance' mechanisms at this position. Such studies have been carried out (Hayamizu, 1969; Hehre, 1976) a sample correlation is shown in equation (3.7) (Hehre, 1976).

$$S_{^1H_{meta}} = 0.24\ \sigma_I + 0.44\ \sigma_R{}^0 \qquad (3.7)$$

It must be pointed out that the coefficients of such correlations are strongly solvent dependent. The relation shown (3.7) was found for shifts extrapolated to infinite dilution in the 'inert' solvent carbon tetrachloride. The transmission of electric field effects as reflected by the coefficient of σ_I in particular depend upon the nature of the solvent. The relative importance of σ_R to the meta-^1H shielding may seem surprising since one would expect the field contribution to be dominant at this position. The observed relation (3.7) might be rationalized on the basis of the π-induced σ effect as described by Topsom (1976) or from an inherent weakness in the dual substituent parameter model. One such weakness may be that the π-interaction between the substituent and the phenyl ring may have a significant effect on the magnitude of the 'ring current'. Substituents which interact strongly with the π-orbitals of the ring diminish the ring current and thus have a partial shielding effect which is of approximately the same value at all ring protons (Yamada, 1970). Therefore, unless the magnitude of this change in the ring-current is known for each substituent, differences in the chemical shifts between different protons within the same species will have more significance with regard to electron distribution effects than the individual substituent chemical shifts. Yamada has shown that this ring-current diminution can be reasonably accounted for by a term proportional to the absolute value of the resonance substituent parameter, $|\sigma_\pi|$ (Yukawa, 1965), in a correlation of the meta-^{1}H SCS with the Hammett substituent parameter, σ_m (3.8).

$$S_{^1H_{meta}} = -0.511\ \sigma_m + 0.509\ |\sigma_\pi|\ \text{(ppm)} \qquad (3.8)$$

Apparently no attempt has been made to account for this effect in the dual substituent parameter analyses involving σ_I and σ_R parameters mentioned above. However, Hehre et. al. (1976) have compared the results of their analysis (3.7) with a similar correlation of the calculated σ-charge at the meta proton (3.9).

$$\Delta q_\sigma^{m-H} = 0.017\ \sigma_I + 0.006\ \sigma_R^{\,o} \qquad (3.9)$$

Comparison of (3.9) with (3.7) shows that the charge, Δq_σ^{m-H}, has relatively little dependence on the resonance parameter compared to the substituent chemical shift, $S_{^1H_{meta}}$. The difference between the two relations is undoubtedly due to the ring-current effect.

(c) Para Proton

For the para-proton substituent chemical shift the main contributions will be from the electron density at the para position and also from the ring-current effect mentioned above. That this chemical shift is highly dependent on the electron density at the para carbon atom is demonstrated by the existence of good correlations with substituent parameters such as σ_p^+, with $^{13}C_{para}$ chemical shifts and with the analogous $^{19}F_{para}$ chemical shifts in fluorinated compounds. The variation in electron density at the para position is dominated by the resonance effect of the substituent as exemplified by the dual substituent parameter relation shown below (Hehre, 1976).

$$S_{^1H_{para}} = 0.27\ \sigma_I + 1.25\ \sigma_R^{o} \qquad (3.10)$$

It must be remembered, however, that the coefficient of σ_R^{o} conceals a contribution from the changes in the ring-current.

To a first approximation the magnitude of the resonance effect may be inferred from the substituent chemical shift of the para proton. Further refinement may involve comparison of this shift with that of the meta proton for which the effects of substituent polarity and of changes in the ring current are of comparable magnitude to those at the para position but the effects due to resonance are considerably reduced. It has been shown that the calculated charge at both the meta and para protons can be related to their substituent chemical shifts by inclusion of a term proportional to the total π-charge transferred to, or from, the ring by the substituent (Hehre, 1976) (3.11).

$$S_{^1H} \propto \Delta q_\sigma^H - 0.14|\Sigma\Delta q_\pi| \qquad (3.11)$$

This is somewhat analogous to Yamada's treatment of the dependence of $S_{^1H_{meta}}$ on σ_m and $|\sigma_\pi|$ (3.8) -- the $|\Sigma\Delta q_\pi|$ term in (3.11) accounting for the effect of the change in the ring current. If such a relationship holds in general then the difference between the para-proton chemical shift and that of the meta-proton should be proportional to the difference in σ-charge densities at these protons since the ring current effect is cancelled out. Similarly the algebraic difference between equations (3.7) and (3.10) should afford the relative dependence of this charge density difference on 'field' and 'resonance' mechanisms. Comparison of these two equations shows that $(\delta_{^1H_{para}} - \delta_{^1H_{meta}})$ is almost exclusively dependent on σ°_R with little contribution from σ_I. This suggests that polar effects are of comparable magnitude at the meta and para protons and that the difference $(\delta_{^1H_{para}} - \delta_{^1H_{meta}})$ is a better measure of the substituent's resonance effect than $S_{^1H_{para}}$ alone.

(ii) Results and Discussion

It has been shown that deprotonation of phenylgermane (Birchall, 1970) or triphenylstannane (Birchall, 1975) results in increased shielding of the meta and para protons while the ortho protons were deshielded in each case. This result was interpreted (Birchall, 1970) as signifying that the dominant effect of the anionic ring substituents in these cases was to polarize the π-electrons of the phenyl group rather than to delocalize the negative charge into the ring. This interpretation was consistent with the observation that phenyl-substitution of germane did not increase the acidity of the remaining protons (Birchall, 1966) because the anions are not stabilized by resonance delocalization of the negative charge. In the present study the phenyl-substituted hydrides of the group 5B elements are similarly investigated to see if the observed increase in acidity of the hydrides (Issleib, 1965) upon phenyl substitution may be related to a resonance delocalization in the anions.

In a preliminary experiment $(C_6H_5)_2PNa$ was generated in THF solution by the reaction of $(C_6H_5)_3P$ with sodium metal. The 90 MHz ^1H NMR spectrum showed, besides a single line attributed to benzene, three complex multiplets, the fine structure of which could not be resolved, (Figure 3.3).

possibly because of line-broadening due to the presence of paramagnetic species or suspended solids in these dark-coloured solutions. A simple homonuclear decoupling experiment, shown in the figure, reveals that the low-field multiplet must be assigned to the ortho protons because it does not display a large coupling to the multiplet at highest field-strength which is clearly attributable to the para proton because of its relative intensity. The relative areas under these multiplets and under the benzene peak are completely consistent with the reaction given by equations (3.12) and (3.13)

$$(C_6H_5)_3P + Na \rightarrow (C_6H_5)_2PNa + C_6H_5^{\bullet} \qquad (3.12)$$

$$C_6H_5^{\bullet} + \text{Solvent} \rightarrow C_6H_6 + (\text{Solvent} - H^{\bullet}) \qquad (3.13)$$

A similar experiment with $(C_6H_5)_3Sb$ did not yield a stable anion at room temperature (see Chapter 2). However the ^1H NMR spectrum of the THF solution, shortly after preparation at reduced temperature, revealed the presence of a species whose ^1H NMR spectrum bore close resemblance to that of $C_6H_5GeH_2Na$ (Birchall, 1970) in the aromatic region. The spectrum of the stibide was not fully analysed because of low resolution and the presence of other unidentified aromatic species. However, the resonances which can reasonably be attributed to $(C_6H_5)_2SbNa$ indicate that the

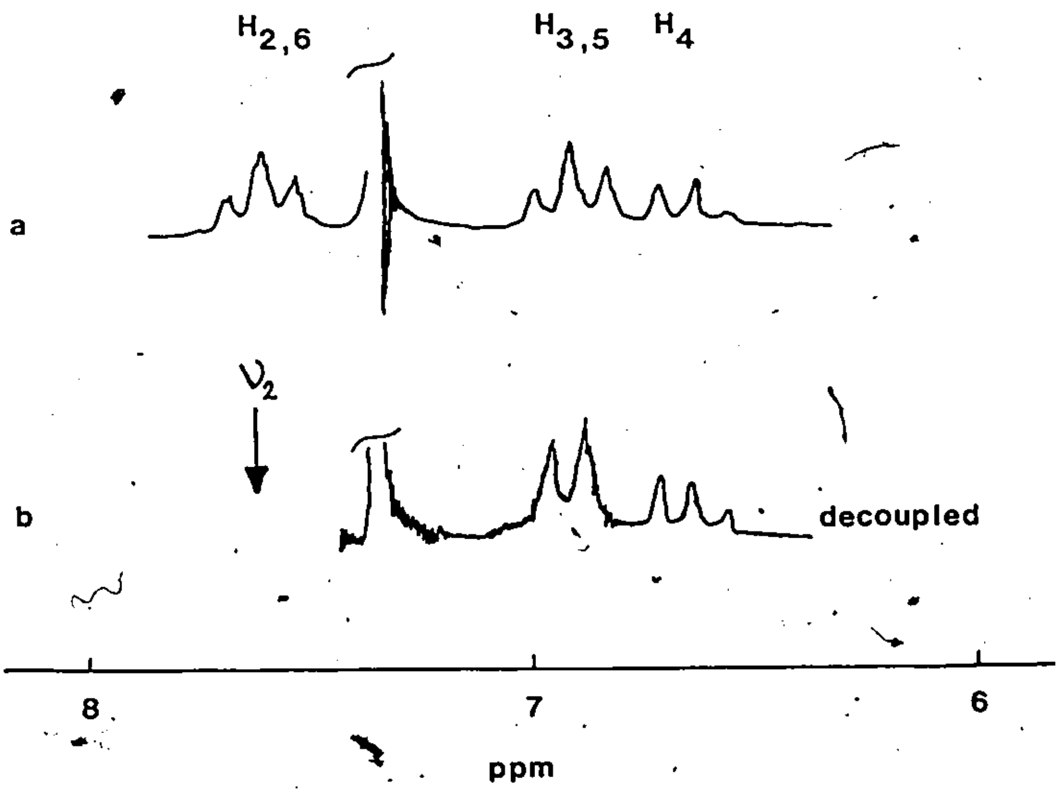


Figure 3.3: Aromatic Region of ^1H NMR Spectrum of $(C_6H_5)_2PNa + C_6H_6$.

(a) Fully coupled spectrum;
(b) Decoupler frequency centred on the low-field multiplet.

ring protons in this species have chemical shifts at: -0.45 ppm ($H_{2,6}$), +0.52 → +0.60 ppm ($H_{3,5}$ and H_4) relative to benzene.

The similar relative positions of the ring-proton resonances in these group 5B anions compared to those found for $C_6H_5GeH_2^-$ (Birchall, 1970) suggested that the electronic interactions of the substituents with the phenyl rings in the group 5B anions might not be significantly different from those in analogous group 4B anions. However it was noted that the para-proton substituent chemical shift of $(C_6H_5)_2PNa$ occurred at somewhat higher field than that of $C_6H_5GeH_2Na$ suggesting that there is possibly greater delocalization of negative charge to the para position in the former species.

It is more appropriate, of course to compare the germanium species with analogous arsenic compounds since these elements belong to the same period. Consequently the complete series of phenyl- and diphenylamines, -phosphines and -arsines along with their respective monosodium salts were studied by ^1H NMR as ~1M tetrahydrofuran solutions. The spectra of the anions, prepared by reaction of the hydrides with Na, displayed greatly improved resolution over those of the anions prepared from reaction of the triphenyl-compounds with Na as the reactions of the hydrides appear to proceed quite cleanly with the production of H_2 gas and with no side reactions.

The aromatic regions of these spectra were computer simulated and the best fits to the experimental spectra were obtained. An example of such a simulation was shown in Figure 2.4. The $^1H-^1H$ and $^1H-^{31}P$ coupling constants were found to be in the normal ranges for monosubstituted benzenes (Becker, 1980; Parr, 1978). Variations in the derived coupling constants from compound to compound, however, were found to be only of comparable magnitude to their individual standard deviations as obtained from the iterative program NUMARIT (Worvill, 1975). Therefore, the discussion in this section shall be confined mainly to the experimental chemical shifts. $^{31}P-^1H$ spin-spin couplings will be discussed in the section on ^{31}P NMR (section 3(d)).

The 80 MHz ^1H spectrum of $(C_6H_5)_2NNa$ in THF is included here (Figure 3.4) since it is an interesting example of a 'deceptively simple' spectrum (Becker, 1980). For this sample the resonances of the ortho and meta protons coincide and the spectrum appears to be independent of the coupling constants between these protons. Also, the observed pseudo-first-order splitting in the spectrum is the average of the ortho-para coupling and the meta-para coupling. A simulated spectrum which agrees closely with the observed spectrum is also shown in Figure 3.4. Because of the features mentioned above, however, not too much reliance should be placed on the coupling constants obtained because they rely to a large extent on speculative assignments of the weaker, poorly

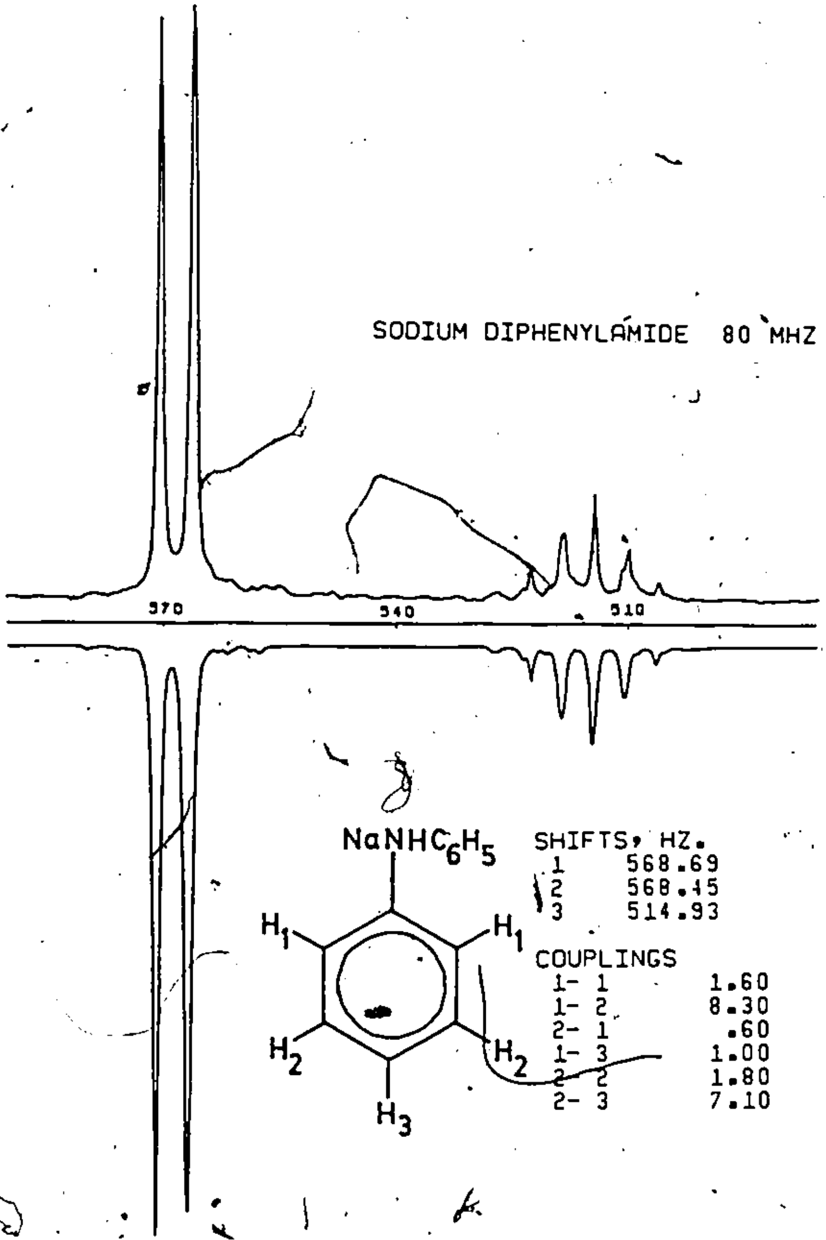


Figure 3.4: Observed (upper) and simulated (lower) ^1H NMR spectra for $(C_6H_5)_2NNa$ in THF: recorded at 80 MHz.

resolved peaks in the spectrum. Thus using a range of different values for some of these couplings very similar spectra can be simulated.

The ^1H chemical shift data for the series of compounds studied is summarized in Table 3.1. Figure 3.5 shows, schematically, the chemical shifts of the aromatic protons relative to benzene. Recently published data (Berestova, 1982) for the lithium salts of the phenyl- and diphenylamines and -phosphines in DMSO solvent display the same trends as observed here for the sodium salts in THF. The data for phenylgermane and sodium phenylgermyl (Birchall, 1970) are included in Table 3.1 and Figure 3.5 for comparison. These latter data were measured using solutions in CCl_4 and NH_3 respectively, therefore caution is required when comparing these data with those for the compounds in the present work where tetrahydrofuran was used as the solvent in all cases. For the neutral hydrides the differing abilities of the solvents to form H-bonded interactions involving the 'hydride' hydrogen atoms (i.e. the hydrogen atom bonded directly to the variable main group element) of the solute are important. Also, more polar solvents will favour contributions from resonance forms of the solute having larger charge separation. These effects may be illustrated by a comparison of the chemical shifts of the aromatic protons of aniline (relative to that of benzene) in the solvents CCl_4 (5% solution) (Spiesecke, 1961) and THF(~1M).

Table 3.1:

^{1}H Chemical Shifts[a] (p.p.m.)

		1(X-H)	2,6 (ortho)	3,5 (meta)	4 (para)
1.	$C_6H_5NH_2$	4.23(br)	6.52	6.98	6.52
2.	$C_6H_5PH_2$	3.90	7.43	7.21	7.21
3.	$C_6H_5AsH_2$	b	7.47	7.20	7.21
4.	C_6H_5NHNa	2.75	6.20	6.65	5.77
5.	C_6H_5PHNa	2.23	7.16	6.58	6.29
6.	C_6H_5AsHNa	1.18	7.36	6.59	6.43
7.	$(C_6H_5)_2NH$	(5.29)[c]	7.04	7.16	6.78
8.	$(C_6H_5)_2PH$	5.17	7.43	7.24	7.21
9.	$(C_6H_5)_2AsH$	4.89	7.44	7.19	7.18
10.	$(C_6H_5)_2NNa$		6.92	6.92	6.25
11.	$(C_6H_5)_2PNa$		7.48	6.79	6.52
12.	$(C_6H_5)_2AsNa$		7.59	6.80	6.63
13.	$C_6H_5GeH_3$[d]	4.29	7.49	7.29	7.32
14.	$C_6H_5GeH_2Na$[e]	3.30	7.51	6.78	6.73

Footnotes for Table 3.1

(a) Unless otherwise indicated, chemical shifts (±0.01 ppm.) are for THF solutions, ~ 1M; measured relative to neat external TMS, and corrected empirically to the value relative to internal TMS; the benzene resonance occurs at 7.31 ppm. relative to internal TMS in THF.

(b) Peak obscured by solvent signal (3.4 → 3.7 ppm.).

(c) Peak not observable because of broadening in THF solvent; the value given was measured in $CDCl_3$ relative to benzene; benzene assigned 7.31 ppm.

(d) Birchall, 1970; Chemical shifts measured in CCl_4 solution (1M) relative to benzene; benzene assigned 7.31 ppm.

(e) Birchall, 1970; Chemical shifts measured in NH_3 solution (1M) relative to benzene; benzene assigned 7.31 ppm.

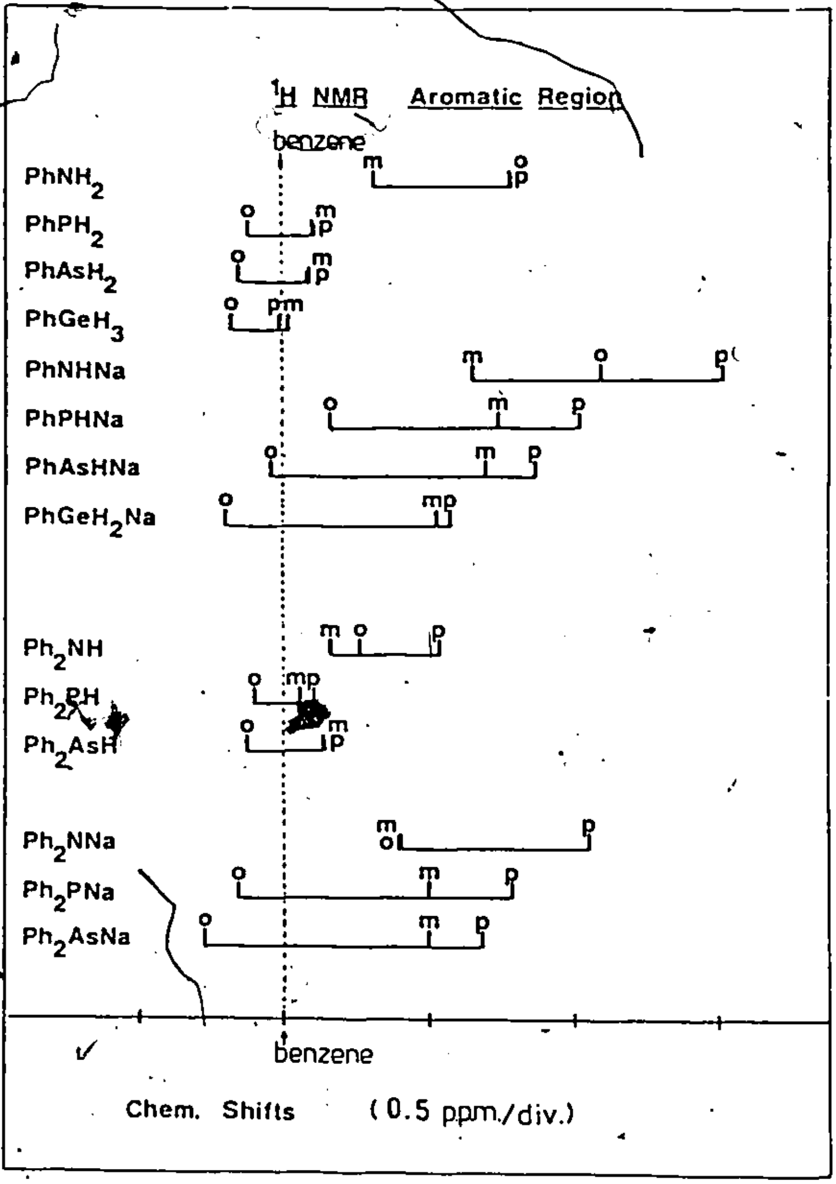


Figure 3.5: Schematic diagram of phenyl-proton chemical shifts; data from Table 3.1.
Ph = phenyl; o = ortho; m = meta; p = para

In CCl_4 the chemical shifts are: $H_{2,6}$, -0.76 ppm; $H_{3,5}$, -0.20 ppm; H_4, -0.63 ppm; whereas in THF they are slightly different: $H_{2,6}$, -0.78 ppm; $H_{3,5}$, -0.32 ppm; H_4, -0.78 ppm. For the THF solution the meta and para ^1H resonances have shifted to higher field strength relative to the ortho ^1H resonance so that in THF the ortho and para resonances coincide. These differences are most likely partly due to the greater ability of the tetrahydrofuran solvent molecules to form hydrogen bonds with the N-H protons. This is further evidenced by the low-field shift of the N-H proton resonance in THF relative to the same resonance in CCl_4 (Ryan, 1965). It is also observed that the N-H resonance of aniline in THF is quite broad (~17Hz) while that of diphenylamine is so broadened as to be not observed in this solvent. In solvents such as chloroform or carbon tetrachloride these same resonances are relatively sharp (~1Hz). This broadening effect is undoubtedly due to the nuclear quadrupole moment on ^{14}N and the differing quadrupolar relaxation rates in the different solvents. Hydrogen-bonded interactions with the solvent are less likely to be important for the hydrides of phosphorus and arsenic compared to those of nitrogen. For example the half-height linewidth of the As-H proton resonance for diphenylarsine in THF is relatively narrow (1.3Hz) despite the fact that ^{75}As is 100% abundant and has a large quadrupole moment.

For the anionic species the ability of the solvent to separate the ion pairs must be considered (O'Brien, 1976). More polar solvents such as NH_3 will favour an increased proportion of solvent separated pairs thus permitting the effect of the anionic charge to be brought to bear more fully on the electron distributions in the phenyl rings.

(a) Protons directly bonded to the group 5B element.

The interpretation of the chemical shift changes observed for the protons directly attached to the group 5B element appears to be relatively straightforward. Successive replacement of the hydrogen atoms of the YH_3 (Y=N,P,As) compounds by phenyl groups results in shifts of the Y-H resonances to lower field strengths. This is as expected since the phenyl group may potentially withdraw electron density from Y either inductively or by resonance thus deshielding the remaining protons. In addition there is the deshielding effect of the ring current associated with the phenyl ring. The effective change in shielding that the phenyl group introduces at the remaining protons of a substituted hydride has been shown (Ryan, 1965) to have a crude dependence on the electronegativity of the substituted element. Therefore the relative values for this shielding, from one compound to the next, may reflect the abilities of these elements to transmit the inductive effect of the phenyl group.

When the phenyl substituted hydrides are deprotonated, there is an upfield shift of the resonance of the remaining proton of 1-2 ppm because of the increased shielding introduced by the negative charge. It is of interest to note that the magnitude of this shift increases as group 5B is descended. This may reflect either the differences in electronegativities of these elements or the varying tendencies of the anions to form ion pairs with the cation Na^+. Perhaps more important however are the relative abilities of the group 5B elements to participate in a $p\pi$-$p\pi$ interaction with the π-system of the phenyl ring thus allowing resonance delocalization of the negative charge of the anions. Unfortunately a comparison with the analogous shift upon deprotonation of phenylgermane (Birchall, 1970) is rendered of doubtful significance because of the use of different solvents in this earlier study.

(b) Ring Protons

The conclusion that delocalization of negative charge from germanium into the phenyl ring does not occur for $C_6H_5GeH_2^-$ (Birchall, 1970) was based upon the fact that the ortho protons resonated to lower field strength of the benzene resonance whereas both the meta and the para protons resonated at higher field strength thus indicating that the dominant effect was the polarization of the phenyl ring caused by the anionic charge being localized on germanium.

The ^{1}H chemical shift trends for the series of compounds shown in Figure 3.5, as well as those for the ^{13}C resonances (see below), essentially confirm this conclusion but the reasons for it perhaps need clarification. It is apparent that there are large contributions to the proton shifts which are not directly related to the charge densities at the sites in question.

The chemical shift of the ortho proton in particular is influenced by a variety of competing factors: inductive, resonance, magnetic anisotropy and electric field effects as well as dispersion forces and steric effects as a result of the proximity of bulky substituents. Most of these effects will be much smaller for the meta proton while resonance is usually the dominant effect for the para proton .

As has been mentioned, only the para-^{1}H chemical shift shows, in general, a good correlation with the analogous ^{13}C chemical shift (Stothers, 1972). Two such correlations, -- one for the data in the present study and another for literature data for some common monosubstituted benzenes (Hayamizu, 1968; Stothers, 1972) -- are shown in Figure 3.6. The fact that these correlations are not greatly divergent suggests that for the anions, as well as for the neutral species, the para-^{1}H substituent chemical shift is an indicator of the electron density at the para-carbon atom. The relatively small displacement of the data in the present study from the correlation of the literature data can be

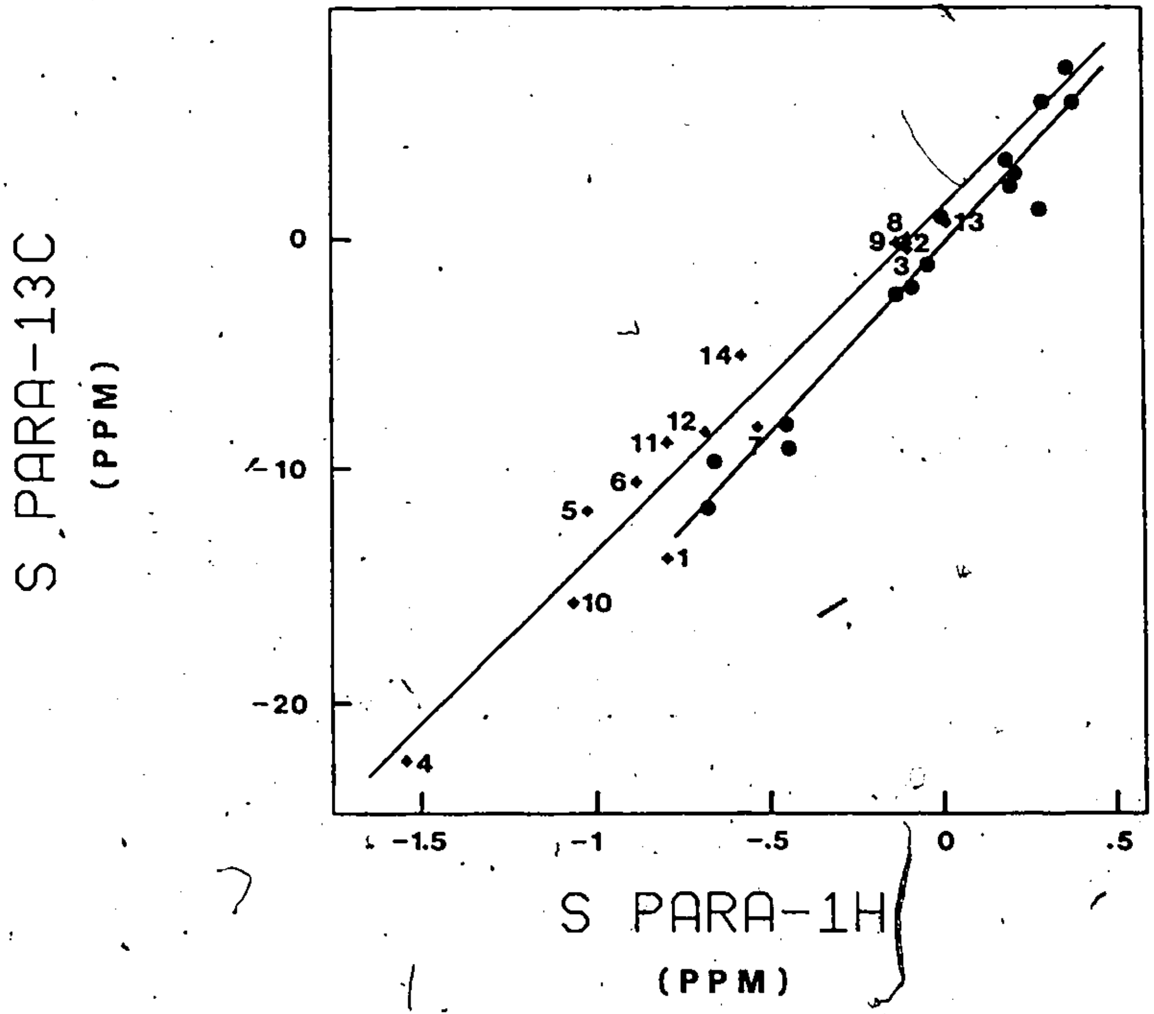


Figure 3.6: Plot of the para-^{13}C substituent chemical shift versus para-^{1}H substituent chemical shift; the numbered points refer to the compounds listed in Table 3.1; the solid circles represent literature data for some common monosubstituted benzenes (Hayamizu, 1968; Stothers, 1972); the upper line represents the best linear fit to the numbered data (slope = 14.888, intercept = 1.434, r = 0.9756); the lower line represents the best linear fit to the literature data (slope = 16.497, intercept = 0.217, r = 0.9798); linear regression analysis of all points gives: slope = 14.316, intercept = 0.374, r = 0.9740.

attributed in part to the use of polar solvents (THF for compounds 1-12, NH_3 for compound 14) whereas the literature data correspond in general to CCl_4 solutions. This will have a more marked effect on the ^1H data than on the ^{13}C data.

To a first approximation the SCS of the para protons might be considered to depend predominantly upon the change in π-electron density at the para carbon as a result of resonance with the substituent. Using this approximation it can be seen that the phenylarside anion exhibits greater delocalization of negative charge to the para carbon atom than does the anion of phenylgermane. The fact that a more polar solvent, NH_3, was used for the latter case only serves to enhance this conclusion. The extent of resonance delocalization in the anions appears to increase further on going from As to P to N as would be expected based upon the degree of overlap possible between the 2p(π) orbital of C, and the 4p, 3p or 2p orbitals of the group 5B elements, respectively. It is also apparent that for the neutral hydrides only the nitrogen containing compounds display a significant resonance effect. (See Figure 3.5)

The relatively large substituent chemical shifts of the meta protons in the anions suggest that the polar effects of the anionic substituents are, as previously concluded (Birchall 1970), contributing to the observed proton chemical shifts as are, also, the ring current effects. Therefore a better estimate of the actual resonance effect of the substituent may be more truly reflected by the relative chemical shift of the para and meta protons. The so-called 'inductive' substituent effect is usually considered to be of nearly equal magnitude at both the meta and para positions and calculations confirm this (Vorpagel, 1981). It may also be noted that in the dual substituent parameter equations (3.7) and (3.10) the coefficients of σ_I are of comparable magnitude.

The trend in the chemical shift difference ($\delta_{^1H_{para}} - \delta_{^1H_{meta}}$) for the series of compounds listed in Table 3.1 is essentially the same as the trend for $S_{^1H_{para}}$ alone therefore the same conclusions can be reached using this 'correction' to the para proton chemical shift. Added information obtained is that despite the relatively large value for $\delta_{^1H_{para}}$ for $C_6H_5GeH_2Na$ the actual resonance interaction in this anion is likely to be small considering the closely comparable substituent chemical shifts for the meta and para protons in this species.

The validity of the above 'correction' to $\delta_{^1H_{para}}$ is brought into question, however, when it is observed that, unlike the para-^{1}H chemical shifts, the meta ^{1}H chemical shifts show no correlation with the analagous ^{13}C chemical shifts (Figure 3.7). This is due, in part, to the fact that the proton chemical shifts include a significant contribution from changes in the magnetic anisotropy associated with the 'ring current' which may be disrupted by substituents which interact strongly with the π-system of the ring. If the nitrogen substituted compounds are excluded, a crude correlation exists which shows that for the other anionic species the effect of the substituent's polarity dominates the ^{1}H meta SCS. In general however, chemical shifts of meta-^{1}H have not been found to correlate well with either calculated electron densities or empirical substituent parameters unless corrections for the 'ring current' effect are made. (Ewing, 1978; Yamada 1970; Hehre, 1976). Such corrections require independent measures of 'resonance' substituent parameters which are not available for most of the species considered here.

Although the ortho proton substituent chemical shifts of monosubstituted benzenes have not been found in general to correlate well with the analogous ^{13}C SCS (Nelson, 1976), the data collected in this study appear to show a rough correlation, Figure 3.8 ($r=0.896$; $n=14$). In particular, the correlation is considerably improved when only the monophenyl derivatives are considered ($r=0.987$; $n=8$). This apparently reasonable correlation is no doubt heavily weighted by the fact that there is a large separation between the data points for the nitrogen containing derivatives and the other data points. When the points for aniline and sodium anilide are excluded the correlation is somewhat worse ($r=0.936$; $n=6$). This correlation is perhaps coincidental, but it is of

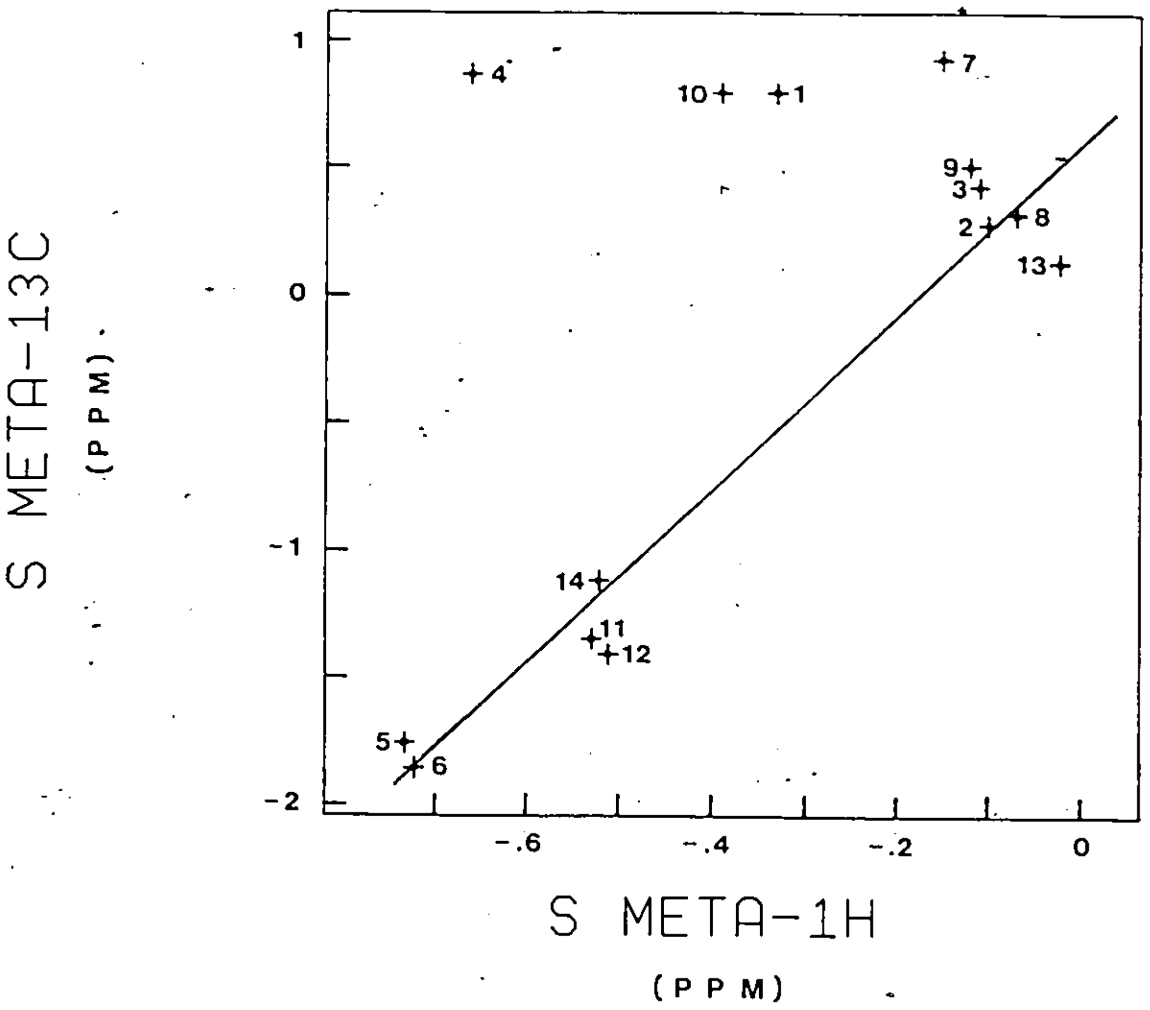


Figure 3.7: Plot of the meta-^{13}C substituent chemical shifts versus the meta-^{1}H substituent chemical shifts for the series of compounds listed in Table 3.1. The line represents the best straight line fit to the data excluding the nitrogen containing compounds -- points 1, 4, 7 and 10; n = 10, r = 0.976.

interest to note that the relative order of $C_6H_5GeH_3$ to $C_6H_5GeH_2Na$ in terms of both ^1H and ^{13}C data is reversed from the orders observed for the neutral species and anions of the group <u>5B</u> compounds.

Although there is considerable uncertainty as to the exact significance of the ^1H substituent chemical shifts it is apparent that there is a considerable change in the nature of the π-interaction between ring and substituent for the phenylgermyl anion and those of the group <u>5B</u> compounds. This difference is most easily rationalized in terms of the differences in resonance delocalization in these compounds. Consideration of the ^{13}C data for these compounds will give more conclusive evidence for this.

C. ^{13}C NMR

Substituent chemical shifts of carbon-13 nuclei occur over a much wider range than do the analogous ^1H-SCS. This is attributed to the fact that ^{13}C-SCS result mainly from changes in the larger paramagnetic term in Ramsey's equation for local electronic shielding (Nelson, 1976). A consequence of this large range of SCS is that the effects of magnetic anisotropies are relatively unimportant and therefore ^{13}C SCS may be more readily related to changes in the local electronic environment of the nucleus in question. ^{13}C NMR spectra, which are usually recorded with ^1H broadband decoupling, more easily yield exact chemical shifts than do

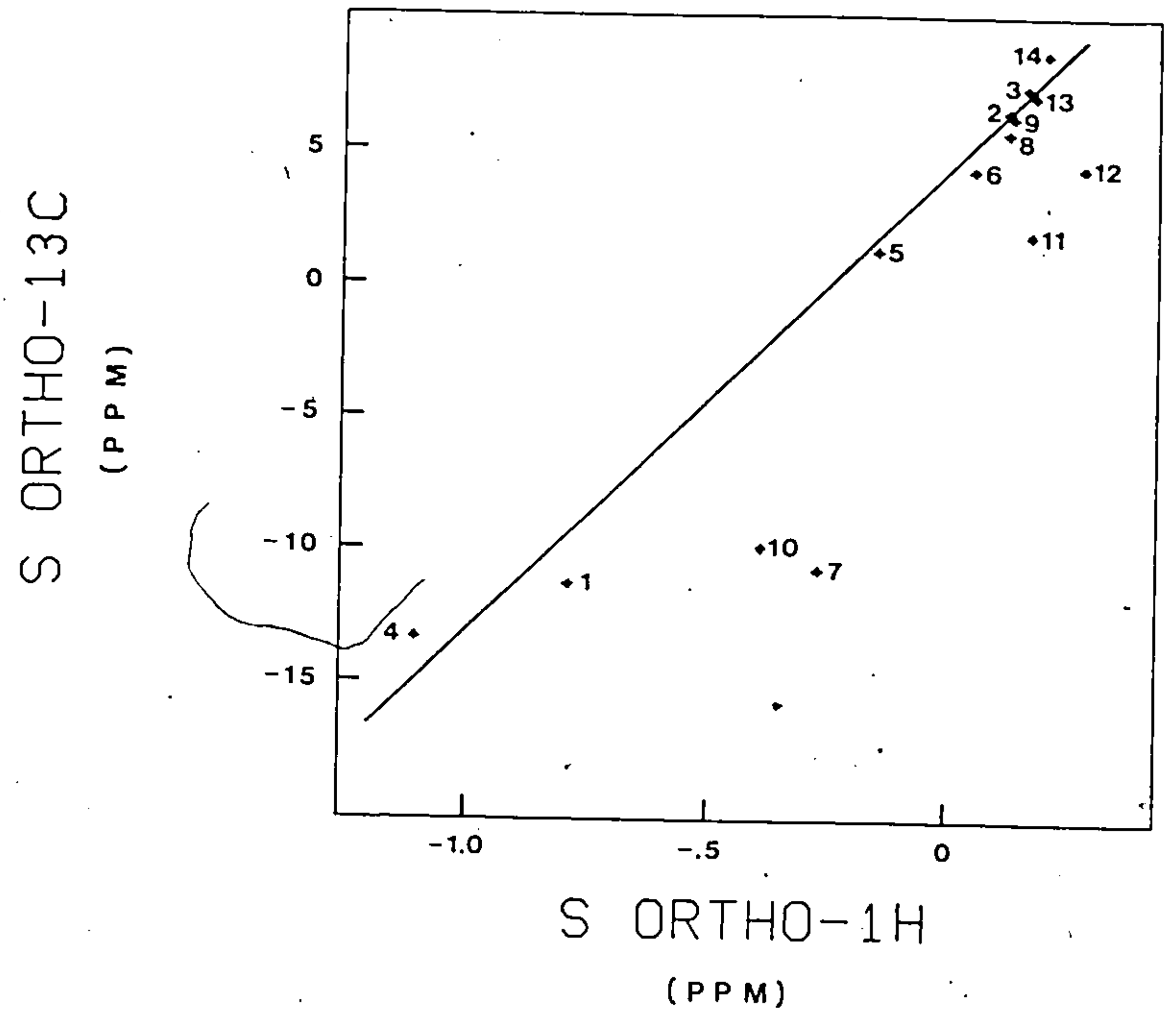


Figure 3.8: Plot of ortho-^{13}C substituent chemical shift versus ortho-^{1}H substituent chemical shift for the compounds listed in Table 3.1. The straight line represents the best linear fit to the data for the monophenyl-compounds only (i.e. excluding points 7-12).

^1H spectra since the low natural abundance of ^{13}C (1.108%) eliminates the complicating factor of homonuclear spin-spin coupling. The paramagnetic term for local shielding, however, is not as readily related to local electron density as is the diamagnetic term.

(i) Monosubstituted Benzenes

In general ^{13}C chemical shifts do not correlate well with either calculated electron densities or to experimental parameters which are related to electron densities (Nelson, 1976). However for ^{13}C nuclei which belong to a series having closely similar environments such correlations may be observed. Karplus and Pople (1963) have presented a theoretical rationale for such observations in series of sp^2 hybridized carbon atoms in conjugated molecules. Consideration of their approximate expression for σ_p^{loc} (3.3) will demonstrate how this rationale may be applied to the individual carbon nuclei in monosubstituted benzenes. Ewing (1979) has summarized the current understanding of ^{13}C SCS in monosubstituted benzenes and has presented a nearly comprehensive list of published chemical shifts for such systems.

(a) Ipso Carbon

The carbon atom which is directly bonded to the variable substituent shows the largest range of substituent chemical shifts. These shifts do not correlate well with charge density although certainly the charge density is a major contributing factor, influencing σ_p^{loc} via the $\langle r^{-3}\rangle_{2p}$ term. It has been suggested that significant contribution to ipso ^{13}C-SCS may arise from local changes in the average excitation energy term in equation 3.3 (Lynch, 1977). Changes in $\sum_B Q_{AB}$ are also likely to have an effect as a result of varying C-X bond orders. Contribution by all of these factors complicate the interpretation of the ipso ^{13}C SCS.

It has been shown that after making an empirical correction for what was loosely termed 'magnetic anisotropy' the ipso ^{13}C chemical shift showed a linear correlation with the electronegativity of the substituent atom for neutral monosubstituted benzenes (Spiesecke, 1961). Both ipso and ortho ^{13}C SCS show considerable dependence on the semi-empirical parameter Q (Hruska, 1965) discussed earlier with regard to ortho ^{1}H SCS. Triple parameter correlations involving σ, resonance and field substituent parameters have also been formulated (Smith, 1972). The significance of these correlations is uncertain although Q may be related to either the ΔE^{-1} term in the expression for σ_p^{loc} or to an alternating through bond inductive effect. (Ewing, 1978)

(b) Ortho Carbon

Ortho ^{13}C substituent chemical shifts cover a smaller range than the ipso ^{13}C SCS. The absence of good single correlations of $S_{^{13}C_{ortho}}$ with charge density or substituent parameters again suggests that contributions to the ΔE^{-1} and

$\sum_{A} Q_{AB}$ terms in the expression for σ_p^{loc} are significant although presumably less so than for $S_{^{13}C_{ipso}}$. This is exemplified by the smaller magnitude of the coefficient of Q in the triple parameter correlation for $S_{^{13}C_{ortho}}$ with field, resonance and Q parameters (Smith, 1972) than for the analogous correlation of $S_{^{13}C_{ipso}}$. The suggestion that the inclusion of the Q parameter represents an alternating through-bond inductive effect arises from the observation that $S_{^{13}C_{ortho}}$ has a reversed dependence on Q than either $S_{^{13}C_{ipso}}$ or $S_{^{1}H_{ortho}}$ (Ewing, 1978). The magnitude of contributions to σ_p^{loc} as a result of close non-bonded contacts between the ortho C-H group and the variable substituent is undetermined but may be considerable. The observed substituent chemical shifts are apparently a result of these competing influences and thus there is no simple interpretation for these values. Isolated comparisons of relative SCS may, with caution, be attributed to one effect or another.

(c) Meta Carbon

The chemical shifts of the meta ^{13}C resonances of monosubstituted benzenes always occur within a few ppm of that of benzene. This is consistent with the expectation that variations in the charge density at this position as a result of the substituents' resonance effects will be minimal. The approximation that ΔE^{-1} is invariant is reasonable for meta carbon. Similarly changes in the electron imbalance term are likely to be small in most cases (Karplus, 1963), but given the small total range of $S_{^{13}C_{meta}}$, this term may still be an important factor. This might account for the apparent lack of correlations of this parameter with either calculated charge densities or with substituent σ-parameters. This lack of correlations may also be because of inherent weaknesses in the charge density calculations and in the uncertainties associated with empirical substituent parameters. Changes in charge density at the meta carbon arise mainly from the overall polarization of the π-system. Consideration of the meta ^{13}C SCS for the anions studied in this work as well as for other anionic and cationic species from the literature (Ewing, 1979), confirm that there is a major dependence of this parameter on the intrinsic polarization of the π-system of the given monosubstituted benzene.

(d) Para Carbon

Para carbon substituent chemical shifts occur over a wide range (~60ppm). As for the meta carbon changes in the ΔE^{-1} term of σ_p^{loc} are expected to be negligible. Similarly contributions to the electron imbalance term will be small in comparison to the effect of changes in π-electron density (Karplus, 1963). There is considerable experimental support for a direct relationship between the para carbon chemical shift and the charge density at this carbon atom as evidenced by numerous correlations of $S_{^{13}C_{para}}$ with Hammett σ-values, calculated charge densities as well as ^{1}H para and ^{19}F para chemical shifts (Ewing, 1979). It is apparent that the dominant effect is the change in the π-electron density and that the variations that result are mainly from resonance with the substituent on the ring. Therefore $S_{^{13}C_{para}}$ is frequently taken to be a measure of the substituent's resonance effect.

A further refinement may be considered in an attempt to separate the resonance contribution to this chemical shift from the generally smaller field effects. Maciel and Natterstad (1965) observed a small improvement in the correlations of ($\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$) with Taft's σ_R or σ_R° constants as compared to correlations involving $S_{^{13}C_{para}}$ alone. Their assumption was that field, and any other small effects, should be of comparable magnitude at the meta and para positions. It was concluded that the difference between the meta ^{13}C and para ^{13}C chemical shifts was a better indication of the change in π-electron density at the para position resulting from resonance with the substituent. More recent studies involving substituents known to have effectively no resonance effect but considerable polarity (Ewing, and Toyne, 1979) have shown that the resultant SCS for the para carbon is approximately twice that for the meta carbon. This is consistent with an overall polarization of the phenyl π-system as the dominant mechanism for transmitting the field effect of the polar substituent to the atoms in the ring. The 'correction', $S_{^{13}C_{para}} - 2S_{^{13}C_{meta}}$, may therefore be a truer estimate of the substituent's resonance effect especially for highly polar substituents which possess only limited ability to conjugate with the ring. In general, regardless of whether $S_{13_{para}}$, $\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$, or $S_{^{13}C_{para}} - 2S_{^{13}C_{meta}}$ are considered the conclusions regarding the extent of electron delocalization to, or from, the phenyl ring are essentially the same because the values of $S_{^{13}C_{meta}}$ are so small. There are perhaps two practical advantages to the simple difference $\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$: (i) it serves as a kind of internal reference when comparing literature data and (ii) semantically it serves as a reminder that in some cases the field contribution to the para chemical shift may be significant.

(ii) Results

(a) Phenylhydrides of Group 5B and their Anions

The same series of compounds (~1M solutions in THF) as were examined by ^{1}H NMR were also analysed by ^{13}C NMR. The chemical shifts are listed in Table 3.2 and are shown schematically relative to that of benzene in Figure 3.9. Similar data for the lithium salts of the phenyl- and diphenyl-nitrogen and phosphorus compounds have been recently published (Berestova, 1982) which are consistent with the results reported here. $^{13}C-^{31}P$ coupling constants will be discussed in the section on ^{31}P NMR.

A sample spectrum is shown in Figure 3.10. Because of their relative intensities, it was comparatively easy to assign the resonances of the ipso and para carbon atoms. Assignment of the ortho and meta carbon resonances was made on the basis of observed trends of these values from literature data (Ewing, 1979) -- mainly upon the fact that the resonance of the meta carbon is generally within a few ppm of that of benzene. In a few cases additional confirmation of the assignments was made by selective proton decoupling experiments. An example of such an experiment is shown in Figure 3.11 for C_6H_5NHNa. Similar experiments were carried out for C_6H_5PHNa, $C_6H_5AsH_2$ and $(C_6H_5)_2AsNa$.

In the case of phenylphosphine the ipso carbon resonance was obscured by the resonances of the meta and para carbon atoms. An ^1H-coupled spectrum was recorded so that when the meta and para resonances were further split by the one-bond $^1H-^{13}C$ coupling the ipso carbon resonance was revealed. An off-resonance experiment (Levy, 1980) was also performed to reduce the long-range $^{13}C-^1H$ coupling constants and thus reveal the splitting caused by the one-bond $^{31}P-^{13}C$ coupling (Figure 3.12). The resonances in this spectrum are still somewhat broadened because of residual long range coupling however further increase in decoupling power would

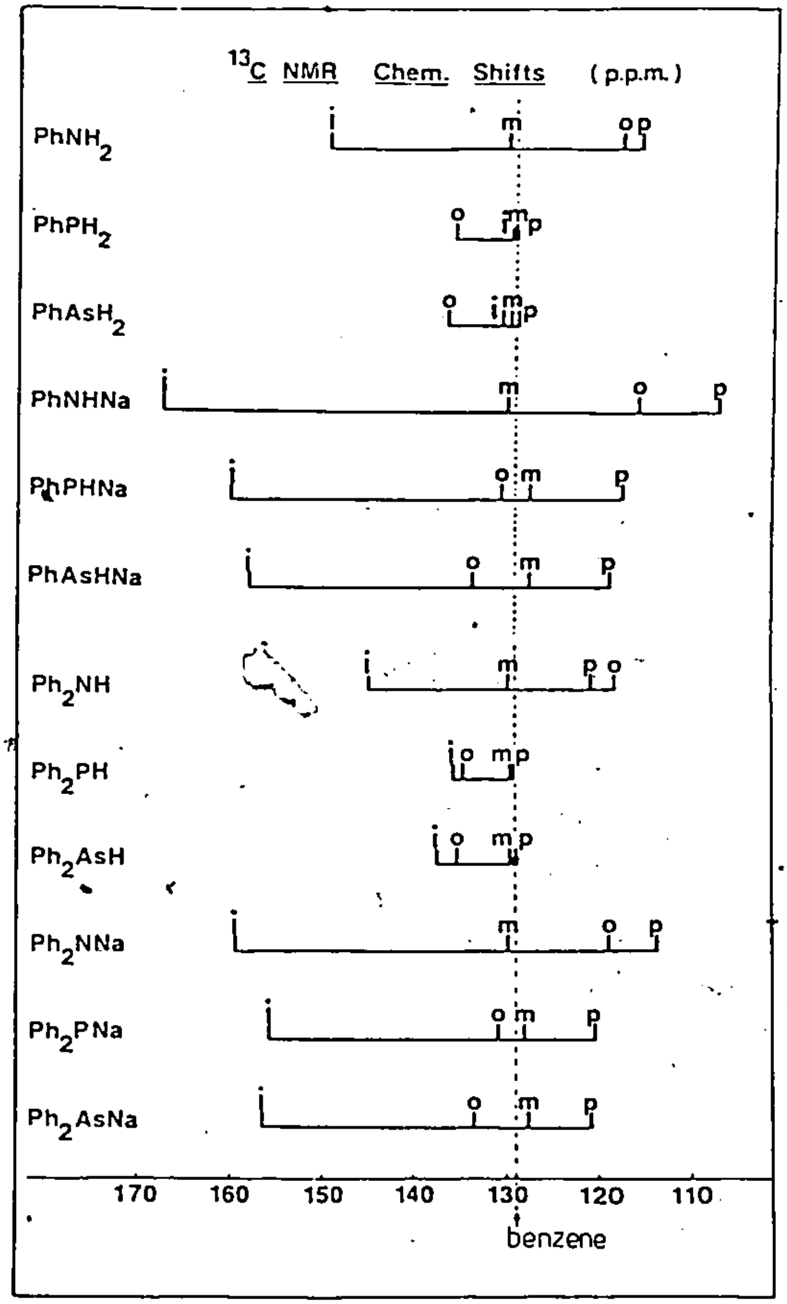


Figure 3.9: Schematic diagram of phenyl-^{13}C chemical shift of group 5B phenylhydrides and anions; i = ipso; other abbreviations as for Figure 3.5.

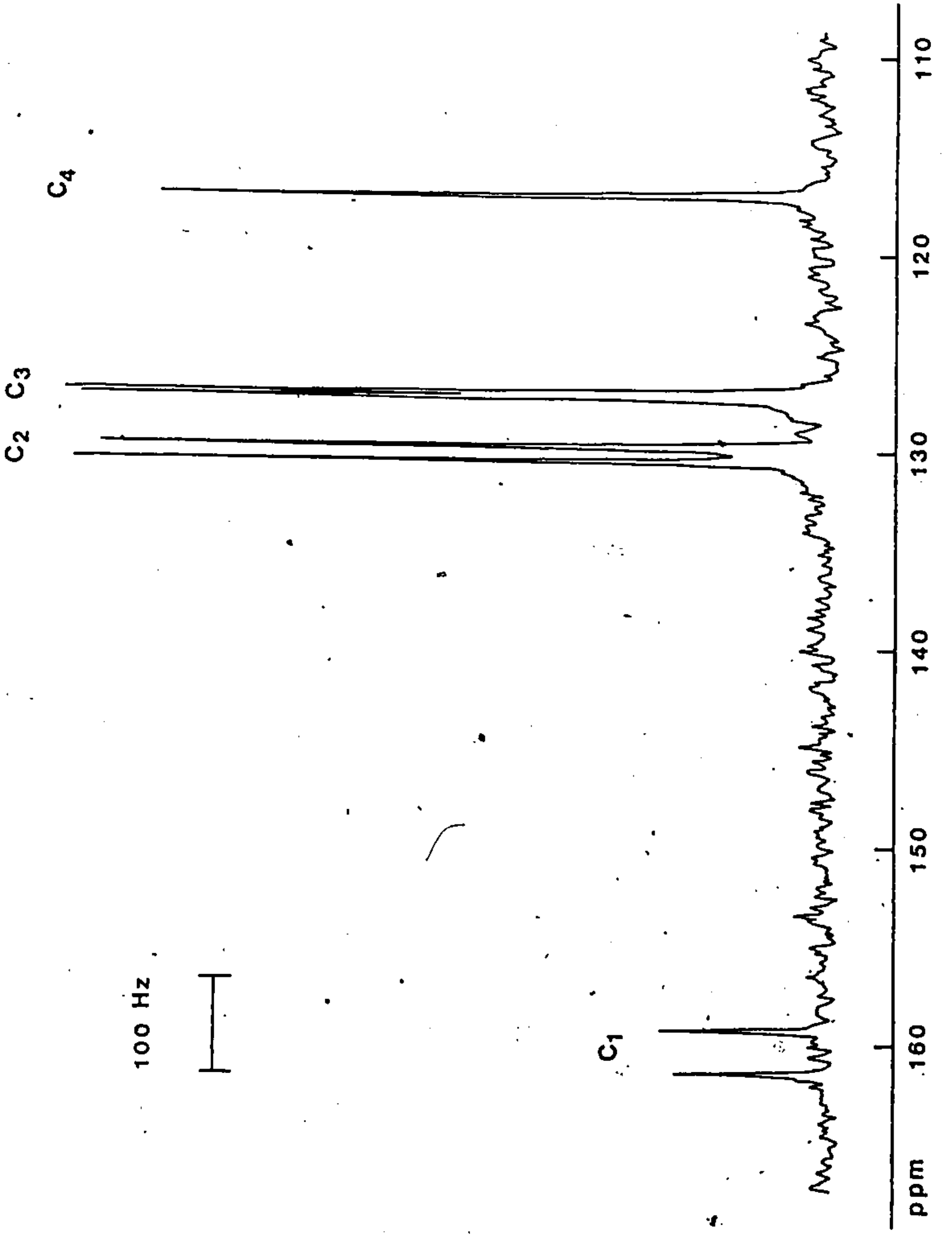


Figure 3.10: 80 MHz ^{13}C NMR spectrum of C_6H_5PHNa, 0.61 M in THF; ^{1}H-broadband decoupled.

Table 3.2:

^{13}C Chemical Shifts^{a} (p.p.m.) of Group 5B Phenylhydrides and Anions

		δ_{C1} (ipso)	δ_{C2} (ortho)	δ_{C3} (meta)	δ_{C4} (para)
1.	$C_6H_5NH_2$	149.22	117.55	129.71	115.21
2.	$C_6H_5PH_2$	129.16	135.45	129.19	128.80
3.	$C_6H_5AsH_2$	130.20	136.36	129.34	128.54
4.	C_6H_5NHNa	167.16	115.54	129.78	106.50
5.	C_6H_5PHNa	159.98	130.18	127.15	117.28
6.	C_6H_5AsHNa	157.70	133.22	127.05	118.53
7.	$(C_6H_5)_2NH$	144.93	118.13	129.84	120.87
8.	$(C_6H_5)_2PH$	135.85	134.64	129.23	129.05
9.	$(C_6H_5)_2AsH$	137.46	135.26	129.42	128.83
10.	$(C_6H_5)_2NNa$	159.49	118.98	129.71	113.33
11.	$(C_6H_5)_2PNa$	155.45	130.81	127.79	120.21
12.	$(C_6H_5)_2AsNa$	156.37	133.35	127.50	120.68

(a) Chemical shifts (± .04 p.p.m.) are relative to neat external TMS; all solutions are approximately 1M in THF; the benzene resonance occurs at 128.91 p.p.m.

result in the ipso resonance again being obscured. Phenylphosphine presented a further problem regarding chemical shift assignments in that the resonances attributed to the meta and para carbon atoms occur as three nearly equally-spaced equal-intensity peaks in the broadband decoupled spectrum -- the meta resonance being split by the three-bond $^{31}P-^{13}C$ coupling. It was not immediately obvious how these three lines should be assigned. However, since typical three-bond $^{31}P-^{13}C$ couplings for ^{31}P substituted benzenes are 6-7 Hz and the meta carbon resonances are usually close to 129 ppm the assignment was chosen which most closely agrees with these values (Table 3.2). This assignment was later confirmed by a ^{13}C spectrum of phenylphosphine recorded at higher frequency (100.6 MHz) and field strength, and is in agreement with a recent literature assignment (Parr, 1978).

The effect of the choice of solvent upon the ^{13}C substituent chemical shifts may be noted by comparison of the values for aniline in CCl_4 (5%) (Spiesecke, 1961) with those obtained here for aniline in THF (~ 1M). The former values (ppm; relative to benzene) are: $S_{c_1} = 19.2$; $S_{c_2} = -12.4$; $S_{c_3} = 1.3$; $S_{c_4} = -9.5$; compared to $S_{c_1} = 20.2$; $S_{c_2} = -11.5$; $S_{c_3} = 0.71$; $S_{c_4} = -13.8$ for the THF solution. In THF the para carbon resonance is shifted to higher field strength from that of the ortho carbon. This shift is analogous to that observed for the para proton resonance for aniline in the same pair of solvents, and is in agreement with the

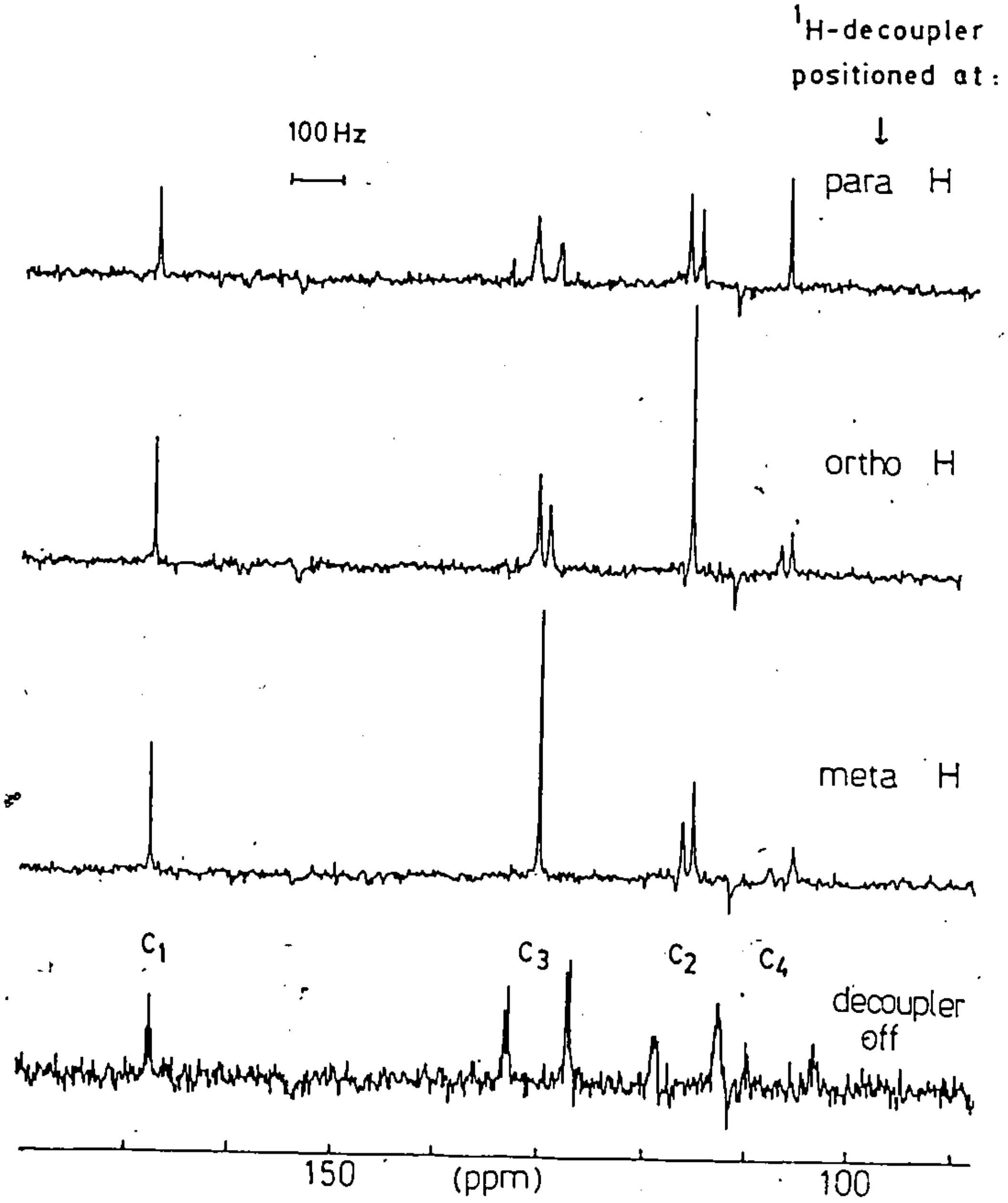
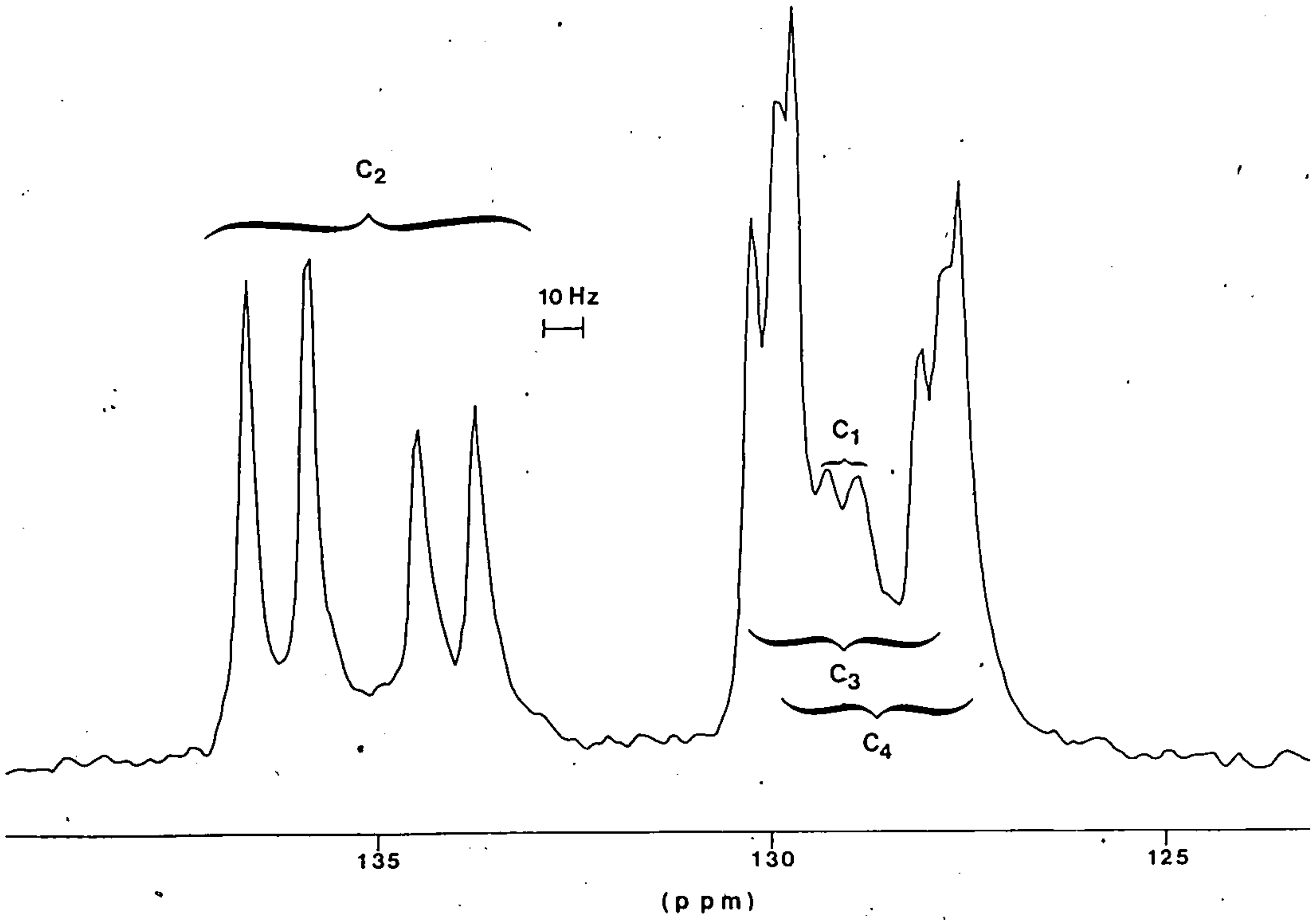


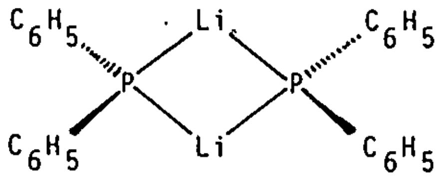
Figure 3.11: ^{13}C NMR spectra of C_6H_5NHNa in THF demonstrating selective ^{1}H-decoupling -- to confirm assignments of ^{13}C resonances.



<u>Figure 3.12</u>: ^{13}C NMR Spectrum of $C_6H_5PH_2$ with off-resonance decoupling of the ^1H region.

suggestion that the change of solvent actually affects the electron distribution in the phenyl ring, probably via interactions such as hydrogen-bonding between the solvent and the $-NH_2$ protons. Such effects are likely to be less significant for the phenyl hydrides of phosphorus and arsenic. For instance it is found that there is not a significant difference between the ^{13}C chemical shifts of phenylarsine in THF solution (Table 3.2) and those of neat phenylarsine: $\delta_{C_1} = 130.73$; $\delta_{C_2} = 136.65$; $\delta_{C_3} = 129.49$; $\delta_{C_4} = 128.68$ (ppm; relative to external neat TMS).

A change of solvent for the anions will have a more important effect. For example, the chemical shift of the para carbon resonance of C_6H_5PHNa shifts from 117.28 ppm in THF solution to 114.13 ppm (relative to external TMS) when measured in NH_3 solvent. This indicates an increase in electron density at the para position in the latter solvent. Presumably this arises because of a greater degree of solvent separation of ion pairs in the more polar NH_3 solvent. As well as equilibria involving solvation of ion pairs there is the possibility of self-association of the ion pairs. An example of this is that, for $(C_6H_5)_2PLi$ in diethylether solution, ^7Li and ^{31}P NMR (Colquhoun, 1982) reveal that this species adopts a dimeric structure. Variation of the



concentration of C_6H_5PHNa in THF, however, causes only minor changes in its ^{13}C chemical shifts (Figure 3.13), the largest observed change being -1.6 ppm for the ipso carbon resonance as the concentration was changed from 0.28M to 2.22M. An analogous but larger ^{31}P chemical shift dependence on concentration is also observed.

(b) Arylgermanes and their Anions

For the purpose of comparison several arylgermanes and their respective monosodium salts were also investigated by ^{13}C NMR. Table 3.3 presents the chemical shifts of these species and of phenyl- and diphenylsilanes along with some literature data for phenyl-silanes and $(C_6H_5)_3SiLi$. Figure 3.14 displays the ^{13}C substituent chemical shifts of the germanium species studied relative to benzene.

Ideally it is desirable to compare chemical shifts obtained from dilute solutions in a common solvent. These conditions could not be realized however, because the germyl anions require a solvent of considerable polarity, namely NH_3, to yield stable solutions, whereas the neutral germanes do not have appreciable solubility in ammonia. Therefore when making comparisons of the ^{13}C NMR data for the germyl anions with other species studied in this work the relative effects of the different solvents must be considered. The diamagnetic correction between various solvents is not significant in comparison to the magnitudes of the ^{13}C

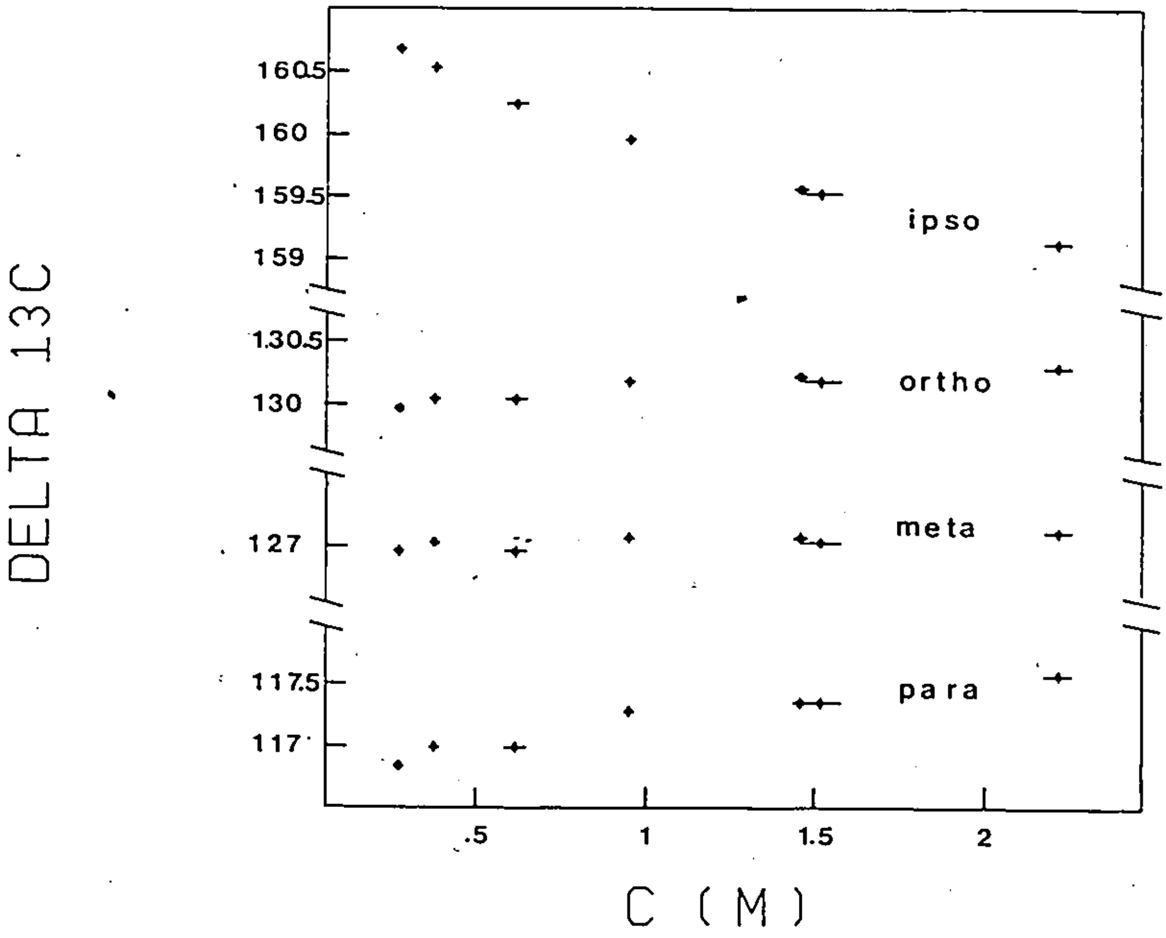


Figure 3.13: Chemical shifts of the carbon-13 atoms of C_6H_5PHNa (ppm; relative to external neat TMS) as a function of concentration (M; in THF).

substituent chemical shifts. Solute-solvent interactions appear to be relatively unimportant for the neutral germanes and silanes because of their non-polar character.

Of most importance is the effect of the different solvents on the chemical shifts of the anions. The questions of solvation or association of ion pairs, already discussed for the group 5B compounds again arises. For example, the differences in the ^{13}C chemical shifts for triphenylsilyl lithium in THF and triphenylgermyl sodium in liquid ammonia most likely reflect the differences in solvation of the salts. The species studied in liquid ammonia will have a higher proportion of solvent separated ion pairs whereas the species dissolved in the less polar THF will be more highly associated. As a result the species dissolved in NH_3 will exhibit more ionic character and the ^{13}C NMR spectra reveal larger substituent chemical shifts as a result of enhanced resonance and polarization effects. The different counter-ions, Li^+ or Na^+ will most likely also influence the ion-pairing equilibria in solution. Presumably with the same counterion and the same solvent the NMR parameters of $(C_6H_5)_3Ge^-$ and $(C_6H_5)_3Si^-$ would more closely resemble one another.

Table 3.3

^{13}C Chemical Shifts (ppm) of Silanes, Germanes and Their Anions.[a]

	δ_{C_1} (ipso)	δ_{C_2} (ortho)	δ_{C_3} (meta)	δ_{C_4} (para)	δ_{me}
$C_6H_5SiH_3$ [b]	128.39	136.51	128.83	130.58	
$C_6H_5SiH_3$ [c]	127.97	135.83	128.10	129.78	
$(C_6H_5)_2SiH_2$ [d]	131.90	136.29	128.68	130.36	
$(C_6H_5)_2SiH_2$ [c]	131.41	135.63	128.08	129.82	
$(C_6H_5)_3SiH$ [e]	133.7	136.1	128.4	130.1	
$(C_6H_5)_3SiH$ [c]	133.30	135.78	128.03	129.78	
$(C_6H_5)_4Si$ [f]	134.17	136.44	127.90	129.61	
$(C_6H_5)_3SiLi$ [g]	145.0	136.1	127.5	128.4	
$C_6H_5GeH_3$ [b]	131.60	136.06	129.04	129.70	
$(C_6H_5)_2GeH_2$ [b]	134.65	135.84	129.11	129.83	
$(C_6H_5)_3GeH$ [b]	136.36	135.78	129.05	129.82	
$(C_6H_5)_4Ge$ [h]	141.5	136.3	128.2	129.0	
$(p\text{-}CH_3C_6H_4)_3GeH$ [b]	133.06	135.69	129.70	139.35	21.35
$C_6H_5GeH_2Na$ [i]	163.28	139.61	127.69	124.11	
$(C_6H_5)_2GeHNa$ [i]	164.39	137.79	126.85	123.49	
$(C_6H_5)_3GeNa$ [i]	165.31	137.31	126.93	123.85	
$(p\text{-}CH_3\text{-}C_6H_4)_3GeNa$ [i]	161.29	137.30	127.65	132.33	21.20

Footnotes for Table 3.3

[a] Unless indicated otherwise solutions are approximately 1M; chemical shifts are relative to neat $(CH_3)_4Si$, external; (±0.06 ppm).

[b] Solutions in tetrahydrofuran; benzene resonance occurs at 128.91 ppm.

[c] Rakita (1976); 20-40% in $CDCl_3$; $CHCl_3$ internal reference assigned 77.20 ppm.

[d] Neat liquid.

[e] Olah (1980); tetrahydrofuran solution; relative to internal $(CH_3)_4Si$.

[f] Rakita (1976); 2% in $CDCl_3$; referenced as for b.

[g] Olah (1980); tetrahydrofuran solution; secondary reference solvent tetrahydrofuran, peaks assigned 26.2 and 78.0 ppm.

[h] Saturated solution in $CDCl_3$; secondary reference, $CDCl_3$ assigned 76.9 ppm.

[i] Solutons in NH_3; benzene resonance occurs at 129.04 ppm.

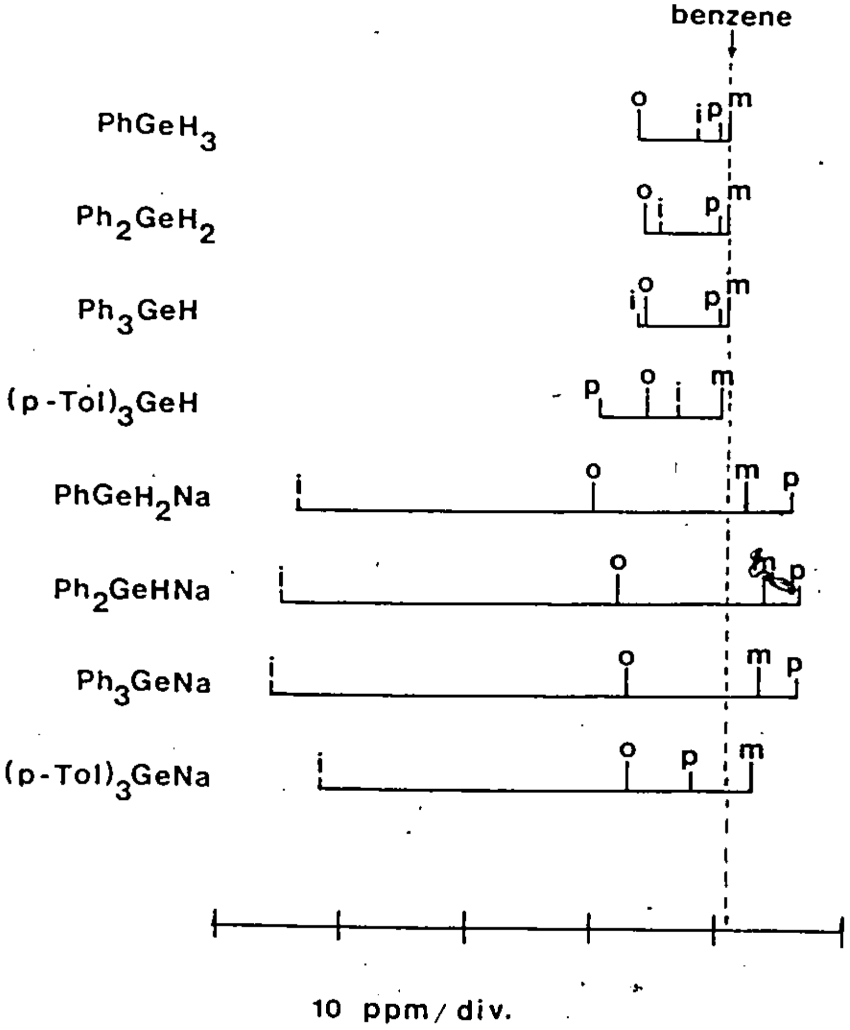


Figure 3.14: Schematic diagram showing the ^{13}C substituent chemical shifts of the ring carbon atom resonances for arylgermanes and their monoanions relative to that of benzene; p-Tol = para-tolyl group, $p\text{-}CH_3C_6H_5$-; other symbols as for Figure 3.9.

(iii) Discussion

Consideration of the trends in the chemical shifts of the individual types of carbon atoms in these series of phenyl-substituted amines, phosphines, arsines, silanes and germanes and their anions will allow some general conclusions to be made regarding the nature of the electronic interactions between the aromatic ring and the main group element substituents.

(a) Ipso Carbon

Although the substituent chemical shift of the ipso carbon atom is not simply related to the electron density at this position the electron density is still likely to be the major contributing influence. Trends in the ipso carbon SCS, in particular the large shifts observed for the anionic species, no doubt reflect relatively large changes in electron density at the ipso carbon atom. Corroborating evidence of this is found by considering the reasonable additivity of substituent chemical shifts for para-disubstituted benzenes (Lynch, 1977). It is apparent that substituents influence the chemical shifts of the carbon atom para to themselves through changes in the π-electron density at this carbon atom. For example the SCS of the para carbon resonance of toluene, $C_6H_5CH_3$, of -3 ppm (Levy, 1980) may be attributed to the increase in π-electron density at this carbon atom (Δq = 0.021; Pross, 1981) relative to benzene. However for a para substituted toluene the proportionality between substituent chemical shift at the carbon atom para to the methyl group and the change in π-electron density induced at that position by the methyl group may be modulated by the influence of the second substituent on the terms ΔE^{-1} and $\Sigma_B Q_{AB}$ in the equation for σ_p^{loc} which are not proportional to electron density. The observation that para-methyl substitution of $(C_6H_5)_3GeH$ or $(C_6H_5)_3GeNa$ (see Table 3.3) results in shifts of the ipso carbon resonance (i.e. that C bonded to Ge) of -3.3 and -4.02 ppm respectively and that these values are of comparable magnitude to the analagous SCS for toluene (-3 ppm) suggests that modulation of the electron density contribution to the chemical shift of this carbon resonance is relatively small. Therefore to a first approximation large shifts of the ipso carbon resonance in such compounds will reflect a relatively large change in electron density at that carbon.

For the neutral phenyl-substituted silanes, germanes, phosphines and arsines the resonance of the ipso carbon is the only resonance which displays major variations in chemical shift upon change in degree of phenyl-substitution or main group element (Figures 3.9 and 3.14). In all these cases the ipso carbon resonance shifts to lower field strength upon increased phenyl-substitution (Fig 3.15). This may be attributed predominantly to the inductive electron withdrawing effect of each additional phenyl group. There

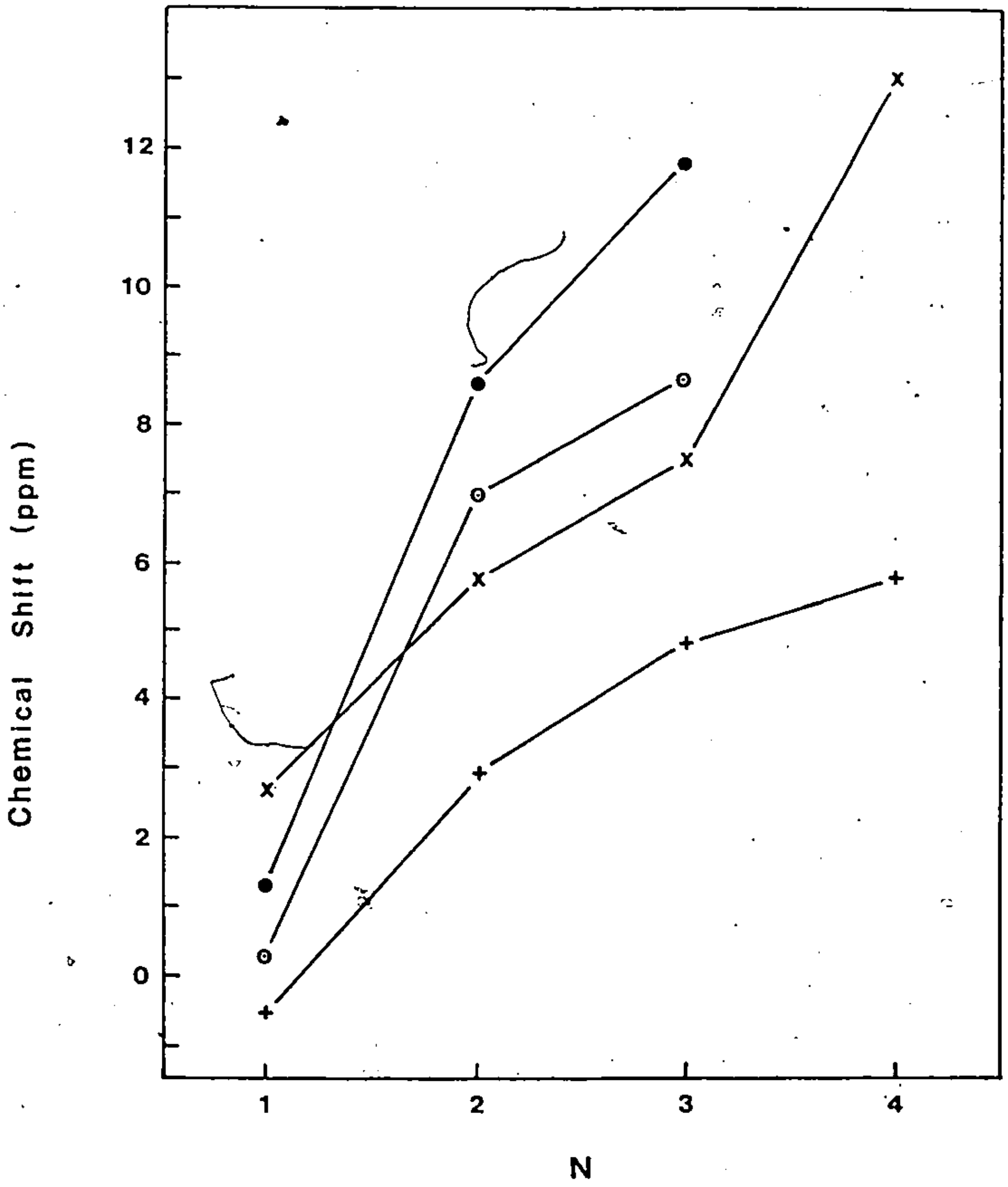


Figure 3.15: Graph of the substituent chemical shift of the ipso carbon atom resonance of phenyl substituted hydrides versus the degree of phenyl-substitution (N); o = phosphines, ● arsines, + = silanes, x = germanes.

may also be a small contribution from the magnetic anisotropy associated with the ring current of each additional phenyl group.

Unlike their phosphorus and arsenic analogues, aniline ($C_6H_5NH_2$) and diphenylamine ($(C_6H_5)_2NH$) display large low-field SCS for their ipso carbon resonances. This is a result of large pπ-pπ interactions between filled nitrogen orbitals and the phenyl rings in these compounds. It has been shown that such interactions which frequently result in net electron transfer to the ring, also cause an alternating polarization (Libit, 1974) with net reduction in π-electron density at the ipso carbon. This is certainly the primary explanation for the observed shifts for the neutral nitrogen containing compounds.

Spiesecke and Schneider (1961) found that, after making an empirical correction for "substituent anisotropy", there was an apparent correlation between the chemical shift of the C_1 atom in a monosubstituted benzene and the substituent's electronegativity. The more electronegative substituents give rise to C_1 resonances at lower field strength. It is of interest to note that, for all of the compounds studied in the present work, deprotonation of the substituent resulted in large shifts to lower field strength for the ipso carbon resonance. These shifts are clearly in the opposite direction to those expected for a decrease in substituent electronegativity. Similar low field shifts have been observed for the ipso ^{13}C resonances of the phenoxide ion (Maciel, 1965), the benzenethiolate ion (Carson, 1981), the phenylmethyl carbanion (O'Brien, 1976), and triphenylsilyl anion (Olah, 1980). It appears that this is a general phenomenon for monosubstituted benzenes in which the substituent atom is the centre of anionic charge. Other literature data (Ewing, 1979) show that substituents which are cationic centres generally cause the opposite effect, namely a large high-field shift of the C_1 resonance. Such shifts may in some cases be attributed partly to the pπ-pπ orbital effect described above. In addition, it is apparent that an electronic charge which is localized on the substituent atom causes a polarization of the π-system of the phenyl ring resulting in a gradual increase, or decrease depending upon the sign of the ionic charge (cf. $C_6H_5NH_3^+$; Pross, 1981), of the π-electron densities as the distance from the substituent increases. It is clear that for the ionic species such field effects predominate over the inductive effect of the substituent in determining the ipso ^{13}C substituent chemical shift.

The relative importance of this electric field effect compared to the pπ-pπ orbital effect, which causes a parallel shift of the ipso ^{13}C resonance, is exemplified by the group 4B element phenyl hydrides and their mono-anions. The triphenylsilyl anion, $(C_6H_5)_3Si^-$, (Olah, 1980) displays considerably less delocalization of negative charge into the phenyl ring than does the analogous carbanion, $(C_6H_5)_3C^-$, as evidenced by the chemical shifts of their para-carbon resonances, yet the ipso carbon resonance of $(C_6H_5)_3Si^-$ displays a larger shift to low field strength relative to that of the neutral hydride $(C_6H_5)_3SiH$ than does that of $(C_6H_5)_3C^-$ relative to $(C_6H_5)_3CH$. Deprotonation of $(C_6H_5)_3GeH$, observed in the present study, results in an even larger shift of the ipso carbon resonance to lower field strength. This latter observation, however, may be attributed, in part, to the choice of solvent, NH_3, as opposed to THF for the carbon and silicon analogues (Olah, 1980). The effect of the more polar solvent will enhance the field effects giving rise to these large shifts (see Figure 3.14 and Table 3.3).

Increased phenyl-substitution of the anions of the germanes studied causes a trend to lower field strength for the ipso ^{13}C chemical shifts which is analogous to that observed for the neutral germanes and which may be attributed to the inductive effect of the additional phenyl groups. The anions of the group <u>5B</u> phenylhydrides, however, show a slight upfield shift for the ipso carbon resonance upon increased phenyl-substitution. This may be evidence of increased delocalization of the negative charge in these anions. An analogous shift is also observed for the neutral diphenylamine relative to aniline.

(b) Ortho Carbon

In general the substituent chemical shifts of the ortho carbon atoms are not well understood. The observed shifts are the net result of a variety of influences because of the proximity of the substituents which possess varying sizes, electronegativities, polarities and resonance interactions. Of the neutral phenyl-hydrides studied here, those of the third and fourth period elements, Si, Ge, P, As, exhibit similar ortho ^{13}C SCS (5-7.5 ppm). These shifts may be largely the result of a close non-bonded contact between the ortho C-H group and the substituent on the ring. Figure 3.16 shows that the ortho ^{13}C resonance undergoes a significant shift to higher field strength with increased phenyl-substitution in the cases of the phosphines and arsines but not in the cases of silanes and germanes. These differences might be related to more severe crowding of the phenyl groups in the group 5B compounds because of the large stereochemical influence of the formally non-bonding pair of electrons. Changes in the polarities of these molecules with changing degree of substitution may also contribute to the observed shifts. For the analogous compounds of nitrogen, aniline and diphenylamine, the ortho ^{13}C shift is clearly dominated by the resonance contribution to the electron density at this position.

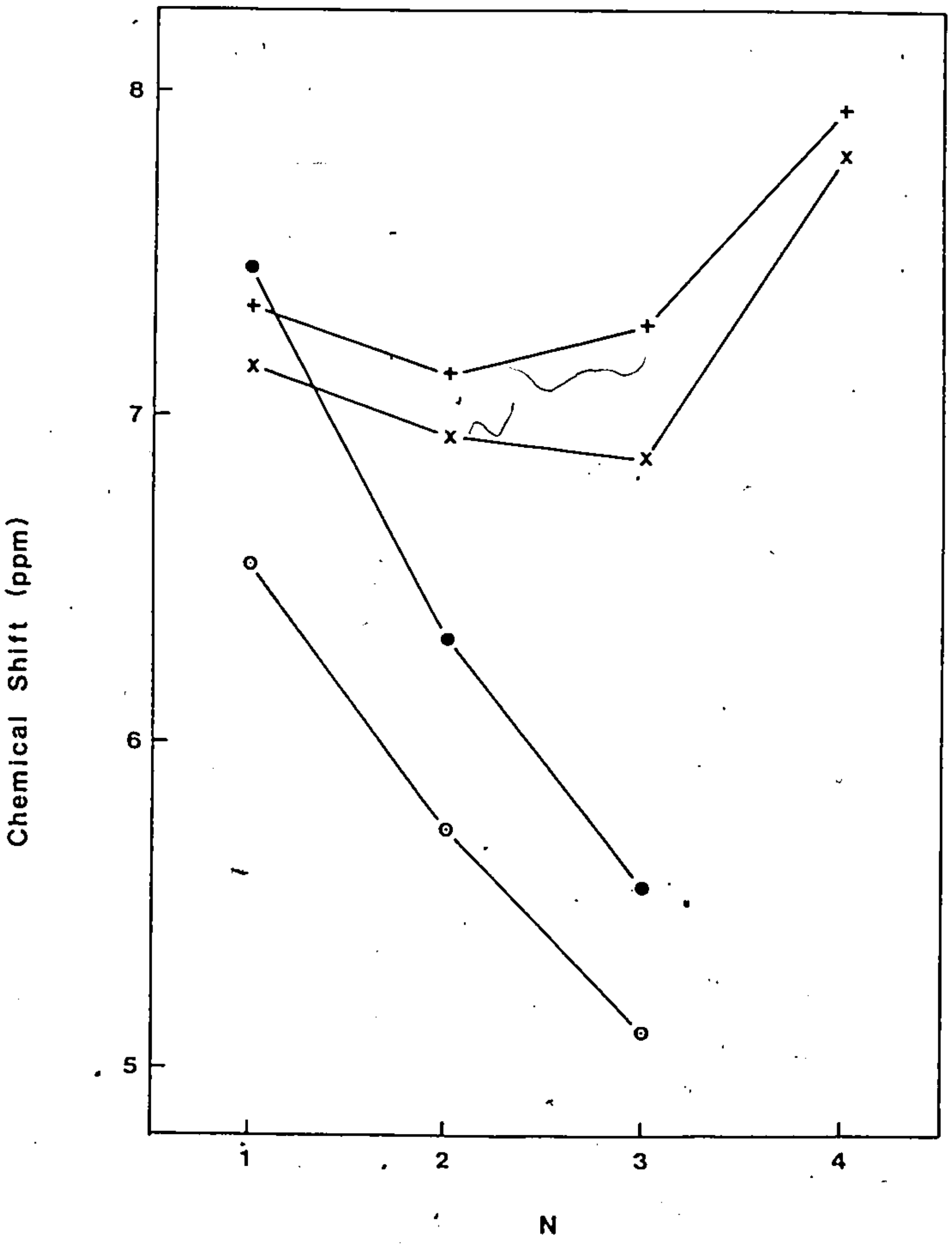


Figure 3.16: Graph of the substituent chemical shift of the ortho carbon atom resonance of phenyl-substituted hydrides versus the degree of phenyl-substitution (N); o = phosphines, ● = arsines, + = silanes, x = germanes.

Deprotonation of the arylgermanes results, in all cases, in a small shift to lower field strength for the ortho carbon resonances. In contrast to this, deprotonation of phenyl- or diphenylphosphines or -arsines causes a small high-field shift of this resonance. This is consistent with the proposed lower degree of delocalization of negative charge for the arylgermyl anions relative to the group 5B anions. The apparent difference, however, is relatively small because the resonance contribution is masked by other effects such as increased field polarization in the anions as well as unknown contributions of the ΔE^{-1} and $\sum_{B} Q_{AB}$ terms to the paramagnetic shielding.

(c) Meta Carbon

As expected the meta carbon chemical shifts of all the species studied do not vary greatly from that of benzene. In all cases this shift is independent of the degree of phenyl substitution, but there are small differences with change of main group element. Although not yet definitively established variations in meta ^{13}C chemical shifts probably reflect the variations in electron density at this position. Of particular note is that deprotonation of the phenyl-substituted germanes, arsines and phosphines results in a shift to higher field strength for the meta ^{13}C resonances of these compounds. Comparison with the literature data for monosubstituted benzenes (Ewing 1979) reveals that these shifts, although small, are among the largest high field SCS observed for meta carbon atoms. Similarly the largest low-field meta ^{13}C SCS occur when the substituent atom is the centre of cationic charge. These observations suggest that for ionic or highly polar substituents the meta ^{13}C SCS depends largely upon the polarization of the π-system as a result of the electronic charge which is to a large degree localized on the substituent atom. By contrast it is noted that deprotonation of either aniline or diphenylamine does not give rise to a significant shift of the meta ^{13}C resonance. This is no doubt a consequence of the stronger $p\pi$-$p\pi$ interaction in these anions which has been noted to cause a small decrease in electron density at the meta position (Pross, 1981). Also the negative charge in these anions is more delocalized thus reducing the effective polarity of the negatively charged substituent.

(d) Para Carbon

In all the phenyl-substituted neutral silanes, germanes, phosphines and arsines the resonances of the para carbon atoms occur within 2 ppm of that of benzene. Like the meta carbon resonances their chemical shifts show no dependence upon degree of phenyl substitution. There is, however, a small but notable difference between the group 4B and group 5B compounds. For the silanes and germanes the para carbon resonance always occurs at lower field strength than the meta carbon resonance, while for the phosphines and arsines the opposite is true. These differences are very small but may be indicative of a weak pπ-dπ interaction in the former case and a weak pπ-pπ interaction in the latter. Compared to the para-carbon substituent chemical shifts observed for the amines and for the anions of the various phenyl-hydrides, however, these effects are hardly significant. Essentially the conclusion must be made that for the neutral phenylhydrides of Si, Ge, P and As net charge transfer between ring and substituent is negligible. For aniline and diphenylamine, however, the large high-field substituent chemical shifts of the para carbon resonance show that there are significant increases in electron density at the para carbon atom resulting from the pπ-pπ interaction between the nitrogen and the ring involving the formally non-bonded electron pair of nitrogen.

While it has been well established that the para carbon SCS show reasonable linear dependence on the π-electron density at this carbon atom for neutral molecules, there has been little systematic investigation of anionic monosubstituted benzenes. Therefore extension of this conclusion to include these anionic species may require some justification. In this regard, it may be noted that the phenoxide ion was included in the study of Maciel and Natterstad (1965) and the data for this anion did not deviate from the observed correlations of para carbon chemical shift with σ_R and $\sigma_R°$ substituent constants. It may also be noted that the data for the anions presented here do not deviate greatly from the correlation of ^{13}C and ^{1}H para chemical shifts shown in Figure 3.6. For these reasons, and also because of the observation that the meta carbon chemical shifts of the anions do not vary greatly from that of benzene, it would appear that no unusual effects are influencing the meta and para carbon chemical shifts other than the 'resonance' and 'field' contributions to the electron density.

A qualitative ranking of the various species studied, in terms of the resonance effect of the substituent on the ring, may be obtained from consideration of the substituent chemical shifts of the para carbon atoms. As has been noted, for compounds in which the relative contribution of the field effect to the para ^{13}C chemical shift is significant, it may be more appropriate to consider the relative chemical shifts of the meta and para carbon atoms. Table 3.4 lists the values of $S_{^{13}C_{para}}$, $\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$, and $S_{^{13}C_{para}} - 2S_{^{13}C_{meta}}$. It can be seen that the observed trends in these values are very similar because the values of $S_{^{13}C_{meta}}$ are very small. For compounds which are highly polar but which display a relatively low value of $S_{^{13}C_{para}}$ the value of

Table 3.4: Relative ^{13}C Chemical Shifts (ppm) Indicative of Substituent Resonance Effects[a]

	$\delta_{^{13}C_{para}}$	$(\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}})$	$(\delta_{^{13}C_{para}} - 2\delta_{^{13}C_{meta}})$
C_6H_5NHNa	-22.41	-23.28	-24.15
$(C_6H_5)_2NNa$	-15.58	-16.38	-17.18
$C_6H_5NH_2$	-13.21	-14.50	-14.81
$(C_6H_5)_2NH$	-8.04	-8.97	-9.90
C_6H_5PHNa	-11.63	-9.87	-8.11
C_6H_5AsHNa	-10.38	-8.52	-6.66
$(C_6H_5)_2PNa$	-8.70	-7.58	-6.46
$(C_6H_5)_2AsNa$	-8.23	-6.82	-5.41
$C_6H_5GeH_2Na$[b]	-4.93	-3.58	-2.23
$(C_6H_5)_2GeHNa$[b]	-5.55	-3.36	-1.17
$(C_6H_5)_3GeNa$[b]	-5.19	-3.08	-0.97
$C_6H_5PH_2$	-0.11	-0.39	-.67
$C_6H_5AsH_2$	-0.37	-0.80	-1.23
$(C_6H_5)_2PH$	+0.14	-0.18	-.50
$(C_6H_5)_2AsH$	-0.08	-0.59	-1.10
$C_6H_5GeH_3$	+0.79	+0.66	+0.53
$(C_6H_5)_2GeH_2$	+0.92	+0.72	+0.52
$(C_6H_5)_3GeH$	+0.91	+0.77	+0.63

(a) All data for tetrahydrofuran solutions unless noted otherwise.
(b) NH_3 solutions.

$S_{^{13}C_{para}} - 2S_{^{13}C_{meta}}$ might be the best indication of the resonance effect. However, when the resonance effects are large relative to the field effects of the substituents then this 'correction' is certainly not significant.

The general qualitative conclusions may be summarized as follows. Clearly both aniline and diphenylamine as well as their monoanions exhibit, particularly for the anions, considerable negative charge transfer from nitrogen into the phenyl rings. The anions of phenyl- and diphenylphosphines and arsines display less delocalization and consequently field effects begin to assume some importance because of the more localized charge, but the resonance contribution is still significant. The resonance effect is small for the phenylgermyl anions and in these cases the negative charge must be largely localized on germanium thus giving rise to relatively large field contributions to the para and meta ^{13}C chemical shifts. The neutral phosphines and arsines show minimal resonance effects and for the neutral germanes a weak pπ-dπ interaction between the ring and germanium might be postulated.

The effect of the use of a different solvent for the germyl anions (NH_3 as opposed to THF for all other species) has already been noted. If it were possible to use the same solvent for all cases it is expected that the differences between the group <u>5B</u> anions and group <u>4B</u> anions would be enhanced and that the phenyl germyl anions would display negligible resonance effects in solvents of lower polarity as is observed for $(C_6H_5)_3Si^-$ in THF (Olah, 1980).

Consideration of the SCS of all four types of carbon atom in the anions studied leads to the conclusion that the distribution of π-electron density in the phenyl rings is mainly a result of the balance between 'resonance' effects, which may be considered to include both charge transfer and π-orbital effects, and 'field' effects as a consequence of the degree of localization of the negative charge on the substituent atom.

D. ^{31}P NMR

The ^{31}P NMR parameters of the phosphines and phosphides studied as well as the coupling constants derived from ^{1}H and ^{13}C NMR spectra are shown in Table 3.5. The available literature data on these species are included for comparison and there is generally good agreement. It has been previously noted that ^{31}P chemical shifts appear to depend not so much on the overall electric charge on the molecule as on the geometry at phosphorus (Van Wazer, 1967). In addition the nature of the substituents bonded to phosphorus, in particular their ability to form bonds of higher order also have an important influence on the ^{31}P chemical shifts. The most notable feature of the observed trends in ^{31}P chemical shift (Table 3.5) is that deprotonation of PH_3 results in a large upfield shift (-58 ppm), while

Table 3.5:

^{31}P N.M.R. Parameters[a]

	$\delta_{^{31}P}$	$^1J_{^{31}P^1H}$	$^3J_{^{31}PCC^1H}$	$^1J_{^{31}P^{13}C}$ [g]	$^2J_{^{31}PC^{13}C}$ [g]	$^3J_{^{31}PCC^{1}}$
PH_2Na [b]	-303.4(1)	147(3)[e]				
PH_2K [c]	-256	134				
PH_3 [b]	-245.4(1)	189(3)[e]				
PH_3 [c]	-240	182				
$C_6H_5PH_2$ [b]	-125.7(1)	198.7(2)[f]	6.9(6)[e]	8.8(8)	16.2(8)	5.9(8)
$C_6H_5PH_2$ [c]	-122	196				
C_6H_5PHNa [b]	-120.9(1)	162.8(2)[f]	5.4(1)[f]	44.1(8)	16.2(8)	5.9(8)
C_6H_5PHNa [d]	- 98.4(1)	152(3)[e]				
$(C_6H_5)_2PH$ [b]	- 41.3(1)	215.4(2)[f]	6.6(8)[e]	11.7(8)	16.2(8)	5.9(8)
$(C_6H_5)_2PH$ [c]	- 41.1	214				
$(C_6H_5)_2PNa$ [b]	- 22.5(1)		6.0(1)[f]	44.1(8)	17.7(8)	4.4(8)
$(C_6H_5)_2PNa$ [c]	- 24.4					

a) Chemical shifts are measured relative to external 85% H_3PO_4; negative val indicate shifts to higher field strength; the estimated error in the las digit is given in parentheses.

b) This work; approximately 1M in THF solution.

c) Reference (Knoll, 1966); DMF solvent.

d) This work; approximately 1M in NH_3 solution.

e) Coupling as measured by ^{31}P NMR.

f) Coupling as measured by ^1H NMR.

g) Couplings as measured by ^{13}C NMR.

deprotonation of phenylphosphine causes a downfield shift (5 ppm) and deprotonation of diphenylphosphine an even larger downfield shift (19 ppm). The latter shift is consistent with that observed for lithium diphenylphosphide (Grim, 1974) but it may be noted that the chemical shift for PH_2Na is at significantly higher field than the previously reported value of PH_2K in dimethylformamide (Knoll, 1966). The downfield shift of the ^{31}P resonances of phenyl- and diphenylphosphines might be attributed to a pπ-pπ interaction with the phenyl groups, as has previously been suggested for $(C_6H_5)_2PLi$ (Grim, 1974) and which is in accord with the present interpretation of ^{13}C and ^{1}H NMR results for such species. These shifts upon deprotonation might also be influenced by the changes in the bond angles, about the phosphorus atoms having varying degrees of substitution.

It is of interest to note that the solvent plays a significant role in determining the ^{31}P chemical shift of C_6H_5PHNa. For a solution of this compound in liquid ammonia the ^{31}P resonance occurs at about 22 ppm to lower field strength than for a THF solution of similar concentration. The parent hydride, $C_6H_5PH_2$, displays the same chemical shift in both solvents. Presumably the ^{31}P chemical shift of C_6H_5PHNa is sensitive to the degree of solvation of this salt. In this regard it was found that the chemical shift

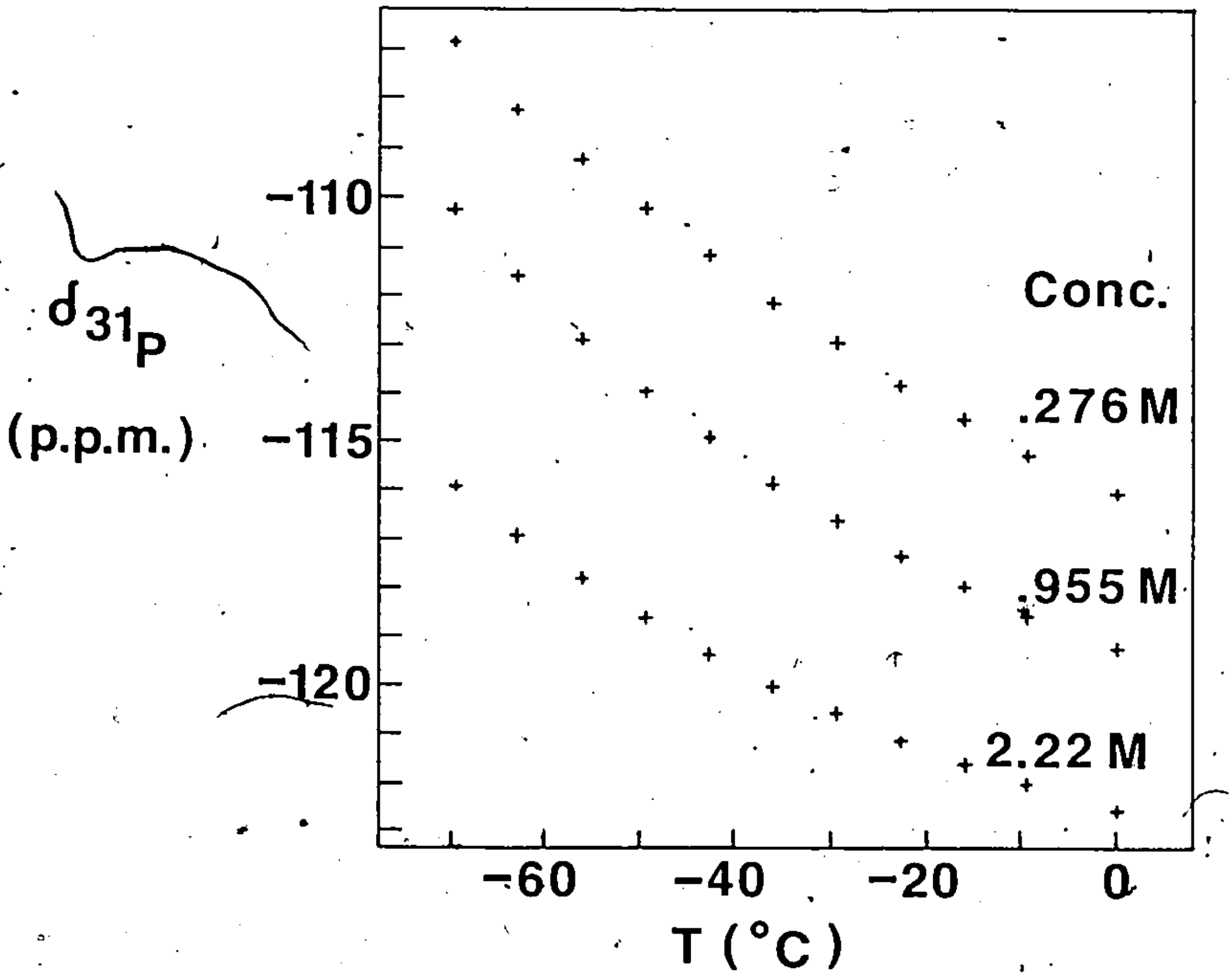


Figure 3.17: ^{31}P Chemical shift of C_6H_5PHNa (relative to 85% H_3PO_4, external) as a function of temperature and concentration.

varied with both temperature and concentration (Figure 3.17). With the limited information available it is not possible to fully describe the equilibria which exist in these solutions, but they are more involved than the simple equilibrium between solvent-separated and contact ion pairs observed for analogous carbanions (e.g. $(C_6H_5)_3CNa$) (Grutzner, 1972; O'Brien, 1976; Buncel, 1978). It is possible that for C_6H_5PHNa the ion pairs may associate to form species of analogous structure to the bridged dimeric species $[(C_6H_5)_2PLi]_2$ (Colquhoun, 1982). This could account for the concentration dependence of the ^{31}P chemical shift which is in addition to the expected temperature dependence.

The one bond ^{31}P - ^{13}C coupling constants for both phenylphosphine and diphenylphosphine (Table 3.5) increase by a factor of four upon deprotonation of these hydrides. The significance of this change is uncertain particularly since the relative signs of these couplings are not known. It has been suggested that a large separation in energy between valence s and p electrons may result in a negative one-bond coupling constant (Weigert, 1969). Also for the neutral compounds, $C_6H_5PH_2$ and $(C_6H_5)_2PH$, it may be noted that the one-bond ^{31}P - ^{13}C coupling constants are smaller in absolute magnitude than the two-bond ^{31}P - ^{13}C coupling constants. The increase in $|^1J_{PC}|$ upon deprotonation may be an indication of a P-C bond order greater than one in the anions.

The two-bond couplings, $^2J_{PC}$, do not change magnitude upon deprotonation of either phenyl- or diphenylphosphines. Studies have indicated that such couplings are always positive (Mavel, 1973). The three-bond couplings, $^3J_{PC}$, also do not change upon deprotonation. All of the ^{31}P - ^{13}C couplings, except for the one-bond couplings in the anions, are of comparable magnitude to the analagous couplings for triphenylphosphine (Bodner, 1975).

The one-bond ^{31}P - ^1H couplings are in reasonable agreement with the previously reported values (Table 3.5). Couplings involving the hydrogen nucleus are said to depend only on the 'contact' term from the electron spin polarization model for spin-spin coupling (Ramsey, 1952) since the 'orbital' and 'dipolar' contributions depend upon p-electrons. Consequently it might be expected that the magnitude of the coupling constant, $^1J_{PH}$, would reflect the s character of the phosphorus hybrid orbital involved in P-H bonding. In this regard it is of interest to note that deprotonation of either phosphine or phenylphosphine results in a decrease in $|^1J_{PH}|$ whereas phenyl-substitution of phosphine results in an increase in this parameter. Unfortunately these couplings most likely result from a sum of large terms of opposite sign as was observed for SnH_3^- (Birchall and Pereira, 1972) therefore changes in $|^1J_{PH}|$ may reflect relative changes in the magnitudes of these terms rather than simply a change in phosphorus s-orbital contribution to the bonding orbital.

The three-bond couplings, $^3J_{PH}$, of phenylphosphine and diphenylphosphine are consistent with previously reported values (Akitt, 1966; Parr 1978). The change in this parameter upon the deprotonation of these molecules is not significant compared to the estimated error in the measurements.

E. Relative Acidities

The NMR results discussed here, in particular the ^{13}C chemical shifts, corroborate the previous explanations of the observed relative acidities of the phenylhydrides of the group 4B and 5B elements (Jolly, 1971; Issleib, 1965; Birchall and Drummond, 1972). The increase in the acidity of group 5B hydrides upon phenyl-substitution may be attributed to increased resonance stabilization of the anions. There is not, however, as significant a degree of delocalization of negative charge in the anions of phenyl-substituted germanes, presumably because the large s→p promotion energy required for rehybridization of the Ge orbitals causes the 'non-bonding' pair of electrons to have predominantly s-orbital character (Jolly, 1971). Consequently there is no resonance stabilization of such anions and the observed decrease in acidity of germ[illegible] upon phenyl-substitution has been rationalized in terms of relative solvation energies as well as steric effects (Birchall and Drummond, 1972). The silanes and stannanes are expected to behave similarly. Phenylmethanes, on the other hand, show considerable increase in acidity relative to methane (Streitwieser, 1980). In this case the highly favourable overlap between the $2p_z$ orbital of the deprotonated methyl carbon atom in the carbanion with the appropriate phenyl pπ-molecular orbitals results in sufficient resonance energy to overcome the necessary s→p promotion energy. That considerable delocalization of negative charge into the phenyl rings of phenylmethyl carbanions occurs is demonstrated by the ^{13}C NMR parameters of such species (O'Brien, 1975; Takahashi, 1970).

The possibility that the observed relative acidity differences between the germanes (Birchall and Drummond, 1972) and the group 5B compounds (phosphines and arsines; Issleib, 1965) are due solely to solvent effects must be considered because the former were measured in liquid ammonia solvent whereas THF was used as the solvent for the arsines and phosphines. In this regard, measured amounts of PH_3 were condensed into both ammonia and tetrahydrofuran solutions containing comparable known amounts of C_6H_5PHNa. After allowing these solutions to equilibrate the ^{31}P or ^{13}C NMR spectra revealed that both samples contained predominantly C_6H_5PHNa and PH_3 and much smaller amounts of $C_6H_5PH_2$ and PH_2Na. This demonstrates that the order of relative acidities of the two hydrides are the same in NH_3 as in THF (i.e. that $C_6H_5PH_2$ is more acidic than PH_3). Therefore the different behaviour of the group 5B phenylhydrides from those of the phenylgermanes cannot be accounted for solely in terms of solvation effects.

It must be pointed out however that considerable uncertainty exists as to the reliability of the reported relative acidities of the phenyl-substituted hydrides of the group 5B elements because the various data used in their determination (Issleib, 1965) represent competitive equilibria involving differing counterions and using different indicators. Furthermore the relative pKa values of phosphine and arsine were not determined but merely suggested as reasonable estimates. It has become apparent that the acidifying effect of the phenyl-substituent on PH_3 and AsH_3 is perhaps not as great as previously suggested. For example the competitive equilibrium (described above):

$$C_6H_5PHNa + PH_3 \overset{K}{\rightleftharpoons} C_6H_5PH_2 + PH_2Na \qquad (3.14)$$

yielded a value of -log K of 0.95 ± 0.2 in THF solution whereas the data of Issleib and Kümmel (1965) implied a value of 4.5. The similar experiment (also described above) using NH_3 as solvent gave a value for -log K of 2.1 ± 0.5.

Also, the acidities of phenyl and diphenyl-phosphines have recently been remeasured with respect to an established acidity scale for hydrocarbon acids in DMSO solvent

(Terekhova, 1982). These findings suggested that further substitution of phenyl-phosphine to give diphenylphosphine actually results in a decrease in the acidity of the remaining proton by 0.7 logarithmic units. These authors reexamined the data of Issleib and Kümmel (1965), for THF solvent, in the light of more appropriate current values for the pKa's of the indicators used, and concluded that the observed equilibrium constants represent an increased acidity of diphenylphosphine relative to phenylphosphine of only 0.5 logarithmic units as opposed to the value of 2.8 suggested earlier (Issleib, 1965). They further rationalized the remaining apparent discrepancy of 1.2 logarithmic units as possibly arising from the use of different counterions in the earlier study. The possible influence of the use of different solvents in the two studies may also be important. In light of the apparent importance of solvent and ion-pairing effects on the equilibria involved in the acidity measurements, the significance of the relative acidities for the phenyl- and diphenylarsines reported by Issleib and Kümmel are also cast into doubt.

Figure 3.18 shows a graph on which is plotted the average change in pKa per phenyl-substituent for various phenyl-substituted hydrides (relative to the unsubstituted parent hydride) versus the parameter, $\delta_{^{13}C_{para}} - \delta_{^{13}C_{meta}}$, of their conjugate anions. The acidity data for this plot (except for those for the $C_6H_5PH_2/PH_3$ couple (mentioned above)) are taken from: Birchall and Drummond (1972), Algrim (1978), Terekhova (1982), and Streitwieser (1980). These data represent the relative acidities in non-hydroxylic, dipolar solvents. ^{13}C NMR data for the phenyl-substituted methyllithium salts, $(C_6H_5)_nCH_{3-n}Li$, are those of Takahashi (1974). The large error-bars indicated for the relative acidity data of the nitrogen and carbon hydrides have been chosen somewhat arbitrarily but are indicative of the uncertainty in the pKa values for NH_3 and CH_4 as a consequence of their very low acidities. Data points for the phenyl-substituted arsines have unfortunately been omitted from the plot because of doubt concerning the reliability of the reported relative acidity data (Issleib, 1965) but the results obtained appear to indicate that the values may be closely comparable to those for the analogous phosphines.

Despite the uncertainties, the effect of phenyl-substitution on the acidity of the hydrides appears to roughly parallel the trend in the ^{13}C NMR chemical shifts. The observed trend suggests that the degree to which the negative charge may be delocalized into the phenyl-rings of the anions is a major factor in the acid strengthening effect of phenyl-substitution. Although the difference in the influence of the phenyl substituent on acidity between the germanes and the group <u>5B</u> hydrides is not as large as previously thought it still appears to be significant and is most likely a consequence of the different degrees of resonance stabilization of the anions.

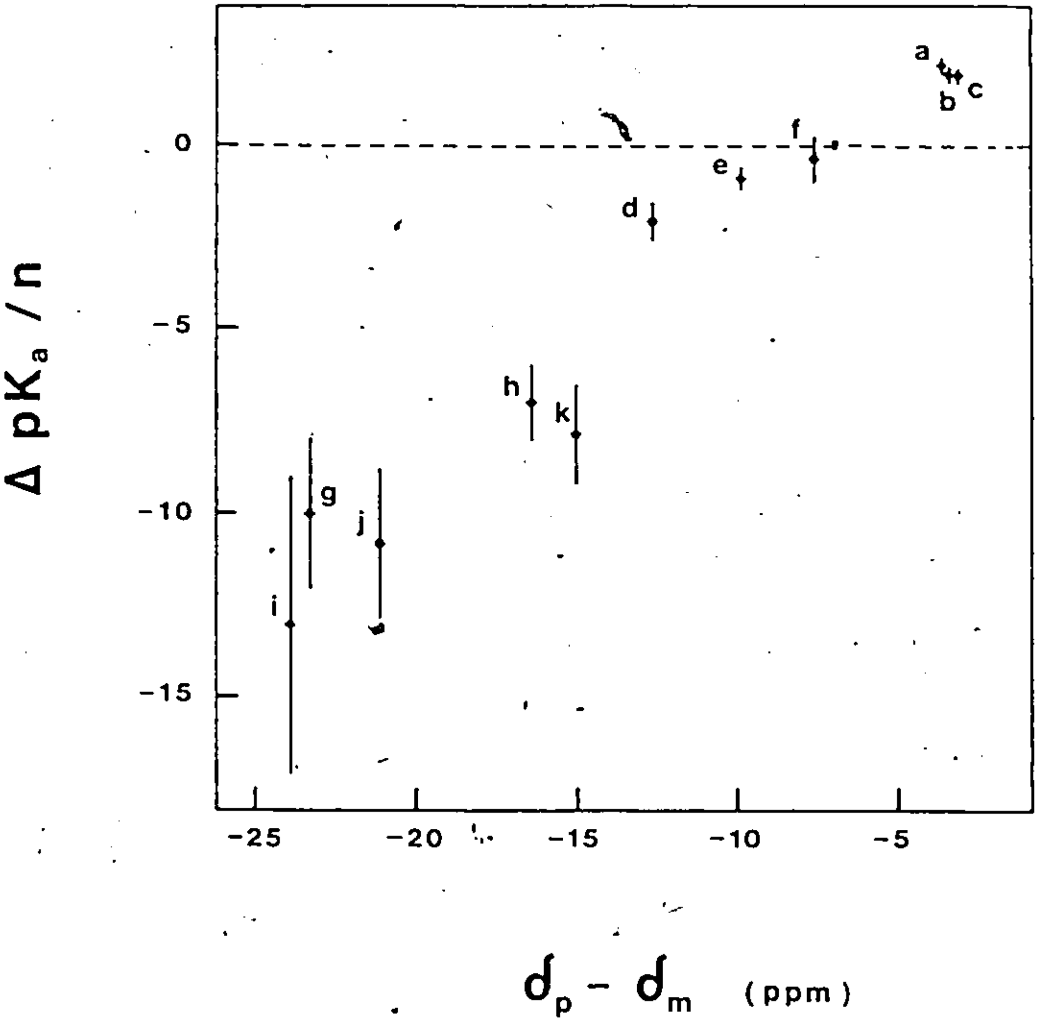


Figure 3.18: Plot of the average change in pK$_a$ per phenyl-substituent for hydrides of carbon, nitrogen, phosphorous and germanium versus the ^{13}C NMR parameter, $\delta_{para}-\delta_{meta}$, for the analogous monoanions;

$$\Delta pK_a/n = [pK_a(Y(C_6H_5)_nH_{m-n}) - pK_a(YH_m)]/n;$$

^{13}C NMR:

a) $C_6H_5GeH_2Na$ (NH_3)
b) $(C_6H_5)_2GeHNa$ (NH_3)
c) $(C_6H_5)_3GeNa$ (NH_3)
d) C_6H_5PHNa (NH_3)
e) C_6H_5PHNa (THF)
f) $(C_6H_5)_2PNa$ (THF)
g) $(C_6H_5)NHNa$ (THF)
h) $(C_6H_5)_2NNa$ (THF)
i) $C_6H_5CH_2Li$ (THF)
j) $(C_6H_5)_2CHLi$ (THF)
k) $(C_6H_5)_3CLi$ (THF)

CHAPTER 4

COORDINATION CHEMISTRY OF PHOSPHINES WITH CUPROUS IODIDE

A. Introduction

Although basicity and donor ability are well known properties of trivalent compounds of the group 5B elements (evidence for this comes from innumerable studies of coordination compounds involving ligands such as triphenylphosphine), there has been relatively little investigation of the coordination chemistry of hydrides and organohydrides of the group 5B elements other than nitrogen. Presumably this is because the tertiary derivatives, especially the triphenyl compounds, are much easier to work with. Triphenylphosphine is a readily available, air stable, solid which is relatively non-volatile and is soluble in many organic solvents. The secondary and primary phosphines and arsines are generally volatile liquids and are very susceptible to oxidation thus requiring handling under an inert atmosphere. It is also reasonable to expect that the coordination chemistry of primary and secondary phosphines will be very similar to that of tertiary derivatives. However potential differences do exist. For example there is evidence for the dissociation of P-H bonds with resultant formation of phosphido complexes (Kraihanzel, 1974). Also it has been noted that the order of basicity for phosphines is tertiary > secondary > primary > PH_3 (Henderson, 1960).

The coordinating ability of a phosphine, however, depends on features other than simple basicity. For example the extent to which π-acidity of the ligand can contribute to the stability of the coordinative interaction has been the centre of much controversy (McAuliffe, 1979). It is unlikely that π-back donation into d-orbitals of the ligand is significant for tertiary organophosphines, but for PF_3 and for phosphites it is apparently important (Emsley, 1976). Vibrational studies on the C-O stretching frequency of a carbonyl group trans to a given phosphine ligand indicate that PH_3 is intermediate in 'π-accepting' ability between tertiary phosphines and phosphites (Emsley, 1976).

It has also been shown that, for tertiary phosphines, the steric bulk of the ligand appears to be the deciding factor in the stability of the coordinative interactions between these ligands and transition metals (Tolman, 1970; Lippard, 1971, 1972). With much smaller phosphine ligands such as PH_3 or the primary phosphines, steric interactions should be greatly reduced (cf. the cone angle of PH_3 is 87° whereas that of $P(C_6H_5)_3$ is 145° (Tolman, 1970)). For complexes containing these small ligands, electronic factors should assume increased importance.

The systems $(CuX)_m(PR_3)_n$ (X = halide) appeared to be potentially useful for investigations concerning the relative importance of steric and electronic factors because a large number of X-ray crystallographic studies (Gill, 1976, and references therein) have shown that the steric bulk of both the phosphine ligands and the halides have a tremendous influence on the degree of association and resulting structure of such complexes. Spectroscopic characterization of these complexes has proven to be somewhat problematic however and as a consequence of this they have been largely studied by X-ray crystallography (McAuliffe, 1979).

In the present work complexes based on cuprous iodide were investigated with the hope that ^{127}I Mössbauer spectroscopy could be used to characterize the different species according to the geometries about the iodine. Iodine can be triply-bridging, doubly-bridging, terminal or potentially ionic in these compounds depending on the CuI to phosphine ratio. It was expected that the differences in these iodine environments would be reflected in the quadrupole coupling constant ~~and~~ the asymmetry parameter for ^{127}I. As shall be seen, however, this turns out not to be the case. NMR and vibrational studies are of limited use for structural characterization of these compounds but are briefly considered. It is still the case therefore that X-ray crystallography must be resorted to for unambiguous characterization of $CuX{\cdot}PR_3$ compounds.

In early vapour pressure studies (Holtje, 1940; Scholder, 1934) it was concluded that cuprous halides could form complexes with PH_3 in ratios of $CuX{\cdot}2PH_3$ and $CuX{\cdot}PH_3$ but that these were unstable to loss of PH_3. Much later, Abel et. al. (1969) studied the complexes formed between $(C_6H_5)_2PH$ and cuprous halides in the hope that vibrational and ^1H NMR spectroscopy, with specific focus on the hydrogen bonded to phosphorus, would yield further information on the characterization of these kinds of complexes. These authors found complexes possessing most of the known stoichiometries for $(CuX)_m(PR_3)_n$, where m/n = 1/3, 1/2, 2/3, 1/1. However, while NMR and infrared spectroscopies could differentiate between free and complexed $(C_6H_5)_2PH$, these techniques could not discriminate between the different stoichiometries and structures of the complexes. These studies appear to be the only previous investigations of cuprous halide complexes of non-tertiary phosphines.

B. ^{127}I Mössbauer Spectroscopy of $CuI{\cdot}nP(C_6H_5)_3$ Adducts

Although a great deal of crystallographic and other work has been published concerning complexes of the cuprous halides with tertiary phospines, no Mössbauer spectroscopy on such species has been previously reported. To establish the utility of ^{127}I Mössbauer spectroscopy for distinguishing between the different types of structures found for CuI·nPR$_3$ complexes, the series of triphenylphosphine adducts was selected since this series of compounds includes the three types of known geometries for the iodine atom environment and the structures of these compounds are established.

The one-to-one adduct is found to form a tetrameric molecule, $[CuIP(C_6H_5)_3]_4$, possessing the 'step' structure, (II) shown in Figure 4.1 (Churchill, 1975). The reason that this molecule has this 'step' structure as opposed to the more common 'tetrahedral' structure, (I) in Figure 4.1, is that the latter structure would have more inherent steric strain as a consequence of the large halide and the bulky triphenylphosphine ligands. The iodine atoms in $[CuIP(C_6H_5)_3]_4$ occur in two different molecular environments namely di-bridging (bent) and triply-bridging (pyramidal), both of which are asymmetric.

The molecule $(CuI)_2[P(C_6H_5)_3]_3$ possesses the dimeric structure (IV) in Figure 4.1 (Eller, 1977). Here the two crystallographically unique iodine atoms are in very similar asymmetrically di-bridging environments. The fact that CuI does not form a 2:4 adduct, (III) in Figure 4.1, with triphenylphosphine is, again, most probably the result of the steric bulk of the ligands which restrict one of the copper atoms to pseudotrigonal coordination.

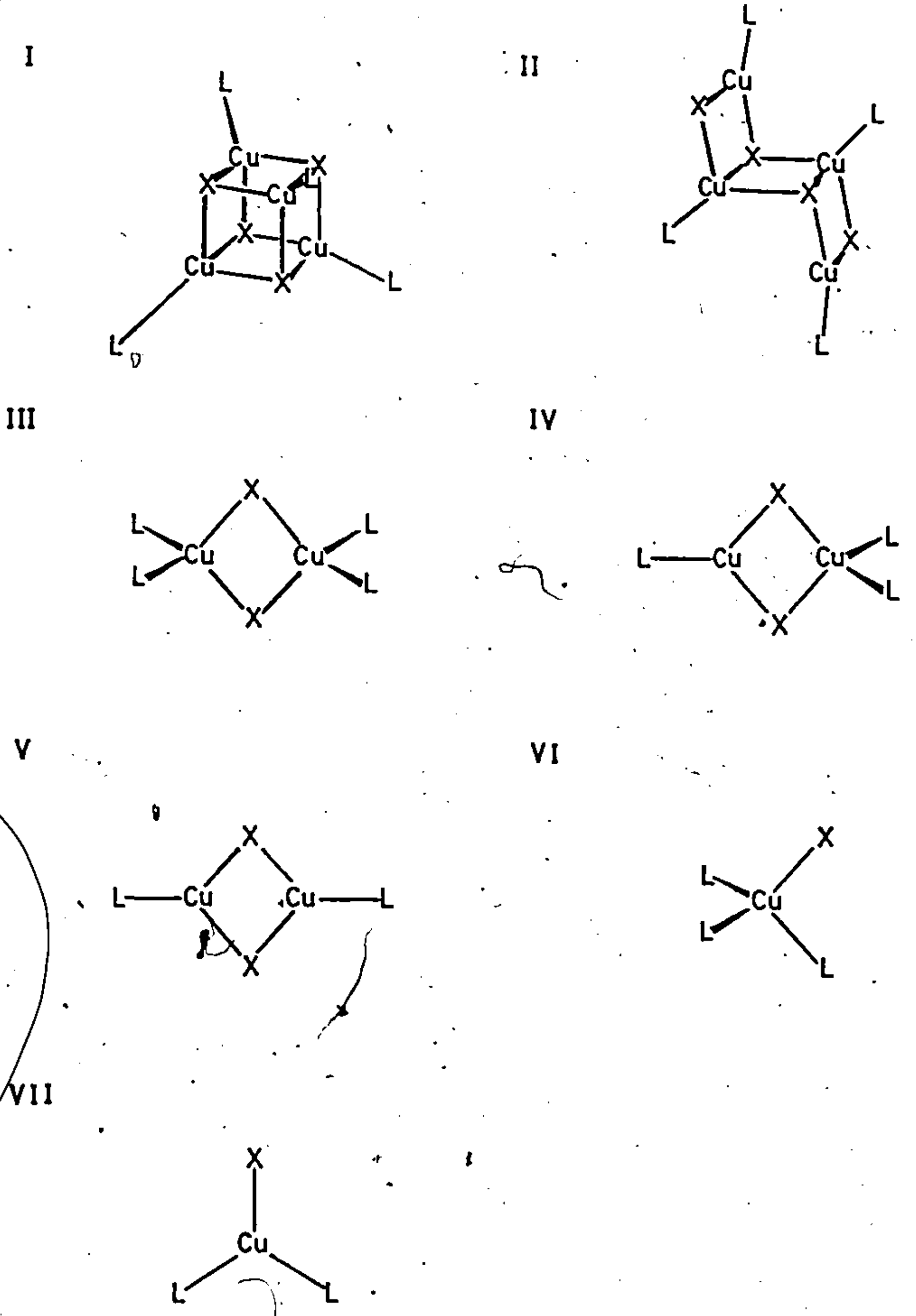


Figure 4.1: Known Geometries of Cuprous Halide-Tertiary-Phosphine Adducts

The structure of $CuI[P(C_6H_5)_3]_3$ does not appear to have been determined, however, it is almost assuredly a pseudotetrahedral monomer, (VI) in Figure 4.1, analogous to the structures of $CuCl[P(C_6H_5)_3]_3$ (Gill, 1976) and $Cu[BF_4][P(C_6H_5)_3]_3$ (Gaughan, 1974). Therefore for $CuI[P(C_6H_5)_3]_3$ the iodine atom is likely to be terminally bonded to copper.

These compounds were expected to display different ^{127}I quadrupolar couplings and asymmetry parameters as a result of the different environments about iodine. This would provide a means of characterizing the complexes. The quadrupole coupling constants were expected to be significant because the Cu-I interatomic distances in these compounds are approximately equal to the sum of the covalent radii (2.61A) (Pauling, 1965), and covalent interactions in these non-spherical environments about iodine should give rise to significant electric field gradients at that nucleus.

The ^{127}I Mössbauer spectra of the triphenylphosphine adducts as well as that of CuI itself are shown in Figure 4.2. The relevant data are summarized in Table 4.1. The single striking feature of these spectra is that none of them display any resolvable quadrupole coupling. In fact the half-height linewidths of these spectra are comparable to that found for CuI in which the tetrahedrally coordinated iodine atoms should experience negligible electric field gradients and hence negligible quadrupole coupling. Although

Table 4.1: ^{127}I Mossbauer Parameters for Complexes of CuI [a,b]

Compound		Isomer Shift[c] (mm s^{-1})	eQV_{zz}[d] (MHz)	Absorber Linewidth (mm s^{-1})	T_A[e]	χ^2/degree of freedom
CuI		-0.17(2)	0.0*	3.77(1)	0.24(1)	0.90
$CuI[P(C_6H_5)_3]_3$	(1)	-0.26(2)	0.0*	2.64(8)	0.200(4)	1.20
	(2)	-0.17(2)	-465(19)	1.7*	0.280(4)	1.07
$[CuI]_2[P(C_6H_5)_3]_3$	(1)	-0.26(2)	0.0*	2.61(7)	0.160(3)	0.91
	(2)	-0.18(2)	-446(18)	1.7*	0.220(3)	0.84
$[CuIP(C_6H_5)_3]_4$	(1)	-0.26(1)	0.0*	3.83(4)	0.478(3)	2.55
	(2)[f]	-0.79(3) +0.28(4)	-624(24) 685(21)	1.7* 1.7*	0.853(5)	1.11
$[CuI(C_6H_5PH_2)_2]_2$	(1)	-0.20(2)	0.0*	2.56(6)	0.196(3)	1.33
	(2)	-0.13(2)	-409(19)	1.7*	0.264(3)	1.44
'$[CuIC_6H_5PH_2]_4$'		-0.29(1)	0.0*	3.40(4)	0.568(4)	2.07

[a] The parameters were obtained from the experimental data using the iterative Mössbauer fitting program GMFP (Ruebenbauer, 1979). The fitted spectra suffer from insufficient extractable information for the number of variable parameters to be determined. Consequently the minima for convergence are ill-defined unless constraints on the parameters are introduced. Therefore there is considerable uncertainty as to the significance of the numbers obtained.

[b] In all cases the source linewidth was fixed at the natural linewidth (1.27 mm s^{-1}); * indicates the values of other parameters which also were not permitted to vary during the fitting procedure.

Table 4.1: (continued)

[c] Isomer shifts measured relative to the source ($Zn^{127m}Te$).

[d] In most cases visually better fits to the experimental data could be obtained by including variable quadrupolar coupling constants. In these cases the absorber linewidth was fixed at a value which represents a reasonable expected minimum (1.7 mm s^{-1}) (Myers, 1982; Birchall, 1981). The fitted values of eQV_{zz}, therefore, represent maximum possible quadrupolar coupling constants. In all cases the asymmetry parameter (η) was fixed at zero although, for some of the sites considered, this condition is not to be expected. Allowing η to vary during the iterative process resulted in non-convergence or in results of dubious significance.

[e] Dimensionless absorber thickness.

[f] Two sites fitted.

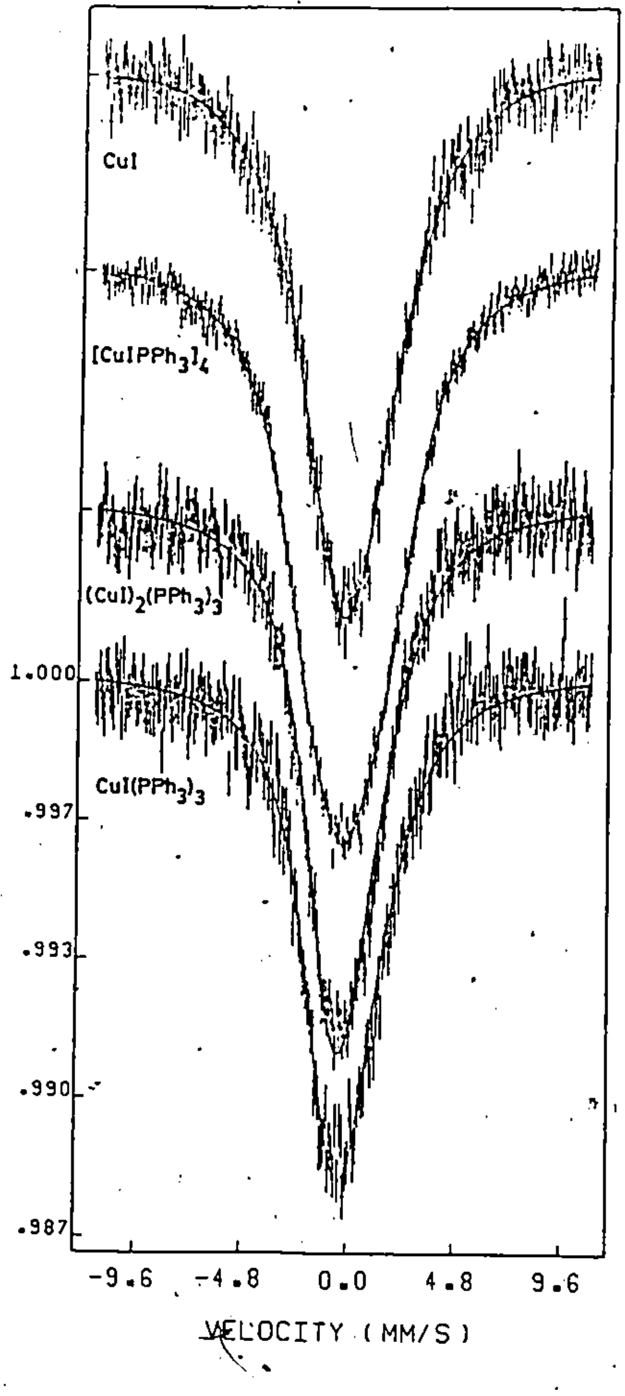


Figure 4.2: ^{127}I Mössbauer spectra of some cuprous iodide complexes

it is noted that the linewidth of the resonance for cuprous iodide can be improved somewhat (i.e., approaches closer to the ideal natural linewidth) by considerably reducing the sample size, it is nevertheless apparent that the quadrupole couplings of the iodine nuclei in the adducts are too small to be resolved by ^{127}I Mössbauer spectroscopy.

The maximum possible magnitudes of the coupling constants (eQV_{zz}) in these adducts are indicated in Table 4.1. By comparison, genuinely covalent interactions of iodine bonded to main group elements in non-cubic configurations can give rise to quadrupole coupling constants as large as 3200 MHz (Birchall, 1981). There have been relatively few iodine Mössbauer investigations of iodide bonded to transition metals however a number of ^{129}I Mössbauer results have been reported for the iodo ligand in Pt(II) coordination compounds (Dale, 1974). Conversion of the ^{129}I quadrupole coupling constants for these species, which contain iodine terminally bonded to platinum, to the corresponding values for ^{127}I yields values ranging from 770 to 1190 MHz. These values are significantly larger than the maximum-possible values for the $CuI \cdot nP(C_6H_5)_3$ complexes.

It must, therefore, be concluded that for the copper(I)-iodo complexes there is little distortion of the electronic environment of iodine from the spherical valence configuration of the purely ionic iodide ion. This would seem to indicate that the nature of the 'bond' between iodine and copper is not covalent despite the short internuclear separation. Alternatively this could imply that, in the bonding, electrons are withdrawn nearly equally from all of the valence p orbitals of iodine. This is conceivable for the triply bridging iodine environment but not for the di-bridging or terminal environments. The possibility that a lattice contribution to the electric field gradient cancels the valence contribution seems rather unlikely. Consequently it must be concluded that, for compounds of copper(I) iodide, comparison of the actual bond lengths with accepted ionic or covalent radii sums is not necessarily a valid indication of the degree of covalency of the bond.

C. Coordination Chemistry of Phenylphosphine with Cuprous Iodide

(i) $CuI \cdot C_6H_5PH_2$

The reaction of excess cuprous iodide with phenylphosphine in THF yielded an infinitely soluble product. The weight of unreacted CuI suggested that the stoichiometry of the soluble product was approximately $(CuI)_{0.8} \cdot C_6H_5PH_2$. The ^{31}P NMR spectrum of this solution consisted of a triplet at $\delta = -106.62(3)$ ppm having the spin-spin coupling $^1J_{PH} = 303(3)$ Hz. (The proton NMR spectrum reveals $^1J_{PH} = 302.2$ Hz). Studies with tertiary phosphines have shown that analogous complexes undergo dissociation in solution and rapidly exchange phosphine ligands at room temperature (Lippard, 1971). Below -70°C the ^{31}P resonance of the above solution broadens considerably and shifts slightly, -109 ppm at -90°C, however no new features were observed before the freezing point of the solution was reached. Since the observed room temperature chemical shift is to low field of that of free phenylphosphine by approximately 20 ppm and the P-H coupling constant is ~ 100 Hz greater than that of free phenylphosphine, it must be concluded that these NMR parameters represent a coordinated ligand. Perhaps these ligands undergo rapid exchange, at room temperature, between species of different geometry and degree of association as has been observed for tertiary phosphine adducts (Lippard, 1972; Muetterties, 1970).

The ^{13}C NMR parameters averaged from two different sample preparations are δ_{C_1} = 125.8(2) ppm, δ_{C_2} = 135.7(2) ppm, δ_{C_3} = 129.5(2) ppm, δ_{C_4} = 130.6(2) ppm, $^{1}J_{PC}$ = 27(2) Hz, $^{2}J_{PC}$ = 12(2) Hz, $^{3}J_{PC}$ = 8(2) Hz. The notable difference between these parameters and those of free phenylphosphine (see Table 3.2) are the shift to higher field strength for the ipso carbon (-3.4 ppm), the shift to lower field strength of the para carbon resonance (1.8 ppm) and the increase in the one-bond P-C coupling constant from 9 Hz for phenylphosphine to 27 Hz for the coordinated ligand. These changes are consistent with a coordinative interaction along with the accompanying changes in hybridization at phosphorus.

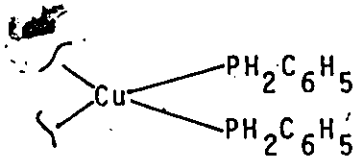
The fact of the high miscibility of the solute with THF along with an apparent slow decomposition of the dissolved adducts to give a dark coloured, THF soluble substance, possibly a phosphido species as a consequence of P-H bond cleavage, prevented the isolation of a pure solid product from the above solutions. However, when the THF solvent was evaporated under vacuum and the viscous glassy residue was immersed in diethylether, colourless crystals slowly grew out of the insoluble mass of residue which ultimately completely solidified. This was accompanied by precipitation of the small amount of dark by-product mentioned above. None of these crystals was found suitable for structure determination by X-ray crystallography. This solid product (density ~ 2.3 g cm^{-3}) was, most likely, a tetrameric 1:1 adduct of CuI with $C_6H_5PH_2$ by analogy with the known stoichiometries and structures of other 1:1 adducts between CuX and tertiary or secondary phosphines (Costa, 1965; Churchill, 1975; Abel, 1969). Attempts to recrystallize the solid from different solvent systems were unsuccessful and were accompanied by further decomposition. At the present time it remains uncharacterized. The ^{127}I Mössbauer parameters of the crude product are included in

Table 4.1. No significant differences from those for the triphenylphosphine adducts are observed.

(ii) $CuI \cdot 2C_6H_5PH_2$

When two equivalents of phenylphosphine were allowed to react with cuprous iodide a crystalline product was obtained after recrystallization from ethanol containing 5% THF. The crystallization was affected by slow evaporation of solvent, the THF evaporating preferentially thus diminishing the THF content of the mixed solvent system. Like the previous solute this substance is infinitely miscible with THF but it has low solubility in ethanol.

A THF solution of the product yielded room temperature ^{31}P and ^{13}C NMR spectra which were essentially identical with those found for the previous solutions prepared using excess CuI. However, the ^{31}P NMR spectrum initially displayed upon cooling, some broadening of the observed triplet until at about -90°C further fine structure was resolved (see Figure 4.3). The low temperature spectrum can be accounted for by postulating a ^{31}P-^{31}P spin-spin coupling between two phenylphosphine ligands bound to the same copper atom.



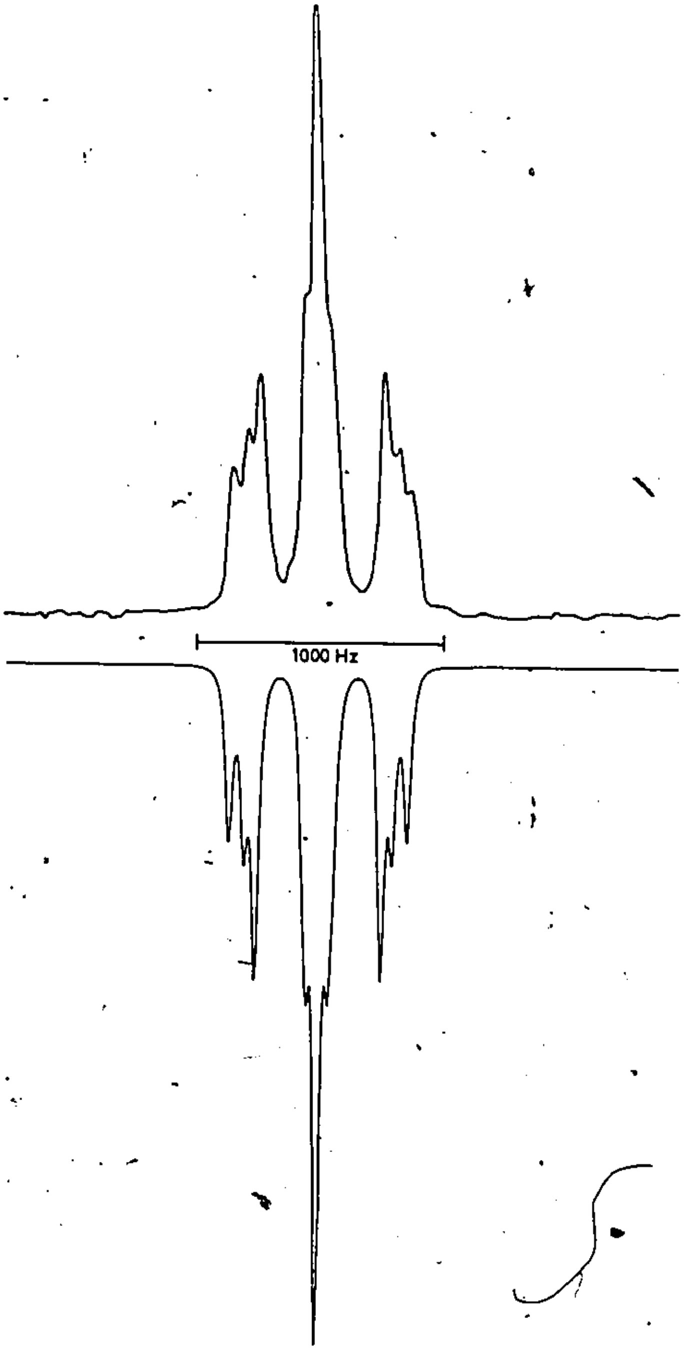
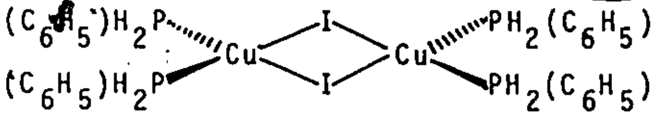


Figure 4.3: Experimental and simulated ^{31}P NMR spectra of $[CuI(C_6H_5PH_2)_2]_2$ in THF at -97°C

Although these two phosphorus atoms are chemically equivalent and thus have the same chemical shift, they are magnetically inequivalent by virtue of the strong coupling to the protons directly bound to them. This kind of second order effect is sometimes known as 'virtual coupling' (Becker, 1980). Figure 4.3 includes a simulated spectrum which represents the best fit to the observed peak positions assuming only coupling between directly bound phosphorus and hydrogen and the two bond ^{31}P-^{31}P coupling. The three bond ^{31}P-^{1}H coupling was fixed at zero for this simulation. The changes in ^{31}P chemical shift and one-bond ^{31}P-^{1}H coupling with reduced temperature were insignificant and no new resonances appeared. Therefore, it is apparent that at room temperature the bound phosphine ligands are being exchanged rapidly between different copper atoms. It is not possible to deduce whether this exchange is inter- or intramolecular. However, since it is known that these kinds of complexes may dissociate in solution, it is quite possible that the exchange is intermolecular in nature. The species in solution at low temperature could be the dimer:



The possibility that a THF solvent molecule assumes one coordination position, and thus breaks-up the dimers, cannot be ruled out.

The crystalline solid obtained from the ethanol/THF recrystallization was found by X-ray crystallography to be, indeed, the bridged dimer, indicated above.

The ^{127}I Mossbauer parameters of $[CuI(C_6H_5PH_2)_2]_2$ are included in Table 4.1 and again, no resolyable quadrupole coupling was observed. Raman and infrared spectra of this solid showed that a significant amount of free phenylphosphine was present in the sample as evidenced by a band at 2290 cm^{-1} corresponding to the P-H stretching vibration of $C_6H_5PH_2$. It is possible that this free $C_6H_5PH_2$ was produced by decomposition of the sample in the laser beam of the Raman spectrometer. Two bands centred at approximately 2322 and 2344 cm^{-1} which occur in both the Raman and infrared spectra may be attributed to the P-H stretching modes of the complexed ligand. Infrared spectra of cuprous halide adducts of diphenylphosphine (Abel, 1969) indicate that the P-H stretch of the coordinated ligand occurs at about 30-40 wavenumbers higher frequency than that of free $(C_6H_5)_2PH$. Solid compounds of higher $C_6H_5PH_2$/CuI ratio were not obtained.

(a) Structure of Tetrakis(phenylphosphine)-di-μ-iodo-dicopper(I)

The experimental data for the X-ray diffraction study of $[CuI(C_6H_5PH_2)_2]_2$ are summarized in Table 4.2. The structure was initially solved using a partial set of intensity data collected at ambient temperature. Because of the low melting point of the compound (65°C), and the somewhat large atomic temperature factors determined in this initial refinement, a full data set was acquired at -65°C.

The symmetry and systematic absences of the weighted reciprocal lattice indicated that C2/c and Cc were possible space groups for the crystal. No solution to the Patterson map could be found in the centrosymmetric space group C2/c. Analysis of the normalized squared structure factors (E^2) gives an average value of $|E^2-1|$ of 0.82. A centrosymmetric structure would be expected to give a value of 0.97 and a noncentrosymmetric structure a value of 0.74 (Sheldrick, 1976).

The structural solution in the non-centrosymmetric space group Cc was fully refined for all non-hydrogen atoms and included anisotropic temperature factors for Cu, I and P. The subsequent final cycles of refinement included the 20 hydrogen atoms of the phenyl-rings, which atoms were fixed at positions 0.95Å (Churchill, 1973) from each carbon atom along a vector bisecting each C-C-C angle and in the plane defined by those atoms. The hydrogen atoms were assigned isotropic

Table 4.2: Crystal and Diffraction Data Acquisition Parameters for $[CuI(C_6H_5PH_2)_2]_2$.

Crystal Parameters (at -65°C).[a]

a = 10.625(2)Å
b = 25.115(8)Å
c = 11.361(2)Å
β = 105.929(15)°
V = 2914.6(12)Å^3
μ(MoK$_\alpha$) = 38.5 cm^{-1}

Monoclinic
Space group Cc
Z = 4
FW = 821.28
$\rho_{(calc)}$ = 1.8716(9) g cm^{-3}
$\rho_{(obs)}$ = 1.8(1) g cm^{-3}

Conditions : hkℓ : h+k = 2n
hOℓ : ℓ = 2n
Crystal dimensions : 0.3 × 0.3 × 0.2 mm[c]

Intensity Measurements

Radiation : MoK$_\alpha$ (λ = 0.71069Å)
Scan Mode : θ:2θ
Scan Range : (K$_{\alpha_1}$ -1.0°) to (K$_{\alpha_2}$ +1.0°)
Scan rates[d] : 5.86 to 29.30° min^{-1}
Reflections measured : ±h,k,±ℓ
Maximum 2θ : 45°
Standard reflections[e] : 5 -5 0 (e.s.d. 2.93%)
: 4 -8 1 (e.s.d. 1.53%)

Table 4.2: (continued)

Details of Refinement[f]

Unique Reflections : 3820
'Unobserved Reflections' : less than 3σ:381, zero intensity:36[g]
R Factors[h] : $R_1 = 0.0460$
: $R_2 = 0.0593$
Weighting Scheme : $w = [\sigma_F^2 + 0.001741\ F^2]^{-1}$
'Second Extinction' : $F^* = F(1-2.9\times10^{-8}F^2/\sin\theta)$
Final|Shift/error| : Maximum 0.090
: Average 0.006
Highest peak[i] in final difference map : 1.010 eA^{-3}
Lowest trough in final difference map : -0.655 eA^{-3}

[a] 15 reflections 20°<2θ<30° were used to determine the cell constants using MoK_{α_1} radiation (λ = 0.70926Å).

[b] Neutral buoyancy in aqueous $ZnBr_2$.

[c] The crystal was a rectangular prism; the dimensions given are approximate; measurement of more precise crystal dimensions was unfortunately forestalled by decomposition and liquefaction of the crystal upon rewarming to room temperature after the acquisition of intensity data.

Table 4.2 (continued)

[d] Dependent on the intensity of a preliminary count.

[e] Measured after every 48 reflections; displayed no systematic deviations in intensity.

[f] Data reduction, including Lorentz and polarization corrections, was performed using programs from the XRAY-76 package of crystallographic programs. Absorption corrections were not applied (estimated maximum error in F is ~35%).

[g] Reflections of zero intensity were given a weight of zero in the refinement.

[h] $R_1 = \Sigma(|F_{(obs)}|-|F_{(calc)}|)/\Sigma(F_{(obs)})$

$R_2 = [\Sigma(w(|F_{(obs)}|-|F_{(calc)}|)^2)/\Sigma(wF_{(obs)}{}^2)]^{1/2}$

[i] This peak occurs at (0.4035, 0.4229, 0.7104) which is 1.00Å from I_1. The second most intense peak occurs at 1.09Å from I_2.

temperature factors fixed at 1.5 times those of the carbon atom to which they were bonded. The positions and temperature factors of the hydrogen atoms were recalculated after each cycle of refinement and were fixed at these new values for the subsequent cycle. The hydrogen atoms bonded to phosphorus could not be found in the electron difference map and were not included in the refinement.

The final positional parameters and equivalent isotropic temperature factors for the atoms are given in Table 4.3. Anisotropic temperature factors for the heavy atoms are listed in Table 4.4. The calculated and observed structure factors and σ-values can be found in the Appendix.

Description of the Structure

The crystal consists of discrete molecular dimers, $[CuI(C_6H_5PH_2)_2]_2$, separated by normal van der Waals distances. The closest intermolecular contacts, none of which are unusually close, are described below. Each molecule comprises one asymmetric unit of the structure.

The packing of the molecules in the unit cell, shown in Figure 4.4, is particularly interesting because it demonstrates how the packing of potentially flexible molecules can cause those molecules to assume asymmetric conformations. The molecules of $[CuI(C_6H_5PH_2)_2]_2$ pack so that three of the phenyl-groups, namely those bonded to P(1),

Table 4.3:

Final Atomic Positional Fractional Coordinates × 10^3 and Equivalent Isotropic Thermal Parameters for $[CuI(C_6H_5PH_2)_2]_2$

	x	y	z	$U_{eq}{}^{a*}$ or $U_{iso}(A^2\times10^{-3})$
I(1)	500^b	423.29(2)	750^b	36.3(5)*
I(2)	591.9	318.56(2)	503.3(1)	39.9(5)*
Cu(1)	530.1(1)	420.58(5)	525.9(1)	39.7(9)*
Cu(2)	575.8(1)	322.41(5)	731.7(1)	40.9(9)*
P(1)	771.9(3)	316.9(1)	871.8(3)	40(2)*
P(2)	336.2(3)	431.0(1)	386.8(3)	39(2)*
P(3)	687.9(3)	477.2(1)	509.7(3)	43(2)*
P(4)	411.9(3)	270.4(1)	754.8(2)	43(2)*
C(1)	786.9(9)	348.9(4)	1018.8(9)	34(2)
C(2)	900(1)	377.0(4)	1080.5(9)	41(2)
C(3)	906(1)	399.0(5)	1189(1)	56(3)
C(4)	808(1)	395.1(5)	1246(1)	56(3)
C(5)	695(1)	366.7(5)	1188(1)	60(3)
C(6)	686(1)	344.9(4)	1073.6(9)	43(3)
C(7)	314.9(9)	402.0(4)	235.1(9)	33(2)
C(8)	259(1)	352.3(5)	205(1)	57(3)
C(9)	253(2)	332.7(7)	85(2)	81(4)
C(10)	294(2)	362.0(6)	6(2)	80(4)
C(11)	350(1)	408.5(6)	37(1)	68(4)
C(12)	361(1)	428.8(4)	150(1)	42(3)
C(13)	859(1)	464.1(4)	590.2(9)	38(2)
C(14)	961(1)	478.2(4)	542(1)	51(3)
C(15)	1089(1)	466.8(5)	609(1)	60(3)
C(16)	1114(1)	442.4(5)	716(1)	63(3)
C(17)	1015(1)	428.8(5)	770(1)	57(3)
C(18)	887(1)	439.3(5)	703(1)	48(3)
C(19)	243(1)	286.6(4)	677.2(9)	39(2)
C(20)	140(1)	270.1(5)	723(1)	58(3)
C(21)	11(1)	284.5(5)	659(1)	61(3)
C(22)	-14(1)	311.9(5)	552(1)	60(3)
C(23)	87(2)	326.5(5)	511(1)	61(3)
C(24)	215(1)	315.3(4)	573(1)	47(3)
H(2)	971^c	380.3	1045	61^d
H(3)	983	418.3	1230	84
H(4)	816	411.5	1323	84
H(5)	626	362.5	1225	90
H(6)	609	326.6	1032	64
H(8)	225	332.3	261	86
H(9)	219	298.0	62	122
H(10)	283	349.1	-75	119
H(11)	384	427.8	-20	101
H(12)	401	462.6	171	64
H(14)	944	495.4	465	76

Table 4.3: (continued)

	x	y	z	U_{iso}
H(15)	1159	476.7	577	89
H(16)	1203	433.8	757	94
H(17)	1035	413.3	850	86
H(18)	817	429.1	735	72
H(20)	156	249.6	796	87
H(21)	-60	274.9	691	92
H(22)	-101	320.5	508	90
H(23)	70	345.5	436	92
H(24)	284	327.7	542	71

equivalent positions: x,y,z; $x+1/2,y+1/2,z$; $x,\overline{y},z+1/2$; $x+1/2,1/2-y,z+1/2$.

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j$

[b] Coordinates fixed arbitrarily to define the origin of the unit cell.

[c] Hydrogen positions are fixed at 0.95Å from their analogous ring-carbon atoms (see Churchill, 1973), along a vector bisecting the C-C-C angle and in the plane of those atoms.

[d] The isotropic temperature factors of the hydrogen atoms are fixed at 1.5 times those of the carbon atoms to which they are bonded.

Table 4.4: Anisotropic Temperature Factors for the Heavy Atoms in $[CuI(C_6H_5PH_2)_2]_2$. $(Å^2 \times 10^{-3})$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	40.3(4)	30.5(4)	32.0(4)	4.0(3)	7.9(3)	-4.6(3)
I(2)	46.3(4)	34.4(4)	33.4(4)	7.3(3)	12.9(3)	-3.8(3)
Cu(1)	36.9(8)	39.2(8)	34.7(8)	0.4(5)	2.2(6)	-1.1(5)
Cu(2)	44.1(8)	37.8(7)	32.6(8)	3.5(5)	3.6(6)	-0.5(5)
P(1)	40(2)	39(2)	32(2)	9(1)	5(1)	3(1)
P(2)	37(2)	41(2)	32(2)	6(1)	5(1)	3(1)
P(3)	43(2)	30(1)	48(2)	1(1)	5(1)	6(1)
P(4)	58(2)	29(1)	35(2)	-4(1)	7(1)	3(1)

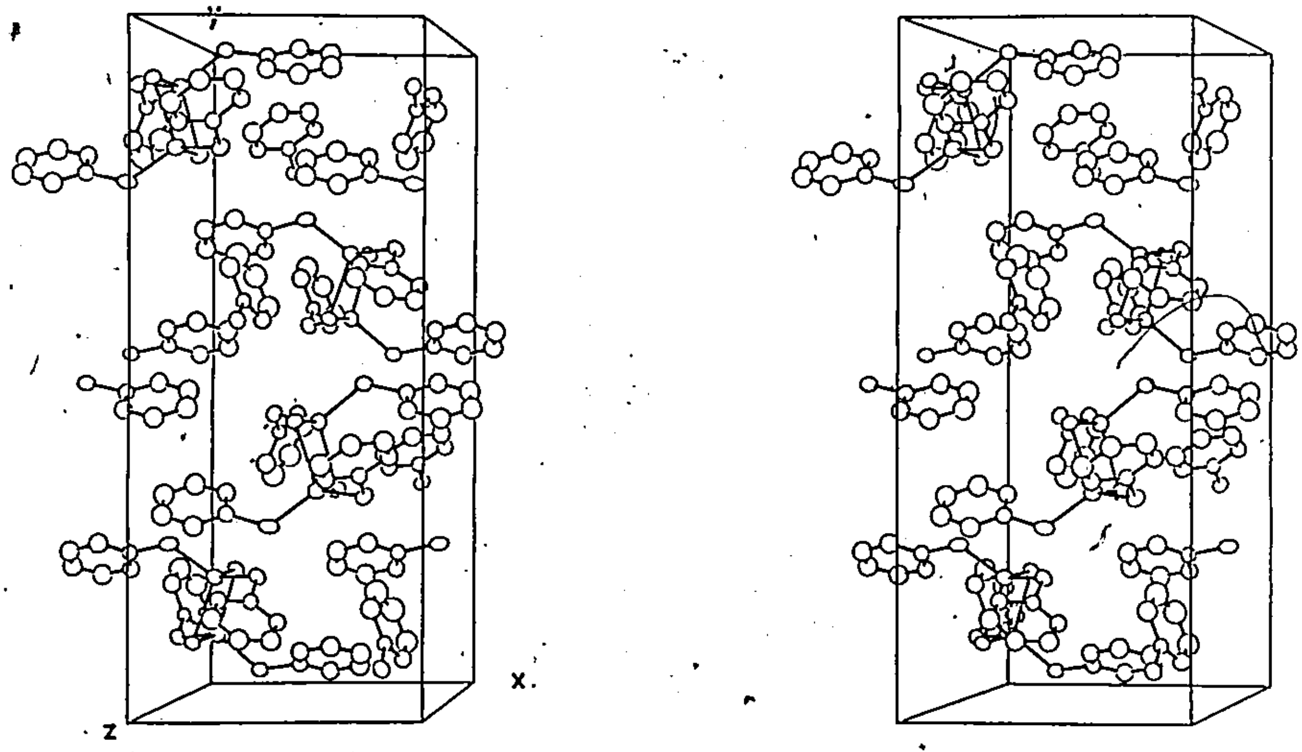


Figure 4.4: Stereoscopic Ortep (Stewart, 1976) drawing of the packing of molecules in $[CuI(C_6H_5PH_2)_2]_2$.

(The diagram includes the non-hydrogen contents of one unit cell plus atoms to complete the four molecules whose Cu_2I_2 cores occur within the cell and atoms to complete all phenylphosphine groups which protrude into the cell.)

P(3) and P(4), from each molecular unit are incorporated into infinite sliding stacks (see Figure 4.4) in which each ring is related to the ring three levels further along the stack by the c-centering operation. Therefore the axes of these 'pseudo-graphitic' stacks are oriented parallel to the $[1,\bar{1},0]$ and $[1,1,0]$ directions. Stacks possessing these two different orientations are related to each other by the c-glide plane. Two of the crystallographically unique rings in a given stack are very nearly parallel to one another. The dihedral angle between them is 4.8° (see planes (V) and (VI) in Table 4.5). The third ring, plane (III) in Table 4.5, is tilted somewhat with respect to the other two, giving dihedral angles of 20.6° and 21.4°. This tilting of the ring bonded to P(1) arises because the fourth crystallographically unique phenyl-ring, bonded to P(2), in the structure is situated between adjacent pseudo-graphitic stacks separated by unit translations along a and is in close contact with the former ring. This last phenyl ring is oriented approximately parallel to the axes of the neighbouring stacks and packs edge to edge with Cu_2I_2 rhombuses of adjacent molecules so that it is nearly coplanar with these latter fragments, (see Figure 4.4). The dihedral angle between the plane of this ring and that of an adjacent Cu_2I_2 rhombus is 11.0° (see also plane (VII) in Table 4.5). The structure, therefore, contains sets of infinite 'ribbons' parallel to $(1,\bar{1},0)$ and $(1,1,0)$ consisting of alternating

Table 4.5: Selected Least Squares Planes[a] and Dihedral Angles for $[CuI(C_6H_5PH_2)_2]_2$

	Atom	Deviation(A)		
Plane Ia:	I(1)	0.036	Plane Ib:	I(1), I(2), Cu(1)
	I(2)	0.036	Plane Ic:	I(1), I(2), Cu(2)
	Cu(I)	-0.036	Plane Id:	Cu(I), Cu(2),I(1)
	Cu(2)	-0.036	Plane Ie:	Cu(1), Cu(2),I(2)
Plane II:	Cu(1)	-0.015		
	Cu(2)	0.094		
	P(1)	-0.014		
	P(2)	0.017		
	P(3)	-0.024		
	P(4)	-0.057		
	I(1)*[b]	-2.041		
	I(2)*	2.105		
Plane III:	C(1)-C(6)	no significant deviation from planarity		
	P(1)*	-0.044		
Plane IV:	C(7)-C(12)	no significant deviation from planarity		
	P(2)*	-0.040		
Plane V:	C(13)-C(18)	no significant deviation from planarity		
	P(3)*	0.006 (not significant)		
Plane VI:	C(19)-C(24)	no significant deviation from planarity		
	P(4)*	0.022		
Plane VII:	C(7)	0.007	I(1)'[d]	-0.136
	C(8)	0.106	I(2)'	0.180
	C(9)	0.085	Cu(1)'	-0.191
	C(10)	0.040	Cu(2)'	0.091
	C(11)	-0.086		
	C(12)	-0.098		

Table 4.5: (continued)

Planes	Dihedral Angles (degrees)[c]
Ia + II	87.6
Ib + Ic	5.0
Id + Ie	4.0
III + IV	40.2
III + V	55.2
III + VI	59.6
IV + V	73.6
IV + VI	75.6
V + VI	4.8
III + V'	20.6
III + VI'	21.4
IV + I'	11.0

[a] Unless otherwise indicated planes are composed of atoms within the same molecule.

[b] * -- indicates atoms which were not included in the calculation of the plane.

[c] Acute dihedral angles given.

[d] Primed numerals or atom labels indicate planes or atoms from a molecule related by (x,1-y,z-1/2) to those denoted by the unprimed labels and numerals.

phenyl-rings and Cu_2I_2 rhombuses. These 'ribbons' are sandwiched between the 'sliding stacks' of phenyl-rings and thus represent another facet of the same packing condition which gives rise to the orientations of the stacks. The absence of significant voids in this structure suggests that it represents an optimum packing geometry.

Molecular Structure

A diagram of an individual molecule is given in Figure 4.5 and shows clearly that the two diametrically opposed phenyl-groups bonded to P(3) and P(4) respectively are nearly parallel to one another (dihedral angle = 4.8°), while the other two rings are tilted with respect to them and with respect to each other (see Table 4.5). There is a slight puckering of the Cu_2I_2 rhombus indicated by the dihedral angle of 5° for planes Ib and Ic in Table 4.5. Such puckering is commonly observed in structures of this type (Eller, 1977) and is no doubt attributable to packing forces. The intramolecular atomic separations are listed in Table 4.6 and the bond angles in Table 4.7.

The dimeric molecule contains two pseudotetrahedrally coordinated copper atoms bridged by two iodine atoms. The other coordination sites are occupied by the phosphorus atoms of the phenylphosphine ligands. This molecule may therefore be described as a 'normal' dimer in that it has the most commonly occurring geometries about halogen and copper

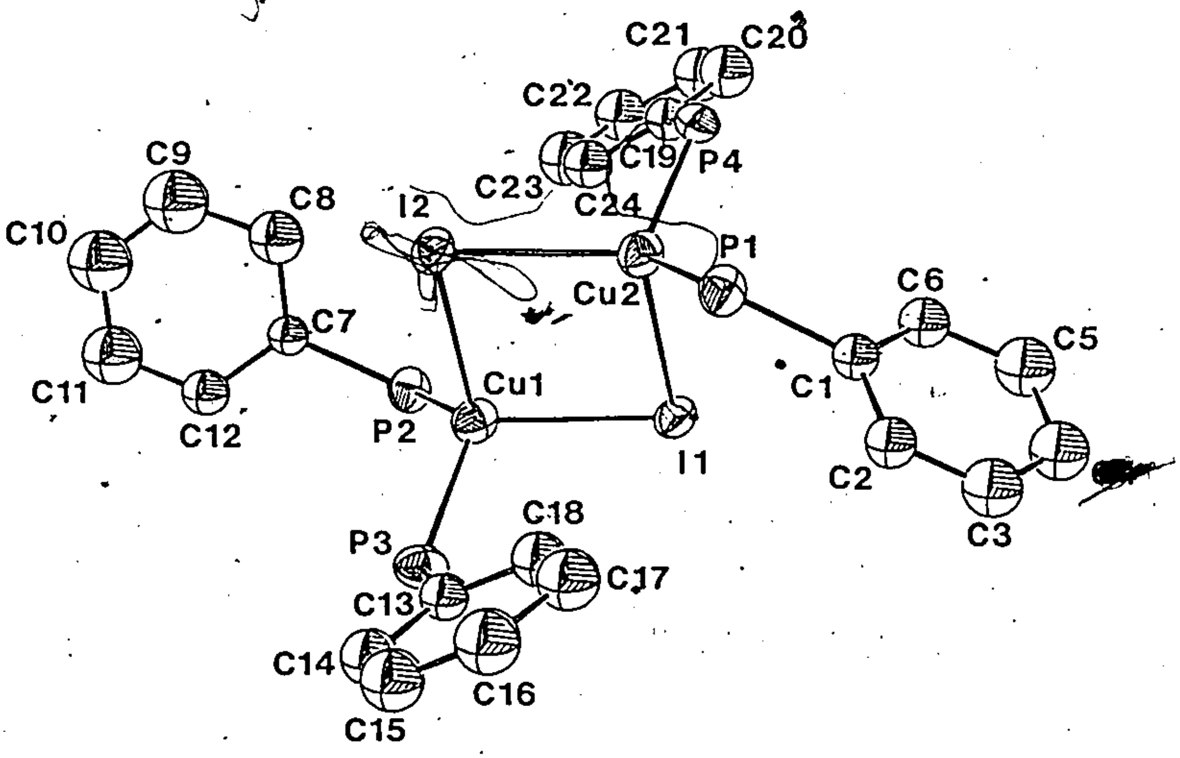


Figure 4.5: Molecule of $[CuI(C_6H_5PH_2)_2]_2$.
(Ortep drawing, XRAY-76: Stewart, 1976)

Table 4.6: Interatomic Distances (Å) for $[CuI(C_6H_5PH_2)_2]_2$ (Intramolecular)

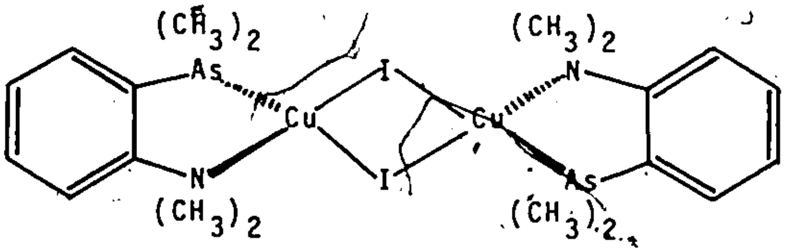
I(1) - Cu(1)	2.652(1)	I(2) - Cu(1)	2.675(1)
I(1) - Cu(2)	2.684(1)	I(2) - Cu(2)	2.648(2)
I(1) - I(2)	4.151(1)	Cu(1) - Cu(2)	3.340(2)
Cu(1) - P(2)	2.241(3)	Cu(2) - P(1)	2.252(3)
Cu(1) - P(3)	2.244(3)	Cu(2) - P(4)	2.249(3)
P(2) - C(7)	1.83(1)	P(1) - C(1)	1.82(1)
P(3) - C(13)	1.83(1)	P(4) - C(19)	1.82(1)
C(1) - C(2)	1.40(1)	C(7) - C(8)	1.39(2)
C(1) - C(6)	1.38(2)	C(7) - C(12)	1.37(2)
C(2) - C(3)	1.34(2)	C(8) - C(9)	1.44(2)
C(3) - C(4)	1.37(2)	C(9) - C(10)	1.33(3)
C(4) - C(5)	1.40(2)	C(10) - C(11)	1.32(2)
C(5) - C(6)	1.39(2)	C(11) - C(12)	1.36(2)
C(13) - C(14)	1.39(2)	C(19) - C(20)	1.40(2)
C(13) - C(18)	1.38(2)	C(19) - C(24)	1.35(2)
C(14) - C(15)	1.39(2)	C(20) - C(21)	1.41(2)
C(15) - C(16)	1.33(2)	C(21) - C(22)	1.36(2)
C(16) - C(17)	1.40(2)	C(22) - C(23)	1.33(2)
C(17) - C(18)	1.40(2)	C(23) - C(24)	1.38(2)

Table 4.7: Bond Angles for $[CuI(C_6H_5PH_2)_2]_2$
(Degrees)

Cu(1) - I(1) - Cu(2)	77.50(4)	Cu(1) - I(2) - Cu(1)	77.73(5)
I(1) - Cu(1) - I(2)	102.36(5)	I(1) - Cu(2) - I(2)	102.24(5)
I(1) - Cu(1) - P(2)	110.2(1)	I(1) - Cu(2) - P(1)	104.03(8)
I(1) - Cu(1) - P(3)	110.60(9)	I(1) - Cu(2) - P(4)	106.3(1)
I(2) - Cu(1) - P(2)	104.26(9)	I(2) - Cu(2) - P(1)	113.2(1)
I(2) - Cu(1) - P(3)	113.00(9)	I(2) - Cu(2) - P(4)	110.72(9)
P(2) - Cu(1) - P(3)	115.5(1)	P(1) - Cu(2) - P(4)	118.5(1)
Cu(1) - P(2) - C(7)	118.1(3)	Cu(2) - P(1) - C(1)	116.9(3)
Cu(1) - P(3) - C(13)	120.5(4)	Cu(2) - P(4) - C(19)	120.5(4)
P(2) - C(7) - C(8)	121.5(9)	P(1) - C(1) - C(2)	121.8(9)
P(2) - C(7) - C(12)	119.6(7)	P(1) - C(1) - C(6)	119.9(7)
P(3) - C(13) - C(14)	122.4(8)	P(4) - C(19) - C(20)	121.7(8)
P(3) - C(13) - C(18)	118.5(9)	P(4) - C(19) - C(24)	119.6(9)
C(8) - C(7) - C(12)	119(1)	C(2) - C(1) - C(6)	118(1)
C(7) - C(8) - C(9)	116(1)	C(1) - C(2) - C(3)	119(1)
C(8) - C(9) - C(10)	121(2)	C(2) - C(3) - C(4)	123(1)
C(9) - C(10) - C(11)	122(2)	C(3) - C(4) - C(5)	119(1)
C(10) - C(11) - C(12)	120(2)	C(4) - C(5) - C(6)	118(1)
C(7) - C(12) - C(11)	122(1)	C(1) - C(6) - C(5)	122(1)
C(14) - C(13) - C(18)	119.2(9)	C(20) - C(19) - C(24)	119(1)
C(13) - C(14) - C(15)	119(1)	C(19) - C(20) - C(21)	119(1)
C(14) - C(15) - C(16)	122(1)	C(20) - C(21) - C(22)	121(1)
C(15) - C(16) - C(17)	122(1)	C(21) - C(22) - C(23)	118(1)
C(16) - C(17) - C(18)	117(1)	C(22) - C(23) - C(24)	123(1)
C(13) - C(18) - C(17)	122(1)	C(19) - C(24) - C(23)	120(1)

found in copper(I) halide-phosphine complexes. Although a number of compounds have been prepared which possess the same stoichiometric ratio of ligand to metal halide and which almost certainly possess the same structure, no crystal structure has previously been reported for a simple 'binary' dimeric complex of this stoichiometric ratio of CuI to monodentate ligand, nor has any similar structure been reported in which the phosphine ligands were not tertiary phosphines.

Only three structures have been published which [illegible]st of dimeric molecules possessing the Cu_2I_2 core. The one which most closely approaches the present structure is for $\{CuI[P(C_6H_5)_2CH_3]_2\}_2 \cdot SO_2$ which has the same general molecular geometry as $[CuI(C_6H_5PH_2)_2]_2$ except that it contains a molecule of SO_2 which is weakly coordinated via sulfur to one of the bridging iodine atoms (Eller, 1977). This shows that the iodine atoms in such structures possess the capability of forming secondary bonds. The molecule $(CuI)_2[P(C_6H_5)_3]_3$ (Eller, 1977) contains a similarly di-bridged Cu_2I_2 core but one of the copper atoms is only pseudo-trigonally coordinated. Coordination of a fourth triphenylphosphine ligand in this molecule is thought to be prohibited as a consequence of the steric bulk of the triphenylphosphine ligands. The former compound containing $P(C_6H_5)_2CH_3$ ligands as well as the compound $[CuI(C_6H_5PH_2)_2]_2$, presented here, both demonstrate that the use of smaller phosphine ligands permits full tetrahedral coordination of the copper atoms. The only other published structure based on the Cu_2I_2 core is that of $[\mathrm{CuI}\underline{o}\text{-}\mathrm{C_6H_4N(CH_3)_2As(CH_3)_2}]_2$ (Graziani, 1971) in which the bidentate ligand binds to the copper atom via both As and N.



Various authors have concluded that the molecular structures of cuprous halide-tertiary phosphine complexes are the net results of electronic, steric and packing factors (Gill, 1976; Eller, 1977; Churchill, 1975). When the phosphine ligands and halide ions are large (e.g. $P(C_6H_5)_3$ and I^-) non-bonded intramolecular interactions are dominant in deciding the structural geometry and stoichiometry in concert with the metal-ligand and metal-halide bond distances which appear to be a function of the coordination number about the metal (Gill, 1976). The bond angles about copper and halogen appear to be quite flexible and adopt values which minimize steric interactions. In $[CuI(C_6H_5PH_2)_2]_2$ as well as in other compounds possessing Cu_2I_2 units the geometry of this unit is apparently governed by the minimum distance of mutual approach of the two iodine atoms

(4.151(1)Å for $[CuI(C_6H_5PH_2)_2]_2$; 4.109(1)Å for $\{CuI[P(C_6H_5)_2CH_3]_2\}_2 \cdot SO_2$; 4.302(1)Å for $(CuI)_2[P(C_6H_5)_3]_3$ and 4.370Å for $[CuI\sigma\text{-}C_6H_4N(CH_3)_2As(CH_3)_2]_2$). Twice the accepted van der Waals radius of iodine is 4.30Å (Pauling, 1965).

The Cu-Cu distance in $[CuI(C_6H_5PH_2)_2]_2$ is non-bonding (3.340(2)Å). The distance in Cu metal is 2.56Å. However, separations of Cu atoms in similar compounds show a considerable range of values and can approach bonding distances. It has been postulated (Hoffmann, 1978) that there may be a net 'soft attractive' interaction between Cu atoms in such complexes rendering the structures relatively indifferent to the magnitude of the metal-metal separation. The result is that this distance is merely a consequence of the minimum halogen-halogen distance and normal Cu-X bond lengths.

The CuI bond lengths, average = 2.665(18)Å, are in the same range normally found for tetrahedrally coordinated copper(I) (2.62-2.81Å) (Churchill, 1975; Eller, 1977). The Cu-P distances, average = 2.247(5)Å, are essentially the same as those found with tertiary phosphines in similar structures, namely 2.24 to 2.27Å (Churchill, 1975; Eller, 1977).

The average of the bond angles about the phosphorus atoms, Cu-P-C = 119(2)°, is larger than an average value of 114° found for triphenylphosphine bound to copper (Churchill, 1975), but it is not abnormally large. It is reasonable to expect this angle to be somewhat larger for a primary phosphine because of the relatively small stereochemical requirements of the P-H hydrogen atoms. The P-C bond lengths, average = 1.823(4)Å, are normal for a phosphorus-carbon single bond. The phosphorus atoms deviate very little from the planes of their associated phenyl-rings (see Table 4.5). The C-C-C, average = 120(2)°, and P-C-C, average = 120.6(14)°, bond angles all deviate by less than 3σ from 120°. Apparent deviations in the C-C bond distances from the expected 1.395Å, especially for those between meta and para carbon atoms, may result from systematic errors caused by rigid-body thermal motions. Specifically wagging motions of the phenylphosphine groups about the P-Cu and P-C bond axes may cause the C-C bond lengths furthest from these axes to be systematically low (Churchill, 1975).

It is perhaps of interest to consider briefly the environment of the iodine atoms in $[CuI(C_6H_5PH_2)_2]_2$ in more detail to look for possible explanations for the small effective electric field gradients at these atoms as indicated above by the ^{127}I Mössbauer results. There are several contacts between the iodine atoms and the projected hydrogen atoms from the phenyl-rings which may be slightly less than the sum of the van der Waals radii for hydrogen and iodine (1.2 + 2.15 = 3.35A). The values range from 2.95 to 3.35A assuming that the hydrogens are located 1.1 angstroms from their respective carbon atoms. Given the uncertainty in the van der Waals radii, these contacts may merely represent ordinary non-bonding separations. The geometry about the phosphorus atom which most closely approaches an iodine atom from an adjacent molecule, P(3)...I(1) = 3.963(3)Å, indicates that the hydrogen atoms bonded to phosphorus are not likely to approach the iodine atom by less than 3.1Å. Although the hydrogen atoms were not located in the structure refinement and therefore their exact positions are not known, there does not appear to be any clear evidence of secondary bonds to iodine which could act to effectively reduce any electric field gradient at iodine caused by the I-Cu bonds.

D. Interaction of PH_3 with CuI

It has been demonstrated (Lippard, 1971) that the steric bulk of a tertiary phosphine ligand is the dominant contributing factor to the dissociation of their complexes with cuprous halides in solution. ~~The~~ bulkier ligands cause a higher degree of dissociation. Complexes between cuprous halides and the much smaller primary phosphines or PH_3 itself might reasonably be expected to be more stable since, in addition to their smaller cone angles (Tolma, 1970) they have also been postulated to have greater π-acidity than tertiary phosphines (Fischer, 1969). In fact a possible order of 'complexing power' of P(III) ligands has been suggested to be as follows:

$$P(OR)_3 > PF_3 > PH_3 > PR_3 > P(OPh)_3 > PPh_3 = PBu^t_3$$

(Emsley, 1976). Such a listing is of course rather arbitrary and no doubt the degree to which the various stabilizing or destabilizing factors (i.e., σ-donor strength, π-acidity, steric effects) contribute to the relative order will depend upon the metal atom involved and upon the geometry of the complex.

Earlier workers (Holtje, 1940; Scholder, 1934) found that adducts between PH_3 and cuprous halides are unstable to loss of PH_3 under standard conditions. This indicates that ligand basicity is the dominant factor contributing to the energetics of the metal-phosphine interaction in the absence of steric effects. The relative basicities of PH_3 and the phenyl-phosphines, as given by the pKa values of the conjugate phosphonium ions, are: $P(C_6H_5)_3$, pka = 2.73; $P(C_6H_5)_2H$, pKa = 0.03; $P(C_6H_5)H_2$, pKa est. (-1.7); PH_3, pKa = -14 (Henderson, 1960). For compounds with Cu(I) it seems that π-back-donation into phosphorus d-orbitals is not sufficient to compensate for the weaker σ-donor ability of PH_3 relative to the phenyl-substituted phosphines. This may be due, in part, to the d^{10} filled-shell configuration of Cu(I).

To confirm the earlier conclusions regarding the interaction between PH_3 and CuI, solutions of PH_3 and CuI in THF were prepared and examined by ^{31}P NMR. It was found that indeed a considerable excess of PH_3 was required in the sealed NMR tubes in order to dissolve all of the cuprous iodide. ^{31}P NMR spectra of these solutions confirmed complex formation by revealing a complexation shift of approximately 20 ppm to low field and an increase in J_{PH} from 187 Hz for free PH_3 to approximately 233 Hz in the solution. The existence of only one ^{31}P signal, an ^{1}H-coupled quartet, regardless of the exact composition of the solution indicated that as with other phosphines the complexes undergo rapid ligand exchange in solution at room temperature. Raman spectra of the solutions confirmed this. A sharp band at 2307 cm^{-1}, attributed to the P-H stretching vibration of free PH_3, as well as a broader, possibly multiple, band centred at 2344 cm^{-1}, attributed to bound PH_3, were observed. Such an increase in P-H stretching frequency is in agreement with the observation (Abel, 1969) that the P-H stretching frequency of $(C_6H_5)_2PH$ increases by about 33 to 41 cm^{-1} upon coordination to copper(I). The NMR and vibrational results are consistent with a strengthening of the P-H bond upon complexation as a result of rehybridization at phosphorus.

When low-temperature ^{31}P NMR spectra of the solutions were recorded, in an attempt to 'freeze out' the ligand exchange process, a white solid precipitated and the time averaged ^{31}P NMR parameters shifted back towards those of free PH_3. This process was observed to be reversible and possibly indicates that $CuI-PH_3$ complex formation is endothermic. Crystals of the precipitated solid were shown by X-ray diffraction to be cuprous iodide (Batchelor, 1982).

CHAPTER 5

CONCLUSION

A. NMR of the Main Group Phenylhydrides and Their Anions

(i) Summary and Discussion

Trends in the ^{1}H NMR chemical shifts of phenyl-substituted amines, phosphines and arsines as well as of their respective monoanions have been studied. The ^{13}C NMR chemical shifts of the same species have also been obtained and have been compared with the ^{1}H results. The chemical shifts have been interpreted in terms of the electron distributions of these compounds although other factors also strongly influence some of the observed shifts. ^{31}P NMR spectra of the phosphines and phosphides were also recorded and the results compared with literature data. The interpretation of the ^{31}P NMR parameters is less clear but they are not inconsistent with the conclusions reached from the ^{1}H and ^{13}C results.

The ^{13}C chemical shifts appear to be the best indicators of the electron distributions in the molecules studied, consequently ^{13}C NMR spectra of a series of aryl-substituted germanes as well as their monoanions were also recorded. The observed chemical shifts were compared with those of the analogous group 5B compounds as well as with literature data for phenyl substituted methanes and their corresponding carbanions. The results indicate a much lower degree of resonance delocalization of the negative charge in the phenyl-substituted germyl anions as compared with either the analogous carbanions or the anions of phenyl-substituted group 5B hydrides. This is consistent with a previously suggested rationale (Jolly, 1971), based on hybridization ideas, for the lowered acidities of germanes upon increased phenyl-substitution (Birchall and Drummond, 1972). Analogous studies with phenyl-substituted silanes were unsuccessful because of their lower acidities and the occurrence of side reactions when attempting the deprotonation of either phenyl- or diphenyl-silanes. However, the ^{13}C NMR spectrum of $(C_6H_5)_3SiLi$ has been reported (Olah, 1980) and reveals no evidence of resonance delocalization in this compound.

Concentration and temperature dependent studies of the ^{31}P NMR of C_6H_5PHNa in THF show that ion-pairing as well as aggregation are important in these solutions. ^{13}C chemical shifts of this species in THF, however, show little dependence on concentration. Change of solvent to NH_3 has a somewhat larger effect on the ^{13}C chemical shifts. However, the observed changes in the NMR spectrum, along with the observation that the order of relative acidity of $C_6H_5PH_2$ compared to PH_3 is the same in either THF or NH_3 solvents indicates that the effect of the different solvents does not account for the opposite trends in acidity of phosphines and arsines compared to germanes upon phenyl-substitution. This was of concern because the earlier studies of the acidities of phenylphosphines and -arsines (Issleib, 1965) and of phenylgermanes (Birchall and Drummond, 1972) were conducted using THF and NH_3 solvents respectively.

The objective of this work was to use NMR spectroscopy to demonstrate that the above mentioned, observed differences in the effect of phenyl-substitution on the acidities of main group hydrides can be traced to electronic interactions in these molecules and their anions. However, it is apparent that correlations between chemical properties, such as thermodynamic equilibrium constants, and the NMR chemical shifts are rather tenuous. Conceptually there are two basic steps required to achieve such an analysis. First, the chemical shifts must be related to electron distributions in the molecules concerned. Second, the electron distributions must be related to the energetics of the chemical process which, in this case, is the acid base equilibrium (5.1).

$$YH_{n-1}^{-} + (C_6H_5)_mYH_{n-m} \rightleftharpoons YH_n + (C_6H_5)_mYH_{n-m-1}^{-} \quad (5.1)$$

The complexity of the theory of chemical shifts necessitates severe approximations in order to allow a rationale for a simple correlation with electron densities (Karplus, 1963). Empirical correlations of chemical shifts with calculated electron densities do show, however, that such approximations may be valid for special sets of selected data (Ewing, 1978; Hehre, 1976; Nelson, 1976 and references therein). The chemical shifts of the nuclei in the para position of monosubstituted benzenes appear to conform to such correlations. Direct correlation of these chemical shifts with substituent parameters such as $\sigma_R{}^\circ$ appears to shortcut the necessity for correlating the electron densities with energy-related parameters although such studies have also been made (Hehre, 1976). Generally, however, consideration of the trends in the various NMR parameters of monosubstituted benzenes permits only qualitative conclusions to be reached regarding the nature of the interaction between the ring and the substituent.

All of the species studied in this work may be considered as substituted benzenes having π-donor substituents, although the extent of π-donation varies drastically. Four limiting cases may be considered:

(a) neutral molecules having poor π-overlap between the ring and the substituent.

(b) neutral molecules with good π-overlap between ring and substituent.

(c) anions with poor π-overlap and therefore little delocalization of negative charge.

(d) anions with good π-overlap and considerable delocalization of negative charge.

Figure 5.1 can be used as a rough guide to the ^{13}C NMR chemical shifts for these four classifications. Ortho carbon chemical shifts are not included because these shifts appear to show a strong dependence on the size of the substituent which is not well understood. However, for small substituents in which the atom bonded to C_1 is a second period element (C, N, O, F) the ortho ^{13}C chemical shifts loosely parallel those of the para carbon (see Stothers, 1972) as is expected from electronic considerations. Most of the species studied in this work represent intermediate stages between the four extreme cases mentioned above.

The nature of the electronic interactions which give rise to the observed distributions in chemical shifts might best be described as a balance between charge transfer or delocalization, simple polarization and a 'π-molecular orbital effect'. The latter effect causes a redistribution of the π-electrons in the ring as a consequence of a

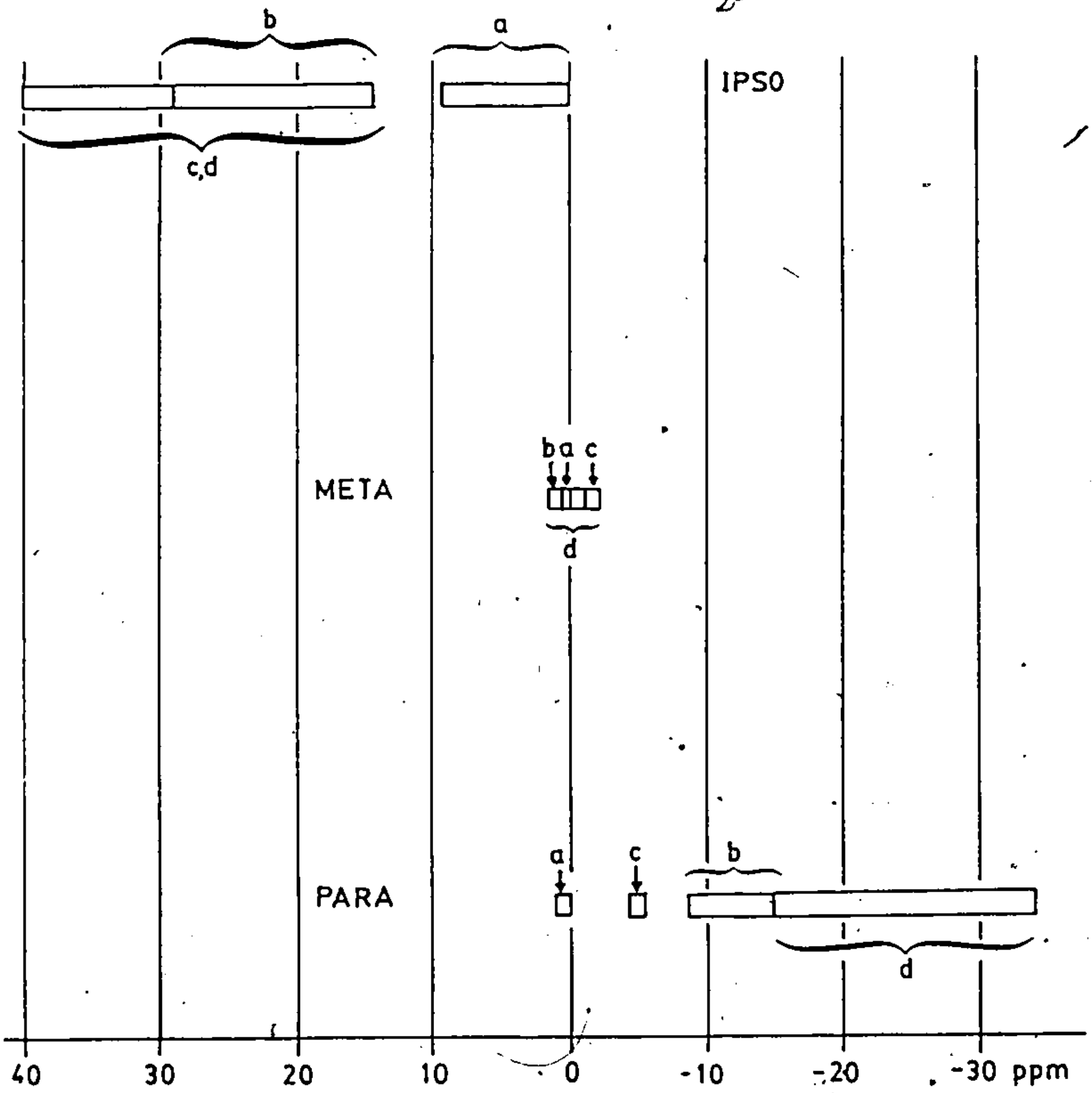


Figure 5.1: Typical ^{13}C NMR chemical shifts for monosubstituted benzenes having potentially π-donating substituents; definitions of a, b, c, d are found on page 175.

repulsive interaction with the electrons in filled orbitals of π-symmetry on the substituent (Libit, 1974; Topsom, 1976) such that π-electron density is shifted from the ipso carbon, and to a lesser extent from the meta carbon, and is accummulated at the ortho and para positions. Examples which distinguish between these influences can be found in calculated electron distributions for various monosubstituted benzenes (Pross, 1981); Figure 5.2. The case of strong delocalization may be represented by the anilide anion. The charge distribution is consistent with a low-field ^{13}C NMR chemical shift for the ipso carbon resonance as well as a high-field shift for the para (and ortho) resonance. The case of simple polarization is exemplified by the anilinium ion in which the completely localized positive charge causes the phenyl-ring to become polarized such that the π-electron density decreases with increasing distance from the positively charged substituent. In the present study, exactly the inverse of this appears to occur for the phenylgermyl anions as evidenced by their large low-field shifts of the ipso ^{13}C resonances and their small upfield shifts of the para and meta ^{13}C resonances.

The case of toluene demonstrates the 'π-orbital' effect (Libit, 1974). For toluene there is little net charge transfer to the ring but the interaction between the ring π-orbitals and orbitals of π-symmetry formed by linear combinations of the C-H σ-orbitals of $-CH_3$ results in mixing

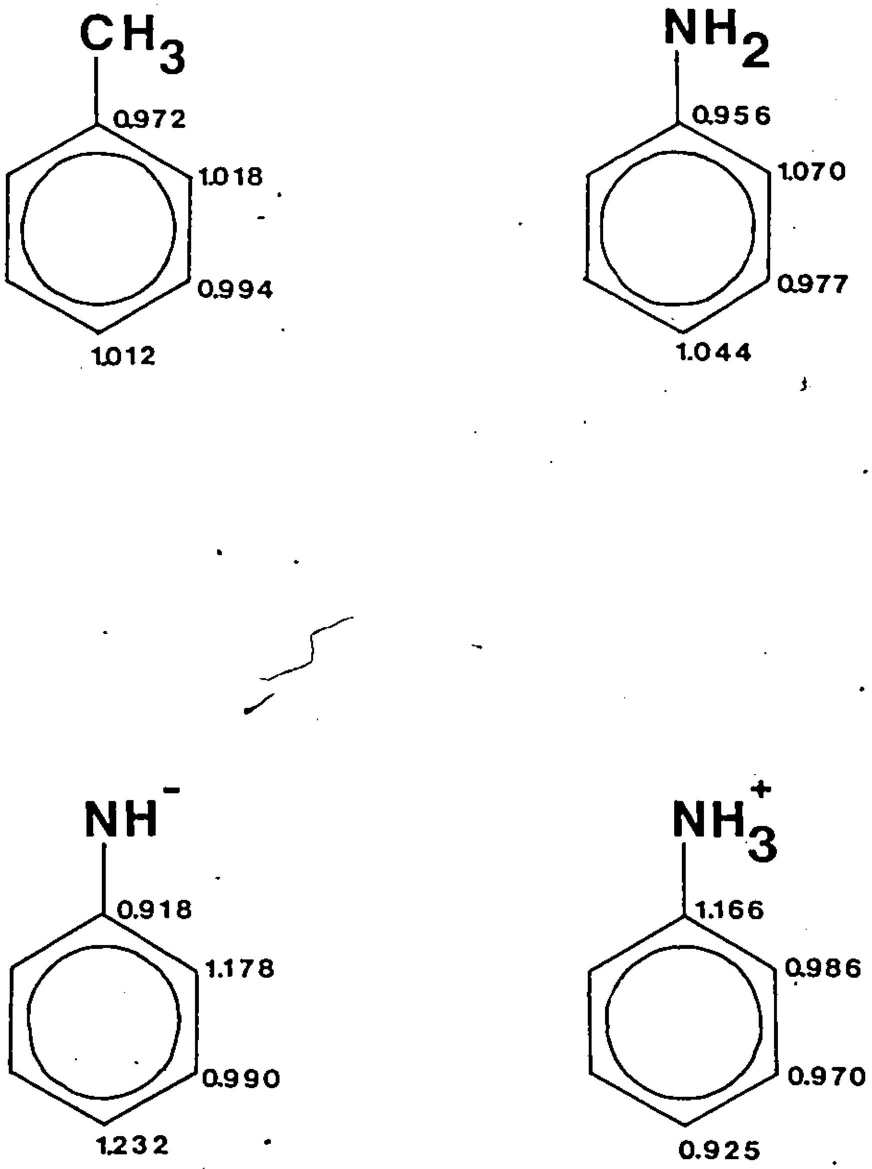


Figure 5.2: Calculated π-electron distributions for some simple monosubstituted benzenes (Pross, 1981).

of π^*-orbitals into the π-orbitals of the ring thus causing the observed redistribution of electrons in the ring. The case of aniline is intermediate between those of toluene and of the anilide ion in that it shows more electron transfer than does toluene but considerably less than the anilide ion.

The above differences in molecular π-electron distribution for benzenes possessing π-donor substituents, viewed in terms of perturbation molecular orbital theory, arise from two things:

(a) the degree of overlap between the filled π-orbitals of the substituent with π or π^* orbitals of the ring.

(b) the relative energies of these orbitals.

It is apparent that for a significant degree of charge transfer to occur the occupied π-orbital of the substituent must be of high enough energy to interact with the π^* orbitals of the benzene ring. Also there will be little net stabilization unless such charge transfer occurs (Pross, 1981) (Fig. 5.3). Thus it can be seen that a π interaction between ring and substituent has a much more stabilizing effect in the case of an anion than in the case of a neutral molecule. Therefore, when attempting to demonstrate the effects of resonance delocalization on the equilibrium shown

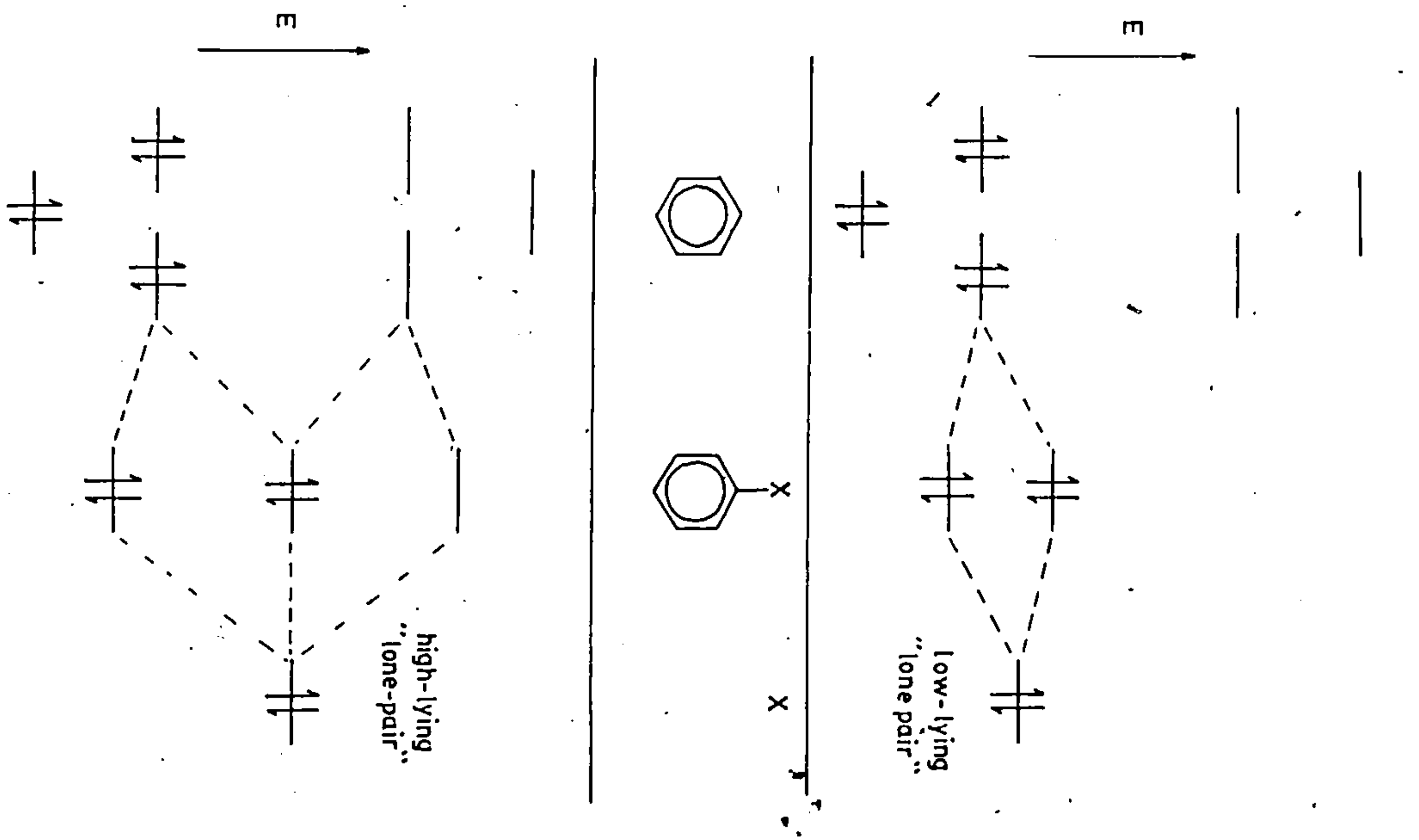


Figure 5.3: Simplified molecular orbital diagrams showing the effect of the relative energy of the substituent 'lone-pair' π-orbital on the interaction with the b_2 π-orbitals of the phenyl-ring (Pross, 1981).

in equation (5.1), only the resonance effects of the anions $(C_6H_5)_mYH^-_{n-m-1}$ need, at first, be considered. It is for this reason that in Fig. 3.18 the change in pKa per phenyl substituent was plotted versus the NMR parameters of the phenyl substituted anions only and that no term was included to account for the electronic interactions in the neutral molecules.

For the monosubstituted benzenes in which the substituent atom is a heavier main group element, such as P, As, Si or Ge, the amount of overlap between the filled π-orbitals of the main group element and the the π-system of the ring is considerably diminished. Thus while aniline displays some charge transfer from nitrogen to the ring as well as considerable accumulation of electron density at the ortho and para positions at the expense of the ipso position, phenylphosphine does not display either of these effects. The ^{13}C NMR spectrum of either $C_6H_5PH_2$ or $C_6H_5AsH_2$ has the resonances for the para, meta and ipso carbons at approximately the same chemical shift as that of benzene. The highest occupied molecular orbital belonging to the $-PH_2$ or $-AsH_2$ fragments in these molecules is the 'non-bonding' orbital containing the 'lone-pair' of electrons. The overlap between this orbital and the benzene π-system is smaller than that for $-NH_2$ not only because of the fact that the C-P or C-As bond lengths are greater than C-N and that the valence orbitals of the heavier elements are more diffuse but also because the 'non-bonding' orbital of $C_6H_5PH_2$ or $C_6H_5AsH_2$ must have a higher degree of P or As s-orbital character. The phenylgermyl anion is isoelectronic with phenylarsine and, no doubt, also displays little π-overlap between the highest occupied molecular orbital of $-GeH_2^-$ and the ring. Consequently the electron distribution in the phenyl ring of this species is predominantly affected by the localized charge on Ge which causes a simple polarization of the ring. The anions $C_6H_5PH^-$ and $C_6H_5AsH^-$ have more p-orbital character in the HOMO's of the substituent fragments than does $C_6H_5GeH_2^-$. Consequently for the group 5B anions there is more significant π-overlap and therefore some delocalization of the negative charge although less than that observed for the anilide-ion.

Although partially obscured, the above effects are mirrored in the NMR parameters of these species. The chemical shifts of the para carbon atoms are appropriately attenuated upon multiple phenyl-substitution. The ipso carbon chemical shift is most strongly affected by variable phenyl-substitution most likely as a consequence of inductive or geometric effects.

(ii) Future work

Calculations of charge distributions for monosubstituted benzenes show that there is a good correlation of either the total charge or the π-charge at the para carbon with the NMR chemical shift for that carbon atom (Hehre, 1976). The reported proportionality constants were 450 and 200 ppm/electron respectively. All of the species studied were, however, neutral molecules. It would be of interest to extend such calculations to the kind of anionic monosubstituted benzenes considered in the present study. A calculated π-electron distribution for the anilide anion has been reported (Pross, 1981). This yields an increase in π-electron density at the para position of 0.232 electrons relative to benzene. The method used for this calculation was the same as was used in the earlier study (Hehre, 1976). This value implies that if the relationship between ^{13}C chemical shift and π-charge density can be extrapolated to include such ionic species then the substituent chemical shift for the para carbon of $C_6H_5NH^-$ would be -46 ppm. The value of -22.41 ppm found in the present work is surely an indication of a high degree of ion pairing for C_6H_5NHNa in THF solution. Calculated electron densities for such anions might best be compared with the NMR parameters obtained from solutions in solvents such as DMSO. Alternatively the calculations could, perhaps, be made to include the effect of ion pairing.

Although the NMR results obtained in this study corroborate the previous explanations for the observed relative acidities of the group <u>4B</u> and <u>5B</u> hydrides and phenylhydrides, the apparent inconsistencies in the reported pKa values (Issleib, 1965; Terekhova, 1982) as well as the gaps in and general lack of acidity data for compounds of these types indicate that further systematic studies of the relative acidities of these species are in order. For example, the solution acidity of AsH_3 does not yet appear to have been measured to any reasonable degree of accuracy.

Two complementary approaches to the establishment of reliable pKa values for the hydrides may be considered. First, the so-called 'absolute' acidities could be measured relative to hydrocarbon indicators which have well established pKa values in various solvent systems. The acidity scales of Bordwell (1977), using dimethylsulfoxide (DMSO) solvent, and of Streitwieser (1980), using cyclohexylamine (CHA) solvent, provide a sound basis for this approach. Second, the relative acidities of the various compounds studied may be compared directly without the intermediation of a scale of indicator acids. By this method the pKa values of a series of similar compounds are determined on a hierarchical basis thus providing the most reliable measure of the <u>differences</u> in the acidities of hydrides having different degree of substitution or having different central elements. This method has been employed for a series of substituted germanes in liquid ammonia (Birchall and Drummond, 1972). The use of NMR spectroscopy for the determination of relative acidities (Birchall, 1965) may be most useful for such studies as it does not require a coloured indicator as do spectrophotometric methods. The NM spectra obtained also can provide information about the nature of the species in solution and about the kinetics of proton exchange.

To aid in the interpretation of the relative acidity and NMR results, it would be worthwhile to make studies of the effects of solvation, ion-pairing and aggregation by use of different solvents. For example, it is generally thought that in DMSO solvent most organo-alkali metal salts are solvated as unpaired ions and therefore acidities in this solvent may reflect more directly the true electronic effect on the acid-base equilibrium, analogous to gas phase data (Streitwieser, 1980). In solvents of lower polarity, such a CHA or THF, ion pairing and aggregation are more important. Temperature and concentration dependent studies of the equilibria as well as use of different cations can provide more information about solvation/aggregation effects. In this regard it is possible that expanded use of multinuclear NMR to include the cation nuclei, such as ^{23}Na or ^{7}Li, may b highly valuable.

A series of aryl- and alkyl-substituted hydrides of the fourth period elements, Ge, As and Se, may prove to be most profitable subjects for such studies. The lower acidit of silanes may make the study of the analogous third period sequences somewhat problematic, whereas the low stability of hydrides of fifth period elements makes these species also experimentally more difficult to study. Careful quantification of the relative acidities of such series of compounds may clarify whether or not hybridization changes upon deprotonation of the various hydrides have a noticeable effect. Since the neutral germanes, unlike the As and Se compounds, must all have essentially sp^3 hybridization it may be expected that the germanes could show anomalous acidities. It has previously been found that GeH_4 is intermediate in acidity between AsH_3 and PH_3 (Birchall, 1966). Comparison of the pKa values for a series of phenylgermanes (Birchall and Drummond, 1972) with those reported for phenylarsines (Issleib, 1965) -- the pKa values were given in both studies relative to a common standard (indene) -- indicates that GeH_4 may actually be more acidic than AsH_3. However, this is most likely a consequence of the use of different solvents, NH_3 and THF, and the more favourable solvation of localized anions in more polar solvents.

It is perhaps of interest to speculate on the effect which phenyl-substitution of group _6B_ hydrides has on their acidities, based on what is now known of the hydrides of groups _4B_ and _5B_. It is apparent that the phenyl-derivatives of the heavier main group hydrides and their anions must possess at least two 'lone pairs' of electrons before a significant π-interaction can take place. Therefore deprotonation of phenylphosphine or phenylarsine receives an extra energetic 'benefit' from delocalization as compared to deprotonation of phenylgermane. In the case of the hydrides and phenylhydrides of the group 6B elements (S, Se, Te) the neutral species already possess two 'non-bonding' pairs of electrons. Consequently it is possible for a significant π-interaction to occur in, for example, the neutral C_6H_5SH. The ^{13}C NMR spectrum of C_6H_5SH in $CDCl_3$ solution has been reported (Senoff, 1975) and the following assignments given: C_1, 130.5 ppm; C_2, 129.1 ppm; C_3, 128.7 ppm; C_4, 124.2 ppm. The parameter, $(\delta_p-\delta_m)_{^{13}C}$ = -3.5 ppm, is evidence of a π interaction in this compound (cf. $(\delta_p-\delta_m)_{^{13}C}$ = 0.39 for $C_6H_5PH_2$ in THF). Such an interaction, however, is not likely to be appreciably stabilizing. The ^{13}C chemical shifts for C_6H_5SNa, in CD_3OD solvent, have also been reported: C_1, 148.9 ppm; C_2, 134.4 ppm; C_3, 128.4 ppm; C_4, 121.7 ppm (Carson, 1981). In this case $(\delta_{para}-\delta_{meta})_{^{13}C}$ = -6.7 ppm confirms the expected increase in π-donation to the ring as compared to the hydride C_6H_5SH, however, this is not as large an effect as was observed for C_6H_5PHNa; $(\delta_{para}-\delta_{meta})_{^{13}C}$ = -9.87 ppm in THF solution. The lower value for C_6H_5SNa may be a consequence of hydrogen bonding by the methanol solvent. It is also worth noting that the electron affinity of sulfur is much greater than that of phosphorus therefore it perhaps should not be surprising that C_6H_5PHNa would display a greater degree of charge transfer to the phenyl-ring than does C_6H_5SNa.

Based on these limited observations one might expect phenyl substitution of H_2S to result in an increase in the acidity of the remaining proton but not so large as is observed for phenyl-substitution of PH_3. The pKa's of H_2S and C_6H_5SH in aqueous solutions at 25°C are reported to be 7.033(6) (Sretenskaya, 1974) and 6.615(5) (De Maria, 1973) respectively. Thus C_6H_5SH is ~ 0.42 logarithmic units more acidic, in H_2O solution, than is H_2S. This is consistent with both the suggested rationale and the NMR parameters. The use of H_2O solvent, however, will favour the formation of HS^- as this small anion will produce greater solvation energy than $C_6H_5S^-$. One would expect therefore that, in a less polar, non-hydroxylic solvent, the acidity difference between C_6H_5SH and H_2S might appear to be larger. It would be of interest to record the ^{13}C NMR parameters of the group <u>6B</u> phenylhydrides and their anions in both THF and NH_3 solvents as well as to measure their acidities relative to the simple binary hydrides in order to make a more direct comparison with the group <u>4B</u> and <u>5B</u> analogues of the present study.

B. Some Coordination Chemistry of PH_3 and $C_6H_5PH_2$

Attempts were made, in this work, to prepare and characterize coordination complexes between cuprous iodide and both phosphine and phenylphosphine analogous to those already known for diphenyl- (Abel, 1969) and triphenyl-phosphines (Costa, 1965). The observation that solutions of $CuI \cdot nPH_3$ in THF precipitate crystals of CuI at reduced temperature suggests that the formation of these adducts in solution from solid CuI and dissolved PH_3 may be endothermic. This observation also suggests a new potential avenue of research in that solutions of PH_3 may be used for the preparation of crystalline samples of CuI and perhaps this can be extended to the crystal growth of other metal iodides as well. Crystallization can be easily controlled by regulation of temperature or of PH_3 pressure. This provides a low-energy alternative to the preparation of such crystals from the melt.

By contrast, $[CuI(C_6H_5PH_2)_2]_2$ dissolved in THF does not precipitate CuI at low temperature. ^{31}P NMR shows that the ligands remain coordinated at -100°C. The stronger coordinating ability of $C_6H_5PH_2$ compared to PH_3 parallels their relative basicities (Henderson, 1960). This suggests that σ-donor strength is the dominant influence on the stability of the coordinative interaction when steric effects are minimal. π-Acceptor ability of these ligands appears not to be a factor.

The structure of $[CuI(C_6H_5PH_2)_2]_2$ demonstrates that full tetrahedral coordination of Cu is achieved when steric considerations permit (cf. structure of (Cu[illegible])$_2$[C$_6$H$_5$)$_3$P]$_3$, Eller, 1977). The use of ^{127}I Mössbauer spectroscopy to characterize different structural geometries in such complexes was found to be unfruitful. The observed spectra are not consistent with simple ideas about I-Cu bond covalency.

Appendix

Moduli of the observed and calculated structure factors and standard deviations for $[CuI(C_6H_5PH_2)_2]_2$. F(000)(x 10) on this scale is 15839.

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE 1 OF 18
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	0	-12	837	877	37	0	4	-10	226	157	28	-3	3	-9	778	763	35
1	1	-12	777	806	35	2	4	-10	337	310	24	-1	3	-9	520	692	29
3	1	-12	345	399	27	4	4	-10	240	154	26	1	3	-9	1174	1196	51
2	2	-12	362	444	26	6	4	-10	389	439	24	3	3	-9	1531	1527	66
4	2	-12	699	706	31	8	4	-10	126	68	44	5	3	-9	1329	1291	57
3	3	-12	682	701	32	-3	5	-10	189	115	34	7	3	-9	345	858	37
2	4	-12	265	211	29	-1	5	-10	798	777	35	9	3	-9	251	329	29
4	4	-12	235	159	34	1	5	-10	1040	1049	45	-4	4	-9	513	565	30
3	5	-12	1020	1034	45	3	5	-10	1119	1082	48	-2	4	-9	760	715	33
-1	1	-11	96	94	53	5	5	-10	188	191	33	0	4	-9	576	649	31
1	1	-11	671	639	31	7	5	-10	177	86	33	2	4	-9	2455	2364	105
3	1	-11	274	233	26	-2	6	-10	630	653	30	4	4	-9	1994	1961	85
5	1	-11	252	218	27	0	6	-10	1199	1192	52	6	4	-9	1543	1557	66
0	2	-11	285	371	27	2	6	-10	1049	990	45	8	4	-9	523	575	27
2	2	-11	431	464	25	4	6	-10	901	813	36	-3	5	-9	39	147	84
4	2	-11	634	615	29	6	6	-10	158	185	38	-1	5	-9	429	447	24
6	2	-11	270	232	27	8	6	-10	141	56	40	1	5	-9	1336	1301	60
-1	3	-11	422	427	25	-3	7	-10	828	837	37	3	5	-9	1437	1400	61
1	3	-11	159	245	28	-1	7	-10	826	791	37	5	5	-9	930	968	43
3	3	-11	148	173	38	1	7	-10	553	560	23	7	5	-9	732	811	35
5	3	-11	477	475	25	3	7	-10	435	378	24	9	5	-9	0+	99	115
7	3	-11	580	672	29	5	7	-10	369	359	25	-4	6	-9	716	741	33
0	4	-11	465	461	26	7	7	-10	271	285	26	-2	6	-9	547	637	30
2	4	-11	94	96	52	-2	8	-10	1048	1034	45	0	6	-9	396	869	39
4	4	-11	130	135	45	0	8	-10	360	320	25	2	6	-9	353	351	24
6	4	-11	1025	1094	48	2	8	-10	483	446	25	4	6	-9	455	422	25
-1	5	-11	456	446	25	4	8	-10	910	930	40	6	6	-9	339	396	24
1	5	-11	290	299	25	6	8	-10	615	633	30	8	6	-9	367	414	25
3	5	-11	0+	97	31	8	8	-10	501	545	27	-3	7	-9	534	497	27
5	5	-11	274	279	30	-1	9	-10	253	292	29	-1	7	-9	315	792	36
7	5	-11	470	529	27	1	9	-10	390	363	24	1	7	-9	1554	1451	61
0	6	-11	350	392	26	3	9	-10	0+	28	110	3	7	-9	1451	1420	62
2	6	-11	337	316	25	5	9	-10	645	578	30	5	7	-9	741	729	33
4	6	-11	247	188	28	7	9	-10	233	306	30	7	7	-9	775	815	35
6	6	-11	362	413	26	-2	10	-10	357	329	26	9	7	-9	335	420	25
-1	7	-11	455	464	26	0	10	-10	53	112	68	-4	8	-9	420	358	25
1	7	-11	345	377	25	2	10	-10	250	250	27	-2	8	-9	427	405	25
3	7	-11	332	347	25	4	10	-10	215	210	31	0	8	-9	841	776	37
5	7	-11	385	398	25	6	10	-10	147	196	41	2	8	-9	1496	1469	64
0	8	-11	335	351	27	-1	11	-10	682	684	32	4	8	-9	729	592	33
2	8	-11	130	141	31	1	11	-10	443	481	25	6	8	-9	630	571	32
4	8	-11	433	463	25	3	11	-10	426	375	25	8	8	-9	429	468	25
6	8	-11	302	261	27	5	11	-10	729	736	33	-3	9	-9	1552	1605	67
1	9	-11	330	392	25	7	11	-10	389	429	23	-1	9	-9	1074	1050	45
3	9	-11	312	354	26	0	12	-10	549	543	22	1	9	-9	1439	1453	64
5	9	-11	713	724	29	2	12	-10	256	252	29	3	9	-9	432	442	25
2	10	-11	339	421	27	4	12	-10	358	333	25	5	9	-9	213	175	29
4	10	-11	571	606	27	6	12	-10	306	329	26	7	9	-9	937	963	63
1	11	-11	340	338	37	-1	13	-10	902	929	40	-2	10	-9	1338	1317	60
3	11	-11	134	147	44	1	13	-10	732	750	34	0	10	-9	1530	1450	68
-2	0	-10	1583	1779	72	3	13	-10	817	925	37	2	10	-9	1137	1146	53
0	0	-10	540	511	27	5	13	-10	75	167	64	4	10	-9	1170	1122	33
2	0	-10	110	31	44	7	13	-10	731	799	36	6	10	-9	305	355	40
6	0	-10	753	360	44	0	14	-10	990	1035	43	8	10	-9	1111	1165	49
8	0	-10	644	657	40	2	14	-10	533	595	28	-3	11	-9	332	330	36
-3	1	-10	929	350	40	4	14	-10	274	275	27	-1	11	-9	553	641	34
-1	1	-10	310	844	24	6	14	-10	489	495	31	1	11	-9	1555	1652	46
1	1	-10	465	391	29	-5	1	-9	652	655	59	3	11	-9	735	657	32
3	1	-10	354	315	24	-3	1	-9	1206	1235	60	5	11	-9	275	277	27
5	1	-10	397	597	35	-1	1	-9	1377	1442	50	7	11	-9	573	656	37
7	1	-10	407	407	44	1	1	-9	1408	1390	30	-2	12	-9	352	369	37
-2	2	-10	737	754	35	3	1	-9	440	444	33	0	12	-9	536	537	29
0	2	-10	1007	1008	44	5	1	-9	654	731	33	2	12	-9	1451	1424	63
2	2	-10	231	151	23	7	1	-9	715	794	72	4	12	-9	739	790	35
4	2	-10	248	232	29	9	1	-9	1259	1367	73	6	12	-9	1013	1073	44
6	2	-10	589	819	29	-4	2	-9	1576	1633	71	-1	13	-9	591	653	44
8	2	-10	591	649	30	-2	2	-9	1633	1709	75	1	13	-9	315	379	33
-3	3	-10	442	468	34	0	2	-9	1017	987	31	3	13	-9	719	633	33
-1	3	-10	374	380	30	2	2	-9	552	551	24	5	13	-9	435	471	35
5	3	-10	523	397	35	4	2	-9	368	327	43	7	13	-9	434	549	37
7	3	-10	323	337	35	6	2	-9	382	331	29	-2	14	-9	572	533	29
-2	4	-10	135	133	28	-5	3	-9	397	376	42	0	14	-9	540	551	23

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE 2 OF 15
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	14	-9	473	452	27	-3	7	-8	356	352	25	0	18	-8	539	641	31
4	14	-9	438	512	27	-1	7	-8	1439	1406	62	2	18	-8	614	599	30
6	14	-9	380	406	26	1	7	-8	1359	1325	58	4	18	-8	708	708	33
-1	15	-9	514	515	28	3	7	-8	1075	1054	47	6	18	-8	456	504	27
1	15	-9	1085	1061	47	5	7	-8	1012	999	44	-1	19	-8	1257	1255	55
3	15	-9	1428	1398	61	7	7	-8	682	725	31	1	19	-8	1208	1219	52
5	15	-9	999	1079	44	9	7	-8	487	525	27	3	19	-8	532	634	29
0	16	-9	636	642	31	-4	8	-8	964	913	42	5	19	-8	154	146	43
2	16	-9	1160	1211	50	-2	8	-8	1385	1293	59	2	20	-8	557	680	29
4	16	-9	1154	1138	50	0	8	-8	2007	1885	85	-7	1	-7	252	295	30
6	16	-9	900	935	36	2	8	-8	1182	1110	51	-5	1	-7	170	136	35
1	17	-9	915	996	41	4	8	-8	1124	1099	49	-3	1	-7	631	652	31
3	17	-9	392	369	26	6	8	-8	523	504	27	-1	1	-7	927	957	40
5	17	-9	352	357	27	8	8	-8	794	817	35	1	1	-7	1116	1047	48
2	18	-9	343	382	27	-5	9	-8	533	526	28	5	1	-7	451	439	23
-6	0	-8	271	319	29	-3	9	-8	662	667	31	7	1	-7	357	319	23
-4	0	-8	1309	1271	56	-1	9	-8	923	920	40	9	1	-7	448	479	25
-2	0	-8	1563	1650	67	1	9	-8	900	899	39	-6	2	-7	237	250	30
0	0	-8	1759	2902	117	3	9	-8	938	913	41	-4	2	-7	526	515	25
6	0	-8	738	893	35	5	9	-8	369	363	24	-2	2	-7	447	431	23
8	0	-8	683	707	31	7	9	-8	732	794	33	0	2	-7	1010	976	43
10	0	-8	1042	1200	45	9	9	-8	462	482	27	2	2	-7	1344	1321	57
-5	1	-8	420	441	26	-4	10	-8	262	276	28	4	2	-7	957	826	37
-3	1	-8	556	533	27	-2	10	-8	518	507	26	6	2	-7	214	212	25
-1	1	-8	1701	1707	72	0	10	-8	510	489	26	8	2	-7	204	209	33
1	1	-8	1551	1608	67	2	10	-8	352	359	24	10	2	-7	347	905	39
5	1	-8	850	891	37	4	10	-8	316	295	24	-7	3	-7	237	298	29
7	1	-8	304	876	35	6	10	-8	174	113	33	-5	3	-7	339	360	25
9	1	-8	505	560	27	8	10	-8	261	315	29	-3	3	-7	519	637	29
-6	2	-8	777	822	35	-5	11	-8	654	661	31	-1	3	-7	158	138	29
-4	2	-8	564	594	28	-3	11	-8	1005	1004	44	1	3	-7	256	190	21
-2	2	-8	242	238	26	-1	11	-8	1401	1346	60	3	3	-7	754	759	33
0	2	-8	501	485	25	1	11	-8	1474	1464	63	5	3	-7	1357	1389	53
2	2	-8	530	607	29	3	11	-8	942	885	41	7	3	-7	958	1018	42
4	2	-8	1421	1487	51	5	11	-8	157	229	35	9	3	-7	825	852	37
6	2	-8	1583	1790	72	7	11	-8	770	772	35	-6	4	-7	259	273	28
8	2	-8	541	560	27	9	11	-8	693	772	33	-4	4	-7	543	646	30
10	2	-8	383	442	26	-4	12	-8	558	544	28	-2	4	-7	1031	1063	47
-5	3	-8	863	826	38	-2	12	-8	1073	1004	46	0	4	-7	232	213	23
-3	3	-8	797	812	36	0	12	-8	1530	1420	66	2	4	-7	421	379	22
-1	3	-8	957	930	42	2	12	-8	761	755	34	4	4	-7	1653	1718	71
1	3	-8	1260	1321	54	4	12	-8	697	689	32	6	4	-7	1325	1409	57
3	3	-8	840	794	37	6	12	-8	553	575	27	8	4	-7	1513	1654	65
5	3	-8	1769	1761	76	8	12	-8	558	716	31	10	4	-7	743	750	34
7	3	-8	1077	1144	47	-3	13	-8	522	501	27	-7	5	-7	0+	52	117
9	3	-8	535	579	27	-1	13	-8	553	521	27	-5	5	-7	403	387	24
-6	4	-8	137	141	45	1	13	-8	1157	1084	50	-3	5	-7	936	906	41
-4	4	-8	672	559	31	3	13	-8	1128	1060	49	-1	5	-7	335	300	22
-2	4	-8	450	436	24	5	13	-8	1311	1308	56	1	5	-7	339	401	22
0	4	-8	354	329	22	7	13	-8	999	924	40	3	5	-7	650	582	29
2	4	-8	423	416	23	-4	14	-8	426	414	26	5	5	-7	921	954	40
4	4	-8	965	955	42	-2	14	-8	779	705	35	7	5	-7	547	680	30
6	4	-8	533	564	27	0	14	-8	752	673	34	9	5	-7	934	972	39
8	4	-8	433	486	26	2	14	-8	1312	1304	56	-6	6	-7	155	130	38
10	4	-8	210	226	33	4	14	-8	1501	1583	69	-4	6	-7	158	136	38
-5	5	-8	575	573	29	6	14	-8	1560	1665	71	-2	6	-7	72	177	55
-3	5	-8	353	337	24	8	14	-8	673	311	32	0	6	-7	251	269	22
-1	5	-8	335	304	24	-3	15	-8	134	91	43	2	6	-7	995	915	43
1	5	-8	1610	1544	69	-1	15	-8	203	217	32	4	6	-7	422	401	23
3	5	-8	1402	1385	60	1	15	-8	460	423	25	6	6	-7	333	194	27
5	5	-8	1975	1917	84	3	15	-8	510	616	29	8	6	-7	371	396	25
7	5	-8	1183	1260	51	5	15	-8	867	879	39	10	6	-7	833	290	27
9	5	-8	575	715	31	7	15	-8	461	450	26	-5	7	-7	151	34	28
-4	6	-8	562	524	27	-2	16	-8	376	349	26	-3	7	-7	335	206	24
-2	6	-8	560	684	33	0	16	-8	763	699	34	-1	7	-7	918	943	40
0	6	-8	732	793	35	2	16	-8	568	622	29	1	7	-7	305	320	21
2	6	-8	1390	1827	30	4	16	-8	875	857	39	3	7	-7	1177	1172	50
4	6	-8	1199	2142	94	6	16	-8	535	563	28	5	7	-7	329	902	36
6	6	-8	1250	2237	97	-1	17	-8	556	577	28	7	7	-7	551	561	27
8	6	-8	351	915	18	1	17	-8	636	581	33	9	7	-7	323	879	37
10	6	-8	533	731	27	3	17	-8	916	904	40	-6	8	-7	51	222	79
-5	7	-8	313	371	27	5	17	-8	1240	1274	54	-4	8	-7	456	456	25

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
(UNOBSERVED REFLECTIONS ARE MARKED +)

PAGE 3 OF18

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-2	8	-7	856	793	38	-2	18	-7	305	290	26	7	5	-6	448	474	24
0	8	-7	182	155	29	0	18	-7	527	527	27	9	5	-6	507	625	29
2	8	-7	581	664	30	2	18	-7	867	856	38	-6	6	-6	1225	1207	53
4	8	-7	1287	1261	55	4	18	-7	779	829	35	-4	6	-6	277	237	25
6	8	-7	588	542	28	6	18	-7	293	249	28	-2	6	-6	398	395	22
8	8	-7	646	699	30	-1	19	-7	279	270	29	0	6	-6	1920	1704	78
10	8	-7	445	479	26	1	19	-7	536	486	27	2	6	-6	1515	1458	65
-5	9	-7	383	404	26	3	19	-7	425	367	25	4	6	-6	135	128	25
-3	9	-7	138	82	38	5	19	-7	323	358	27	6	6	-6	34	26	47
-1	9	-7	837	846	37	-2	20	-7	417	401	26	8	6	-6	538	531	27
1	9	-7	521	495	25	0	20	-7	402	436	26	10	6	-6	501	502	26
3	9	-7	1417	1389	61	2	20	-7	620	630	30	-7	7	-6	507	515	27
5	9	-7	775	778	35	4	20	-7	279	344	29	-5	7	-6	1251	1196	54
7	9	-7	183	211	32	-1	21	-7	380	407	28	-3	7	-6	1211	1181	52
9	9	-7	704	717	33	1	21	-7	622	623	30	-1	7	-6	975	953	42
-6	10	-7	473	503	27	3	21	-7	502	546	27	1	7	-6	1131	1114	50
-4	10	-7	404	433	25	-2	22	-7	331	366	28	3	7	-6	465	417	22
-2	10	-7	825	725	36	-8	0	-6	496	490	27	5	7	-6	343	311	22
0	10	-7	650	589	30	-6	0	-6	1044	975	45	7	7	-6	545	630	30
2	10	-7	1210	1170	52	-4	0	-6	1709	1763	73	9	7	-6	331	324	25
4	10	-7	1640	1620	71	-2	0	-6	1672	1715	71	-6	8	-6	1354	1026	46
6	10	-7	200	154	29	0	0	-6	2572	2502	108	-4	8	-6	1738	1741	77
8	10	-7	291	313	26	4	0	-6	409	418	21	-2	8	-6	852	802	35
-5	11	-7	344	314	25	6	0	-6	1068	1182	46	0	8	-6	1176	1231	50
-3	11	-7	431	388	25	8	0	-6	563	593	27	2	8	-6	133	158	25
-1	11	-7	723	565	32	10	0	-6	230	252	29	4	8	-6	720	671	32
1	11	-7	347	345	23	-7	1	-6	649	657	31	6	8	-6	1236	1249	53
3	11	-7	584	629	31	-5	1	-6	1273	1272	55	8	8	-6	372	408	24
5	11	-7	356	270	24	-3	1	-6	1310	1350	56	10	8	-6	123	43	47
7	11	-7	332	332	24	-1	1	-6	1340	1364	57	-7	9	-6	236	216	31
9	11	-7	756	788	35	1	1	-6	230	194	20	-5	9	-6	990	951	43
-4	12	-7	343	342	35	3	1	-6	678	625	30	-3	9	-6	449	410	24
-2	12	-7	838	869	37	5	1	-6	191	196	24	-1	9	-6	736	693	33
0	12	-7	619	557	29	7	1	-6	570	601	27	1	9	-6	510	479	24
2	12	-7	234	249	24	9	1	-6	265	340	25	3	9	-6	241	162	22
4	12	-7	1201	1188	52	11	1	-6	0+	61	117	5	9	-6	602	595	29
6	12	-7	633	671	30	-8	2	-6	630	634	30	7	9	-6	533	544	26
8	12	-7	632	646	30	-6	2	-6	970	957	42	9	9	-6	243	229	29
-5	13	-7	381	204	28	-4	2	-6	610	601	28	-6	10	-6	310	292	27
-3	13	-7	271	215	26	-2	2	-6	273	235	21	-4	10	-6	440	432	24
-1	13	-7	381	366	24	0	2	-6	745	715	33	-2	10	-6	492	465	24
1	13	-7	577	530	27	2	2	-6	1354	1337	58	0	10	-6	521	527	25
3	13	-7	560	549	27	4	2	-6	1045	1025	45	2	10	-6	404	375	22
5	13	-7	345	360	24	6	2	-6	138	110	32	4	10	-6	131	220	29
7	13	-7	297	353	26	8	2	-6	794	865	35	6	10	-6	427	433	24
9	13	-7	556	615	29	10	2	-6	237	177	28	8	10	-6	0+	103	112
-4	14	-7	104	131	50	-7	3	-6	622	609	30	10	10	-6	0+	25	115
-2	14	-7	560	547	27	-5	3	-6	803	774	36	-5	11	-6	1232	1159	53
0	14	-7	444	418	25	-3	3	-6	685	678	31	-3	11	-6	820	796	36
2	14	-7	267	309	27	-1	3	-6	557	536	25	-1	11	-6	1134	1026	48
4	14	-7	515	518	26	1	3	-6	873	813	38	1	11	-6	720	706	32
6	14	-7	466	431	25	3	3	-6	588	605	26	3	11	-6	251	219	23
8	14	-7	474	474	27	5	3	-6	657	717	29	5	11	-6	679	661	31
-3	15	-7	711	705	33	7	3	-6	594	661	28	7	11	-6	672	712	31
-1	15	-7	471	455	25	9	3	-6	255	247	27	9	11	-6	215	202	33
1	15	-7	104	134	50	11	3	-6	327	194	30	-6	12	-6	714	686	33
3	15	-7	480	474	25	-6	4	-6	534	540	27	-4	12	-6	1374	1337	59
5	15	-7	995	1006	43	-4	4	-6	810	819	36	-2	12	-6	750	736	34
7	15	-7	1034	1065	45	-2	4	-6	0+	51	98	0	12	-6	1012	952	44
-4	16	-7	530	465	27	0	4	-6	658	665	29	2	12	-6	329	257	22
-2	16	-7	315	250	25	2	4	-6	268	254	19	4	12	-6	436	476	25
0	16	-7	137	146	40	4	4	-6	226	220	22	6	12	-6	537	577	29
2	16	-7	344	295	24	6	4	-6	432	466	23	8	12	-6	259	235	25
4	16	-7	334	793	37	8	4	-6	118	185	43	-5	13	-6	515	623	30
6	16	-7	1121	1132	49	10	4	-6	22	135	93	-3	13	-6	507	461	26
8	16	-7	793	837	36	-7	5	-6	818	786	36	-1	13	-6	1003	979	44
-3	17	-7	295	194	27	-5	5	-6	809	785	36	1	13	-6	1751	1666	75
-1	17	-7	354	354	25	-3	5	-6	291	244	22	3	13	-6	332	331	23
1	17	-7	334	602	44	-1	5	-6	500	482	24	5	13	-6	511	481	26
3	17	-7	1313	990	44	1	5	-6	1719	1677	73	7	13	-6	92	159	52
5	17	-7	617	560	29	3	5	-6	593	642	31	9	13	-6	552	566	29
7	17	-7	434	429	26	5	5	-6	594	649	27	-6	14	-6	755	759	35

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-4	14	-6	79	101	57	8	2	-5	697	775	31	-2	10	-5	3095	2968	130
-2	14	-6	701	623	32	10	2	-5	812	809	36	0	10	-5	2626	2519	111
0	14	-6	1023	979	45	-7	3	-5	1442	1414	62	2	10	-5	1936	1866	81
2	14	-6	1266	1207	55	-5	3	-5	1256	1216	54	4	10	-5	733	732	32
4	14	-6	101	169	50	-3	3	-5	1236	1234	53	6	10	-5	1231	1276	53
6	14	-6	167	139	34	-1	3	-5	1718	1693	73	8	10	-5	909	909	40
8	14	-6	501	518	27	1	3	-5	1238	1202	53	10	10	-5	905	828	36
-5	15	-6	517	509	27	3	3	-5	1961	2038	83	-7	11	-5	533	572	29
-3	15	-6	76	81	50	5	3	-5	1768	1903	75	-5	11	-5	705	689	32
-1	15	-6	0+	39	110	7	3	-5	582	599	27	-3	11	-5	1354	1314	58
1	15	-6	504	479	26	9	3	-5	178	188	34	-1	11	-5	1478	1437	63
3	15	-6	305	312	24	11	3	-5	158	259	40	1	11	-5	1131	1172	51
5	15	-6	511	532	26	-8	4	-5	1570	1562	67	3	11	-5	1157	1164	50
7	15	-6	509	530	27	-6	4	-5	1916	1826	82	5	11	-5	797	811	35
-4	16	-6	679	716	32	-4	4	-5	1116	1091	48	7	11	-5	523	506	26
-2	16	-6	292	238	25	-2	4	-5	357	289	20	9	11	-5	273	284	27
0	16	-6	490	530	25	0	4	-5	2414	2299	102	-6	12	-5	358	797	38
2	16	-6	223	325	10	2	4	-5	2156	2050	91	-4	12	-5	517	529	26
4	16	-6	533	512	27	4	4	-5	3486	3545	146	-2	12	-5	951	927	41
6	16	-6	625	612	29	6	4	-5	1695	1776	72	0	12	-5	1594	1569	68
8	16	-6	472	453	26	8	4	-5	733	720	33	2	12	-5	1377	1324	59
-5	17	-6	362	362	20	10	4	-5	189	208	34	4	12	-5	1319	1351	56
-3	17	-6	293	339	26	-7	5	-5	1243	1226	54	6	12	-5	748	761	33
-1	17	-6	230	234	29	-5	5	-5	887	863	39	8	12	-5	756	790	35
1	17	-6	544	489	26	-3	5	-5	967	987	42	10	12	-5	248	265	30
3	17	-6	342	343	24	-1	5	-5	852	843	37	-7	13	-5	550	530	29
5	17	-6	0+	123	111	1	5	-5	1430	1404	61	-5	13	-5	552	594	30
7	17	-6	516	518	27	3	5	-5	1564	1576	67	-3	13	-5	1248	1195	54
-4	18	-6	507	513	28	5	5	-5	1632	1678	70	-1	13	-5	1344	1331	57
-2	18	-6	437	445	26	7	5	-5	569	629	27	1	13	-5	1545	1541	66
0	18	-6	284	296	27	9	5	-5	242	228	28	3	13	-5	721	694	32
2	18	-6	412	368	25	11	5	-5	256	243	29	5	13	-5	334	391	39
4	18	-6	419	406	25	-8	6	-5	173	147	38	7	13	-5	344	385	25
6	18	-6	330	347	25	-6	6	-5	581	565	28	9	13	-5	448	493	26
-3	19	-6	927	958	41	-4	6	-5	330	251	23	-6	14	-5	452	438	27
-1	19	-6	1006	982	44	-2	6	-5	1544	1554	66	-4	14	-5	459	400	25
1	19	-6	328	328	36	0	6	-5	2059	1915	87	-2	14	-5	910	965	40
3	19	-6	703	634	32	2	6	-5	487	421	23	0	14	-5	839	844	39
5	19	-6	339	363	25	4	6	-5	568	595	26	2	14	-5	715	555	32
7	19	-6	506	543	28	6	6	-5	595	624	27	4	14	-5	736	697	32
-2	20	-6	1062	1015	46	8	6	-5	202	241	30	6	14	-5	578	604	28
0	20	-6	593	570	29	10	6	-5	576	612	28	8	14	-5	154	212	33
2	20	-6	433	465	25	-7	7	-5	976	962	43	-5	15	-5	956	903	42
4	20	-6	353	317	25	-5	7	-5	950	958	42	-3	15	-5	510	550	29
6	20	-6	293	295	28	-3	7	-5	1411	1389	60	-1	15	-5	713	651	32
-1	21	-6	415	379	26	-1	7	-5	1543	1542	66	1	15	-5	1371	1323	59
1	21	-6	603	602	29	1	7	-5	2043	2034	87	3	15	-5	1801	1756	77
3	21	-6	495	493	27	3	7	-5	1941	1896	83	5	15	-5	1756	1757	75
5	21	-6	381	411	26	5	7	-5	1275	1255	54	7	15	-5	548	623	28
0	22	-6	403	393	25	7	7	-5	790	844	35	9	15	-5	107	243	56
2	22	-6	656	693	31	9	7	-5	647	677	30	-6	16	-5	1354	1343	59
4	22	-6	472	492	26	-8	8	-5	740	722	34	-4	16	-5	595	623	29
1	23	-6	216	275	33	-6	8	-5	619	611	29	-2	16	-5	371	375	24
3	23	-6	90	48	59	-4	8	-5	1067	1034	46	0	16	-5	1052	987	46
-7	1	-5	712	723	32	-2	8	-5	682	700	31	2	16	-5	1222	1184	52
-5	1	-5	1253	1235	34	0	8	-5	1110	1056	48	4	16	-5	1935	1910	81
-3	1	-5	1905	1955	81	2	8	-5	1415	1382	60	6	16	-5	916	965	40
-1	1	-5	3199	3155	130	4	8	-5	932	952	36	8	16	-5	142	157	43
1	1	-5	1343	1331	57	6	8	-5	617	617	28	-5	17	-5	933	877	40
3	1	-5	1209	1220	51	8	8	-5	691	761	31	-3	17	-5	976	902	43
5	1	-5	751	774	33	10	8	-5	146	157	40	-1	17	-5	1770	1679	75
7	1	-5	459	482	23	-7	9	-5	546	526	28	1	17	-5	551	553	30
9	1	-5	380	936	39	-5	9	-5	1529	1532	66	3	17	-5	737	767	35
11	1	-5	472	452	26	-3	9	-5	2222	2131	95	5	17	-5	521	474	26
-8	2	-5	249	226	29	-1	9	-5	2657	2553	112	7	17	-5	505	517	27
-6	2	-5	1401	1362	60	1	9	-5	1690	1613	72	-4	18	-5	1014	954	44
-4	2	-5	1570	1555	67	3	9	-5	1671	1655	71	-2	18	-5	1594	1629	69
-2	2	-5	3568	3606	150	5	9	-5	591	621	27	0	18	-5	1933	1902	85
0	2	-5	2583	2590	109	7	9	-5	950	851	37	2	18	-5	771	714	33
2	2	-5	1074	1374	48	9	9	-5	524	545	27	4	18	-5	420	441	24
4	2	-5	140	129	26	-6	10	-5	1437	1399	62	6	18	-5	746	761	34
6	2	-5	745	778	33	-4	10	-5	2333	2317	99	8	18	-5	351	347	27

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE 5 OF18

(UNOBSERVED REFLECTIONS ARE MARKED *)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-5	19	-5	365	284	28	0	4	-4	1081	1001	46	5	11	-4	492	486	24
-3	19	-5	449	390	26	2	4	-4	834	870	36	7	11	-4	605	651	28
-1	19	-5	896	895	39	4	4	-4	1422	1402	61	9	11	-4	939	873	37
1	19	-5	172	165	36	6	4	-4	428	428	22	-8	12	-4	132	197	48
3	19	-5	419	432	25	8	4	-4	642	635	30	-6	12	-4	356	386	25
5	19	-5	65	137	67	10	4	-4	318	320	26	-4	12	-4	1277	1286	55
7	19	-5	95	141	57	-9	5	-4	676	666	32	-2	12	-4	2012	1974	86
-4	20	-5	561	649	31	-7	5	-4	1212	1197	52	0	12	-4	2498	2355	105
-2	20	-5	799	813	36	-5	5	-4	1330	1331	57	2	12	-4	2583	2481	109
0	20	-5	681	651	32	-3	5	-4	1621	1580	69	4	12	-4	758	749	33
2	20	-5	461	464	25	-1	5	-4	358	346	19	6	12	-4	422	394	23
4	20	-5	498	533	26	1	5	-4	1293	1237	55	8	12	-4	794	789	35
6	20	-5	292	255	27	3	5	-4	2794	2879	117	10	12	-4	749	749	34
-3	21	-5	1124	1144	49	5	5	-4	2176	2325	92	-7	13	-4	815	750	37
-1	21	-5	1520	1517	65	7	5	-4	1802	1954	77	-5	13	-4	929	899	41
1	21	-5	950	950	42	9	5	-4	965	984	42	-3	13	-4	1747	1725	75
3	21	-5	389	387	25	11	5	-4	287	246	27	-1	13	-4	550	535	26
5	21	-5	588	597	29	-8	6	-4	1298	1248	56	1	13	-4	1247	1208	53
-2	22	-5	747	720	34	-6	6	-4	1255	1177	54	3	13	-4	2236	2189	95
0	22	-5	914	863	40	-4	6	-4	1806	1777	77	5	13	-4	1557	1556	66
2	22	-5	591	554	29	-2	6	-4	1015	969	44	7	13	-4	1451	1469	62
4	22	-5	522	614	30	0	6	-4	429	372	20	9	13	-4	894	917	40
-1	23	-5	360	341	26	2	6	-4	2865	2788	120	-6	14	-4	991	924	43
1	23	-5	852	830	38	4	6	-4	3350	3478	140	-4	14	-4	1539	1602	68
3	23	-5	890	912	39	6	6	-4	2229	2331	95	-2	14	-4	649	611	29
0	24	-5	533	693	31	8	6	-4	1987	2101	85	0	14	-4	205	220	26
2	24	-5	704	769	33	10	6	-4	724	723	33	2	14	-4	1736	1741	74
-8	0	-4	204	246	32	-7	7	-4	367	381	25	4	14	-4	2412	2481	102
-6	0	-4	542	635	29	-5	7	-4	665	657	30	6	14	-4	1456	1490	63
-4	0	-4	1591	1643	68	-3	7	-4	1935	1895	83	8	14	-4	1744	1821	75
-2	0	-4	3734	3989	158	-1	7	-4	1933	1864	82	-7	15	-4	499	464	29
0	0	-4	4915	5011	205	1	7	-4	2112	2095	89	-5	15	-4	592	595	29
4	0	-4	793	854	34	3	7	-4	2324	2378	98	-3	15	-4	734	736	35
6	0	-4	297	264	20	5	7	-4	1175	1171	50	-1	15	-4	159	215	31
8	0	-4	513	558	26	7	7	-4	863	904	38	1	15	-4	113	71	41
10	0	-4	1342	1422	58	9	7	-4	945	993	42	3	15	-4	1351	1336	58
-9	1	-4	331	339	27	11	7	-4	330	368	27	5	15	-4	1021	1018	44
-7	1	-4	449	446	25	-8	8	-4	379	371	26	7	15	-4	570	558	29
-5	1	-4	725	728	32	-6	8	-4	562	520	27	9	15	-4	315	383	27
-3	1	-4	1754	1821	75	-4	8	-4	1605	1580	69	-6	16	-4	425	414	26
-1	1	-4	2439	2533	102	-2	8	-4	3313	3186	139	-4	16	-4	710	737	32
1	1	-4	3237	3121	137	0	8	-4	2390	2295	101	-2	16	-4	1476	1393	63
3	1	-4	1818	1889	77	2	8	-4	3989	3900	167	0	16	-4	530	516	26
5	1	-4	870	932	38	4	8	-4	816	812	35	2	16	-4	1545	1578	66
7	1	-4	592	647	27	6	8	-4	393	398	22	4	16	-4	727	728	33
9	1	-4	1036	1059	45	8	8	-4	877	914	38	6	16	-4	722	782	33
11	1	-4	705	677	33	10	8	-4	1035	1003	45	8	16	-4	640	656	31
-8	2	-4	713	739	33	-7	9	-4	424	404	25	-5	17	-4	815	762	36
-6	2	-4	1259	1232	54	-5	9	-4	249	249	25	-3	17	-4	691	676	31
-4	2	-4	1793	1853	77	-3	9	-4	1734	1700	74	-1	17	-4	553	633	30
-2	2	-4	314	351	19	-1	9	-4	1351	1327	57	1	17	-4	530	617	29
0	2	-4	517	485	23	1	9	-4	1772	1693	76	3	17	-4	1142	1138	49
2	2	-4	1114	1156	52	3	9	-4	1833	1880	78	5	17	-4	1552	1604	67
4	2	-4	3378	3065	121	5	9	-4	681	674	30	7	17	-4	1157	1151	51
6	2	-4	1834	2066	91	7	9	-4	450	544	25	-6	18	-4	524	596	31
8	2	-4	1224	1230	53	9	9	-4	735	699	33	-4	18	-4	545	630	30
10	2	-4	386	361	25	-8	10	-4	307	288	27	-2	18	-4	751	736	34
-9	3	-4	425	454	26	-6	10	-4	242	220	28	0	18	-4	971	944	42
-7	3	-4	851	804	38	-4	10	-4	603	584	28	2	18	-4	910	879	40
-5	3	-4	1314	1317	56	-2	10	-4	711	691	32	4	18	-4	1130	1128	49
-3	3	-4	1765	1757	75	0	10	-4	835	812	35	6	18	-4	945	940	42
-1	3	-4	1957	1941	79	2	10	-4	679	705	30	8	18	-4	239	246	35
1	3	-4	1719	1573	73	4	10	-4	660	628	29	-5	19	-4	355	315	26
3	3	-4	2031	2098	90	6	10	-4	143	152	34	-3	19	-4	1236	1152	52
5	3	-4	1698	1874	72	8	10	-4	615	645	29	-1	19	-4	2352	2020	88
7	3	-4	1569	1675	67	10	10	-4	222	172	31	1	19	-4	2130	2047	91
9	3	-4	639	708	31	-7	11	-4	485	447	25	3	19	-4	1225	1228	53
11	3	-4	349	354	26	-5	11	-4	656	629	30	5	19	-4	235	201	29
-8	4	-4	0*	119	119	-3	11	-4	2154	2088	92	7	19	-4	0*	92	117
-6	4	-4	161	139	35	-1	11	-4	2647	2516	112	-4	20	-4	521	469	27
-4	4	-4	1292	1265	55	1	11	-4	2189	2114	93	-2	20	-4	1931	1795	81
-2	4	-4	862	895	37	3	11	-4	2238	2237	95	0	20	-4	1912	1719	77

OBSERVED AND CALCULATED STFUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	20	-4	1652	1653	71	-1	5	-3	1020	946	44	2	12	-3	1146	1168	49
4	20	-4	181	183	35	1	5	-3	1655	1568	70	4	12	-3	910	867	35
6	20	-4	246	241	29	3	5	-3	1269	1300	54	6	12	-3	1232	1340	55
-3	21	-4	566	567	28	5	5	-3	999	1090	43	8	12	-3	857	871	38
-1	21	-4	411	385	26	7	5	-3	1570	1685	67	10	12	-3	839	882	40
1	21	-4	674	642	31	9	5	-3	677	725	31	-7	13	-3	176	179	36
3	21	-4	717	710	33	11	5	-3	521	463	28	-5	13	-3	498	463	25
5	21	-4	714	738	33	-8	6	-3	218	211	31	-3	13	-3	644	550	29
-4	22	-4	389	1012	43	-6	6	-3	370	339	23	-1	13	-3	532	619	26
-2	22	-4	635	622	30	-4	6	-3	377	377	21	1	13	-3	1278	1272	55
0	22	-4	634	639	30	-2	6	-3	206	168	20	3	13	-3	1051	1049	45
2	22	-4	420	440	25	0	6	-3	1196	1150	51	5	13	-3	367	396	23
4	22	-4	1126	1143	49	2	6	-3	1031	1077	44	7	13	-3	637	757	31
6	22	-4	695	795	33	4	6	-3	557	565	25	9	13	-3	373	361	25
-3	23	-4	587	624	29	6	6	-3	383	379	21	-8	14	-3	33	52	91
-1	23	-4	765	769	35	8	6	-3	267	277	26	-6	14	-3	366	326	24
1	23	-4	443	453	26	10	6	-3	194	179	34	-4	14	-3	555	517	27
3	23	-4	332	384	27	-9	7	-3	249	280	31	-2	14	-3	433	381	23
5	23	-4	249	234	30	-7	7	-3	201	250	31	0	14	-3	707	666	31
-2	24	-4	334	300	26	-5	7	-3	581	582	27	2	14	-3	356	359	21
0	24	-4	223	180	30	-3	7	-3	838	791	36	4	14	-3	438	521	24
2	24	-4	339	384	27	-1	7	-3	1080	1036	46	6	14	-3	555	662	30
4	24	-4	700	794	33	1	7	-3	1682	1638	71	8	14	-3	554	539	28
-1	25	-4	0+	171	122	3	7	-3	1850	1890	78	-7	15	-3	30	70	57
1	25	-4	468	476	27	5	7	-3	1427	1514	61	-5	15	-3	876	846	39
3	25	-4	1109	1226	48	7	7	-3	1200	1229	52	-3	15	-3	1019	981	44
-9	1	-3	334	300	26	9	7	-3	917	948	40	-1	15	-3	756	715	34
-7	1	-3	270	199	25	11	7	-3	643	600	31	1	15	-3	38	67	45
-5	1	-3	522	491	25	-8	8	-3	152	107	38	3	15	-3	1128	1115	48
-3	1	-3	549	540	25	-6	8	-3	259	254	26	5	15	-3	1439	1562	64
-1	1	-3	1083	1135	46	-4	8	-3	221	237	23	7	15	-3	1704	1776	73
1	1	-3	3689	3455	154	-2	8	-3	1067	998	46	9	15	-3	811	844	36
3	1	-3	1429	1489	61	0	8	-3	1032	1029	44	-6	16	-3	468	432	26
5	1	-3	1113	1161	47	2	8	-3	1273	1366	54	-4	16	-3	1145	1122	49
7	1	-3	580	620	27	4	8	-3	1329	1363	57	-2	16	-3	290	282	24
9	1	-3	681	558	31	6	8	-3	940	1000	41	0	16	-3	359	305	23
11	1	-3	697	624	32	8	8	-3	1127	1212	49	2	16	-3	956	853	38
-8	2	-3	443	434	25	10	8	-3	538	505	28	4	16	-3	881	860	38
-6	2	-3	475	449	24	-9	9	-3	314	325	28	6	16	-3	1779	1936	75
-4	2	-3	373	378	20	-7	9	-3	642	645	30	8	16	-3	1051	1049	46
-2	2	-3	1104	1082	47	-5	9	-3	659	648	30	-7	17	-3	555	505	29
0	2	-3	2823	2705	118	-3	9	-3	1125	1125	48	-5	17	-3	513	434	27
2	2	-3	3191	3232	133	-1	9	-3	1114	1080	48	-3	17	-3	353	314	24
4	2	-3	921	889	35	1	9	-3	2268	2232	96	-1	17	-3	439	438	25
6	2	-3	1082	1128	46	3	9	-3	1826	1739	78	1	17	-3	1450	1476	62
8	2	-3	495	551	25	5	9	-3	1777	1853	75	3	17	-3	1041	1030	45
10	2	-3	504	618	29	7	9	-3	234	207	26	5	17	-3	1294	1231	52
-9	3	-3	308	269	27	9	9	-3	769	809	35	7	17	-3	726	749	33
-7	3	-3	578	571	28	-8	10	-3	451	390	26	-6	18	-3	445	409	26
-5	3	-3	1095	1115	47	-6	10	-3	1136	1103	49	-4	18	-3	474	473	25
-3	3	-3	539	512	24	-4	10	-3	919	921	40	-2	18	-3	70	82	62
-1	3	-3	722	722	31	-2	10	-3	1451	1428	62	0	18	-3	1753	1676	75
1	3	-3	1173	1113	50	0	10	-3	2447	2311	103	2	18	-3	1733	1758	75
3	3	-3	1043	1104	44	2	10	-3	2449	2411	103	4	18	-3	635	726	31
5	3	-3	1463	1620	63	4	10	-3	2154	2180	91	6	18	-3	650	649	30
7	3	-3	2097	2248	89	6	10	-3	1092	1161	47	8	18	-3	1035	1081	45
9	3	-3	702	694	32	8	10	-3	1052	1120	46	-5	19	-3	139	132	42
11	3	-3	583	577	29	10	10	-3	645	630	31	-3	19	-3	207	197	31
-8	4	-3	287	254	26	-7	11	-3	285	260	25	-1	19	-3	323	303	25
-6	4	-3	747	740	33	-5	11	-3	567	567	27	1	19	-3	947	920	38
-4	4	-3	2036	2049	86	-3	11	-3	409	420	22	3	19	-3	419	439	25
-2	4	-3	1199	1148	51	-1	11	-3	1402	1390	60	5	19	-3	397	422	25
0	4	-3	1276	1147	55	1	11	-3	563	549	25	7	19	-3	0+	177	119
2	4	-3	1341	1271	57	3	11	-3	1026	989	44	-6	20	-3	344	362	27
4	4	-3	1906	1972	81	5	11	-3	708	751	31	-4	20	-3	459	468	26
6	4	-3	3312	3010	118	7	11	-3	753	753	34	-2	20	-3	332	309	25
8	4	-3	2191	2241	94	9	11	-3	630	640	30	0	20	-3	941	911	41
10	4	-3	1064	1039	46	-8	12	-3	222	215	32	2	20	-3	910	829	36
-9	5	-3	0+	40	117	-6	12	-3	391	315	24	4	20	-3	551	543	27
-7	5	-3	122	106	44	-4	12	-3	705	659	31	6	20	-3	256	274	28
-5	5	-3	335	363	25	-2	12	-3	966	925	42	-5	21	-3	415	391	26
-3	5	-3	1033	1048	46	0	12	-3	2408	2302	102	-3	21	-3	343	320	25

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-1	21	-3	698	667	32	-4	4	-2	505	518	23	-7	11	-2	695	653	31
1	21	-3	1493	1484	64	-2	4	-2	342	276	18	-5	11	-2	1147	1134	49
3	21	-3	810	797	36	0	4	-2	290	258	16	-3	11	-2	1264	1209	54
5	21	-3	494	513	26	2	4	-2	0+	97	80	-1	11	-2	958	969	41
7	21	-3	171	234	40	4	4	-2	851	894	37	1	11	-2	552	530	25
-4	22	-3	425	377	26	6	4	-2	490	527	23	3	11	-2	554	553	25
-2	22	-3	394	420	25	8	4	-2	429	434	24	5	11	-2	1071	1094	46
0	22	-3	747	705	34	10	4	-2	193	253	34	7	11	-2	456	506	24
2	22	-3	627	616	30	-9	5	-2	967	926	43	9	11	-2	148	91	38
4	22	-3	692	653	32	-7	5	-2	1027	1023	45	-8	12	-2	381	344	26
6	22	-3	450	474	27	-5	5	-2	1013	966	44	-6	12	-2	810	738	36
-3	23	-3	676	612	32	-3	5	-2	474	421	22	-4	12	-2	875	847	38
-1	23	-3	629	569	30	-1	5	-2	1566	1463	66	-2	12	-2	1235	1204	55
1	23	-3	192	213	34	1	5	-2	1524	1444	64	0	12	-2	308	307	19
3	23	-3	175	203	35	3	5	-2	1032	1099	44	2	12	-2	487	458	23
5	23	-3	789	787	36	5	5	-2	316	353	19	4	12	-2	739	764	32
-2	24	-3	492	417	26	7	5	-2	695	701	31	6	12	-2	555	599	30
0	24	-3	515	459	27	9	5	-2	804	855	36	8	12	-2	314	310	25
2	24	-3	333	357	27	11	5	-2	719	654	33	10	12	-2	438	428	26
4	24	-3	545	572	28	-10	6	-2	1014	962	45	-7	13	-2	590	641	32
-1	25	-3	288	253	28	-8	6	-2	1392	1352	60	-5	13	-2	495	454	25
1	25	-3	604	597	29	-6	6	-2	815	842	36	-3	13	-2	323	305	21
3	25	-3	354	328	27	-4	6	-2	864	868	37	-1	13	-2	1429	1370	61
0	26	-3	408	445	26	-2	6	-2	541	502	24	1	13	-2	739	721	34
2	26	-3	535	598	28	0	6	-2	3564	3266	149	3	13	-2	744	758	33
-10	0	-2	201	211	34	2	6	-2	1289	1240	55	5	13	-2	452	510	24
-8	0	-2	704	701	32	4	6	-2	358	360	19	7	13	-2	330	359	24
-6	0	-2	1342	1330	58	6	6	-2	1097	1174	47	9	13	-2	750	770	34
-4	0	-2	1017	1074	44	8	6	-2	431	433	24	-8	14	-2	1353	1284	59
-2	0	-2	2321	2772	118	10	6	-2	1244	1215	54	-6	14	-2	357	295	24
0	0	-2	2143	2285	90	-9	7	-2	690	636	32	-4	14	-2	824	816	36
2	0	-2	1315	1142	43	-7	7	-2	845	814	37	-2	14	-2	1130	1099	51
4	0	-2	1844	1930	78	-5	7	-2	1056	929	45	0	14	-2	1530	1479	65
6	0	-2	463	505	22	-3	7	-2	1675	1660	71	2	14	-2	919	862	40
8	0	-2	1041	1018	45	-1	7	-2	166	207	22	4	14	-2	391	373	22
10	0	-2	293	342	27	1	7	-2	458	461	21	6	14	-2	529	521	26
-9	1	-2	432	490	26	3	7	-2	547	567	24	8	14	-2	557	580	29
-7	1	-2	1025	1027	44	5	7	-2	1251	1275	53	-7	15	-2	691	632	32
-5	1	-2	882	892	38	7	7	-2	480	466	24	-5	15	-2	530	561	28
-3	1	-2	2067	2124	87	9	7	-2	470	480	26	-3	15	-2	370	359	23
-1	1	-2	774	731	33	11	7	-2	708	659	33	-1	15	-2	434	380	22
1	1	-2	1113	1047	47	-8	8	-2	316	318	25	1	15	-2	333	339	21
3	1	-2	962	991	41	-6	8	-2	1345	1307	58	3	15	-2	276	256	23
5	1	-2	983	1010	42	-4	8	-2	1205	1247	52	5	15	-2	859	898	39
7	1	-2	613	637	28	-2	8	-2	1856	1804	79	7	15	-2	417	415	25
9	1	-2	431	471	24	0	8	-2	204	216	20	9	15	-2	343	364	26
11	1	-2	564	479	28	2	8	-2	66	139	41	-8	16	-2	359	348	27
-10	2	-2	407	414	27	4	8	-2	1434	1485	61	-6	16	-2	832	804	37
-8	2	-2	1218	1145	52	6	8	-2	876	877	38	-4	16	-2	354	311	24
-6	2	-2	604	580	28	8	8	-2	600	624	28	-2	16	-2	517	564	25
-4	2	-2	804	723	34	10	8	-2	86	144	57	0	16	-2	571	538	27
-2	2	-2	513	568	23	-9	9	-2	275	220	28	2	16	-2	391	394	22
0	2	-2	379	393	17	-7	9	-2	689	620	31	4	16	-2	875	892	38
2	2	-2	1227	1215	52	-5	9	-2	696	675	31	6	16	-2	592	635	28
4	2	-2	574+	647	26	-3	9	-2	851	801	37	8	16	-2	332	335	25
6	2	-2	921	942	40	-1	9	-2	349	317	19	-7	17	-2	879	872	39
8	2	-2	735	731	33	1	9	-2	384	353	19	-5	17	-2	327	345	25
10	2	-2	797	802	36	3	9	-2	396	405	20	-3	17	-2	665	644	30
-9	3	-2	613	612	29	5	9	-2	1210	1246	51	-1	17	-2	241	173	26
-7	3	-2	973	1014	42	7	9	-2	127	49	58	1	17	-2	167	66	31
-5	3	-2	462	444	23	9	9	-2	184	188	33	3	17	-2	546	520	26
-3	3	-2	856	827	37	-6	10	-2	236	222	29	5	17	-2	332	433	24
-1	3	-2	1042	961	44	-6	10	-2	591	569	28	7	17	-2	545	585	28
1	3	-2	538	447	23	-4	10	-2	411	383	21	-6	18	-2	797	725	35
3	3	-2	1675	1737	71	-2	10	-2	1183	1109	51	-4	18	-2	540	510	27
5	3	-2	835	861	36	0	10	-2	531	516	24	-2	18	-2	444	427	24
7	3	-2	652	711	29	2	10	-2	520	536	23	0	18	-2	559	540	27
9	3	-2	125	164	43	4	10	-2	356	377	20	2	18	-2	124	200	41
11	3	-2	399	315	28	6	10	-2	280	294	22	4	18	-2	551	545	27
-10	4	-2	299	325	28	8	10	-2	165	112	34	6	18	-2	451	449	25
-8	4	-2	334	298	25	10	10	-2	207	185	33	8	18	-2	579	624	29
-6	4	-2	761	747	33	-9	11	-2	122	162	50	-7	19	-2	727	658	34

```
OBSERVED AND CALCULATED STFUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
(UNOBSERVED REFLECTIONS ARE MARKED +)                                             PAGE 8 OF18

 H   K   L    FO     FC SIG     H   K   L    FO     FC SIG     H   K   L    FO     FC SIG

-5  19  -2   646    633  30     1   3  -1  1654   1607  69    -4  10  -1  3220   3155 135
-3  19  -2  1365   1343  59     3   3  -1  2486   2655 104    -2  10  -1  3009   2921 126
-1  19  -2   740    693  33     5   3  -1  1250   1287  53     0  10  -1  2752   2655 115
 1  19  -2   412    381  24     7   3  -1   519    530  25     2  10  -1  2644   2693 111
 3  19  -2   941    925  41     9   3  -1   167    199  36     4  10  -1   108    252  35
 5  19  -2   672    647  31    11   3  -1   150    149  43     6  10  -1   543    620  26
 7  19  -2   398    397  26   -10   4  -1  1160   1080  50     8  10  -1   913    591  40
-6  20  -2   562    528  29    -8   4  -1  2206   2127  95    10  10  -1   235    307  27
-4  20  -2   642    602  30    -6   4  -1  2451   2438 104    -9  11  -1   730    756  36
-2  20  -2  1208   1195  52    -4   4  -1  2550   2557 107    -7  11  -1   346    333  25
 0  20  -2   124    156  45    -2   4  -1  1212   1116  52    -5  11  -1  1347   1263  58
 2  20  -2   483    448  25     0   4  -1    24    145  46    -3  11  -1  1928   1891  82
 4  20  -2   758    742  34     2   4  -1  3176   3223 133    -1  11  -1   907    793  35
 6  20  -2   176    270  36     4   4  -1  2008   2187  85     1  11  -1  1902   1865  81
-5  21  -2    49    136  77     6   4  -1  1641   1751  70     3  11  -1  1338   1353  57
-3  21  -2   538    479  27     8   4  -1   294    276  24     5  11  -1   325    329  21
-1  21  -2   766    736  34    10   4  -1   357    363  25     7  11  -1   661    687  30
 1  21  -2   355    301  25    -9   5  -1  1078   1046  47     9  11  -1   134    125  33
 3  21  -2   777    783  35    -7   5  -1  1161   1135  50    -8  12  -1  1121   1062  49
 5  21  -2   146     81  38    -5   5  -1  2446   2448 103    -6  12  -1  1002    962  44
 7  21  -2   319    304  27    -3   5  -1  1128   1010  48    -4  12  -1  1250   1260  53
-4  22  -2   292    327  27    -1   5  -1   313    302  16    -2  12  -1   581    686  30
-2  22  -2   647    648  30     1   5  -1   817    748  35     0  12  -1  1509   1516  68
 0  22  -2   309    307  25     3   5  -1  1740   1882  74     2  12  -1  2334   2472 101
 2  22  -2   525    562  27     5   5  -1  1128   1227  48     4  12  -1   456    442  23
 4  22  -2   747    769  34     7   5  -1   843    918  37     6  12  -1   748    773  33
 6  22  -2   286    346  28     9   5  -1   287    282  26     8  12  -1   745    794  33
-5  23  -2   219    221  33    11   5  -1   116     32  50    10  12  -1   193    130  37
-3  23  -2   117     86  47   -10   6  -1   388    356  26    -9  13  -1   510    592  30
-1  23  -2   170    157  37    -8   6  -1   483    505  26    -7  13  -1   427    436  25
 1  23  -2   298    289  25    -6   6  -1   328    285  22    -5  13  -1   872    879  39
 3  23  -2   339    361  25    -4   6  -1   912    890  39    -3  13  -1  1116   1085  49
 5  23  -2     0+    82 117    -2   6  -1  1292   1234  55    -1  13  -1  1705   1697  72
-4  24  -2   305    280  28     0   6  -1  4310   4071 180     1  13  -1  1417   1374  61
-2  24  -2   501    522  27     2   6  -1   612    628  27     3  13  -1  1001   1045  43
 0  24  -2   327    391  26     4   6  -1   400    448  20     5  13  -1   439    411  24
 2  24  -2   437    455  26     6   6  -1   447    456  22     7  13  -1   593    629  28
 4  24  -2    73     89  64     8   6  -1   693    666  31     9  13  -1   179    190  35
-3  25  -2    57    166  73    10   6  -1   486    471  26    -8  14  -1   534    499  29
-1  25  -2   595    653  32    -9   7  -1  1168   1126  51    -6  14  -1   512    553  29
 1  25  -2   517    497  27    -7   7  -1  1055   1016  46    -4  14  -1   633    636  29
 3  25  -2   226    252  32    -5   7  -1  1479   1467  63    -2  14  -1  1054    995  45
-2  26  -2   366    307  26    -3   7  -1  2341   2262  98     0  14  -1   757    771  33
 0  26  -2   425    387  26    -1   7  -1   737    680  32     2  14  -1   757    741  34
 2  26  -2   296    280  28     1   7  -1  2233   2118  94     4  14  -1   433    462  23
-9   1  -1   272    309  27     3   7  -1  1584   1687  67     6  14  -1   370    368  23
-7   1  -1   712    732  32     5   7  -1   499    576  23     8  14  -1   130    195  34
-5   1  -1  1249   1302  53     7   7  -1   988   1032  43    -7  15  -1  1408   1363  61
-3   1  -1  3143   3167 131     9   7  -1   233    207  27    -5  15  -1  1870   1837  80
-1   1  -1  2249   2296  94   -10   8  -1   719    662  33    -3  15  -1   906    794  35
 1   1  -1  2072   2002  86    -8   8  -1  1341   1327  58    -1  15  -1   427    391  22
 3   1  -1   556    611  25    -6   8  -1   902    856  39     1  15  -1  1051   1004  45
 5   1  -1  1064   1116  45    -4   8  -1  2445   2425 103     3  15  -1  1531   1607  70
 7   1  -1   591    616  27    -2   8  -1   613    593  27     5  15  -1  1015   1080  44
 9   1  -1   419    447  24     0   8  -1  1017    975  43     7  15  -1   636    693  30
11   1  -1   315    343  27     2   8  -1  1302   1372  55     9  15  -1   125    150  48
-10  2  -1   744    722  34     4   8  -1   974    954  41    -8  16  -1  1256   1170  54
-8   2  -1   152    148  36     6   8  -1   605    632  28    -6  16  -1  1752   1672  75
-6   2  -1   703    699  31     8   8  -1   488    469  26    -4  16  -1  1516   1422  65
-4   2  -1  2622   2671 110    10   8  -1     0+    66 116    -2  16  -1   505    517  25
-2   2  -1  4627   4548 193    -9   9  -1   423    423  25     0  16  -1   354    291  21
 0   2  -1  2995   2831 125    -7   9  -1   478    445  25     2  16  -1  1297   1231  55
 2   2  -1  3266   3505 136    -5   9  -1  1524   1468  65     4  16  -1  1534   1644  68
 4   2  -1    48     26  49    -3   9  -1  3336   3198 140     6  16  -1   934    874  35
 6   2  -1   279    281  20    -1   9  -1  2212   2096  93     8  16  -1   158    106  38
 8   2  -1  1242   1289  54     1   9  -1  3073   2972 129    -7  17  -1   747    704  34
10   2  -1  1315   1290  56     3   9  -1  1137   1216  49    -5  17  -1  1116   1097  49
-9   3  -1  1270   1292  55     5   9  -1   407    414  21    -3  17  -1  1934   1748  79
-7   3  -1  1559   1543  66     7   9  -1   785    820  35    -1  17  -1  1275   1231  55
-5   3  -1  2369   2435 100     9   9  -1   471    480  26     1  17  -1  1507   1469  64
-3   3  -1  2041   2004  86    -8  10  -1     0+    85 114     3  17  -1   357    362  23
-1   3  -1  1210   1252  51    -6  10  -1   867    854  38     5  17  -1   317    242  24
```

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE 9 OF18
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
7	17	-1	479	469	26	1	1	0	2815	2945	117	-4	8	0	2744	2614	115
-6	18	-1	354	239	30	3	1	0	1637	1728	69	-2	8	0	3351	3101	141
-4	18	-1	1355	1343	58	5	1	0	1643	1707	70	0	8	0	5008	4763	209
-2	18	-1	1867	1795	80	7	1	0	628	671	28	2	8	0	3011	3097	126
0	18	-1	2186	2080	93	9	1	0	200	259	32	4	8	0	2439	2611	103
2	18	-1	770	804	34	11	1	0	702	707	33	6	8	0	326	348	22
4	18	-1	200	248	30	-10	2	0	462	421	26	8	8	0	341	945	41
6	18	-1	253	229	29	-8	2	0	610	596	28	10	8	0	530	530	29
8	18	-1	631	663	30	-6	2	0	2560	2617	108	-9	9	0	450	420	26
-7	19	-1	362	366	26	-4	2	0	1368	1321	58	-7	9	0	541	553	26
-5	19	-1	72	163	52	-2	2	0	1791	1886	75	-5	9	0	925	904	40
-3	19	-1	714	698	32	0	2	0	187	174	9	-3	9	0	1755	1637	75
-1	19	-1	701	651	22	2	2	0	1554	1889	69	-1	9	0	2328	2176	98
1	19	-1	501	539	28	4	2	0	1221	1303	52	1	9	0	2135	2175	89
3	19	-1	220	207	29	6	2	0	2460	2625	104	3	9	0	1593	1631	67
5	19	-1	229	257	30	8	2	0	574	575	27	5	9	0	331	887	36
7	19	-1	243	101	28	10	2	0	413	424	26	7	9	0	555	594	27
-6	20	-1	345	313	26	-9	3	0	761	769	34	9	9	0	395	401	25
-4	20	-1	502	593	29	-7	3	0	1314	1256	57	-10	10	0	201	174	38
-2	20	-1	1106	1117	49	-5	3	0	2473	2417	104	-8	10	0	234	180	29
0	20	-1	450	338	37	-3	3	0	2554	2439	107	-6	10	0	256	235	25
2	20	-1	672	726	31	-1	3	0	2340	2257	98	-4	10	0	700	666	31
4	20	-1	393	375	34	1	3	0	2162	2238	91	-2	10	0	953	926	41
6	20	-1	419	424	35	3	3	0	2306	2432	97	0	10	0	904	889	39
-5	21	-1	510	567	39	5	3	0	2329	2443	98	2	10	0	953	904	37
-3	21	-1	1449	1405	52	7	3	0	1218	1279	52	4	10	0	590	638	27
-1	21	-1	1575	1565	68	9	3	0	674	755	31	6	10	0	234	244	27
1	21	-1	1129	1107	49	-10	4	0	212	248	33	8	10	0	137	131	33
3	21	-1	432	440	33	-8	4	0	273	225	26	10	10	0	90	190	63
5	21	-1	200	234	33	-6	4	0	263	266	22	-9	11	0	552	511	28
7	21	-1	336	339	30	-4	4	0	1655	1580	70	-7	11	0	594	664	31
-6	22	-1	537	485	29	-2	4	0	379	347	18	-5	11	0	1534	1469	65
-4	22	-1	913	888	40	0	4	0	2011	2073	84	-3	11	0	2512	2374	106
-2	22	-1	894	895	39	2	4	0	299	276	16	-1	11	0	3414	3214	143
0	22	-1	1053	1022	46	4	4	0	1501	1592	64	1	11	0	3253	3238	137
2	22	-1	589	620	23	6	4	0	240	245	22	3	11	0	2334	2385	99
4	22	-1	549	535	27	8	4	0	242	227	27	5	11	0	1400	1471	60
6	22	-1	306	307	27	10	4	0	228	244	31	7	11	0	572	712	31
-5	23	-1	1122	1089	49	-9	5	0	310	332	40	9	11	0	457	503	26
-3	23	-1	[illegible]	1116	43	-7	5	0	1843	1801	79	-8	12	0	371	374	25
-1	23	-1	1296	1335	37	-5	5	0	3049	2964	128	-6	12	0	435	457	25
1	23	-1	622	595	30	-3	5	0	1984	1902	94	-4	12	0	1702	1626	72
3	23	-1	1555	1176	30	-1	5	0	1608	1463	68	-2	12	0	2259	2188	96
5	23	-1	755	786	35	1	5	0	1570	1491	66	0	12	0	3357	3190	140
-4	24	-1	755	717	55	3	5	0	1800	1915	76	2	12	0	2118	2150	90
-2	24	-1	0+	45	115	5	5	0	2853	2987	119	4	12	0	1541	1533	65
0	24	-1	262	241	28	7	5	0	1643	1743	70	6	12	0	406	425	23
2	24	-1	1039	1005	44	9	5	0	836	818	37	8	12	0	348	364	25
4	24	-1	539	651	31	-10	6	0	1103	1032	48	-9	13	0	744	659	34
-3	25	-1	527	527	28	-8	6	0	1623	1542	69	-7	13	0	1406	1293	60
-1	25	-1	267	247	28	-6	6	0	3005	2947	126	-5	13	0	1955	1719	79
1	25	-1	370	329	26	-4	6	0	1965	1880	83	-3	13	0	1559	1434	67
3	25	-1	392	350	26	-2	6	0	3952	3637	165	-1	13	0	2179	2042	92
-2	26	-1	454	532	27	0	6	0	266	261	16	1	13	0	2058	2013	88
0	26	-1	535	644	30	2	6	0	3601	3629	150	3	13	0	1437	1435	61
2	26	-1	453	475	37	4	6	0	1796	1876	76	5	13	0	1555	1719	70
-10	0	0	1121	1061	47	6	6	0	3770	2951	117	7	13	0	1224	1299	53
-8	0	0	579	567	27	8	6	0	1519	1525	65	9	13	0	539	637	31
-6	0	0	564	532	16	10	6	0	1164	1135	48	-8	14	0	[illegible]	1173	56
-4	0	0	2344	2540	109	-9	7	0	453	453	26	-6	14	0	2243	2171	69
-2	0	0	2944	2990	127	-7	7	0	958	961	42	-4	14	0	2133	1396	91
2	0	0	2413	2372	107	-5	7	0	1304	1293	56	-2	14	0	1753	1739	76
4	0	0	2333	2549	110	-3	7	0	2055	1952	87	0	14	0	139	239	23
6	0	0	524	525	24	-1	7	0	3084	2833	129	2	14	0	1751	1738	74
8	0	0	584	572	23	1	7	0	2774	2739	116	4	14	0	1375	2030	90
10	0	0	1053	1057	46	3	7	0	1637	1915	78	6	14	0	2055	2179	99
-11	1	0	707	701	31	5	7	0	1250	1350	53	8	14	0	1156	1153	50
-9	1	0	314	307	35	7	7	0	809	914	36	-9	15	0	211	168	44
-7	1	0	643	677	59	9	7	0	453	467	25	-7	15	0	716	750	45
-5	1	0	1685	1735	72	-10	8	0	612	534	30	-5	15	0	1033	1025	47
-3	1	0	1557	1559	70	-8	8	0	1012	927	44	-3	15	0	555	527	26
-1	1	0	3389	3936	129	-6	8	0	362	349	22	-1	15	0	541	561	29

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	15	0	652	553	29	1	25	0	498	488	27	-9	7	1	151	196	39
3	15	0	551	558	26	3	25	0	944	964	41	-7	7	1	1097	1023	47
5	15	0	984	1051	43	-2	26	0	846	779	38	-5	7	1	510	611	27
7	15	0	688	710	32	0	26	0	529	473	28	-3	7	1	1675	1653	71
9	15	0	124	171	50	2	26	0	763	767	35	-1	7	1	2254	2072	95
-8	16	0	528	495	28	1	27	0	984	940	43	1	7	1	821	795	35
-6	16	0	667	659	31	-11	1	1	310	349	22	3	7	1	2056	2253	87
-4	16	0	1134	1110	49	-9	1	1	393	415	25	5	7	1	1404	1463	60
-2	16	0	1127	1006	48	-7	1	1	636	623	29	7	7	1	951	1000	42
0	16	0	1117	1146	48	-5	1	1	1116	1112	48	9	7	1	1073	1106	47
2	16	0	1030	995	44	-3	1	1	545	543	24	-10	8	1	124	66	49
4	16	0	1013	1100	44	-1	1	1	2200	2045	92	-8	8	1	525	458	26
6	16	0	634	666	30	1	1	1	2116	2265	88	-6	8	1	633	637	30
8	16	0	494	521	27	3	1	1	2982	3113	125	-4	8	1	1034	962	47
-7	17	0	1063	989	46	5	1	1	1258	1363	54	-2	8	1	1442	1381	62
-5	17	0	1685	1621	72	7	1	1	699	723	31	0	8	1	1030	1005	44
-3	17	0	886	893	39	9	1	1	265	299	28	2	8	1	645	669	28
-1	17	0	749	717	33	-10	2	1	330	295	25	4	8	1	2356	2409	99
1	17	0	702	704	31	-8	2	1	1305	1269	56	6	8	1	851	861	37
3	17	0	833	873	37	-6	2	1	279	296	21	8	8	1	1249	1328	54
5	17	0	1509	1607	65	-4	2	1	0+	72	86	10	8	1	585	660	32
7	17	0	974	1015	43	-2	2	1	3558	3502	148	-9	9	1	515	485	27
-8	18	0	264	246	30	0	2	1	2859	2837	119	-7	9	1	833	805	37
-6	18	0	934	866	41	2	2	1	4309	4551	180	-5	9	1	451	461	22
-4	18	0	1201	1111	52	4	2	1	2489	2671	105	-3	9	1	1228	1189	52
-2	18	0	890	809	38	6	2	1	653	685	29	-1	9	1	3250	2977	136
0	18	0	1158	1135	50	8	2	1	153	172	38	1	9	1	2134	2103	90
2	18	0	824	836	36	10	2	1	732	726	33	3	9	1	3054	3205	129
4	18	0	1064	1099	46	-11	3	1	200	153	35	5	9	1	1409	1471	60
6	18	0	835	856	37	-9	3	1	204	199	30	7	9	1	454	461	24
8	18	0	248	226	30	-7	3	1	583	538	27	9	9	1	377	420	25
-7	19	0	197	120	32	-5	3	1	1340	1315	57	-10	10	1	371	368	27
-5	19	0	774	733	35	-3	3	1	2772	2666	116	-8	10	1	974	869	43
-3	19	0	1192	1166	51	-1	3	1	1661	1527	70	-6	10	1	616	609	28
-1	19	0	2539	2512	112	1	3	1	1183	1303	50	-4	10	1	233	261	23
1	19	0	2504	2521	110	3	3	1	1878	2025	79	-2	10	1	2936	2695	119
3	19	0	1150	1157	50	5	3	1	2246	2410	95	0	10	1	2745	2657	115
5	19	0	722	739	33	7	3	1	1444	1540	62	2	10	1	2819	2919	119
7	19	0	152	119	41	9	3	1	1224	1298	53	4	10	1	2993	3153	125
-6	20	0	273	279	29	-10	4	1	353	340	25	6	10	1	739	857	35
-4	20	0	775	682	35	-8	4	1	307	264	24	8	10	1	159	103	37
-2	20	0	1796	1693	77	-6	4	1	1738	1751	74	-9	11	1	174	123	35
0	20	0	2837	2738	120	-4	4	1	2252	2192	95	-7	11	1	753	699	34
2	20	0	1649	1683	70	-2	4	1	3493	3217	146	-5	11	1	347	325	22
4	20	0	687	679	31	0	4	1	104	182	20	-3	11	1	1442	1370	62
6	20	0	262	271	28	2	4	1	1115	1118	47	-1	11	1	1930	1851	82
-5	21	0	1003	917	44	4	4	1	2358	2552	99	1	11	1	823	812	36
-3	21	0	315	283	26	6	4	1	2296	2427	97	3	11	1	1831	1877	76
-1	21	0	510	555	29	8	4	1	2098	2131	89	5	11	1	1250	1256	54
1	21	0	581	550	28	10	4	1	1119	1076	49	7	11	1	270	269	26
3	21	0	323	285	24	-11	5	1	58	32	75	9	11	1	774	765	35
5	21	0	939	906	39	-9	5	1	253	290	28	-10	12	1	210	121	34
-6	22	0	1219	1181	53	-7	5	1	880	978	39	-8	12	1	841	785	37
-4	22	0	959	899	42	-5	5	1	1234	1243	53	-6	12	1	929	773	37
-2	22	0	730	729	33	-3	5	1	1977	1903	83	-4	12	1	525	472	24
0	22	0	690	715	32	-1	5	1	961	831	41	-2	12	1	2507	2450	106
2	22	0	689	723	32	1	5	1	295	316	16	0	12	1	1555	1493	66
4	22	0	959	837	38	3	5	1	1047	1053	45	2	12	1	650	703	29
6	22	0	1114	1195	48	5	5	1	2259	2406	96	4	12	1	1170	1263	50
-5	23	0	363	395	28	7	5	1	1110	1171	48	6	12	1	895	946	39
-3	23	0	825	765	37	9	5	1	1008	1066	44	8	12	1	1036	1059	45
-1	23	0	634	604	30	-10	6	1	485	466	27	-9	13	1	209	170	33
1	23	0	621	597	30	-8	6	1	750	651	34	-7	13	1	578	627	30
3	23	0	756	746	34	-6	6	1	503	484	24	-5	13	1	509	450	25
5	23	0	361	419	26	-4	6	1	390	415	20	-3	13	1	1031	993	44
-4	24	0	685	600	32	-2	6	1	662	604	29	-1	13	1	1475	1354	63
-2	24	0	587	533	29	0	6	1	4249	4080	177	1	13	1	1741	1729	74
0	24	0	473	480	26	2	6	1	1158	1234	49	3	13	1	1050	1079	45
2	24	0	563	553	28	4	6	1	855	891	37	5	13	1	850	399	38
4	24	0	614	610	30	6	6	1	329	303	22	7	13	1	351	386	24
-3	25	0	1033	948	45	8	6	1	466	484	26	9	13 *	1	575	593	29
-1	25	0	483	489	17	10	6	1	400	363	26	-8	14	1	157	189	40

OBSERVED AND CALCULATED STFUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-6	14	1	410	369	24	-3	23	1	1218	1160	53	-11	5	2	653	649	32
-4	14	1	504	498	25	-1	23	1	652	600	31	-9	5	2	830	865	39
-2	14	1	789	758	34	1	23	1	299	245	26	-7	5	2	672	664	30
0	14	1	765	769	33	3	23	1	189	107	34	-5	5	2	361	357	20
2	14	1	1011	1004	44	5	23	1	1048	1090	46	-3	5	2	1130	1091	48
4	14	1	557	588	26	-4	24	1	679	655	32	-1	5	2	1494	1381	63
6	14	1	559	561	27	-2	24	1	1069	992	47	1	5	2	1505	1479	64
8	14	1	481	519	27	0	24	1	273	237	26	3	5	2	397	401	19
-9	15	1	132	124	48	2	24	1	122	17	45	5	5	2	994	1008	42
-7	15	1	732	672	33	4	24	1	703	724	33	7	5	2	960	1003	42
-5	15	1	1132	1073	49	-3	25	1	374	363	26	9	5	2	913	914	40
-3	15	1	1756	1612	75	-1	25	1	318	329	27	-10	6	2	1255	1202	55
-1	15	1	1111	1032	48	1	25	1	248	250	30	-8	6	2	493	453	25
1	15	1	422	395	22	3	25	1	521	532	27	-6	6	2	1177	1174	50
3	15	1	742	761	33	-2	26	1	461	476	27	-4	6	2	409	367	20
5	15	1	1772	1813	75	0	26	1	613	637	30	-2	6	2	1331	1234	59
7	15	1	1301	1369	56	2	26	1	501	527	27	0	6	2	3491	3276	146
-8	16	1	137	132	45	-10	0	2	329	285	25	2	6	2	494	512	22
-6	16	1	915	876	40	-8	0	2	1016	981	44	4	6	2	836	878	36
-4	16	1	1766	1644	76	-6	0	2	523	541	24	6	6	2	801	842	35
-2	16	1	1415	1280	60	-4	0	2	1862	1919	79	8	6	2	1339	1353	57
0	16	1	282	279	22	-2	0	2	1016	1138	43	10	6	2	1021	963	45
2	16	1	547	560	26	0	0	2	2126	2286	89	-11	7	2	740	648	34
4	16	1	1441	1431	61	2	0	2	2873	2777	120	-9	7	2	517	463	26
6	16	1	1519	1665	69	4	0	2	998	1054	43	-7	7	2	510	459	25
8	16	1	1136	1173	49	6	0	2	1312	1341	56	-5	7	2	1353	1276	58
-7	17	1	534	478	27	8	0	2	740	727	33	-3	7	2	516	564	27
-5	17	1	293	243	26	10	0	2	271	233	28	-1	7	2	437	478	23
-3	17	1	418	394	23	-11	1	2	536	494	28	1	7	2	130	205	19
-1	17	1	1476	1439	63	-9	1	2	428	443	25	3	7	2	1516	1651	64
1	17	1	1295	1243	55	-7	1	2	665	667	30	5	7	2	930	949	43
3	17	1	1747	1792	75	-5	1	2	983	983	42	7	7	2	826	849	37
5	17	1	1046	1093	46	-3	1	2	1010	975	43	9	7	2	643	625	31
7	17	1	696	693	32	-1	1	2	1075	1062	46	-10	8	2	56	135	73
-8	18	1	673	647	32	1	1	2	751	749	32	-8	8	2	643	611	30
-6	18	1	346	338	25	3	1	2	2043	2151	86	-6	8	2	944	872	41
-4	18	1	193	207	33	5	1	2	796	850	35	-4	8	2	1555	1479	66
-2	18	1	801	783	35	7	1	2	996	1039	43	-2	8	2	150	158	24
0	18	1	2181	2052	93	9	1	2	474	495	26	0	8	2	191	196	20
2	18	1	1812	1790	77	-10	2	2	814	793	36	2	8	2	1531	1806	72
4	18	1	1275	1331	55	-8	2	2	760	732	34	4	8	2	1149	1248	49
6	18	1	262	259	28	-6	2	2	917	943	40	6	8	2	1272	1312	55
-7	19	1	129	88	43	-4	2	2	638	643	28	8	8	2	295	326	26
-5	19	1	296	257	25	-2	2	2	1271	1214	54	-9	9	2	191	196	33
-3	19	1	226	220	29	0	2	2	301	386	15	-7	9	2	51	68	61
-1	19	1	610	636	29	2	2	2	479	574	22	-5	9	2	1325	1246	57
1	19	1	659	626	30	4	2	2	761	734	33	-3	9	2	417	379	20
3	19	1	598	708	32	6	2	2	541	572	25	-1	9	2	415	344	20
5	19	1	198	156	31	8	2	2	1186	1149	51	1	9	2	317	284	19
7	19	1	355	363	27	10	2	2	374	404	27	3	9	2	739	800	34
-6	20	1	425	422	25	-11	3	2	326	316	27	5	9	2	570	671	30
-4	20	1	372	363	25	-9	3	2	150	191	38	7	9	2	532	603	28
-2	20	1	711	702	32	-7	3	2	678	701	30	9	9	2	301	233	27
0	20	1	864	866	38	-5	3	2	894	869	38	-10	10	2	210	191	34
2	20	1	1044	1089	45	-3	3	2	1843	1756	78	-8	10	2	33	106	53
4	20	1	626	614	29	-1	3	2	560	470	24	-6	10	2	231	291	23
6	20	1	234	314	31	1	3	2	918	933	39	-4	10	2	375	388	20
-7	21	1	364	328	26	3	3	2	817	848	35	-2	10	2	520	544	24
-5	21	1	252	268	29	5	3	2	439	417	22	0	10	2	490	502	22
-3	21	1	427	416	25	7	3	2	948	1002	41	2	10	2	1112	1095	47
-1	21	1	1191	1126	51	9	3	2	606	614	29	4	10	2	419	417	22
1	21	1	1600	1570	69	-10	4	2	279	246	27	6	10	2	559	557	27
3	21	1	1345	1369	58	-8	4	2	453	453	24	8	10	2	216	233	30
5	21	1	594	623	29	-6	4	2	520	515	24	-9	11	2	118	97	52
-6	22	1	401	325	26	-4	4	2	964	889	41	-7	11	2	517	512	26
-4	22	1	578	543	29	-2	4	2	149	103	21	-5	11	2	1178	1085	51
-2	22	1	590	639	32	0	4	2	278	252	15	-3	11	2	576	564	25
0	22	1	1086	1031	47	2	4	2	320	296	18	-1	11	2	618	564	27
2	22	1	909	908	40	4	4	2	443	513	21	1	11	2	875	920	38
4	22	1	904	899	40	6	4	2	740	765	33	3	11	2	1197	1250	51
6	22	1	487	485	27	8	4	2	252	279	28	5	11	2	1332	1143	47
-5	23	1	870	804	39	10	4	2	312	313	27	7	11	2	532	538	23

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE12 OF18
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
9	11	2	122	162	50	-4	20	2	800	743	36	-4	4	3	2077	1989	88
-10	12	2	427	415	27	-2	20	2	488	452	26	-2	4	3	1393	1263	59
-8	12	2	333	286	25	0	20	2	156	166	37	0	4	3	1176	1158	50
-6	12	2	703	583	31	2	20	2	1135	1190	49	2	4	3	1069	1148	46
-4	12	2	786	756	34	4	20	2	650	602	30	4	4	3	1927	2068	82
-2	12	2	546	474	25	6	20	2	521	535	27	6	4	3	727	753	32
0	12	2	365	352	19	-7	21	2	320	302	27	8	4	3	234	252	25
2	12	2	1205	1211	52	-5	21	2	142	72	39	-11	5	3	439	463	28
4	12	2	818	843	36	-3	21	2	808	786	36	-9	5	3	733	735	33
6	12	2	780	751	35	-1	21	2	327	329	25	-7	5	3	1700	1638	73
8	12	2	375	370	25	1	21	2	751	735	34	-5	5	3	1060	1079	45
-9	13	2	793	743	36	3	21	2	504	478	26	-3	5	3	1355	1310	58
-7	13	2	409	394	24	5	21	2	146	144	40	-1	5	3	1634	1554	71
-5	13	2	525	520	26	-6	22	2	360	346	27	1	5	3	846	935	38
-3	13	2	785	763	34	-4	22	2	799	771	36	3	5	3	926	1015	40
-1	13	2	909	729	35	-2	22	2	603	566	29	5	5	3	521	591	25
1	13	2	1367	1348	58	0	22	2	293	299	25	7	5	3	172	90	32
3	13	2	267	295	22	2	22	2	631	641	30	9	5	3	174	53	36
5	13	2	434	456	24	4	22	2	252	314	29	-10	6	3	271	212	28
7	13	2	638	636	30	-5	23	2	151	87	43	-8	6	3	370	301	24
-8	14	2	613	589	30	-3	23	2	347	356	26	-6	6	3	331	372	21
-6	14	2	597	517	28	-1	23	2	331	302	25	-4	6	3	576	552	26
-4	14	2	413	363	22	1	23	2	0+	139	114	-2	6	3	1062	1084	45
-2	14	2	927	855	40	3	23	2	31	70	84	0	6	3	1118	1148	48
0	14	2	1524	1481	65	5	23	2	177	216	40	2	6	3	193	201	20
2	14	2	1139	1112	49	-4	24	2	70	108	68	4	6	3	338	368	20
4	14	2	792	815	35	-2	24	2	467	454	26	6	6	3	334	351	23
6	14	2	298	300	25	0	24	2	392	381	25	8	6	3	136	201	34
8	14	2	1309	1285	57	2	24	2	519	539	27	-11	7	3	658	612	32
-9	15	2	412	373	26	4	24	2	320	283	27	-9	7	3	958	938	42
-7	15	2	434	408	25	-3	25	2	231	252	31	-7	7	3	1236	1235	56
-5	15	2	939	901	41	-1	25	2	537	490	28	-5	7	3	1528	1563	69
-3	15	2	247	229	24	1	25	2	677	653	32	-3	7	3	1912	1951	81
-1	15	2	341	325	21	3	25	2	0+	156	118	-1	7	3	1728	1646	73
1	15	2	443	396	23	-2	26	2	291	265	28	1	7	3	1016	1048	43
3	15	2	338	354	23	0	26	2	422	392	26	3	7	3	753	803	33
5	15	2	565	579	27	2	26	2	395	330	26	5	7	3	530	605	27
7	15	2	666	652	31	-11	1	3	683	622	32	7	7	3	232	246	30
-8	16	2	409	332	26	-9	1	3	642	649	30	9	7	3	300	267	26
-6	16	2	652	637	30	-7	1	3	595	628	27	-10	8	3	562	510	29
-4	16	2	940	902	41	-5	1	3	1125	1186	48	-8	8	3	1246	1218	54
-2	16	2	474	420	24	-3	1	3	1463	1511	62	-6	8	3	1003	981	43
0	16	2	532	516	25	-1	1	3	3611	3459	151	-4	8	3	1397	1357	60
2	16	2	491	554	24	1	1	3	1026	1129	44	-2	8	3	1321	1373	56
4	16	2	323	294	24	3	1	3	540	562	24	0	8	3	970	994	41
6	16	2	742	793	33	5	1	3	509	512	24	2	8	3	954	993	41
8	16	2	343	346	27	7	1	3	201	203	30	4	8	3	142	206	32
-7	17	2	620	581	30	9	1	3	356	307	25	6	8	3	258	254	26
-5	17	2	433	442	25	-10	2	3	618	635	30	8	8	3	75	112	61
-3	17	2	560	529	27	-8	2	3	487	535	25	-9	9	3	832	793	37
-1	17	2	60	74	61	-6	2	3	1106	1111	48	-7	9	3	251	226	26
1	17	2	216	161	27	-4	2	3	891	904	38	-5	9	3	1915	1840	82
3	17	2	642	612	29	-2	2	3	3287	3237	137	-3	9	3	1945	1769	83
5	17	2	303	344	26	0	2	3	2491	2709	104	-1	9	3	2329	2222	95
7	17	2	844	866	38	2	2	3	1075	1077	46	1	9	3	1003	1043	43
-8	18	2	675	622	32	4	2	3	338	388	20	3	9	3	932	1118	42
-6	18	2	453	440	25	6	2	3	438	468	23	5	9	3	641	662	29
-4	18	2	575	516	28	8	2	3	428	450	25	7	9	3	665	676	31
-2	18	2	203	171	29	-11	3	3	605	561	30	9	9	3	356	330	26
0	18	2	521	530	26	-9	3	3	782	744	35	-10	10	3	730	645	34
2	18	2	468	451	25	-7	3	3	2231	2249	95	-8	10	3	1134	1130	51
4	18	2	374	557	29	-5	3	3	1550	1583	66	-6	10	3	1157	1149	50
6	18	2	739	724	33	-3	3	3	1082	1061	46	-4	10	3	2327	2181	98
-7	19	2	433	399	26	-1	3	3	1153	1088	49	-2	10	3	2569	2419	108
-5	19	2	710	635	32	1	3	3	633	703	28	0	10	3	2333	2308	100
-3	19	2	961	926	42	3	3	3	532	526	24	2	10	3	1301	1434	55
-1	19	2	430	364	24	5	3	3	1018	1114	44	4	10	3	958	921	37
1	19	2	725	703	32	7	3	3	536	564	26	6	10	3	1370	1127	46
3	19	2	1335	1347	57	9	3	3	258	271	29	8	10	3	423	397	35
5	19	2	609	625	29	-10	4	3	1104	1043	46	-9	11	3	642	661	32
7	19	2	690	669	32	-8	4	3	2346	2249	100	-7	11	3	779	751	35
-6	20	2	325	270	25	-6	4	3	2935	3007	123	-5	11	3	746	702	33

```
OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
                                                                     PAGE13 OF19
(UNOBSERVED REFLECTIONS ARE MARKED +)

  H   K   L    FO     FC SIG    H   K   L    FO     FC SIG    H   K   L    FO     FC SIG

 -3  11   3  1099   1026  47    3  19   3   195    185  32   -1   3   4  1619   1644  69
 -1  11   3   594    565  27    5  19   3   110    121  49    1   3   4  1629   1756  69
  1  11   3  1302   1361  55   -6  20   3   291    265  27    3   3   4  1676   1753  71
  3  11   3   441    441  22   -4  20   3   598    570  29    5   3   4  1301   1345  56
  5  11   3   511    548  25   -2  20   3   829    809  37    7   3   4   798    805  36
  7  11   3   266    266  26    0  20   3   919    941  40    9   3   4   517    475  27
-10  12   3   935    888  43    2  20   3   279    288  26  -10   4   4   331    323  26
 -8  12   3   895    884  43    4  20   3   445    473  25   -8   4   4   710    648  32
 -6  12   3  1392   1335  59    6  20   3   303    369  28   -6   4   4   478    444  23
 -4  12   3   916    886  40   -7  21   3   273    245  29   -4   4   4  1434   1382  62
 -2  12   3  1198   1145  51   -5  21   3   550    507  28   -2   4   4   838    878  36
  0  12   3  2378   2345 100   -3  21   3   871    838  38    0   4   4   934    997  42
  2  12   3   935    919  40   -1  21   3  1551   1483  66    2   4   4   787    897  34
  4  12   3   651    663  29    1  21   3   661    657  31    4   4   4  1246   1273  54
  6  12   3   348    320  24    3  21   3   326    310  25    6   4   4     0+   111 111
  8  12   3   213    216  31    5  21   3   426    405  26    8   4   4   173    115  44
 -9  13   3   386    360  26   -6  22   3   501    472  27  -11   5   4   253    235  31
 -7  13   3   779    773  35   -4  22   3   740    630  34   -9   5   4   975    964  43
 -5  13   3   393    375  23   -2  22   3   669    620  31   -7   5   4  1940   1931  83
 -3  13   3  1067   1047  46    0  22   3   724    690  33   -5   5   4  2320   2320  99
 -1  13   3  1283   1249  55    2  22   3   400    411  25   -3   5   4  3011   2869 125
  1  13   3   554    624  26    4  22   3   342    350  26   -1   5   4  1310   1286  56
  3  13   3   590    570  27   -5  23   3   849    773  38    1   5   4   371    337  18
  5  13   3   510    476  26   -3  23   3   233    214  30    3   5   4  1493   1604  63
  7  13   3   179    168  34   -1  23   3   203    204  32    5   5   4  1254   1323  54
 -8  14   3   549    508  28    1  23   3   598    574  29    7   5   4  1114   1164  48
 -6  14   3   700    661  32    3  23   3   668    629  31    9   5   4   657    664  32
 -4  14   3   535    535  26   -4  24   3   614    574  30  -10   6   4   748    738  34
 -2  14   3   376    354  21   -2  24   3   360    362  26   -8   6   4  2157   2099  93
  0  14   3   710    668  31    0  24   3   490    470  26   -6   6   4  2418   2342 102
  2  14   3   373    377  22    2  24   3   456    417  26   -4   6   4  3653   3460 153
  4  14   3   513    487  26   -3  25   3   357    345  27   -2   6   4  2930   2798 124
  6  14   3   344    330  24   -1  25   3   608    590  30    0   6   4   310    292  18
  8  14   3    77     65  63    1  25   3   238    246  32    2   6   4   903    968  39
 -9  15   3   931    852  41   -2  26   3   634    606  31    4   6   4  1713   1776  73
 -7  15   3  1749   1753  79    0  26   3   472    470  27    6   6   4  1159   1156  50
 -5  15   3  1704   1619  73  -10   0   4  1422   1423  61    8   6   4  1250   1255  54
 -3  15   3  1149   1104  50   -8   0   4   542    566  26  -11   7   4   423    383  27
 -1  15   3    34     38  48   -6   0   4   275    261  21   -9   7   4  1053   1010  46
  1  15   3   755    732  33   -4   0   4   810    853  35   -7   7   4   937    877  39
  3  15   3   931    950  40   -2   0   4  4166   4071 174   -5   7   4  1299   1170  55
  5  15   3   828    870  37    0   0   4  4974   5019 208   -3   7   4  2490   2337 104
  7  15   3     0+    82 117    2   0   4  3898   3998 163   -1   7   4  2214   2118  93
 -8  16   3  1160   1062  50    4   0   4  1629   1633  69    1   7   4  1736   1874  75
 -6  16   3  1996   1932  85    6   0   4   651    640  30    3   7   4  1731   1863  73
 -4  16   3   889    836  39    8   0   4   244    245  28    5   7   4   555    509  26
 -2  16   3   862    849  38  -11   1   4   698    697  33    7   7   4   353    394  25
  0  16   3   334    285  22   -9   1   4  1087   1075  47  -10   8   4  1042   1020  46
  2  16   3   253    265  25   -7   1   4   585    611  27   -8   8   4   959    903  42
  4  16   3  1065   1139  46   -5   1   4   869    936  38   -6   8   4   335    406  22
  6  16   3   456    442  25   -3   1   4  1767   1875  75   -4   8   4   850    815  36
 -7  17   3   811    765  36   -1   1   4  3163   3079 132   -2   8   4  4134   3933 173
 -5  17   3  1251   1211  55    1   1   4  2464   2556 103    0   8   4  2251   2301  95
 -3  17   3  1090    991  47    3   1   4  1717   1821  73    2   8   4  3016   3149 129
 -1  17   3  1434   1459  64    5   1   4   638    673  29    4   8   4  1435   1543  64
  1  17   3   497    470  25    7   1   4   468    463  25    6   8   4   571    522  25
  3  17   3   368    297  24    9   1   4   359    332  25    8   8   4   415    393  25
  5  17   3   522    432  27  -10   2   4   377    373  26   -9   9   4   735    636  35
  7  17   3   437    431  27   -8   2   4  1283   1223  55   -7   9   4   513    536  26
 -8  18   3   241    184  30   -6   2   4  2229   2079  96   -5   9   4   733    658  32
 -6  18   3   724    661  33   -4   2   4  3033   3068 127   -3   9   4  1975   1899  84
 -4  18   3   691    708  31   -2   2   4  1170   1160  50   -1   9   4  1748   1638  75
 -2  18   3  1815   1783  82    0   2   4   488    490  22    1   9   4  1310   1351  56
  0  18   3  1715   1694  74    2   2   4   292    301  18    3   9   4  1574   1705  67
  2  18   3    51     30  71    4   2   4  1769   1866  75    5   9   4   373    238  24
  4  18   3   413    468  25    6   2   4  1220   1222  52    7   9   4   375    413  24
  6  18   3   334    419  26    8   2   4   716    745  33  -10  10   4   117    156  56
 -7  19   3   190    163  34  -11   3   4   348    349  27   -8  10   4   590    656  32
 -5  19   3   123    134  35   -9   3   4   679    669  31   -6  10   4   825    655  38
 -3  19   3   422    410  25   -7   3   4  1683   1670  72   -4  10   4   573    609  30
 -1  19   3   905    856  40   -5   3   4  1765   1830  76   -2  10   4   757    720  33
  1  19   3   311    274  24   -3   3   4  2144   2111  90    0  10   4   779    921  34
```

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE14 OF18
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
2	10	4	636	684	29	-7	19	4	138	126	43	0	4	5	2167	2298	91
4	10	4	592	602	28	-5	19	4	247	221	29	2	4	5	283	289	20
6	10	4	237	192	27	-3	19	4	1239	1222	53	4	4	5	1044	1072	45
8	10	4	292	294	27	-1	19	4	2136	2031	91	6	4	5	1847	1831	79
-9	11	4	329	376	41	1	19	4	1976	1981	84	8	4	5	1570	1562	67
-7	11	4	665	633	30	3	19	4	1167	1195	50	-11	5	5	235	232	32
-5	11	4	510	511	25	5	19	4	303	282	27	-9	5	5	257	244	27
-3	11	4	2264	2209	36	-6	20	4	258	227	29	-7	5	5	572	603	27
-1	11	4	2172	2088	92	-4	20	4	283	236	26	-5	5	5	1656	1662	71
1	11	4	2459	2509	104	-2	20	4	1788	1647	76	-3	5	5	1713	1614	73
3	11	4	2035	2116	35	0	20	4	1774	1734	76	-1	5	5	1354	1401	58
5	11	4	565	605	25	2	20	4	1801	1801	77	1	5	5	791	835	34
7	11	4	470	465	26	4	20	4	443	413	25	3	5	5	898	981	38
-10	12	4	813	753	37	-7	21	4	721	653	34	5	5	5	848	844	37
-8	12	4	849	793	38	-5	21	4	817	767	37	7	5	5	1134	1244	52
-6	12	4	423	393	24	-3	21	4	787	717	35	-10	6	5	618	607	30
-4	12	4	915	769	36	-1	21	4	650	597	31	-8	6	5	256	269	27
-2	12	4	2639	2478	111	1	21	4	463	431	26	-6	6	5	508	601	28
0	12	4	2419	2367	102	3	21	4	513	553	27	-4	6	5	623	612	28
2	12	4	1871	1961	79	-6	22	4	815	801	37	-2	6	5	392	345	20
4	12	4	1205	1285	52	-4	22	4	1224	1139	53	0	6	5	1893	1926	80
6	12	4	320	386	25	-2	22	4	463	457	26	2	6	5	1415	1559	60
8	12	4	225	191	31	0	22	4	621	645	30	4	6	5	239	242	23
-9	13	4	929	908	41	2	22	4	544	578	28	6	6	5	597	563	29
-7	13	4	1558	1467	57	4	22	4	988	1041	43	8	6	5	159	147	39
-5	13	4	1668	1577	72	-5	23	4	256	247	32	-9	7	5	718	673	33
-3	13	4	2320	2204	98	-3	23	4	393	381	26	-7	7	5	978	845	39
-1	13	4	1299	1210	55	-1	23	4	544	494	28	-5	7	5	1330	1262	57
1	13	4	540	568	25	1	23	4	726	734	33	-3	7	5	2041	1993	87
3	13	4	1597	1700	68	3	23	4	624	644	30	-1	7	5	1916	1984	81
5	13	4	842	851	37	-4	24	4	761	751	35	1	7	5	1392	1521	60
7	13	4	763	761	35	-2	24	4	431	405	26	3	7	5	1342	1442	57
-8	14	4	1975	1324	55	0	24	4	234	207	30	5	7	5	875	932	38
-6	14	4	1585	1500	58	2	24	4	303	296	28	7	7	5	922	954	40
-4	14	4	2604	2469	110	-3	25	4	1316	1220	57	-10	8	5	145	158	44
-2	14	4	1862	1747	79	-1	25	4	469	476	28	-8	8	5	755	752	34
0	14	4	257	279	33	1	25	4	230	174	30	-6	8	5	552	629	29
2	14	4	603	619	28	-11	1	5	485	447	27	-4	8	5	857	840	38
4	14	4	1544	1610	66	-9	1	5	931	922	41	-2	8	5	1417	1389	61
6	14	4	857	910	38	-7	1	5	492	491	24	0	8	5	1024	1073	44
-9	15	4	392	397	26	-5	1	5	759	765	33	2	8	5	570	698	29
-7	15	4	539	545	29	-3	1	5	1119	1222	48	4	8	5	956	992	42
-5	15	4	1113	1033	46	-1	1	5	1367	1354	58	6	8	5	572	624	28
-3	15	4	1364	1309	59	1	1	5	3039	3152	127	8	8	5	753	713	34
-1	15	4	31	60	77	3	1	5	1820	1919	78	-9	9	5	547	540	28
1	15	4	231	230	25	5	1	5	1182	1236	51	-7	9	5	896	857	39
3	15	4	786	766	35	7	1	5	714	729	33	-5	9	5	557	629	30
5	15	4	542	568	27	-10	2	5	816	805	36	-3	9	5	1738	1655	75
7	15	4	465	460	27	-8	2	5	747	780	33	-1	9	5	1656	1629	71
-8	16	4	593	629	32	-6	2	5	787	773	34	1	9	5	2432	2551	103
-6	16	4	303	304	36	-4	2	5	63	89	47	3	9	5	2029	2107	87
-4	16	4	737	705	35	-2	2	5	2109	1976	89	5	9	5	1444	1517	62
-2	16	4	1691	1504	72	0	2	5	2348	2598	99	7	9	5	485	513	26
0	16	4	513	495	25	2	2	5	3456	3605	145	-10	10	5	908	824	40
2	16	4	1334	1393	59	4	2	5	1482	1545	64	-8	10	5	1019	914	44
4	16	4	565	731	34	6	2	5	1387	1359	60	-6	10	5	1379	1256	57
6	16	4	373	424	26	8	2	5	256	202	28	-4	10	5	741	730	33
-7	17	4	1273	1176	55	-11	3	5	199	213	34	-2	10	5	1949	1877	83
-5	17	4	1677	1590	72	-9	3	5	208	193	30	0	10	5	2472	2517	104
-3	17	4	1238	1180	52	-7	3	5	641	623	29	2	10	5	2749	2968	119
-1	17	4	510	604	29	-5	3	5	1882	1923	85	4	10	5	2231	2321	94
1	17	4	593	613	28	-3	3	5	1942	2001	82	6	10	5	1374	1409	59
3	17	4	699	673	32	-1	3	5	1080	1187	46	-9	11	5	245	260	30
5	17	4	768	798	25	1	3	5	1678	1711	72	-7	11	5	572	555	27
-8	18	4	300	264	28	3	3	5	1129	1221	48	-5	11	5	340	917	37
-6	18	4	1113	946	44	5	3	5	1239	1223	53	-3	11	5	1152	1148	50
-4	18	4	1303	1154	52	7	3	5	1461	1408	61	-1	11	5	1239	1238	54
-2	18	4	423	369	44	-10	4	5	211	230	33	1	11	5	1472	1435	61
0	18	4	455	961	42	-8	4	5	799	725	35	3	11	5	1237	1264	54
2	18	4	719	751	32	-6	4	5	1794	1779	76	5	11	5	683	704	31
4	18	4	551	605	29	-4	4	5	3654	3549	153	7	11	5	551	557	29
6	18	4	614	583	30	-2	4	5	2166	2061	91	-10	12	5	316	272	27

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
(UNOBSERVED REFLECTIONS ARE MARKED +) PAGE15 OF18

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
-8	12	5	356	801	38	3	21	5	1154	1131	50	-4	6	6	140	131	30
-6	12	5	312	749	35	-4	22	5	663	607	32	-2	6	6	1529	1463	65
-4	12	5	1382	1341	59	-2	22	5	621	574	30	0	6	6	1550	1718	70
-2	12	5	1388	1334	59	0	22	5	920	863	41	2	6	6	357	393	21
0	12	5	1489	1540	63	2	22	5	758	724	35	4	6	6	316	313	24
2	12	5	926	968	45	-5	23	5	1210	1127	53	6	6	6	1229	1202	53
4	12	5	425	474	35	-3	23	5	982	923	43	-9	7	6	352	324	25
6	12	5	835	792	37	-1	23	5	854	813	38	-7	7	6	633	664	31
-9	13	5	506	475	33	1	23	5	367	357	26	-5	7	6	296	293	23
-7	13	5	413	408	24	-2	24	5	876	783	39	-3	7	6	471	443	23
-5	13	5	387	371	40	0	24	5	696	683	37	-1	7	6	1119	1145	48
-3	13	5	702	678	31	-10	0	6	226	226	30	1	7	6	936	962	39
-1	13	5	1530	1504	65	-8	0	6	525	543	26	3	7	6	1053	1166	46
1	13	5	1257	1306	54	-6	0	6	1045	1150	45	5	7	6	1213	1205	52
3	13	5	1208	1242	52	-4	0	6	425	424	21	7	7	6	495	502	27
5	13	5	612	575	29	-2	0	6	1410	1298	59	-10	8	6	0+	34	118
7	13	5	549	571	38	0	0	6	2611	2508	110	-8	8	6	335	404	25
-8	14	5	197	229	34	2	0	6	1676	1720	71	-6	8	6	1296	1243	56
-6	14	5	581	572	28	4	0	6	1746	1752	75	-4	8	6	718	666	31
-4	14	5	770	726	34	6	0	6	1106	969	44	-2	8	6	119	155	34
-2	14	5	747	599	33	8	0	6	514	493	28	0	8	6	1119	1231	43
0	14	5	343	345	37	-11	1	6	153	67	41	2	8	6	732	791	34
2	14	5	933	970	39	-9	1	6	344	334	25	4	8	6	1565	1746	71
4	14	5	352	354	34	-7	1	6	617	595	28	6	8	6	1355	1023	46
6	14	5	385	406	36	-5	1	6	187	167	25	-9	9	6	234	232	30
-9	15	5	324	252	38	-3	1	6	667	638	29	-7	9	6	542	534	27
-7	15	5	633	631	31	-1	1	6	217	193	20	-5	9	6	593	601	27
-5	15	5	1897	1750	81	1	1	6	1315	1343	56	-3	9	6	136	156	31
-3	15	5	1910	1795	92	3	1	6	1357	1396	58	-1	9	6	450	456	23
-1	15	5	1319	1299	57	5	1	6	1250	1265	54	1	9	6	573	673	30
1	15	5	680	656	34	7	1	6	653	635	31	3	9	6	359	419	23
3	15	5	589	559	38	-10	2	6	166	189	39	5	9	6	343	937	41
5	15	5	357	383	38	-8	2	6	869	858	38	7	9	6	153	209	29
-8	16	5	190	173	36	-6	2	6	180	110	27	-10	10	6	38	34	58
-6	16	5	1014	977	44	-4	2	6	1047	1030	45	-8	10	6	54	132	63
-4	16	5	2003	1914	36	-2	2	6	1362	1337	58	-6	10	6	422	438	24
-2	16	5	1296	1177	55	0	2	6	594	713	30	-4	10	6	112	172	40
0	16	5	1066	1001	46	2	2	6	220	235	23	-2	10	6	331	369	22
2	16	5	369	374	28	4	2	6	590	605	23	0	10	6	434	521	24
4	16	5	675	639	28	6	2	6	978	957	43	2	10	6	424	449	23
6	16	5	1344	1345	27	8	2	6	628	634	31	4	10	6	427	440	25
-7	17	5	524	519	28	-11	3	6	164	203	40	6	10	6	259	285	28
-5	17	5	574	432	27	-9	3	6	234	230	29	-9	11	6	272	205	27
-3	17	5	777	737	28	-7	3	6	620	651	29	-7	11	6	539	700	32
-1	17	5	630	623	29	-5	3	6	670	715	30	-5	11	6	728	669	32
1	17	5	1733	1688	74	-3	3	6	604	606	27	-3	11	6	221	195	25
3	17	5	921	906	40	-1	3	6	746	800	33	-1	11	6	659	674	30
5	17	5	403	877	39	1	3	6	549	563	25	1	11	6	1325	1023	45
-8	18	5	402	399	27	3	3	6	624	630	28	3	11	6	774	800	34
-6	18	5	757	738	25	5	3	6	726	750	33	5	11	6	1174	1167	51
-4	18	5	565	419	25	7	3	6	608	611	30	-8	12	6	139	224	35
-2	18	5	743	701	54	-10	4	6	102	121	54	-6	12	6	506	567	28
0	18	5	1999	1925	55	-8	4	6	204	193	29	-4	12	6	517	483	35
2	18	5	1522	1620	65	-6	4	6	429	460	23	-2	12	6	318	284	22
4	18	5	422	953	40	-4	4	6	250	223	20	0	12	6	952	961	42
-7	19	5	1136	1142	35	-2	4	6	253	361	20	2	12	6	722	740	31
-5	19	5	194	131	33	0	4	6	582	660	26	4	12	6	1278	1346	55
-3	19	5	436	412	25	2	4	6	42	64	64	6	12	6	634	686	32
-1	19	5	223	423	30	4	4	6	770	826	34	-9	13	6	535	551	29
1	19	5	951	904	38	6	4	6	524	553	27	-7	13	6	155	183	34
3	19	5	384	342	25	-9	5	6	648	634	30	-5	13	6	540	437	27
5	19	5	333	303	28	-7	5	6	474	457	24	-3	13	6	345	336	23
-6	20	5	272	238	27	-5	5	6	631	661	29	-1	13	6	1728	1687	74
-4	20	5	303	515	27	-3	5	6	697	616	31	1	13	6	346	969	41
-2	20	5	403	482	30	-1	5	6	1573	1555	67	3	13	6	447	457	25
0	20	5	673	662	34	1	5	6	460	509	23	5	13	6	593	615	29
2	20	5	770	813	35	3	5	6	306	260	22	-8	14	6	373	513	28
4	20	5	635	624	33	5	5	6	804	794	36	-6	14	6	353	135	36
-5	21	5	502	590	30	7	5	6	777	776	35	-4	14	6	339	162	28
-3	21	5	402	380	25	-10	6	6	524	501	28	-2	14	6	1237	1206	55
-1	21	5	975	963	30	-8	6	6	539	524	27	0	14	6	1325	981	44
1	21	5	1523	1511	30	-6	6	6	0+	26	102	2	14	6	549	630	31

```
OBSERVED AND CALCULATED STFUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
(UNOBSERVED REFLECTIONS ARE MARKED +)                          PAGE16 OF18

  H   K   L    FO     FC SIG     H   K   L    FO     FC SIG     H   K   L    FO     FC SIG

  4  14   6   145    107  39     1   3   7   126    161  34    -8  12   7   712    647  32
  6  14   6   723    762  33     3   3   7   606    647  28    -6  12   7   658    580  31
 -7  15   6   560    542  28     5   3   7   354    368  25    -4  12   7  1296   1190  56
 -5  15   6   557    513  27     7   3   7   321    324  27    -2  12   7   279    268  24
 -3  15   6   312    297  24   -10   4   7   793    758  36     0  12   7   593    572  27
 -1  15   6   498    459  26    -8   4   7  1683   1650  72     2  12   7   732    882  35
  1  15   6    57     57  65    -6   4   7  1385   1422  59     4  12   7   355    350  25
  3  15   6    31    109  55    -4   4   7  1721   1723  73    -9  13   7   572    637  32
  5  15   6   501    527  27    -2   4   7   376    367  21    -7  13   7   256    230  27
 -8  16   6   471    452  27     0   4   7   176    213  27    -5  13   7   335    340  25
 -6  16   6   517    611  29     2   4   7  1074   1081  46    -3  13   7   532    555  28
 -4  16   6   553    514  27     4   4   7   646    673  30    -1  13   7   502    549  28
 -2  16   6   312    320  24     6   4   7   280    303  28     1  13   7   375    376  24
  0  16   6   498    538  26    -9   5   7   953    959  42     3  13   7   245    231  27
  2  16   6   292    277  25    -7   5   7   703    682  32     5  13   7   218    192  33
  4  16   6   665    707  31    -5   5   7   938    958  41    -8  14   7   439    449  27
 -7  17   6   544    518  28    -3   5   7   657    574  29    -6  14   7   440    431  25
 -5  17   6   195    141  22    -1   5   7   555    392  21    -4  14   7   551    539  27
 -3  17   6   145    340  24     1   5   7   310    299  21    -2  14   7   250    298  27
 -1  17   6   501    466  26     3   5   7   858    910  38     0  14   7   333    429  24
  1  17   6   210    236  35     5   5   7   371    371  25     2  14   7   541    531  27
  3  17   6   310    313  25     7   5   7   159     76  40     4  14   7    34    135  59
  5  17   6   295    343  29   -10   6   7   314    284  28    -7  15   7  1134   1058  48
 -6  18   6   363    343  25    -8   6   7   426    413  25    -5  15   7  1126   1022  48
 -4  18   6   514    444  27    -6   6   7   154    173  35    -3  15   7   437    499  26
 -2  18   6   476    369  25    -4   6   7   447    395  23    -1  15   7     0+   123 112
  0  18   6   227    232  30    -2   6   7   950    926  41     1  15   7   422    458  25
  2  18   6   557    476  20     0   6   7   209    259  24     3  15   7   535    707  32
  4  18   6   553    524  28     2   6   7   183    184  28    -8  16   7   955    838  43
 -7  19   6   533    542  29     4   6   7   131    123  42    -6  16   7  1236   1137  53
 -5  19   6   413    391  25     6   6   7     0+   113 114    -4  16   7   332    777  37
 -3  19   6   616    519  31    -9   7   7   904    987  40    -2  16   7   230    242  25
 -1  19   6   303    392  35    -7   7   7   618    593  29     0  16   7     0+   152 110
  1  19   6   940    979  43    -5   7   7   846    873  37     2  16   7   245    259  28
  3  19   6   936    976  41    -3   7   7  1252   1191  54     4  16   7   539    491  29
 -6  20   6   304    284  17    -1   7   7   320    353  21    -7  17   7   436    413  27
 -4  20   6   323    319  26     1   7   7   956    855  37    -5  17   7   519    576  30
 -2  20   6   469    487  26     3   7   7   315    295  24    -3  17   7  1041    977  45
  0  20   6   572    575  23     5   7   7    69     77  64    -1  17   7   512    585  29
  2  20   6  1012   1014  44   -10   8   7   526    480  28     1  17   7   356    360  25
 -5  21   6   423    414  45    -8   8   7   718    693  33     3  17   7   271    206  27
 -3  21   6   523    501  27    -6   8   7   507    537  28    -6  18   7   257    248  29
 -1  21   6   544    597  36    -4   8   7  1340   1263  57    -4  18   7   970    840  37
  1  21   6   385    373  29    -2   8   7   669    669  30    -2  18   7   972    872  41
 -4  22   6   535    493  32     0   8   7   142    139  33     0  18   7   515    527  27
 -2  22   6   687    683  26     2   8   7   805    802  35     2  18   7   315    299  26
  0  22   6   436    392  29     4   8   7   454    440  25    -5  19   7   334    342  28
 -3  23   6     0+   358 129     6   8   7   188    222  35    -3  19   7   336    385  25
 -1  23   6   283    296  29    -9   9   7   785    711  35    -1  19   7   551    497  28
 -9   1   7   505    495  26    -7   9   7   176    187  32     1  19   7   254    271  29
 -7   1   7   357    343  23    -5   9   7   771    754  34    -4  20   7   236    325  28
 -5   1   7   404    404  20    -3   9   7  1425   1385  61    -2  20   7   545    651  31
 -3   1   7  1417   1385  50    -1   9   7   458    471  24     0  20   7   425    392  25
 -1   1   7  1105   1039  48     1   9   7   788    834  35     2  20   7   373    407  25
  1   1   7   951    950  40     3   9   7   114     74  44    -3  21   7   524    564  30
  3   1   7   537    567  22     5   9   7   401    412  25    -1  21   7   631    621  32
  5   1   7     0+   149 112    -8  10   7   319    312  25     1  21   7   442    394  27
  7   1   7   201    231  28    -6  10   7   167    150  35    -2  22   7   337    364  27
-10   2   7   935    910  28    -4  10   7  1702   1626  73   -10   0   8  1230   1139  53
 -8   2   7   260    553  28    -2  10   7  1224   1169  53    -8   0   8   727    725  32
 -6   2   7   199    533  28     0  10   7   600    574  28    -6   0   8   327    831  36
 -4   2   7   793    829  35     2  10   7   742    733  33    -4   0   8   939    976  40
 -2   2   7  1402   1360  60     4  10   7   370    437  24    -2   0   8  1313   1311  59
  0   2   7   975    979  42     6  10   7   534    515  28     0   0   8  2970   2936 122
  2   2   7   451    438  23    -9  11   7   836    784  39     2   0   8  1552   1544  66
  4   2   7   545    522  27    -7  11   7   312    297  24     4   0   8  1358   1242  58
  6   2   7   192    232  40    -5  11   7   353    374  24     6   0   8   231    319  57
 -9   3   7   899    861  40    -3  11   7   686    623  31    -9   1   8   553    570  29
 -7   3   7  1325   1307  57    -1  11   7   339    317  23    -7   1   8   343    833  37
 -5   3   7  1321   1391  57     1  11   7   641    673  29    -5   1   8   733    861  35
 -3   3   7   271    727  30     3  11   7   590    587  24    -3   1   8   744    649  32
 -1   3   7   202    163  33     5  11   7   306    298  27    -1   1   8  1539   1624  69
```

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2
PAGE17 OF18
(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
1	1	8	1714	1733	73	0	10	8	485	496	25	-5	3	9	1222	1334	53
3	1	8	475	456	25	2	10	8	480	533	25	-3	3	9	1533	1523	69
5	1	8	445	446	26	4	10	8	244	258	29	-1	3	9	1132	1174	49
-10	2	8	489	440	27	-9	11	8	327	796	37	1	3	9	654	701	30
-8	2	8	559	576	27	-7	11	8	767	757	34	3	3	9	304	805	36
-6	2	8	1701	1795	73	-5	11	8	235	232	28	5	3	9	917	857	40
-4	2	8	1594	1491	59	-3	11	8	947	897	41	-8	4	9	573	575	28
-2	2	8	641	601	29	-1	11	8	1390	1423	60	-6	4	9	1473	1555	63
0	2	8	480	481	24	1	11	8	1333	1372	57	-4	4	9	1372	1980	94
2	2	8	203	229	29	3	11	8	997	1006	43	-2	4	9	2279	2354	97
4	2	8	507	606	29	5	11	8	580	646	29	0	4	9	558	645	30
6	2	8	355	838	28	-8	12	8	798	723	36	2	4	9	749	716	33
-9	3	8	571	550	28	-6	12	8	581	573	28	4	4	9	508	674	32
-7	3	8	1110	1128	48	-4	12	8	737	665	33	-9	5	9	119	114	51
-5	3	8	1835	1785	72	-2	12	8	830	758	37	-7	5	9	913	806	36
-3	3	8	874	808	38	0	12	8	1452	1424	62	-5	5	9	939	915	40
-1	3	8	1196	1313	52	2	12	8	1008	985	44	-3	5	9	1394	1423	60
1	3	8	333	943	40	4	12	8	540	539	28	-1	5	9	1273	1291	55
3	3	8	770	734	34	-7	13	8	999	941	44	1	5	9	412	429	24
5	3	8	871	341	39	-5	13	8	1346	1298	58	3	5	9	131	138	43
-10	4	8	227	210	33	-3	13	8	1102	1071	48	-8	6	9	436	411	26
-8	4	8	511	501	26	-1	13	8	1151	1089	50	-6	6	9	415	393	25
-6	4	8	521	576	26	1	13	8	466	486	25	-4	6	9	453	401	25
-4	4	8	941	915	41	3	13	8	518	491	27	-2	6	9	327	333	24
-2	4	8	413	423	23	-8	14	8	879	822	39	0	6	9	955	868	38
0	4	8	502	311	23	-6	14	8	1774	1672	76	2	6	9	515	696	29
2	4	8	451	434	24	-4	14	8	1676	1580	72	4	6	9	750	745	34
4	4	8	654	564	40	-2	14	8	1383	1311	60	-9	7	9	332	415	27
6	4	8	127	125	43	0	14	8	708	679	32	-7	7	9	353	306	38
-9	5	8	721	715	33	2	14	8	765	725	34	-5	7	9	738	759	35
-7	5	8	1259	1273	53	4	14	8	426	398	25	-3	7	9	1372	1397	60
-5	5	8	1987	1914	35	-7	15	8	521	477	28	-1	7	9	1455	1463	62
-3	5	8	1415	1377	64	-5	15	8	935	862	41	1	7	9	759	789	34
-1	5	8	1498	1563	64	-3	15	8	596	577	29	3	7	9	435	508	26
1	5	8	297	335	24	-1	15	8	466	443	26	-8	8	9	517	470	27
3	5	8	555	339	24	1	15	8	177	193	34	-6	8	9	533	674	32
5	5	8	545	565	44	3	15	8	0+	99	113	-4	8	9	755	690	34
-10	6	8	721	725	34	-6	16	8	535	540	29	-2	8	9	1330	1479	60
-8	6	8	974	931	43	-4	16	8	939	893	41	0	8	9	733	793	34
-6	6	8	2255	2290	97	-2	16	8	613	614	29	2	8	9	379	335	24
-4	6	8	2261	2150	97	0	16	8	741	705	34	4	8	9	415	362	26
-2	6	8	1769	1839	76	2	16	8	379	356	26	-7	9	9	1011	968	44
0	6	8	694	778	31	-5	17	8	1309	1276	57	-5	9	9	139	201	31
2	6	8	552	637	30	-3	17	8	932	905	41	-3	9	9	479	466	26
4	6	8	505	517	26	-1	17	8	619	599	30	-1	9	9	1334	1439	60
-9	7	8	551	515	25	1	17	8	558	589	28	1	9	9	332	1071	43
-7	7	8	764	739	34	-6	18	8	597	508	30	3	9	9	1555	1590	67
-5	7	8	1052	965	44	-4	18	8	772	700	35	-8	10	9	1234	1163	54
-3	7	8	1113	1039	47	-2	18	8	571	577	29	-6	10	9	918	866	40
-1	7	8	1182	1344	55	0	18	8	641	632	31	-4	10	9	151	127	36
1	7	8	1283	1374	55	-5	19	8	241	153	30	-2	10	9	1174	1152	51
3	7	8	290	296	25	-3	19	8	642	625	31	0	10	9	1439	1433	62
5	7	8	350	367	26	-1	19	8	1299	1226	56	2	10	9	1310	1317	56
-8	8	8	434	322	39	1	19	8	1299	1259	56	-7	11	9	577	643	32
-6	8	8	436	453	36	-2	20	8	685	681	32	-5	11	9	333	307	24
-4	8	8	1239	[illegible]	62	-9	1	9	792	783	36	-3	11	9	713	676	32
-2	8	8	1352	1107	52	-7	1	9	673	699	31	-1	11	9	1043	1074	45
0	8	8	1347	1394	79	-5	1	9	450	465	25	1	11	9	515	611	29
2	8	8	1353	1298	54	-3	1	9	563	555	25	3	11	9	949	835	38
4	8	8	913	923	40	-1	1	9	1447	1392	62	-6	12	9	1112	1074	49
-9	9	8	570	534	39	1	1	9	1478	1450	63	-4	12	9	326	795	36
-7	9	8	753	792	24	3	1	9	1201	1211	52	-2	12	9	1436	1420	64
-5	9	8	433	408	24	5	1	9	649	638	31	0	12	9	550	585	27
-3	9	8	323	313	40	-8	2	9	1067	1091	46	2	12	9	371	367	25
-1	9	8	340	886	17	-6	2	9	386	352	24	-7	13	9	524	553	30
1	9	8	495	938	39	-4	2	9	698	663	31	-5	13	9	437	433	26
3	9	8	575	671	31	-2	2	9	1045	983	45	-3	13	9	727	656	33
5	9	8	525	532	57	0	2	9	1039	1712	72	-1	13	9	330	355	39
-8	10	8	214	325	34	2	2	9	1657	1636	71	1	13	9	543	666	30
-6	10	8	194	1034	55	4	2	9	1340	1369	59	-6	14	9	439	346	27
-4	10	8	273	331	35	-9	3	9	365	371	26	-4	14	9	570	533	29
-2	10	8	355	351	24	-7	3	9	340	357	37	-2	14	9	514	472	27

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR (CUI(PH2C6H5)2)2 PAGE18 OF18

(UNOBSERVED REFLECTIONS ARE MARKED +)

H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG	H	K	L	FO	FC	SIG
0	14	9	543	547	27	-8	6	10	107	67	51	1	1	11	157	86	37
2	14	9	575	534	29	-6	6	10	201	187	32	-6	2	11	274	248	27
-5	15	9	1154	1092	50	-4	6	10	815	811	36	-4	2	11	573	616	31
-3	15	9	1466	1400	55	-2	6	10	954	1001	42	-2	2	11	490	467	26
-1	15	9	1105	1069	48	0	6	10	1145	1192	50	0	2	11	371	381	24
1	15	9	477	487	27	2	6	10	645	668	30	-7	3	11	554	667	31
-6	16	9	971	937	43	-7	7	10	315	277	25	-5	3	11	456	447	26
-4	16	9	1291	1209	56	-5	7	10	409	362	24	-3	3	11	71	152	62
-2	16	9	1265	1204	55	-3	7	10	376	388	24	-1	3	11	251	251	27
0	16	9	644	636	31	-1	7	10	587	586	28	1	3	11	420	436	26
-5	17	9	372	351	27	1	7	10	812	813	36	-6	4	11	1045	1100	46
-3	17	9	423	396	26	3	7	10	807	820	36	-4	4	11	57	121	65
-1	17	9	952	965	42	-8	8	10	539	541	28	-2	4	11	170	99	54
-2	18	9	369	368	26	-6	8	10	667	635	31	0	4	11	479	463	25
-8	0	10	710	659	35	-4	8	10	946	925	42	-7	5	11	536	525	28
-6	0	10	773	353	35	-2	8	10	441	454	25	-5	5	11	256	305	28
-4	0	10	333	832	38	0	8	10	317	303	25	-3	5	11	145	105	37
-2	0	10	23	37	82	2	8	10	357	1022	42	-1	5	11	235	294	26
0	0	10	541	509	27	-7	9	10	271	304	23	1	5	11	414	451	26
2	0	10	1300	1786	77	-5	9	10	665	565	31	-6	6	11	353	423	25
-7	1	10	311	316	25	-3	9	10	81	44	55	-4	6	11	315	199	49
-5	1	10	241	279	20	-1	9	10	326	359	26	-2	6	11	233	317	26
-3	1	10	493	466	23	1	9	10	199	275	32	0	6	11	334	396	26
-1	1	10	419	410	44	-6	10	10	124	183	46	-5	7	11	358	397	25
1	1	10	360	846	38	-4	10	10	249	200	27	-3	7	11	357	348	24
3	1	10	1333	949	44	-2	10	10	234	246	29	-1	7	11	402	376	25
-8	2	10	215	227	31	0	10	10	59	136	67	1	7	11	457	475	26
-6	2	10	0+	129	111	2	10	10	246	312	31	-6	8	11	212	245	33
-4	2	10	1099	1015	48	-7	11	10	470	439	26	-4	8	11	516	473	27
-2	2	10	311	754	26	-5	11	10	770	712	35	-2	8	11	76	137	61
0	2	10	405	376	24	-3	11	10	413	366	25	0	8	11	346	354	25
2	2	10	617	605	20	-1	11	10	456	473	26	-5	9	11	731	719	35
-7	3	10	235	322	25	1	11	10	679	648	32	-3	9	11	355	342	25
-5	3	10	437	485	26	-6	12	10	397	331	26	-1	9	11	407	397	25
-3	3	10	325	870	40	-4	12	10	398	351	25	-4	10	11	545	606	31
-1	3	10	442	490	25	-2	12	10	247	273	29	-2	10	11	437	421	26
1	3	10	595	618	29	0	12	10	541	560	28	-3	11	11	156	150	39
3	3	10	593	596	29	-5	13	10	155	171	41	-1	11	11	237	342	29
-8	4	10	0+	74	112	-3	13	10	850	824	38	-4	0	12	132	332	25
-6	4	10	365	440	25	-1	13	10	797	770	36	-2	0	12	322	382	41
-4	4	10	150	140	35	-4	14	10	584	584	29	-5	1	12	359	340	21
-2	4	10	319	311	34	-2	14	10	1065	1018	47	-3	1	12	416	399	25
0	4	10	220	116	30	0	14	10	775	800	35	-1	1	12	927	786	37
2	4	10	71	104	36	-3	15	10	516	483	25	-4	2	12	737	724	36
-7	5	10	166	99	35	-1	15	10	248	247	31	-2	2	12	457	439	35
-5	5	10	175	233	35	-7	1	11	224	224	31	-3	3	12	779	703	38
-3	5	10	157	1080	44	-5	1	11	323	353	20	-4	4	12	130	150	38
-1	5	10	1038	1040	34	-3	1	11	291	246	26	-2	4	12	157	227	39
1	5	10	755	750	44	-1	1	11	730	720	33	-3	5	12	1336	1026	45
3	5	10	0+	114	114												

REFERENCES

Abel, E. W.; McLean, R. A.N.; Sabherwal, I. H. (1969) J. Chem. Soc. (A), 133.

Akitt, J. W.; Cragg, R. H.; Greenwood, N. N. (1966) J. Chem. Soc. Chem. Comm. 5, 134.

Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. J. (1978) J. Org. Chem. 43, 5024.

Batchelor, R.; Birchall, T. (1982) Acta Cryst. B38, 1260.

Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. (1979) Acc. Chem. Res. 12, 176.

Becker, E. D. (1980) "High Resolution NMR", Academic Press, New York.

Benkeser, R. A.; Landesman, H.; Foster, D. J. (1952) J. Amer. Chem. Soc. 74, 648.

Berestova, S. S.; Terekhova, M. I.; Bondarenko, N. A.; Bogachev, Yu. S.; Petrov, E. S.; Shatenshtein, A. I. (1982) Zh. Obshch. Khim. 52, 513.

Birchall, T.; Jolly, W. L. (1966a) Inorg. Chem. 5, 2177.

Birchall, T.; Jolly, W. L. (1966b) J. Amer. Chem. Soc. 88, 5439.

Birchall, T.; Drummond, I. (1970) J. Chem. Soc. (A), 1401.

Birchall, T.; Drummond, I. (1972) Inorg. Chem. 11, 250.

Birchall, T.; Pereira, A. R. (1972) J. Chem. Soc. Chem. Comm. 1150.

Birchall, T.; Pereira, A. R. (1975) J. Chem. Soc. Dalton Trans. 1087.

Birchall, T.; Myers, R. D. (1981) 'Advances in Chemistry Series, No. 194' J. G. Stevens and G. K. Shenoy, eds. p. 377, Amer. Chem. Soc., Washington, D.C.

Bodner, G. M.; Gaul, M. (1975) J. Organomet. Chem. 101, 63.

Bordwell, F. G. (1977) Pure and Applied Chem. 49, 963.

Bordwell, F.; Algrim, D.; Vanier, N. R. (1977) J. Org. Chem. 42, 1817.

Buncel, E.; Menon, B. (1978), J. Chem. Soc. Chem. Comm. 758.

Carson, G. K.; Dean, P. A. W.; Stillman, M. J. (1981) Inorganica Chimica Acta, 56(B3), 59.

Charton, M. (1971) J. Org. Chem. 36, 266.

Churchill, M. R. (1973) Inorg. Chem. 12, 1213.

Churchill, M. R.; DeBoer, B. G.; Donovan, D. J. (1975) Inorg. Chem. 14(3), 617.

Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. (1982) J. Chem. Soc. Chem. Comm. 220.

Cook, D. I.; Fields, R.; Green, M.; Haszeldine, R. W.; Iles, B. R.; Newlands, M. J. (1966) J. Chem. Soc. (A) 887.

Costa, G.; Reisenhofer, E.; Stefani, L. (1965) J. Inorg. Nucl. Chem. 27, 2581.

Cromer, D. T. (1974) 'International Tables for X-Ray Crystallography' Vol. IV, Table 2.3.1, p. 149. Birmingham: Kynoch Press.

Cromer, D. T.; Waber, J. T. (1974) 'International Tables for X-Ray Crystallography' Vol. IV, Table 2.2A, p. 72, Birmingham: Kynoch Press.

Curtis, M. D. (1969) J. Amer. Chem. Soc. 91, 6011.

Dale, B. W.; Dickinson, R. J.; Parish, R. V. (1974) J. Chem. Soc. Chem. Comm. 35.

Day, M. C.; Selbin, J. (1969) 'Theoretical Inorganic Chemistry', 2nd Ed. p. 383, Reinhold: New York.

Dean, P. A. W.,; Gillespie, R. J.; Ummat, P. K. (1974) Inorg. Synth. 15, 213.

Debies, T. P.; Rabalais, J. W. (1974) Inorg. Chem. 13(2), 308.

DeMaria, P.; Fini, A.; Hall, F. M. (1973) J. Chem. Soc. Perkin Trans. 2, 14, 1969.

Drummond, I. (1970) Ph.D. Thesis, McMaster University.

Eller, P. G.; Kubas, G. J.; Ryan, R. R. (1977) Inorg. Chem. 16(10), 2454.

Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. (1965) 'High Resolution N.M.R. Spectroscopy', Vol. 2. Pergamon Press: London.

Emsley, J.; Hall, D. (1976) 'The Chemistry of Phosphorus' Halsted Press (John Wiley and Sons): New York.

Ewing, D. F. (1978) 'Correlation Analysis in Chemistry', N. B. Chapman and J. Shorter, eds., Chapter 8. Plenum: New York.

Ewing, D. F. (1979) Org. Magn. Res. 12(9), 499.

Ewing, D. F.; Toyne, K. J. (1979) J. Chem. Soc. Perkin Trans. 2, 243.

Fischer, E. O.; Louis, E.; Kreiter, C. G. (1969) Angew. Chem. Int. Ed. Eng., 8, 377.

Gaughan, A. P. Jr.; Dori, Z.; Ibers, J. A. (1974) Inorg. Chem. 13, 1657.

Gill, J. T.; Mayerle, J. J.; Welker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. (1976) Inorg. Chem. 15(5), 1155.

Gillespie, R. J. (1960) J. Amer. Chem. Soc. 82, 5978.

Gillespie, R. J.; Spekkens, P.; Milne, J. B.; Moffett, J. (1976) Fluorine Chem. 7, 43.

Goldwhite, H. (1981) 'Introduction to Phosphorus Chemistry' Cambridge University Press.

Grant, D. M.; Cheney, B. V. (1967) J. Amer. Chem. Soc. 89, 5315.

Graziani, R.; Bombieri, G.; Forsellini, E. (1971) J. Chem. Soc. (A), 2331.

Grim, S. O.; Molenda, R. P. (1974) Phosphorus, 4, 189.

Grutzner, J. B.; Lawlor, J. M.; Jackman, L. M. (1972) J. Amer. Chem. Soc. 94, 2306.

Hamnett, A.; Hood, S. T.; Brion, C. E. (1977) J. Electron Spectrosc. Relat. Phenom. 11, 263.

Hayamizu, K.; Yamamoto, O. (1968) J. Mol. Spectrosc. 28, 89.

Hayamizu, K.; Yamamoto, O. (1969) J. Mol. Spectrosc. 29, 183.

Hehre, W. J.; Taft, R. W.; Topsom, R. D. (1976) Prog. Phys. Org. Chem. 12, 159.

Henderson, W. A.; Streuli, G. A. (1960) J. Amer. Chem. Soc. 82, 5791.

Hoffman, R. (1978) Inorg. Chem. 17, 2187.

Holtje, R.; Schlegel, H. (1940) Z. Anorg. Allg. Chem. 243, 246.

Hruska, F.; Hutton, H. M.; Schaefer, T. (1965) Can. J. Chem. 43, 2392.

Issleib, K.; Kümmel, R. J. (1965) J. Organomet. Chem. 3, 84.

Johnson, O. H. (1951) Chem. Rev. 48, 259.

Johnson, O. H.; Harris, D. M. (1957) Inorg. Synth. 5, 74.

Johnson, O. H.; Nebergall, W. H.; Harris, D. M. (1957) Inorg. Synth. 5, 76.

Jolly, W. L. (1971) Inorg. Chem. 10, 2364.

Karplus, M.; Pople, J. A. (1963) J. Chem. Phys. 38, 2803.

Knoll, F.; Bergerhoff, G. (1966) Monatsh. Chem. 97, 808.

Kosolapoff, G. M.; Maier, L. (1972), 'Organic Phosphorus Compounds', p. 293. New York: Wiley-Interscience.

Kraihanzel, C. S. (1974) J. Organomet. Chem. 73, 137.

Kühlein, K.; Neumann, W. P. (1967) J. L. Annalen der Chemie, 702, 17.

Lamb, W. (1941) Phys. Rev. 60, 817.

Lebedeva, T. I.; Kolseova, V. A.; Gerasimovich, L. L.; Kefchivan, G. A.; Petrov, E. S.; Strepikheev, Yu. A.; Shatenshtein, A. I. (1977), Zh. Org. Khim. 13, 1137.

Levy, G. C.; Lichter, R. L.; Nelson, G. L. (1980) "Carbon-13 N.M.R. Spectroscopy", 2nd Ed. John Wiley and Sons: New York.

Libit, L.; Hoffman, R. (1974) J. Amer. Chem. Soc. 96, 1370.

Lippard, S. J.; Palenik, G. J. (1971) Inorg. Chem. 10, 1322.

Lippard, S. J.; Mayerle, J. J. (1972) Inorg. Chem. 11, 753.

Lynch, B. M. (1977) Can. J. Chem. 55, 541.

Maciel, G. E.; Natterstad, J. J. (1965) J. Chem. Phys. 42(7), 2427.

Malatesta, L.; Cenini, S. (1974) 'Zerovalent Compounds of Metals', Academic Press: London.

Mann, F. G.; Pragnell, M. J. (1965) J. Chem. Soc. 4120.

Mavel, G. (1973) Ann. Rep. NMR Spectrosc. 5B, 71.

McAuliffe, C. A.; Levason, W. L. (1979) 'Phosphine, Arsine and Stibine Complexes of the Transition Elements', Elsevier: New York.

Muetterties, E. L.; Alegranti, C. W. (1970) J. Amer. Chem. Soc. 92, 4114.

Myers, R. D. (1982) Ph.D. Thesis, McMaster University.

Nelson, G. L.; Williams, E. A. (1976) Prog. Phys. Org. Chem. 12, 229.

O'Brien, D. H.; Hart, A. J.; Russell, C. R. (1975) J. Amer. Chem. Soc. 97, 4410.

O'Brien, D. H.; Russell, C. R.; Hart, A. J. (1976) J. Amer. Chem. Soc. 98, 7427.

Olah, G. A.; Hunadi, R. J. (1980) J. Amer. Chem. Soc. 102, 6989.

Parr, W. J. E. (1978) J. Chem. Soc. Faraday Trans. 2, 74, 933.

Pauling, L. (1960) 'The Nature of the Chemical Bond', 3rd Ed. Ithaca, New York: Cornell University Press.

Pople, J. A. (1962) J. Chem. Phys. 37, 53.

Pross, A.; Radom, L. (1981) Prog. Phys. Org. Chem. 13, 1.

Rakita, P. E.; Srebro, J. P.; Worsham, L. S. (1976) J. Organomet. Chem. 104, 27.

Ramsey, N. F. (1950) Phys. Rev. 78, 699.

Ramsey. N. F.; Purcell, E. M. (1952) Phys. Rev. 85, 143.

Raynes, W. T. (1971) Mol. Phys. 20, 321.

Raynes, W. T. (1974) 'Nuclear Magnetic Resonance', Vol. 3, p. 13. The Chemical Society: London.

Rijkens, F.; Van der Kerk, G. J. M. (1964) 'Organogermanium Chemistry', Schotanus and Jens: Utrecht.

Ruby, S. L. (1973) 'Mössbauer Effect Methodology', I. J. Gruverman and C. W. Seidel, eds., vol. 8, p. 263. Plenum Press: New York.

Ruebenbauer, K.; Birchall, T. (1979) Hyperfine Interactions, 7, 125.

Ryan, M. T.; Lehn, W. L. (1965) Organomet. Chem. 4, 455.

Saika, A.; Slichter, C. P. (1954) J. Chem. Phys. 22, 26.

Sandrock, G. D.; Snape, E. (1980) 'Hydrogen Production and Marketing', W. N. Smith and J. G. Santangelo, eds. American Chemical Society: Washington, D.C.

Schaefer, T.; Reynolds, W. F.; Yonemoto, T. (1963) Can. J. Chem. 41, 2968.

Scholder, R.; Pattock, K. (1934) Z. Anorg. Allg. Chem. 220, 250.

Senoff, C. V.; Ward, J. E. H. (1975) Inorg. Chem. 14, 278.

Shaw, B. L. (1967) 'Inorganic Hydrides', Oxford, New York: Pergamon Press.

Sheldrick, G. M. (1976) 'SHELX 76. Program for Crystal Structure Determination', University of Cambridge, England.

Smith, W. B.; Roark, J. L. (1967) J. Amer. Chem. Soc. 89, 5018.

Smith, W. B.; Ihrig, A. M.; Roark, J. L. (1970) J. Phys. Chem. 74, 812.

Smith, W. B.; Deavenport, D. L. (1972) J. Magn. Res. 7, 364.

Spiesecke, H.; Schneider, W. G. (1961) J. Chem. Phys. 35(2), 731.

Sretenskaya, N. G. (1974) Geokhimiya, 7, 996.

Stewart, J. M. (1976) 'X-RAY 76: System of Crystallographic Programs', Tech. Rep. TR-446, University of Maryland, College Park, Maryland.

Stothers, J. B. (1972) 'Carbon-13 NMR Spectroscopy', Academic Press: New York.

Stout, G. H.; Jensen, L. H. (1968) 'X-Ray Structure Determination', Macmillan: London.

Streitwieser, A. Jr.; Juaristi, E.; Nebenzahl, L. L. (1980) 'Comprehensive Carbanion Chemistry', Part A, E. Buncel and T. Durst, eds. Elsevier: New York.

Sutton, L. E. (1958) 'Interatomic Distances', Chemical Society Special Publication No. 11.

Takahashi, K.; Kondo, Y.; Asami, R.; Inoue, Y. (1974) Org. Magn. Res. 6, 580.

Terekhova, M. J.; Bondarenko, N. A.; Malakhova, I. G.; Tsvetkov, E. N.; Petrov, E. S.; Shatenshtein, A. I. (1982) Zh. Obshch. Khim. 52(3), 516.

Tolman, C. A. (1970) J. Amer. Chem. Soc. 92, 2956.

Topsom, R. D. (1976) Prog. Phys. Org. Chem. 12, 1.

Turner, G. (1976) Ph.D. Thesis, McMaster University.

Tzschach, A.; Pacholke, G. (1964) Chem. Ber. 97, 419.

Van Wazer, J. R.; Letcher, J. H. (1967) Topics in Phosphorus Chemistry, 5, 169. Interscience: New York.

Vorpagel, E. R.; Streitwieser, A. Jr.; Alexandratos, S. D. (1981) J. Amer. Chem. Soc. 103, 3777.

Wan, Y-P.; O'Brien, D. H.; Smentowski, F. J. (1972) J. Amer. Chem. Soc. 94, 7680.

Weaver, J. R.; Parry, R. W. (1966) Inorg. Chem. 5, 718.

Weigert, F. J.; Roberts, J. D. (1969) J. Amer. Chem. Soc. 91, 4940.

Weston, R. E.; Bigeleisen, J. (1954) J. Amer. Chem. Soc. 76, 3074.

Wiberg, E. (1971) 'Hydrides of the Elements of Main Groups I-IV'. New York: Elsevier.

Wiberg, E.; Mödritzer, K. (1957) Z. Naturforsch. 12B, 127.

Wiberg, E.; Nöth, H. (1957) Z. Naturforsch. 12B, 125.

Woolfson, M. M. (1970) 'An Introduction to X-Ray Crystallography'. Cambridge University Press.

Worvill, K. M.; Martin. J. S. (1975) "NUMARIT: Iterative NMR Spectral Analysis Program" a development of NUMAR: A. R. Quirt and J. S. Martin, J. Magn. Res. 5, 318 (1971).

Yamada, H.; Tsuno, Y.; Yukawa, Y. (1970) Bull. Chem. Soc. Japan, 43, 1459.

Yukawa, Y.; Tsuno, Y. (1965) Nippon Kagaku Zusshi, 86, 873.