STRUCTURAL STUDIES OF COMPOUNDS
CONTAINING DICOVALENT SULFUR CHAINS

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SCOPE AND CONTENTS:

Because of interest which has been shown in the structure and bonding in polysulfide chains as evidenced by the wide variety of hypotheses which have been proposed in explanation thereof, it was considered of interest to investigate differences among a series of compounds which differ only in the number of sulfur atoms in their polysulfide chains. Furthermore, some controversy existed concerning the molecular structure of a compound which had been prepared and studied in this laboratory, and which was a member of the aforementioned homologous series. Therefore, the x-ray crystal and molecular structures of the benzylidenimine tetra-, tri- and disulfides were sought, and the determinations are herein reported. Similarities and differences among the three compounds are analyzed with detailed consideration of their significance with respect to the precisions and accuracies of the determinations.

A pattern of short-long-short sulfur-sulfur single bonds is observed in benzylidenimine tetrasulfide which is of particular interest with reference to previous findings. A number of possible theoretical explanations for this effect are considered critically, taking into account trends in sulfur-sulfur bond length among the three compounds as well as in other reported polysulfide structures, and also available spectral, kinetic and synthetic information concerning these compounds. It is possible to reject some earlier proposed hypotheses concerning sulfur-sulfur bonding as incompatible with the trends observed in the benzylidenimine polysulfides.

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CHAPTER 1: INTRODUCTION

A. Dicovalent Sulfur Chains

There is considerable interest in the nature of the bonding in polysulfide chains.[1,2] The possibility of branching in polysulfur chains[1] remains controversial, as does the explanation for the barrier to rotation about S-S single bonds.[3] The extent to which s-orbitals,[4] and still more the extent to which d-orbitals, contribute to sulfur-sulfur bonding are likewise unresolved questions. These questions remain despite the large number of compounds containing sulfur chains which have been synthesized and studied, with increasing frequency and with increasingly sophisticated and refined techniques. It therefore seemed desirable that any new study of polysulfide chains address itself to resolving some of these unsolved questions.

One of the more interesting and potentially informative aspects of bonding is suggested by the apparent alternation of bond length in chains of four or more sulfur atoms. This result has been reported several times in the past, but with a lack of consistency or conviction which leaves conclusions based on it open to considerable uncertainty. A major problem until recently has been that of attaining sufficient precision in crystallographic studies to be able to state categorically that two sulfur-sulfur bond lengths (distances) are significantly different. Thus, the triclinic form of $BaS_5O_6.2H_2O$ (barium pentathionate) was studied in 1955 by Foss and Tjomsland.[5] The two inner sulfur-sulfur bond lengths were found to be 2.04(4)Å[*] while the two outer sulfur-sulfur bond lengths were 2.10(4) and 2.12(4)Å. The difference between the two sets is less than two standard deviations, so that the significance of this difference, even though it amounts to 0.07Å, remains doubtful.

Another example is barium tetrasulfide. When Abrahams[6] first studied the crystal structure of $BaS_4.H_2O$ in 1954, he

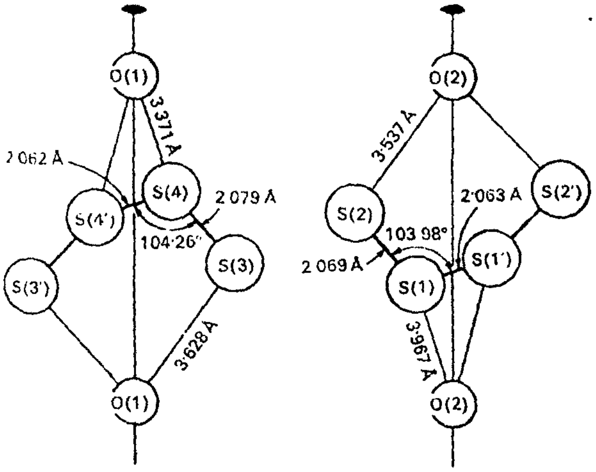

Figure 1. $BaS_4.H_2O$[6]

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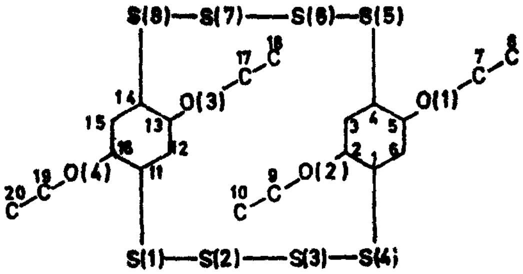
[*] Throughout this thesis the uncertainty in a measurement (standard deviation or σ where least squares is involved) will be designated by including the error in the final digit(s) in parentheses; e.g. 2.04(4)Å is equivalent to 2.04±.04Å.

found bond length alternation; the inner bond was 2.07(4)Å and the outer two were 2.03(4)Å and 2.02(4)Å. The differences, which are quite large in absolute terms are only of the order of one standard deviation. Fifteen years later, with the availability of superior data collection and processing equipment, Abrahams[7] redetermined the bond lengths in this compound, obtaining 2.0690(35)Å and 2.0633(38)Å for the two crystallographically independent inner sulfur-sulfur distances, and 2.0793(33)Å and 2.0624(36)Å for the two outer sulfur-sulfur distances (Figure 1.). The new results are within one standard deviation of the old, but no longer indicate substantial bond length alternation. The authors considered in detail the statistical implications of their new results and finally concluded that "In view of this uncertainty [in bond lengths] the hypothesis that the inner S-S bonds are equivalent in length to the outer S-S bonds should not be rejected."[8]

The clearest example yet found of significant bond length alternation in a chain of dicovalent sulfur atoms was reported by Ricci and Bernal[9] in 1969. They studied 7,15,17,19-tetraethoxy-2,3,4,5,10,11,12,13-octathiatricyclo [12,2,2,$2^{6,9}$] eicosa-6,8,14,16,17,19-hexaene (I), a compound containing two tetrasulfur chains bridging aromatic rings. The outer sulfur-sulfur bonds of the chains averaged 2.028(1)Å, while the inner bonds averaged 2.066(2)Å. The authors on the basis of these data and the slight shortening



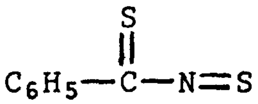
I

of the carbon-sulfur distance from the usual 1.817(5)Å[10] to 1.764(8)Å conclude that "The implication is that conjugation of the two rings across an S_4 fragment has been achieved, which obviously requires the formation of C-S and S-S π-bonds."[9a] Also found in the structure, however, were substantial non-bonded interactions between oxygen and the terminal sulfurs of the chains [2.775(20)Å, less by 0.5Å than the sum of Van der Waal's radii] ; these interactions leave their conclusion open to some question. Considering the significance which has apparently been attached to this conclusion[2], it would seem to be desirable to investigate less ambiguous instances of polysulfur chains connecting aromatic systems.

B. Benzylidenimine Polysulfides

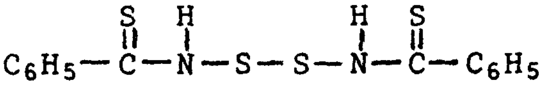
A stable yellow solid of mp 101° has been reported several times over the past century.[11,12,13] Reactions leading to this material include benzylamine with tetrasulfur tetranitride,[11,14a] elemental sulfur with benzylamine in the presence of lead oxide,[12,14b] either sulfur monochloride[13,14b] or trisulfur dichloride with benzylamine,[13] and the decomposition of either benzylamine disulfide[14] or N-benzylheptasulfurimide.[15]

Elemental analyses* are in agreement with the structures II (except for molecular weight), III, IV, V and VI.



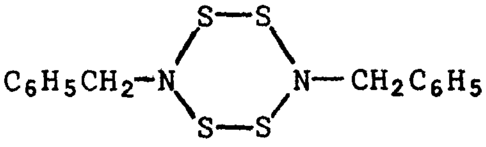
$C_6H_5-C(=S)-N=S$

II

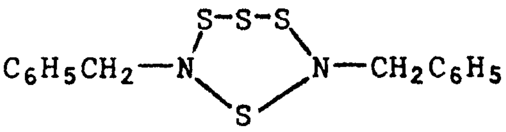


$C_6H_5-C(=S)-NH-S-S-NH-C(=S)-C_6H_5$

III



IV



V

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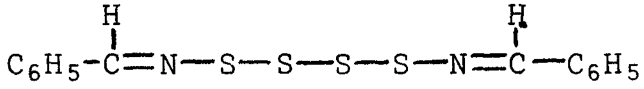
*Calculated for $C_{14}H_{12}N_2S_4$ (molecular weight 336): C,49.97; H,3.59; N,8.32; S,38.11. Found[14c] (332): C,49.54; H,3.67; N,8.70; S,37.70.



$$C_6H_5-\overset{H}{\overset{|}{C}}=N-S-S-S-S-N=\overset{H}{\overset{|}{C}}-C_6H_5$$

VI

All five of these have been suggested at one time or another.[11,12,13,14] Most recently,[13,14a] the same physical data, i.e. nmr and ir spectra, have been interpreted in terms of two different structures (V and VI). Sasaki and Olsen base their formulation VI (abbreviated henceforth as BITS, BenzylidenImine TetraSulfide) on the nmr spectrum, which shows a sharp singlet at -7.87 ppm of area 1 and a multiplet at -7.12 to -7.55 ppm of area 5, the latter due to the phenyl group. The one-proton singlet would appear to be in agreement only with structures III and VI, although the thioamide singlet might be expected to be broader than that observed, and the infrared spectrum did not show the N-H stretching absorption,[13,14,16] expected for a thioamide.

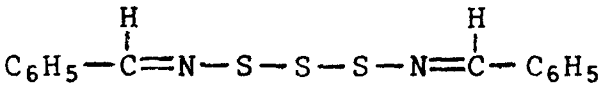
Although he was unable to explain the uncharacteristic benzyl group absorptions and the "quite atypical"[13] methylene C-H stretching region, Pond[13] tentatively assigned the 1,3-diimide structure V (product obtained from the reaction of benzylamine with S_3Cl_2) by analogy with reaction of other primary amines with S_3Cl_2.[17] The shift of 2.8 ppm downfield for the "methylene" protons relative to those in the 1,4 isomer III, was also difficult to rationalize. He also notes that the area ratio of phenyl to methylene proton absorptions of 4.4:1 "is not in agreement with the calculated ratio of 2.5:1 expected for benzyl groups." He did not consider the possibility of the benzylidenimine tetrasulfide structure.

C. Aims of the Present Work

In view of these differing opinions it would be desirable to settle unequivocally the question of the structure of BITS by an X-ray crystallographic determination.

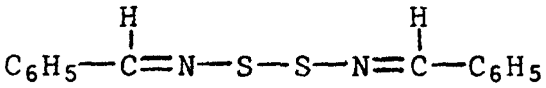
If the compound is indeed benzylidenimine tetrasulfide as expected, then it is an immediate analog of Ricci and Bernal's compound. A chain of four sulfurs connects two aromatic systems (through conjugated imine nitrogens). If the hypothesis of Ricci and Bernal[9] of conjugation across an S_4 fragment is correct, then alternation in bond lengths should be found in BITS. This alternation, if found, would require an explanation based on S-S bonding since, unlike the compound of Ricci and Bernal (I), opportunities for non-bonding interactions are unlikely. Contrariwise, if alternation in bond lengths were not found in BITS, then the explanation put forth by Ricci and Bernal for their compound would require revision. "Butadiene-like"[9b] conjugation is not the only hypothesis that might explain bond length alternation in a tetrasulfur chain. Some other possible explanations might include: (1) the short S...O non-bonding interaction affecting the outer S-S bond lengths already mentioned; (2) inductive effects originating in the substituents on the ends of the tetrasulfur chains which would be expected to affect the outer sulfur atoms of the chain more than the inner; (3) the possibility that a chain of four sulfur atoms is capable of internally stabilizing itself in some fashion employing dπ-pπ or dπ-dπ interactions.

If Sasaki and Olsen's compound is BITS, the homologous compounds BenzylidenImine TriSulfide (BITrS) and BenzylidenImine DiSulfide (BIDS) are available. These are



$$C_6H_5-\overset{H}{\overset{|}{C}}=N-S-S-S-N=\overset{H}{\overset{|}{C}}-C_6H_5$$

BITrS



$$C_6H_5-\overset{H}{\overset{|}{C}}=N-S-S-N=\overset{H}{\overset{|}{C}}-C_6H_5$$

BIDS

obtained as byproducts in some of the same reactions which produce BITS, particularly the reaction of benzylamine with tetrasulfur tetranitride[14] and with sulfur in the presence of lead oxide.[14c] Adjustment of the stoichiometric ratio of the reactants in the latter case can be made to favor the production of these byproducts. Determination of the corresponding sulfur-sulfur distances in these homologs could aid in distinguishing among the various hypotheses.

The work described in this thesis then is undertaken with the aim of establishing the structure of BITS, first in regard to the overall structure, and second in regard to the possibility of alternation of S-S bond lengths. If the inner and outer S-S bonds are found to differ by a statistically significant amount, then the structure of BITrS and BIDS will also be undertaken with the aim of proposing an explanation for this effect.

CHAPTER 2: METHODS AND TECHNIQUES

The crystal and molecular structural determinations described herein used certain common techniques and methods and are founded on a common theoretical base.

A. Interaction of X-Rays With Matter[18]

A crystal may be defined as an array of atoms whose average positions are described by the operation in three dimensions of translational symmetry upon a smaller finite array of atoms. A beam of x-rays incident upon a crystal interacts with the electrons of the atoms and exits coherently only in certain directions. If $\underline{k}'$[*] and $\underline{k}$ are the wave vectors of the incident and diffracted beams of x-rays respectively, then $\underline{K} = \underline{k} - \underline{k}'$ may be used to define the conditions under which diffraction will occur. The repetitive unit of the translationally symmetric array is known as the "unit cell", whose edges are described by the vectors $\underline{a}$, $\underline{b}$, and $\underline{c}$. The following relationships (Laue equations) must be satisfied:

$$\underline{a}.\underline{K} = 2\pi h$$

$$\underline{b}.\underline{K} = 2\pi k$$

$$\underline{c}.\underline{K} = 2\pi \ell$$

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[*] A vector is indicated by underlining.

The Miller indices h, k and ℓ of a plane indicate respectively the integral number of times the cell edges $\underline{a}$, $\underline{b}$ and $\underline{c}$ are intersected by that plane. Thus the diffracting planes may only intersect the unit cell edges at integral fractions of those edges.

It is generally more convenient to define a reciprocal space using as basis vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ defined by:

$$\underline{a}^* = \frac{\underline{b} \times \underline{c}}{V};$$

$$\underline{b}^* = \frac{\underline{c} \times \underline{a}}{V};$$

$$\underline{c}^* = \frac{\underline{a} \times \underline{b}}{V};$$

where V is the volume of a unit cell, defined by $\underline{a}.\underline{b} \times \underline{c}$ Then the solutions to the Laue equations are points in reciprocal space and it is the space that has translational symmetry. The distance H of one of these points from the origin of reciprocal space is given by the Bragg equation:

$$H = \frac{2\sin\,\theta_{(H)}}{\lambda} = \frac{1}{d_H}$$

where λ is the wavelength of the x-radiation used, 2θ is the scattering angle between the incident and diffracted beams, d_H is the distance between two of the planes hkℓ, and

$$\underline{H} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^* \qquad (H = |\underline{H}|)$$

$$\frac{1}{d^2} = h^2\underline{a}^{*2} + k^2\underline{b}^{*2} + \ell^2\underline{c}^{*2} + 2k\ell\underline{b}^*\underline{c}^*\cos\alpha^* + 2h\ell\underline{a}^*\underline{c}^*\cos\beta^* + 2hk\underline{b}^*\underline{c}^*\cos\gamma^*$$

where α^*, β^*, and γ^* are respectively the angles between the b^* and c^*, a^* and c^*, and a^* and b^* axes. Systematic extinctions of reflections (zero intensity) may arise from symmetry operators involving a translation of some integral fraction of the unit cell edges, e.g. screw axes and glide planes.

The symmetry classification or space group of the unit cell of a particular crystal may usually be determined by consideration of the symmetry of the intensity distribution of the diffracted x-rays, together with the systematic extinctions.

The intensity, $I_{hk\ell}$, of a reflection is primarily determined by the arrangement of the atoms in the unit cell, but it is also modified by other factors. $I_{hk\ell}$ may be written:

$$I_{hk\ell} = C(Lp)A|F_{hk\ell}|^2 \qquad (1)$$

Here, C is a constant which depends on the volume and density of the crystal, the intensity of the incident beam, the scattering power of the individual electrons in the atoms of the unit cell, and the efficiency of detection of the diffracted beam of x-rays.

L is the Lorentz factor, and depends upon the manner in which the crystal passes through the conditions for diffraction of a particular reflection, which in turn depends upon the orientation of the incident and diffracted beam relative to the axis of rotation, i.e. upon the geometry of the collection process. The polarization factor, p, arises because the diffracted beam is partially polarized parallel to the plane it is diffracted from. For a direct incident beam,

$$p = \frac{1 + \cos^2 2\theta}{2}$$

If the incident beam passes first through a monochromator, it is thus partially polarized, and p is modified by the (2θ) angle between the direct beam and the monochromatized beam. The Lorentz and polarization corrections are usually applied together.*

Absorption of the x-ray beam by a given crystal is proportional to the instantaneous intensity of the beam, and to the distance x travelled in the crystal:

$$I_{(x)} = I_o e^{-\mu x}$$

where μ is characteristic of the atoms in the crystal and is

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*See page 17.

calculated from the atomic mass absorption coefficients;[19] $e^{-\mu x}$ is known as the transmission factor. The path length x depends generally upon the angle between incident and diffracted beams, and on the shape of the crystal.

Another phenomenon whose effect is similar to that of absorption in reducing the intensity is extinction. If all the unit cells are perfectly aligned with each other throughout the crystal, the energy of the incident beam will be depleted by the amount of energy which has been transferred into the diffracted beam. This phenomenon is known as primary extinction, and is rarely observed and may be ignored in soft organic crystals, because such crystals are mosaics of tiny crystals, all slightly misaligned with respect to one another. In such an array of small blocks of perfectly aligned unit cells which are then nearly but not quite aligned with other such blocks, the diffracted beam leaving one block can be rediffracted back into the incident beam, thus depleting the diffracted beam. This phenomenon is known as secondary extinction. Only very strong reflections are affected, and the magnitude of the effect is usually small compared to random errors. Therefore corrections for secondary extinction have not often been made.

The last term in equation (1), $|F(\underline{H})|^2$, is the one of greatest significance since it is the one which is sensitive to the locations of the atoms in the unit cell. For the purposes of this work, an atom may be considered as a spherical concentration of electron density with an approximately Gaussian cross section. Since this sphere is of finite size, x-rays scattered from a volume element in one part of the sphere are not necessarily in phase with those scattered from another part; the straighter the beam (incident and diffracted) passes through an atom, the more of it will be in phase, and the more intense will be the diffracted beam. Each atom may be described as a mathematical point with an angular variation in scattering power described by the function f(H) known as the atomic scattering factor. These scattering factors are tabulated[19] for each atom as a function of sin θ/λ. The calculated structure factor $F_c(\underline{H})$ then is the sum over all atoms in the unit cell:

$$F_c(\underline{H}) = \sum_{j=1}^{n} f_j(H)\exp(-2\pi i\underline{H}.\underline{r}_j)^*,$$

where n is the number of atoms in the unit cell and $\exp(-2\pi i\underline{H}.\underline{r}_j)$ represents the dependence of the phase of the structure factor on the position of the j'th atom in the unit cell, $\underline{r}_j$ being the vector from the atom to an arbitrary origin in the unit cell.

The effect of thermal vibration is to smear the atomic point-center over a region of space, and is taken into account by a temperature factor. If the vibration of each

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$^*H = hx + ky + \ell z$.

atom is assumed to be isotropic, a single parameter B_j modifies the $F_c(\underline{H})$ by $\exp[-B_j(\sin^2\theta/\lambda^2)]$. If anisotropic vibration is allowed for, six components of the symmetrical second-order tensor $\underline{\underline{U}}_j$ must be determined, to modify $F_c(\underline{H})$ by $\exp(2\pi^2\underline{H}.\underline{\underline{U}}_j.\underline{H})$. The square root of the component U_{ii} of $\underline{\underline{U}}$ gives directly the average root mean square displacement (RMSD) of an atom in the i'th direction. In general, it is necessary to determine the three positional r_i and the temperature factor only for the atoms in the unit cell which are not related by symmetry, that is, the atoms in the asymmetric unit.

B. Data Collection and Reduction

Intensities were recorded either as proportional to the number of counts registered by a scintillation counter, or as proportional to the darkening of a spot on a photographic film, each film containing the reflections of one plane in reciprocal space, i.e. one layer line. Experimental methods of intensity estimation are discussed theoretically in Zachariasen,[18a] and more practically in Chapter 6 of Buerger[20] and Chapters 5 and 6 of Stout and Jensen.[21]

Two geometries for film data collection were used in this study, the Weissenberg method[21a] and the precession method,[22] both rotating crystal methods using monochromatic x-radiation. The directly and quickly obtained peak intensity (non-integrated) photographs obtained by these methods are useful in assessing the quality and symmetry of the crystal. However, more uniform and reproducible intensities are obtained from integrated photographs.[21b] Each reflection was obtained as a chart tracing from a Joyce-Loebl microdensitometer; the height of the peak was measured from the background (typically 5 mm but sometimes much higher), the unobserved reflections were flagged and assigned an intensity equal to the maximum value that it could have (see p. 25 for subsequent treatment of these unobserved or "less-than" reflections).

The narrow range of linear response of the film (a factor of 5 to 10) was overcome by one of two methods. In the Weissenberg case, where film-to-crystal distance was not critical, three films were exposed at once, each one acting as a filter for the one behind. For the precession technique, a series of timed exposures was taken. The different ranges of intensities were scaled together on the basis of common reflections, each pair of films of the same layer scaled using only those common reflections which lay in the region of linear response on both films. An "unobserved" reflection was one with an intensity indistinguishable from background even on the film with the greatest exposure.

The FORTRAN programs WEILPC and PRELPC (written by A. K. Das and I. D. Brown in this laboratory) applied Lorentz and polarization corrections to the intensities (from

Weissenberg and precession films respectively) and converted them to structure factors.

Each layer was scaled independently in the ultimate refinement, but for purposes of structure solution it was often useful to put all data on a common scale. This was done by least squares adjustment of common reflections using the FORTRAN program SCALE, written by J. S. Stephens in this laboratory.

The other method of recording intensity used a scintillation counter and was employed in conjunction with the Syntex computer controlled automatic four-circle diffractometer. The principles of the methods of crystal alignment and intensity collection are found in Stout & Jensen.[21c] The $2\theta/\theta$ scanning technique was employed. Standard deviations on the reflections were calculated according to:

$$\sigma(F_o^2) = [\sigma^2\text{counting} + (SF_o^2)^2]^{1/2}$$

where S is a machine instability constant, which generally lies between 0.01 and 0.1. After preliminary treatment by the program SYNTEX to make the diffractometer data compatible with the XRAY67 system, assignment of "unobserved" reflections as those measuring less than 3 $\sigma(F_o^2)$, Lorentz and polarization corrections, and conversion to structure factors were carried out by the XRAY67 system FORTRAN programs, DATCO3 and DATRDN.

Absolute statistical data scaling was carried out as a preliminary to calculation of three-dimensional Patterson Fourier synthesis and to direct methods of structure solution by the XRAY67 FORTRAN program DATFIX, using a variation of Wilson's method.[28] This gave an overall scale factor, an overall temperature factor, the E values[*] required for input into statistical phase determination (direct methods) and a summary of statistical agreement of the E's with the distribution for centric and acentric structures.

C. The Phase Problem and Fourier Methods

The electron density at a point x,y,z in the cell is given by:[21d]

$$\rho(x,y,z) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{\ell} F_{hk\ell}\exp[-2\pi i(hx+ky+lz)]$$

The structure factor (page 15) may be written in expanded form as:

$$F_{hk\ell} = \sum_{j} f_j \exp(2\pi i(hx_j+ky_j+\ell z_j))$$

Thus the electron density is the Fourier transform of the structure factors, and the structure factors are the Fourier transform of the electron density. However, in order to calculate the electron density it is necessary to know the phases of the structure factors, information which is not contained in the measured intensity data.

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[*] See page 22.

1. The Patterson Method.- One method of finding phases is to locate atom positions using the Patterson function,

$$P(\underline{s}) = \frac{1}{V}\sum_{hk\ell}\sum\sum |F_{o_{hk\ell}}|^2\cos(2\pi\underline{H}\cdot\underline{s}).$$

P is large only when $\underline{s}$ corresponds to an interatomic vector in the real unit cell; P is proportional to the product of electron densities of the two atoms defining the interatomic vector. The two dimensional, or projection Patterson is given by, e.g.:

$$P(x,y) = \frac{1}{A}\sum_{hk}\sum |F_{hk0}|^2\cos 2\pi(hx+ky)$$

Since $P(\underline{s})$ only requires the square of the structure factor, the Patterson Fourier can be calculated directly from the F_o's. The problem then is to find a consistent set of interatomic vectors which fit the resultant peaks. Resolution is poor, however, and overlap is large (the number of peaks is n^2-n, where n is the number of atoms in the unit cell). Only peaks due to the heaviest atoms are likely to be identifiable. Then the phases calculated for $F_c(\underline{H})$ for the heavier atoms may be assigned to $F_o(\underline{H})$'s in order to calculate $\rho(x,y,z)$. If these heavier atom positions represent enough electrons, and are well enough located, peaks may show up on the $\rho(x,y,z)$ (electron density) map for further atoms.

2. Electron Density Difference Synthesis.- Another helpful Fourier map may be calculated by substituting $F_o(\underline{H}) - F_c(\underline{H})$ for the $F_o(\underline{H})$'s in the expression for $\rho(x,y,z)$ to obtain a difference synthesis. In this map atoms which are located in the wrong place (i.e. excess electron density) appear as negative regions, and missing atoms appear as positive regions.

The locally written (J. S. Rutherford) FORTRAN program SYMFOU and the XRAY67 system FORTRAN program FOURR were used to calculate the Fourier maps of this study.

D. Direct Methods of Phase Determination*

The structural information in the intensities $(F(\underline{H})^2)$, which the Patterson function brings out, can be attacked more directly by statistical consideration of the probabilities of occurrence of relatively intense reflections, i.e. those measuring a substantial fraction of the intensity of $F_{000}{}^2$. These amplitudes must of necessity represent the in-phase scattering of most of the electrons in the unit cell, and therefore can provide structural information. In particular, relationships between the indices of two relatively strong reflections can lead to a high probability for the phase (or sign, since these methods have found practical applications mainly for centrosymmetric structures)

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*A brief discussion of the theoretical basis for direct methods can be found in Stout and Jensen, Chapter 13.[21e] For a more thorough treatment see Woolfson.[23]

of a third strong reflection related to the first two by the sum or difference of their Miller indices:

$$S(F_{hk\ell})\ S(F_{h'k'\ell'}).S(F_{h-h',k-k',\ell-\ell'}) \qquad (2)$$

where S means "sign of." A statistical analysis of all such relationships among the strong reflections can provide sufficient phases to lead to a solution of the structure.

The chances of success (the resolution) is increased if the atoms can be considered as vibrationless point atoms, and for this purpose a unitary structure factor is defined:

$$U_{hk\ell} = \frac{F_{hk\ell}}{e^{-B(\sin^2\theta/\lambda^2)}\{\sum_i^N f_{oi}\}}$$

where f_o's are the scattering factors[19] and B is an overall temperature factor. The average value of $|U|$ drops as the number of atoms in the cell increase, i.e. as the probability of all atoms diffracting in phases decreases, but the sign relationships are still of value in phase determination, though based on probabilities rather than certainties. To scale the structure factors relative to the number and sizes of atoms present, Karle and Hauptman[24b] have introduced the normalized structure factor E_{hk}, defined by

$$E^2_{hk\ell} = \frac{U^2_{hk\ell}}{U^2}$$

where $\overline{U}^2$ is determined for each class of reflections in the cell, as determined by the space groups symmetry. Cochran and Woolfson[25] proposed that the probability of equation (2) being true is:

$$P = 1/2 + 1/2 \tanh\{(\sigma_3/\sigma_2^{3/2})|E_{hk\ell} \cdot E_{h'k'\ell} \cdot E_{h-h',k-k',\ell-\ell}|\}$$

$$\text{where } \sigma_3 = \sum_i^N n_i^3,\ \sigma_2 = \sum_i^N n_i^2, \text{ and } n_i = \frac{fi}{\sum_j f_j}.$$

The XRAY67 system FORTRAN program SIGMA2 and PHASE were used to calculate the sign relationships and statistical correlations necessary to arrive at a set of signed E values. Fourier syntheses (E-maps) of these signed E's were then prepared by the XRAY67 system program FOURR.

E. Least Squares Refinement

The procedure of least squares refinement makes small adjustments to parameters describing the model of the structure so as to minimize the function R_2:

$$R_2^2 = \frac{\sum_{\underline{H}} w(\underline{H})\,||F_o(\underline{H})|-|F_c(\underline{H})||^2}{\sum w(\underline{H})\,|F_o(\underline{H})|^2}$$

where $w(\underline{H})$ is a weight assigned to the reflection $\underline{H}$.* R_2 is known as the "normalized residue" or "weighted R-factor."

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*See p.24 for methods of assigning weights; p.26 for use of these weights in calculating standard deviations in the parameters. The purpose of such weighting is to make the refinement on the structure factors independent of their average magnitudes.

More commonly used as an indicator of quality of fit between data and model is the "unweighted R-factor", or just "R-factor":

$$R_1 = \frac{\sum ||F_o(\underline{H})|-|F_c(\underline{H})||}{\sum\limits_{(\underline{H})} |F_o(\underline{H})|}$$

The FORTRAN program CUDLS, written by J. S. Stephens in this laboratory, was used to calculate structure factors and perform the least squares refinements. Where it was necessary to refine groups of atoms (e.g. benzene rings) as rigid bodies the related program GROUPLS, by the same author, was used. These programs also calculated interatomic distances and angles and their standard deviations, and prepared the data for input to SYMFOU, the Fourier mapping program by J. S. Rutherford.

There are several methods of assigning weights $w(\underline{H})$ to reflections. The most direct way is to assign an estimate of the error in the individual reflection (estimated standard deviation, $\sigma(\underline{H})$). For diffractometer data this is based on the counting statistics (see p.18); $w(\underline{H})$ then is most simply $\frac{1}{\sigma(\underline{H})^2}$. The effects of some systematic errors, however, are not readily apparent, and are not taken into account in considering counting statistics alone. For early stages of refinement, when phases are more likely to be correct for stronger reflections, the use of unit weights

($w(\underline{H}) = 1$ for all reflections) tends to force convergence of the refinement. But to account for much of the unknown systematic errors, which are often a function of $|F_o(\underline{H})|$, weights can be chosen so that the function $w(\underline{H})||F_o(\underline{H})|-|F_c(\underline{H})||^2$, (or $w(\underline{H})\Delta_F{}^2$) is on the average not a function of $|F_o(\underline{H})|$.[26] This is done by fitting the curve of the average value of $||F_o(\underline{H})||^2$ to a power series in $|F_o(\underline{H})|$:

$$\frac{1}{w(\underline{H})} = A + B|F_o(\underline{H})| + C|F_o(\underline{H})|^2.$$

Information from counting statistics can be incorporated into this Cruickshank[26] weighting scheme:

$$\frac{1}{w(\underline{H})^2} = A + B|F_o(\underline{H})| + C|F_o(\underline{H})|^2 + D\left|\frac{\sigma_F}{F_o(\underline{H})}\right|^2,$$

where σ_F, the estimated standard deviation in the structure factor, is derived from the counting statistics.*

Reflections unobserved on films were treated in the refinement as being "less than" the lowest intensity measurable in that region of that film. Thus if the structure factor (F_c) calculates less than the maximum F_o value that the reflection could have had and still not be observed, it is ignored in the least squares refinement; whereas if it calculates more than that amount, then the model is in disagreement with observation to at least the extent of the excess of F_c over F_o. The contribution to the

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*See page 18.

least squares refinement is then taken as $[F_c - (\text{fmin})F_o]$, where fmin was usually taken as 0.90 or 0.95, to reflect the probability that the intensity of the "unobserved" reflection is somewhat less than the upper limit possible.

Diffractometer measured reflections whose intensities were less than three standard deviations (as estimated from the counting statistics) were also treated as "unobserved" reflections in the least squares refinement (fmin = 1.0); reflections with negative intensities were discarded.

F. Errors in Structural Parameters

The general equation for the estimated standard deviation σ for any parameter p_i is[27]

$$\sigma^2_{pi} = \frac{b_{ii}\left(\sum_{r=1}^{m} w_r \Delta F_r^{\,2}\right)}{m-n}$$

where b_{ii} is the ith diagonal element of the inverse matrix, w_r the weight of the rth ΔF, m the number of F_o's, and n the number of parameters. Comparison of the least-squares parameter shifts to the errors in them (shift/error) can be used as a guide to the course of refinement. Refinement by full-matrix least squares is usually considered completed when (parameter change)/σ_p, or shift/error, <0.3 for each parameter in a centric structure; for acentric structures, where the phases as well as the parameters can make small adjustments to fit the structure factors, refinement is usually continued until the maximum shift/error is 0.05.[21 f]

The standard deviation in a bond length L between two uncorrelated atoms can be derived from the σ_p's;[21g] for the monoclinic case:

$$\sigma_L{}^2 = (\sigma_{x_1}{}^2 + \sigma_{x_2}{}^2)\left(\frac{a\Delta x + c\Delta y\cos\beta}{L}\right)^2 + (\sigma_{y_1}{}^2)\left(\frac{b\Delta y}{L}\right)^2$$

$$+ (\sigma_{z_1}{}^2 + \sigma_{z_2}{}^2)\left(\frac{c\Delta z + a\Delta x\cos\beta}{L}\right)^2$$

where σ_{x_1} and σ_{x_2} are the standard deviation (σ_p's) of atoms 1 and 2 in the direction, and similarly for σ_{y_1}, σ_{y_2}, σ_{z_1}, σ_{z_2}; Δx is $x_2 - x_1$, etc., and L is the bond length.

For the orthorhombic case:

$$\sigma_L{}^2 = (\sigma_{x_1}{}^2 + \sigma_{x_2}{}^2)\left\{\frac{a\Delta x}{L}\right\}^2 + (\sigma_{y_1}{}^2 + \sigma_{y_2}{}^2)\frac{b\Delta y^2}{L}$$

$$+ (\sigma_{z_1}{}^2 + \sigma_{z_2}{}^2)\frac{c\Delta z^2}{L}.$$

General equations of this type are used by CUDLS in arriving at errors in bond length.

If the errors are isotropic, the equations reduce to $\sigma_L{}^2 = \sigma_A{}^2 + \sigma_B{}^2$, where A and B are the two atoms. Similarly for the comparison of two bond lengths, the standard deviation in the difference between them is $\sigma_\Delta{}^2 = \sigma_1{}^2 + \sigma_2{}^2$. In averaging bonds of the "same kind" to obtain a "best value" for that type of length[29a]:

$$\bar{x} = \frac{\sum_i x_i/\sigma_i^2}{\sum_i 1/\sigma_i^2} \quad \text{and} \quad \sigma^2\,(x) = \frac{1}{\sum(1/\sigma_i^2)},$$

where x_i is a bond length and σ_i is its estimated standard deviation.

These considerations apply strictly only to independent uncorrelated atoms. More generally, $\sigma_\ell^2 = \sigma_A^2 + \sigma_B^2 - 2\mathrm{cov}(A,B)$[27a] where cov(A,B) is a measure of the dependence of the positions of A and B upon each other[27] (see below). For example, for averaging two bond lengths which are correlated through a shared atom, neglecting other correlations and assuming isotropic errors,[21h]

$$\sigma_L^2 = 1/4[2\sigma_A^2\cos^2(\theta/2) + \sigma_B^2] + 1/4[2\sigma_A^2\cos^2(\theta/2) + \sigma_C^2].$$

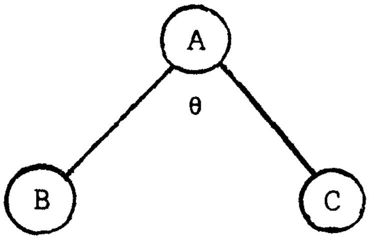

Figure 2

And for comparison between two such shared-atom bond lengths,

$$\sigma_\Delta^2 = \sigma_{AB}^2 + \sigma_{AC}^2 + \sigma_A^2\cos\theta,$$

where σ_Δ is the standard deviation in the difference between the two bonds, σ_{AB} and σ_{AC} are the errors in the two bonds,

σ_A is the positional error in the shared atom, θ is the bond angle (see Figure 1.), and $(-\sigma_A{}^2\cos\theta)$ is the covariance in the bonds. For a bond angle of 107°, common in polysulfur chains, the resulting increase in σ_A is about 6%. All other correlations were assumed to be smaller than this, and were neglected. Standard deviations in bond angles are calculated similarly; for isotropic errors and uncorrelated atoms,

$$\sigma_{(\theta)}{}^2 = \frac{\sigma_B{}^2}{(AB)^2} + \frac{\sigma_C{}^2}{(AC)^2} + \frac{\sigma_A{}^2\,(BC)^2}{(AB)^2(AC)^2}.$$

Preliminary cell parameters were measured from peak-intensity films, but more accurate parameters were measured in all cases in this study by careful centering of several (15-30) reflections on the Syntex diffractometer and least squares analysis of the 2θ values[21 i] obtained by the XRAY67 system FORTRAN program PARAM. This program calculates the standard deviations in the cell parameters, which are then incorporated into the bond lengths and angles by the FORTRAN program MOLG, locally written by I. D. Brown, et. al.

CHAPTER 3: CRYSTAL AND MOLECULAR STRUCTURE OF BENZYLIDENIMINE TETRASULFIDE (BITS)

A. Solution of the Structure

The compound was obtained from the reaction of sulfur plus benzylamine, with lead oxide as a sulfide scavenger:*

$$7S + 2C_6H_5CH_2NH_2 + 3PbO \rightarrow 3PbS + C_6H_5CHNS_4NCHC_6H_5 + 3H_2O.$$

The product was purified by chromatography on a silica gel column, followed by recrystallization from hot methanol to give yellow needles melting at 100.5-102°C. Crystals for x-ray analysis were grown from benzene solution.

hk0 and hkl Weissenberg photographs were used to establish the crystal class as monoclinic. These films and all subsequent ones were consistent only with systematic absences of the type $h0\ell$ for h odd and 0k0 for k odd, establishing the space group as $P2_1/a$. Accurate unit cell parameters were determined by least squares adjustment of a, b,c and β to the 2θ angles of 15 well-centered reflections (measured on the Syntex automatic diffractometer) to be: $a=13.851(4)$Å, $b=19.721(16)$Å, $c=5.981(2)$Å, $\beta=101.33(4)^\circ$.

The density of benzylidenimine tetrasulfide (BITS) was found by flotation in n-heptane/CCl_4 to be $1.395 g/cm^3$; calculated for $Z=4$: $1.404 g/cm^3$.

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*See page 4 and reference (14) for other methods of synthesis.

Intensity data were obtained from integrated Weissenberg and precession photographs. Hkn data with n=0-5 were recorded with CuKα radiation using an integrating Weissenberg camera from a crystal measuring 0.30x0.34x0.58mm, mounted with the axis in the needle direction (001). Skl data, s=0-4, were recorded with MoKα radiation using an integrating Buerger procession camera from a crystal measuring 0.12x0.24x0.6mm, mounted in the needle direction (which in this case, however, was the 010.) The intensities were measured with a Joyce-Loebl microdensitometer.

No absorption corrections were made. The maximum variations in transmission factors for the two crystals were ±9% (first crystal, CuKα, $\mu = 52\ cm^{-1}$), and ±3% (2nd crystal, MoKα, $\mu = 5.6\ cm^{-1}$).

The structure factors obtained after Lorentz and polarization corrections were scaled together by a least squares adjustment of common reflections. The XRAY67 program DATFIX* was then used to estimate the overall temperature factor and scale factor and to calculate quasi-normalized structure factors (E's). The XRAY67 programs SIGMA2 and PHASE were applied to the resulting E's to obtain phases (signs); PHASE determined signs of 207 of the strongest E_H's, 114 plus and 93 minus. From the subsequently prepared Fourier synthesis (by the XRAY67 program FOURR)

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*See pages 21-23 for the use of direct methods programs.

the positions of the four sulfur atoms could be discerned. Electron density and difference syntheses* using the phases obtained from these sulfur positions for all the structure factors (F_o's) yielded the positions of the two nitrogen atoms and two of the carbon atoms. A least squares cycle (CUDLS) using these positions followed by another set of electron density and difference syntheses (maps) yielded two new carbon atoms. Planarity of the C_7NS moiety was assumed, on the basis of sp^2 hybridization at the carbon and nitrogen atoms, and of the results of the solved structure of benzylidenimine trisulfide (see Chapter 4). The position of the atoms of the benzylidene group were calculated on the reasonable assumption of 120^o bond angles at carbon and nitrogen. Structure factor least squares refinement was continued restricting the carbon atoms of the benzene rings to move only as a rigid group (GROUPLS) until the R-factor was down to 0.20. By then enough of the phases were correct that refinement of all carbon atoms was well-behaved and use of the least squares program CUDLS was resumed. Cruickshank weighting schemes $w^2=1/(A+BF_o+CF_o^2)$ were applied so as to normalize $w(F_o-F_c)^2$ over the range of intensities. Up to this point isotropic temperature factors had been applied to all atoms.

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*This and all subsequent Fourier syntheses were carried out by the FORTRAN program SYMFOU.

Anisotropic temperature factors were refined first on the sulfur atoms only, then on all non-hydrogen atoms. Hydrogen atoms were located in the least-squares planes of the benzene rings, 0.97Å from the appropriate carbon atom in each case, with C-C-H angles of 120° and an isotropic temperature factor arbitrarily taken to be .07Å^2. None of the hydrogen atom parameters was refined. The R-factor at this point was 0.075.

The standard deviation on the bond lengths in the benzene rings was 0.013Å, but the average deviation from the mean ring C-C distance (1.372Å) was .017Å, and the maximum deviation from the mean was 0.054Å. Large thermal ellipsoids, elongated primarily out of the plane, were also noted for the ring atoms, suggesting libration or disorder effects in the rings. An attempt was made to correct for these effects by substituting two half-atoms for the most discrepant carbon atoms in each benzene ring and refining the positions and populations of the two fractional atoms separately in each case. Two best least-squares planes for each benzene ring were then selected from among the possible combinations of 6 atom rings, and carbon atom positions for two idealized hexagonal rings calculated; these rings were refined as rigid groups by the program GROUPLS. The number of variables for two rings with one fractional population each and isotropic temperature factors on each of the individual atoms was 26, compared with 24 for a single ring with unit population on each carbon atom varied independently with isotropic temperature factors, and 54 variables with anisotropic temperature factors on the carbon atoms. No R-factor improvement was obtained from the disordered ring model, and so the undisordered model was restored.

However, in order to take some cognizance of the deviations of the rings from the accepted hexagonal shape, an increase in the standard deviations derived from the least-squares fit by a factor of $\sqrt{2}$ was applied. This had the effect of reducing the maximum deviation from the mean C-C distance in the benzene rings from 4σ to less than 3σ.

Increasing all the σ's by a factor does not, of course, substitute for making systematic corrections, but doing so would reflect the greater uncertainties that arise, and the possibility that the data may contain a greater degree of random error than is reflected in the R-factor. Evidence for such a possibility was found during averaging (see below), when about 20% of reflections common to two films were found to differ by 10-25%. In some cases it was possible to decide which was the less reliable by inspection of the films; in other cases they were averaged. Such a possibility is further suggested by the difference between the two carbon-nitrogen bond lengths, which approaches significance despite the apparent chemical equivalence.

Recollection of the data by diffractometer to obtain high quality data on a common scale, is recommended to resolve the anomolous benzene ring and improve confidence in all bond lengths.

Common reflections were averaged on the basis of scales least-squares adjusted for each layer to the F_c's at an R-factor of 0.075. The total number of symmetry independent reflections was 2565, 1211 of which were intense enough to measure on at least one film. Hydrogens were readjusted to the least-squares planes of the carbon atoms of the appropriate ring, and to C-H distances of 0.97(1)Å and C-C-H angles of 120(2)°, before the last cycle. Refinement was taken as completed when the maximum shift/error was 0.56, the average shift/error at that point being 0.12. The final unweighted R-factor was 0.063. The final Cruickshank weighting scheme coefficients were A=0.54, B=-0.004, C=0.0037, and the final weighted R-factor for all reflections was R=0.084.

B. Description of the Structure

The final values of the refined positional and thermal parameters of all non-hydrogen atoms, and the assumed parameters for the hydrogen atoms, are given in Table 1. Table 2 lists observed structure factors and those calculated from the final positional and thermal parameters of the refinement. Table 3 summarizes the bond lengths and angles, and Table 4 some inter-and intra-molecular contact distances, dihedral angles, and least-squares planes. Figure 3 shows a stereoscopic view of the molecule down the a axis and

Table 1: BITS Positional and Thermal Parameters (U_{ij} in A^2x10^3)

Atom	x/a	y/b	z/c	U11	U22	U33	U12	U13	U23	RMSD1	RMSD2	RMSD3	Atom
S1	.5695(2)	.3790(1)	.5514(4)	98(2)	87(1)	85(1)	4(1)	4(1)	-12(1)	.339	.296	.270	S1
S2	.5429(2)	.44208(9)	.2793(4)	84(2)	57(1)	120(1)	-10(1)	15(1)	0(1)	.350	.295	.232	S2
S3	.3903(2)	.44981(9)	.1828(4)	93(2)	53(1)	119(1)	7(1)	10(1)	-2(1)	.355	.302	.227	S3
S4	.3518(2)	.3953(1)	.8913(3)	104(2)	69(1)	93(1)	-4(1)	0(1)	11(1)	.354	.289	.255	S4
N1	.5851(5)	.2982(3)	.4703(10	90(5)	81(4)	80(4)	0(3)	13(3)	-1(3)	.304	.284	.281	N1
N2	.3289(5)	.3140(3)	.9511(10)	101(5)	66(3)	76(4)	-7(3)	9(3)	-5(3)	.326	.279	.250	N2
C1	.5767(6)	.2785(4)	.2671(11)	71(5)	78(4)	75(4)	14(4)	7(3)	7(3)	.293	.276	.254	C1
C2	.5877(6)	.2066(3)	.2136(12)	65(5)	73(4)	83(4)	5(4)	11(3)	8(3)	.297	.271	.248	C2
C3	.5607(7)	.1844(4)	.9957(13)	93(7)	89(5)	85(5)	15(5)	1(4)	5(4)	.337	.304	.260	C3
C4	.5698(8)	.1165(5)	.9400(16)	100(8)	114(7)	115(7)	7(6)	10(6)	-28(5)	.386	.311	.294	C4
C5	.6100(9)	.0715(4)	.1122(20)	132(9)	79(5)	135(8)	7(6)	31(7)	-5(5)	.371	.360	.278	C5
C6	.6405(9)	.0940(5)	.3218(17)	141(10)	98(6)	110(7)	22(6)	19(6)	23(5)	.388	.352	.277	C6
C7	.6322(8)	.1629(4)	.3824(14)	134(9)	79(5)	98(6)	20(5)	15(5)	6(4)	.379	.315	.268	C7
C8	.3403(5)	.2909(3)	.1457(11)	57(5)	66(4)	79(4)	0(3)	13(3)	-12(3)	.295	.243	.238	C8
C9	.3240(5)	.2190(3)	.1924(11)	46(4)	66(4)	80(4)	-2(3)	9(3)	-3(3)	.286	.256	.214	C9
C10	.3506(6)	.1934(4)	.4094(12)	96(7)	89(5)	75(4)	-15(5)	8(4)	-1(4)	.332	.286	.266	C10
C11	.3378(8)	.1257(5)	.4487(14)	114(8)	101(6)	88(5)	-4(5)	2(5)	23(4)	.370	.323	.263	C11
C12	.2970(7)	.0831(4)	.2780(15)	93(7)	65(4)	115(6)	-16(4)	10(5)	8(4)	.355	.307	.238	C12
C13	.2687(7)	.1088(4)	.0639(14)	97(7)	80(5)	96(5)	-12(5)	4(4)	-8(4)	.339	.308	.262	C13
C14	.2812(6)	.1759(3)	.0184(12)	65(5)	64(4)	93(4)	-6(3)	3(4)	2(3)	.319	.260	.241	C14

H1	.5497	.3114	.1510	H8	.3691	.3202	.2699
H3	.5295	.2153	.8755	H10	.3816	.2242	.5290
H4	.5481	.0996	.7873	H11	.3570	.1074	.6015
H5	.6192	.0243	.0764	H12	.2865	.0354	.3088
H6	.6695	.0647	.4489	H13	.2399	.0781	-.0566
H7	.6524	.1788	.5399	H14	.2626	.1941	-.1361

Table 2: BITS Observed and Calculated Structure Factors (x10)
Unobserved and unreliable indicated by * and U respectively

Table 2. (continued)

[illegible]

Table 3

Molecular geometry of benzylidenimine tetrasulfide (BITS)

(e.s.d.'s in parentheses)

Bond distances in Å

S_1-S_2	2.024(4)	C_1-C_2	1.467(14)	C_8-C_9	1.469(13)
S_2-S_3	2.084(4)	C_2-C_3	1.356(14)	C_9-C_{10}	1.373(13)
S_3-S_4	2.028(4)	C_3-C_4	1.392(18)	$C_{10}-C_{11}$	1.373(17)
S_1-N_1	1.691(9)	C_4-C_5	1.389(20)	$C_{11}-C_{12}$	1.357(17)
S_4-N_2	1.686(9)	C_5-C_6	1.319(21)	$C_{12}-C_{13}$	1.362(17)
N_1-C_1	1.260(13)	C_6-C_7	1.417(18)	$C_{13}-C_{14}$	1.369(14)
N_2-C_8	1.232(13)	C_7-C_2	1.381(14)	$C_{14}-C_9$	1.384(13)

Bond angles in degrees

$S_1-S_2-S_3$	106.4(3)	$C_6-C_7-C_2$	117.4(13)
$S_2-S_3-S_4$	106.3(3)	$C_7-C_2-C_3$	120.1(14)
$N_1-S_1-S_2$	111.2(4)	$C_7-C_2-C_1$	119.7(13)
$N_2-S_4-S_3$	110.5(4)	$N_2-C_8-C_9$	122.8(11)
$S_1-N_1-C_1$	125.1(6)	$C_8-C_9-C_{10}$	120.7(11)
$S_4-N_2-C_8$	124.0(6)	$C_9-C_{10}-C_{11}$	120.0(12)
$N_1-C_1-C_2$	121.0(11)	$C_{10}-C_{11}-C_{12}$	121.5(14)
$C_1-C_2-C_3$	120.1(13)	$C_{11}-C_{12}-C_{13}$	118.5(15)
$C_2-C_3-C_4$	121.4(13)	$C_{12}-C_{13}-C_{14}$	121.5(15)
$C_3-C_4-C_5$	118.6(16)	$C_{14}-C_9-C_{10}$	118.7(12)
$C_4-C_5-C_6$	119.8(17)	$C_{14}-C_9-C_8$	120.6(12)
$C_5-C_6-C_7$	122.6(19)		

Table 4: BITS Molecular Geometry

Selected intermolecular contact distances (Å)

$S_1 \ldots S_3$	3.727(4)	$S_2 \ldots C_{12}$	3.556(14)	$C_7 \ldots C_8$	3.570(18)
$S_2 \ldots S_3$	3.747(4)	$C_1 \ldots C_9$	3.540(14)	$C_2 \ldots C_8$	3.601(16)
$S_2 \ldots S_4$	3.747(4)	$C_1 \ldots C_{14}$	3.564(16)	$C_2 \ldots C_9$	3.611(14)

Selected intramolecular contact distances (Å)

$C_1 \ldots C_8$	3.221(14)	$C_1 \ldots C_9$	3.635(14)	$C_2 \ldots C_9$	3.639(14)

Selected dihedral angles

$S_1\text{-}S_2\text{-}S_3\text{-}S_4$	105.0°	$N_1\text{-}S_1\text{-}S_2\text{-}S_3$	93.8°	$N_2\text{-}S_4\text{-}S_3\text{-}S_2$	89.8°

Selected least squares planes

Atoms in plane		Direction cosines of plane			Deviation from plane (|Å|)	
Determining	Relative	α	β	γ	Maximum	Average
$C_2\text{-}C_7$		.96262	.19232	-.19071	.029	.015
	S_1				.378	
	N_1				.294	
	C_1				.024	
$C_9\text{-}C_{14}$		.96223	-.20191	-.18260	.011	.006
	S_4				.343	
	N_2				.231	
	C_8				.045	
$C_1\text{-}C_7$		.96192	.19673	-.18973	.022	.015
$C_8\text{-}C_{14}$		.96072	-.21037	-.18100	.019	.010
$N_1, C_1\text{-}C_7$		.96178	.22300	-.15887	.132	.058
$N_2, C_8\text{-}C_{14}$		.95994	-.23008	-.15991	.094	.043
$S_1, N_1, C_1\text{-}C_7$		.95998	.23603	-.15073	.126	.066
$S_4, N_2, C_8\text{-}C_{14}$		.95769	-.24374	-.15306	.092	.052

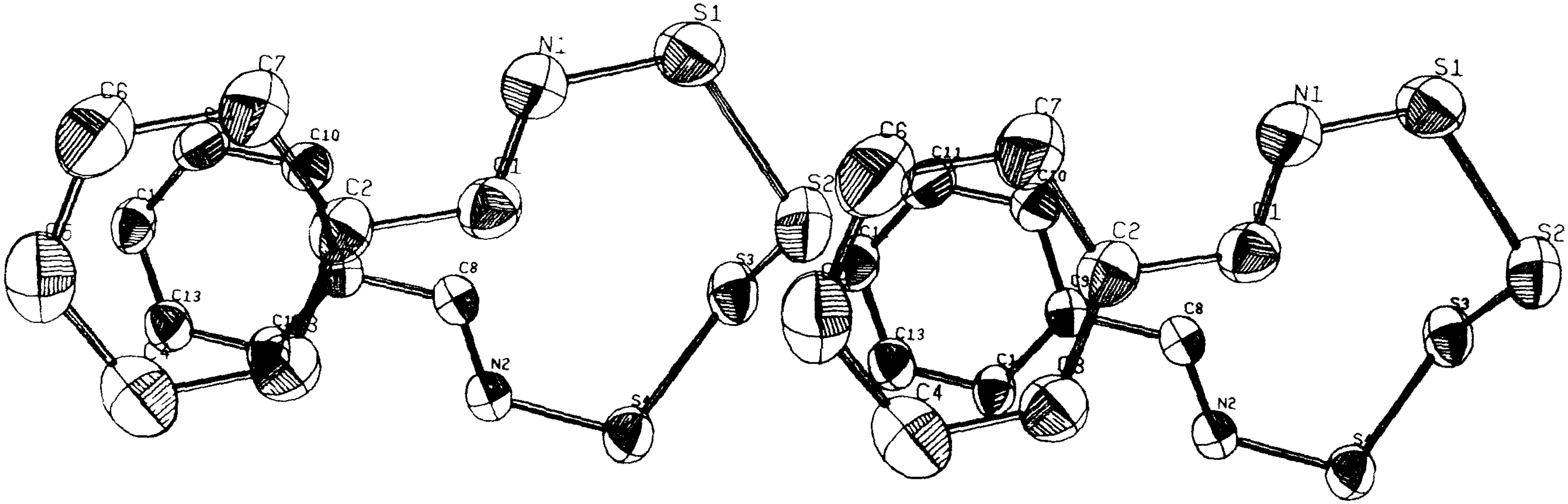


Figure 3.

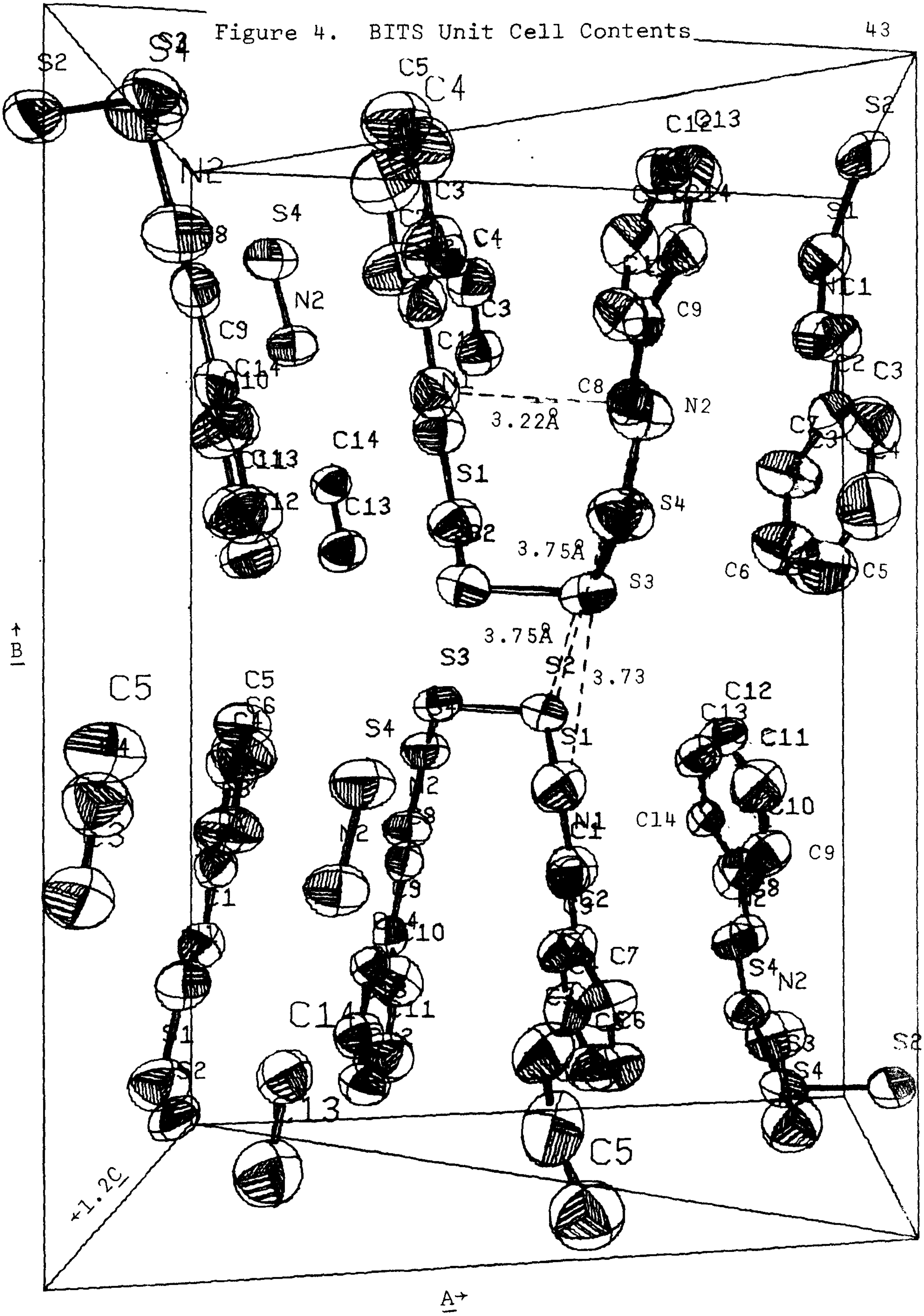
Stereoscopic view of the BITS molecule down the *a* axis

Figure 4 shows packing of the molecules in the unit cell.

The structure contains a chain of four sulfur atoms with the molecule folding back upon itself in such a way that the two phenyl groups are nearly superimposed when projected down the a axis. The planes of the phenyl rings deviate by about 9.2° from coplanarity with the closest approach being the C(1)-C(8) separation of 3.22(1)Å. The atoms of the S_4 chain form a spiral nearly showing a non-crystallographic 3_1 axis extending over the four sulfurs, which intersects the planes of the phenyl groups at 60° and 62° (Figure 5).

The largest deviation from planarity of any atom in the benzene rings is 0.03Å(for C_2). The average C-C distances for the two rings are 1.375Å for C_2-C_7 and 1.370Å for C_9-C_{14}. The overall mean ring C-C bond length is 1.372, with the maximum and average deviations from the mean being 0.053Å and 0.017Å, respectively. The average C-C-C angles for both rings are 120.0. The maximum and average deviations from the mean for both rings are 2.65° and 1.11°, respectively. The average N-S, C=N, and benzylidene C-C distances are respectively 1.689(6)Å, 1.246(9)Å and 1.468(10)Å. The average SSS, SSN, SNC, and NCC angles are respectively 106.34(20)°, 110.9(3)°, 124.5(4)°, and 121.9(8)°. The average SSSN dihedral angle is 91.8°. These bond lengths and angles are reasonable in comparison with known structures--see Chapter 6.

Figure 4. BITS Unit Cell Contents



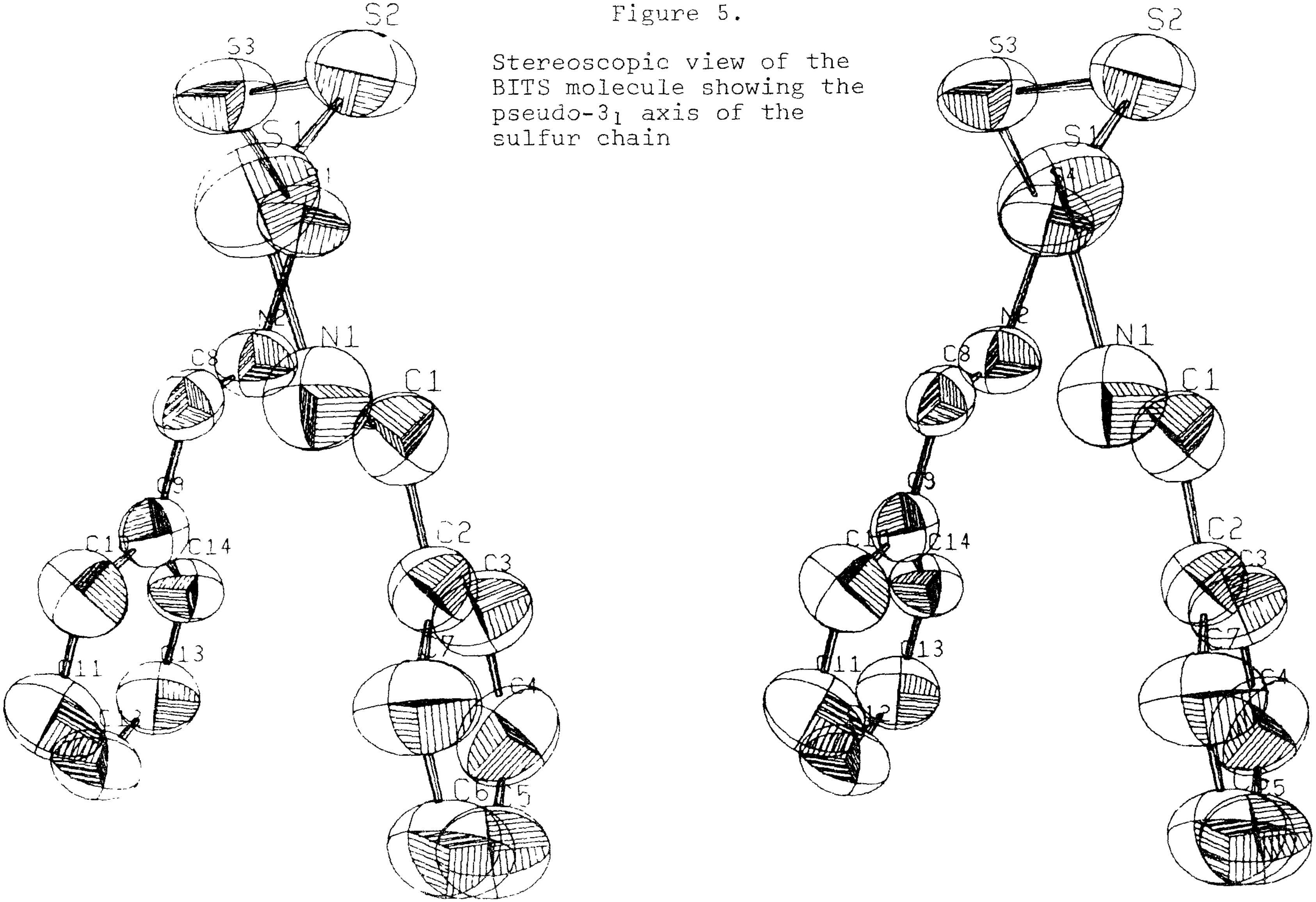


Figure 5.

Stereoscopic view of the BITS molecule showing the pseudo-3_1 axis of the sulfur chain

The sulfur-sulfur bond lengths, 2.024(4), 2.084(4), and 2.028(4)Å, showed distinct alternation, and therefore (as discussed in the Introduction) the solutions of the structures of BITrS and BIDS were sought. These bond lengths are discussed further in Chapter 6. Thermal parameters are reasonable considering the low melting point of the compound, with the exceptions noted on page 33.

The benzylidinimine tetrasulfide molecule features a spiral of sulfur atoms with the rest of the molecule on one side of the spiral. Within the unit cell two spirals pack back-to-back making van der Waals contact (3.75Å). These pairs then stack throughout the crystal along the $\underline{c}$ direction, such that there are columns of sulfur atoms with radii of about 3Å passing through the crystal in the $\underline{c}$ direction. The separation from periphery to periphery is about 5Å. Looking down the $\underline{a}$ axis of the cell or through the cell center in the $\underline{a}$ direction there is a space about 3 3/4 Å wide. On either side are alternately sulfur atoms S_2 and S_3 of the chain, then the edges of the two benzene rings, then the two sulfur atoms again, and so on.

The closest intermolecular contact distance (ignoring hydrogen atoms) is 3.54Å ($C_1 \ldots C_9$, effective thickness of aromatic ring 3.4Å); the closest one involving sulfur ($C_{12} \ldots S_2$) is 3.56Å (van der Waals sum 3.25Å). Pauling's estimate of the van der Waals radius for sulfur is 1.85Å; the closest S...S intermolecular contact is 3.73Å, with two others at 3.75Å. No unusually close non-bonding distances are found.

CHAPTER 4: CRYSTAL AND MOLECULAR STRUCTURE OF BENZYLIDENIMINE TRISULFIDE (BITrS)

A. Solution of the Structure

The same reactions which produce benzylidenimine tetrasulfide[14] also produce the trisulfide and disulfide as byproducts in much smaller yields. Yields of desired polysulfide can be optimized from some of these reactions by adjustment of the sulfur-amine ratios to the necessary stoichiometric values,[14] i.e.:

$$(3+x)S + 2C_6H_5CH_2NH_2 + 3PbO \rightarrow 3PbS + C_6H_5CHNS_xNCHC_6H_5 + 3H_2O$$

Specifically for benzylidenimine trisulfide (BITrS):

$$6S + 2C_6H_5CH_2NH_2 + 3PbO \rightarrow 3PbS + BITrS,$$

i.e. a 3:1 ratio of sulfur to benzylamine. The concentration of BITrS in the product was increased by chromatography on a silica gel column to give the trisulfide containing only small amounts of di- and tetrasulfide. This enriched mixture was then subjected to fractional crystalization from benzene to give white needles melting at 125-126°C.[14c] The size of crystal that could be obtained for x-ray studies was limited by the tendency of the compound to decompose on standing in solution.

Study of hk0 and hk1 Weissenberg photographs established that the crystals belong to the orthorhombic system. These photographs and all subsequent ones were in agreement only with systematic absences of type h00 for h odd and 0k0 for k odd, characteristic of the space group $P2_1 2_1 2$. Accurate unit cell parameters were determined by least squares refinement of a, b, and c to the measured 2θ angles of 22 well-centered reflections, to be a= 16.639(12), b= 10.003(13), c= 4.287(5)Å.

hk0, hk1, and hk2 intensity data were recorded with CuKα radiation using an integrating Weissenberg camera from a crystal 0.02x0.02x0.41 mm mounted in the needle direction (001). The rest of the data was obtained from a crystal 0.06x0.12x0.175 mm, again mounted in the needle direction (which this time, however, was 010). h0ℓ and h1ℓ photographs were recorded with CuKα radiation using an integrating Weissenberg camera; pkℓ data, p= 0-2, hkq data, q= 0-1, and (ℓ+m)kℓ data, m= 0-5 were recorded with MoKα radiation using an integrating precession camera. No absorption corrections were made. For the first crystal, μr(cylindrical)= 0.03. The second crystal was more irregular, the maximum variation in transmission factors being ±12% for CuKα(μ = 44.8 cm^{-1}) radiation and ±1.5% for MoKα(μ = 4.94 cm^{-1}). The intensities were measured with a Joyce-Loebl microdensitometer; the totals are summarized in Table 5.

Density and cell volume (see Table 6) required that there be two molecules per unit cell, implying 1/2 molecule per asymmetric unit. Thus the central sulfur had to lie on the two-fold axis. The hk0 projection Patterson (Figure 6)

Table 5

BITrS observed and calculated structure factors(x10)

Unobserved reflections indicated by *

H	K		FOBS	FCLC
			L = 0	
2	0		155	155
4	0		326	300
6	0		396	334
8	0		639	637
10	0		205	225
12	0		200	196
14	0	*	77	33
16	0	*	78	46
18	0	*	60	47
1	1		409	563
2	1		76	63
3	1		593	674
4	1		257	255
5	1		458	450
6	1		121	130
7	1		398	425
8	1		148	146
9	1		95	86
10	1		224	202
11	1		106	152
12	1		233	215
13	1		131	165
14	1		83	75
15	1	*	78	4
16	1		87	95
17	1		64	55
18	1		65	65
19	1	*	53	21
0	2		182	207
2	2	*	63	25
3	2		201	240
4	2	*	65	46
5	2		142	144
7	2	*	73	34
8	2	*	73	3
9	2		321	291
10	2		116	114
11	2		136	121
12	2	*	81	7
13	2		290	255
14	2	*	84	65
15	2	*	76	52
16	2		86	85
17	2	*	64	37
18	2	*	59	19
19	2		63	62
1	3		590	595
2	3		137	152
3	3		76	59
4	3		340	294
5	3	*	61	0
6	3		110	109
7	3		91	93
8	3		127	119
9	3		182	164
10	3	*	75	21
11	3	*	79	5
12	3		83	76
13	3		174	167
14	3		78	85
15	3	*	78	15
16	3	*	70	24
0	4	*	53	31
1	4		120	119
2	4		139	142
3	4		124	125
4	4	*	77	13
5	4		115	115
6	4		159	131
7	4		85	79
8	4	*	84	45
9	4		155	121
10	4	*	75	25
11	4		199	191
12	4	*	76	32
13	4		78	81
14	4		96	101
15	4		77	77
16	4		64	55
1	5		195	205
2	5		80	81
3	5		459	440
4	5		185	174
5	5	*	79	32
6	5	*	82	25
7	5		140	142
8	5		163	102
9	5		166	165
10	5		162	170
11	5		149	145
12	5		136	144
13	5	*	78	18
0	6		404	386
1	6	*	80	49
2	6		307	355
3	6		70	65
4	6		185	177
5	6	*	81	37
6	6		249	227
7	6	*	79	10
8	6		223	200
9	6	*	75	36
10	6		217	216
11	6	*	78	68
12	6	*	78	55
13	6	*	77	6
1	7		177	169
2	7		95	97
3	7		229	227
4	7		129	125
5	7		123	123
6	7	*	82	10
7	7		124	115
8	7	*	77	23
9	7		109	112
10	7		78	89
11	7	*	78	62
12	7		135	141
13	7	*	74	57
0	8	*	72	30
1	8		98	91
2	8	*	75	40
3	8		120	121
4	8	*	70	14
5	8	*	83	38
6	8	*	84	12
7	8	*	83	60
8	8	*	85	0
9	8	*	84	52
10	8		79	74
11	8		152	137
1	9		151	159
2	9	*	84	1
3	9	*	78	11
4	9	*	68	4
5	9	*	68	11
6	9	*	67	29
7	9	*	67	47
8	9	*	60	10
0	10		79	70
1	10	*	110	63
2	10		102	97
3	10	*	150	7
H	K		L = 1	
0	0		541	542
1	0		359	358
2	0		366	379
3	0		206	210
4	0		260	269
5	0		287	284
6	0		360	319
7	0		122	113
8	0		76	81
9	0		212	206
10	0		111	123
11	0		78	84
12	0	*	74	7
13	0	*	77	40
14	0	*	66	17
15	0		138	115
16	0	*	84	12
0	1		394	394
1	1		521	529
2	1		728	790
3	1		101	110
4	1		275	294
5	1	*	116	95
6	1		260	273
7	1		260	247
8	1		154	153
9	1		76	65
10	1		221	215
11	1	*	79	32
12	1		172	173
13	1	*	77	31
14	1		198	198
15	1		98	101
16	1	*	84	22
0	2	*	54	27
1	2		372	382
2	2		547	566
3	2		142	131
4	2		111	113
5	2		98	90
6	2	*	79	69
7	2		237	249
8	2		168	179
9	2		250	245
10	2		150	168
11	2		154	169
12	2	*	75	21
13	2		135	129
14	2	*	69	10
15	2		100	126
16	2	*	83	46
0	3		70	76
1	3		581	639
2	3		210	201
3	3		219	218
4	3		155	153
5	3		289	291
6	3	*	74	22
7	3		190	194
8	3		136	144
9	3		253	242
10	3	*	79	44
11	3		123	120
12	3	*	134	112
13	3	*	85	53
14	3	*	86	20
15	3	*	85	33
0	4		283	284
1	4		207	240
2	4		167	160
3	4		244	247
4	4		192	201
5	4		161	172
6	4		201	219
7	4	*	106	76
8	4		149	156
9	4		129	140
10	4	*	74	11
11	4		246	250
12	4		79	85
13	4	*	86	68
14	4	*	85	54
0	5	*	62	38
1	5	*	91	51
2	5		127	128
3	5	*	74	68
4	5		235	241
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6	5		144	100
7	5	*	77	61
8	5	*	118	89
9	5	*	74	55
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11	5	*	79	61
12	5		167	189
13	5	*	86	25
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1	6		150	148
2	6		299	227
3	6		75	79
4	6	*	107	85
5	6		166	171
6	6	*	80	53
7	6		69	82
8	6		95	97
9	6		82	76
10	6		140	132
11	6	*	86	34
12	6	*	68	45
13	6	*	67	59
0	7	*	80	77
1	7		80	65
2	7	*	81	58
3	7		168	159
4	7		151	155
5	7	*	85	30
6	7		66	77
7	7	*	67	51
8	7		79	93
9	7		69	75
11	7	*	68	26
0	8		97	77
1	8		107	103
2	8	*	132	97
3	8		67	84
4	8	*	68	11
5	8	*	68	60
6	8	*	69	41
7	8	*	69	56
8	8	*	69	57
9	8	*	68	81
10	8	*	66	38
0	9	*	69	9
1	9		139	131
2	9	*	69	64
3	9		105	111
4	9	*	69	40
5	9		79	98
6	9	*	68	25
7	9	*	67	69
8	9	*	65	12
0	10		109	104
1	10	*	67	60
2	10	*	66	63
3	10	*	66	40
H	K		L = 2	
0	0		262	267
1	0		171	172
2	0		215	241
3	0		84	83
4	0	*	59	17
5	0		137	128
6	0		184	172
7	0	*	70	73
8	0	*	62	6
9	0		111	114
10	0	*	94	22
11	0	*	96	1
12	0	*	101	30
13	0	*	102	39
14	0	*	102	41
15	0	*	99	54
0	1		240	222
1	1		64	76
2	1	*	58	53
3	1		139	144
4	1		120	127
5	1		157	146
6	1		101	151
7	1	*	66	51
8	1		106	125
9	1	*	177	49
10	1	*	184	128
0	2		484	445
1	2		171	146
2	2		225	222
3	2		272	264
4	2		203	187
5	2		94	63
6	2		178	175
7	2		199	224
8	2		187	241
0	3		157	138
1	3		280	260
2	3	*	58	34
3	3		470	443
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5	3		254	255
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7	3		171	184
0	4		295	290
1	4		110	108
2	4		256	243
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6	4		147	156
7	4	*	145	107
0	5	*	66	14
1	5	*	69	52
2	5		114	113
3	5	*	71	31
4	5	*	96	70
5	5	*	117	73
6	5	*	115	100
7	5	*	159	81
0	6		70	67
1	6	*	126	43
2	6		85	69
3	6	*	135	60
4	6		155	157
5	6	*	126	82
6	6	*	124	37
7	6	*	174	28
0	7	*	75	9
1	7	*	134	70
2	7	*	72	45
3	7	*	143	74
4	7	*	106	60
5	7	*	134	45
6	7	*	135	42
7	7	*	187	38
0	8		11:	111
1	8	*	141	8
2	8	*	74	42
3	8	*	200	60
5	8	*	141	90
6	8	*	141	83
7	8	*	200	42
0	9	*	71	5
1	9	*	145	114
2	9	*	70	23
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1	0	*	86	71
2	0		296	289
3	0		102	103
4	0		237	228
5	0	*	91	67
6	0		186	189
7	0		96	86
8	0		138	145
0	1	*	65	47
1	1		191	195
2	1	*	106	58
3	1		125	127
4	1	*	124	52
5	1		183	174
6	1	*	112	73
7	1	*	109	115
8	1	*	153	108
0	2	*	66	6
1	2		93	42
2	2	*	116	76
3	2	*	66	49
4	2	*	127	74
5	2		102	103
6	2	*	115	87
7	2		137	134
8	2	*	157	50
0	3	*	68	3
1	3	*	166	76
2	3		115	109
3	3		102	94
4	3		130	148
5	3		106	103
6	3		119	130
7	3	*	116	91
8	3	*	163	20
0	4	*	76	24
1	4	*	111	82
2	4	*	120	19
3	4		86	74
4	4	*	135	49
5	4		111	116
6	4	*	124	75
7	4	*	122	60
8	4	*	172	88
0	5	*	72	31
1	5	*	115	84
2	5	*	125	23
3	5		91	75
4	5	*	141	113
5	5		120	130
6	5	*	130	87
7	5	*	129	93
8	5	*	181	74
0	6		138	144
1	6	*	110	20
2	6		131	131
3	6	*	74	13
4	6	*	140	125
5	6	*	110	71
6	6	*	136	68
7	6	*	135	31
8	6	*	192	112
0	7	*	142	33
1	7	*	114	68
2	7	*	130	13
3	7		94	85
4	7	*	150	17
5	7	*	124	93
6	7	*	142	53
H	K		L = 4	
0	0		83	88
1	0	*	102	79
2	0	*	102	97
3	0		125	139
4	0		74	72
5	0	*	102	86
6	0	*	108	63
7	0	*	132	90
8	0	*	130	53
9	0	*	183	60
0	1		100	88
1	1	*	135	17
2	1	*	118	69
3	1	*	145	73
4	1		139	135
5	1	*	145	103
6	1	*	118	79
8	1	*	131	67
9	1	*	104	35
0	2	*	75	0
1	2	*	137	39
2	2	*	109	43
3	2	*	147	53
4	2	*	72	24
5	2	*	147	43
6	2	*	120	74
7	2	*	135	52
8	2	*	132	43
9	2	*	107	71
0	3	*	76	11
1	3	*	139	33
2	3	*	111	10
3	3	*	148	76
4	3	*	76	3
5	3	*	148	66
6	3	*	111	29
7	3	*	137	42
0	4	*	77	29
1	4	*	141	47
2	4	*	134	15

Table 6.

Cell data for BITrS ($C_{14}H_{12}N_2S_3$, M.W.304.46)

Space group $P2_12_12$

a = 16.639(12)Å

b = 10.003(13)Å

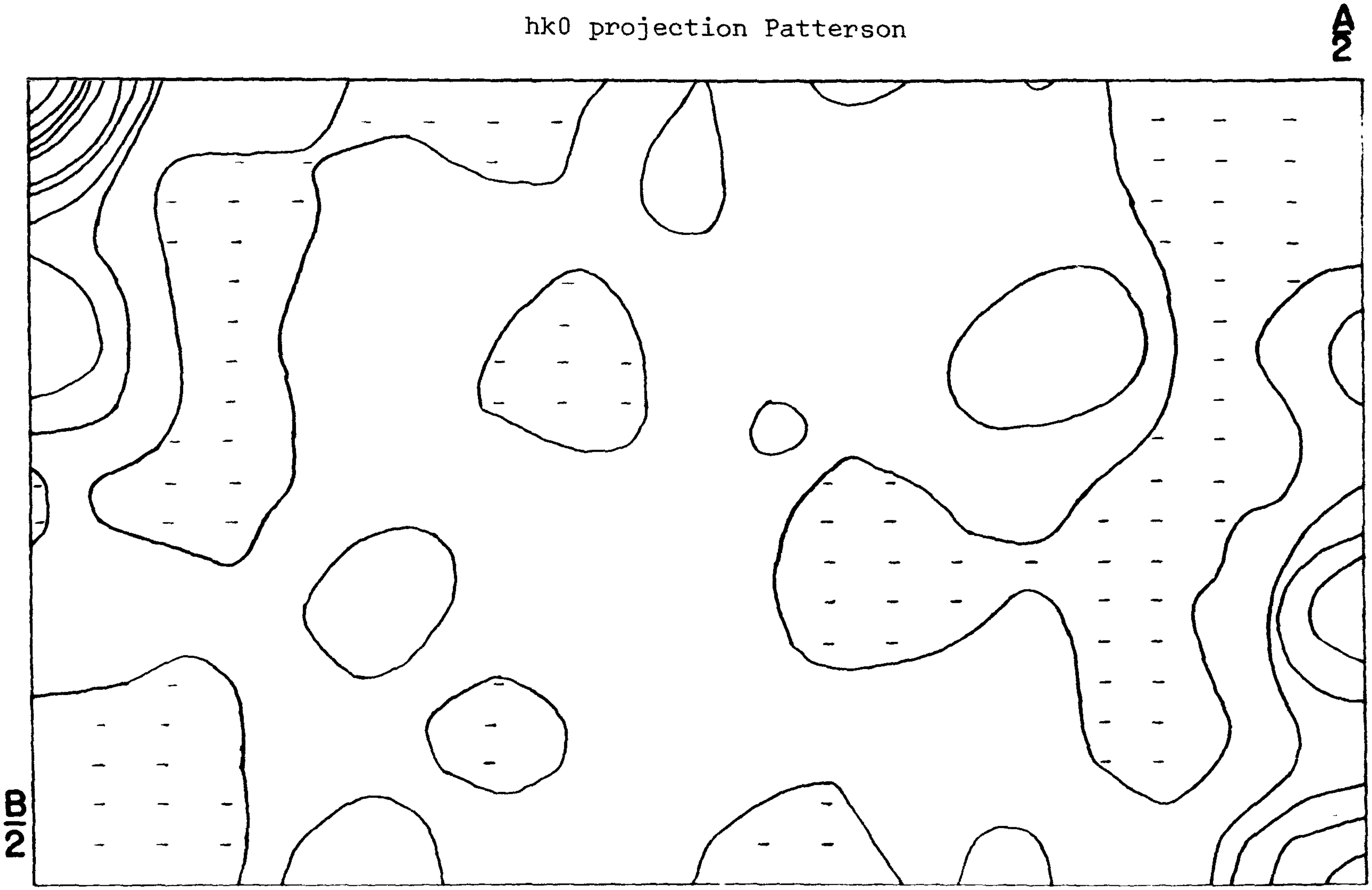
c = 4.287(5)Å

V = 713(2)$Å^3$

ρ_{calc} for 2 molecules per unit cell = 1.426(5)g/cm^3

Figure 6.

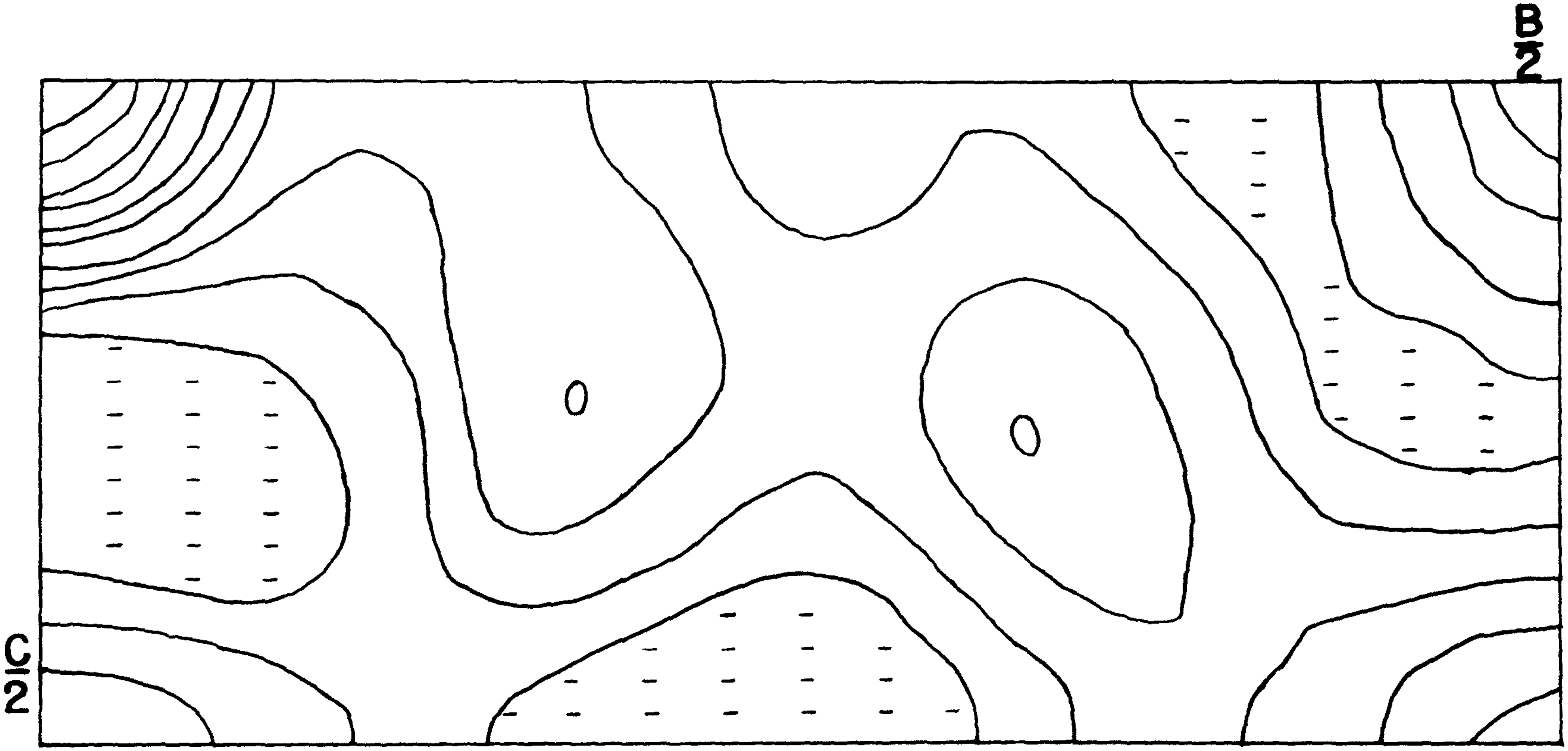
hk0 projection Patterson



then gave the x- and y-coordinates of the other unique sulfur atom, and by subtraction those of the nitrogen atom. The $0k\ell$ projection Patterson (Figure 7) yielded for the central sulfur atom its only unknown coordinate, z, and with the aid of the y-coordinates from the hk0 projection, the z-coordinates also of S_2 and N. Carbon atoms were located from electron density and difference Fourier syntheses calculated from the positions of the two sulfurs and the nitrogen. When enough of these had been located to indicate the orientation of the phenyl ring, the positions of the rest of the ring were calculated assuming a hexagon with sides of 1.397Å. Least squares refinement proceeded allowing the phenyl ring to move only as a rigid hexagon, until the R-factor was down to 0.096, at which time the atom positions were allowed to refine independently. Anisotropic temperature factors were refined first for the sulfur atoms. Anisotropic temperature factors were then refined for the nitrogen atom, but all components were less than two standard deviations from being isotropic, and no improvement in the R-factor was noted, so isotropic temperature factor refinement was restored for nitrogen. Positions for the hydrogen atoms were calculated assuming sp^2 hybridization at all carbons, a C-H bond length of 0.97Å, and isotropic temperature factor $B = 0.07\text{Å}^2$. These were held fixed while the positional and thermal parameters of the other atoms were refined. The sixteen different batches of film data were reduced to a

Figure 7.

0kℓ projection Patterson



common scale by least squares adjustment of common reflections, yielding 484 symmetry independent reflections of which 245 were intense enough to distinguish from background on at least one film. A Cruickshank weighting scheme was applied, with final coefficients A= 1.6, B= -0.154, C= 0.0085. The ratio of unique observed structure factors to variables refining anisotropic temperature factors on sulfur only and one overall scale was 5.2:1; with anisotropic temperature factors on nitrogen it would have been 4.7:1. The final maximum shift/error was 0.035 at R_1= 0.056 (observed reflections only) and R_2= 0.073 (all reflections).

B. Description of the Structure

The final values of positional and thermal parameters of all atoms are given in Table 7. Table 5 lists observed structure factors and those calculated using the final positional and thermal parameters of the refinement. Figure 8 is a stereoscopic view of the molecule viewed down the b axis; Figure 9 indicates the packing of the molecules within the unit cell. Table 8 gives bond lengths and angles, and Table 9 some intermolecular contact distances, dihedral angles and least-squares planes.

One half of the molecule is related to the other by a crystallographic two-fold axis. The unique half-molecule, but for the central sulfur atom, is nearly planar, the maximum deviation from the least-squares plane being .06Å; the angle between the planes of the two halves is 107.0°.

Table 7

Atomic coordinates of BITrS (e.s.d's in parentheses)

	x/a	y/b	z/c	$B(A^2)$
S_1	0.	0.	0.3047(14)	-
S_2	0.0167(2)	0.1628(4)	0.0218(10)	-
N	0.1114(5)	0.1681(11)	0.896(3)	0.048(3)
C_1	0.1638(7)	0.0794(12)	0.920(3)	0.047(4)
C_2	0.2437(7)	0.0895(15)	0.785(4)	0.045(4)
C_3	0.2644(8)	0.1986(14)	0.601(4)	0.056(4)
C_4	0.3393(9)	0.2050(14)	0.481(4)	0.072(5)
C_5	0.3958(9)	0.1072(14)	0.532(5)	0.067(5)
C_6	0.3755(9)	0.0042(16)	0.715(4)	0.067(4)
C_7	0.3044(9)	0.0101(16)	0.838(4)	0.066(4)
H_1	0.150	0.003	1.050	0.07
H_3	0.228	0.273	0.563	0.07
H_4	0.354	0.284	0.359	0.07
H_5	0.460	0.113	0.444	0.07
H_6	0.411	-0.071	0.757	0.07
H_7	0.282	-0.084	0.967	0.07

Anisotropic thermal coordinates ($Å^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S_1	58(4)	86(4)	50(4)	1(3)	0	0
S_2	53(2)	59(2)	67(3)	2(2)	-5(3)	-8(3)

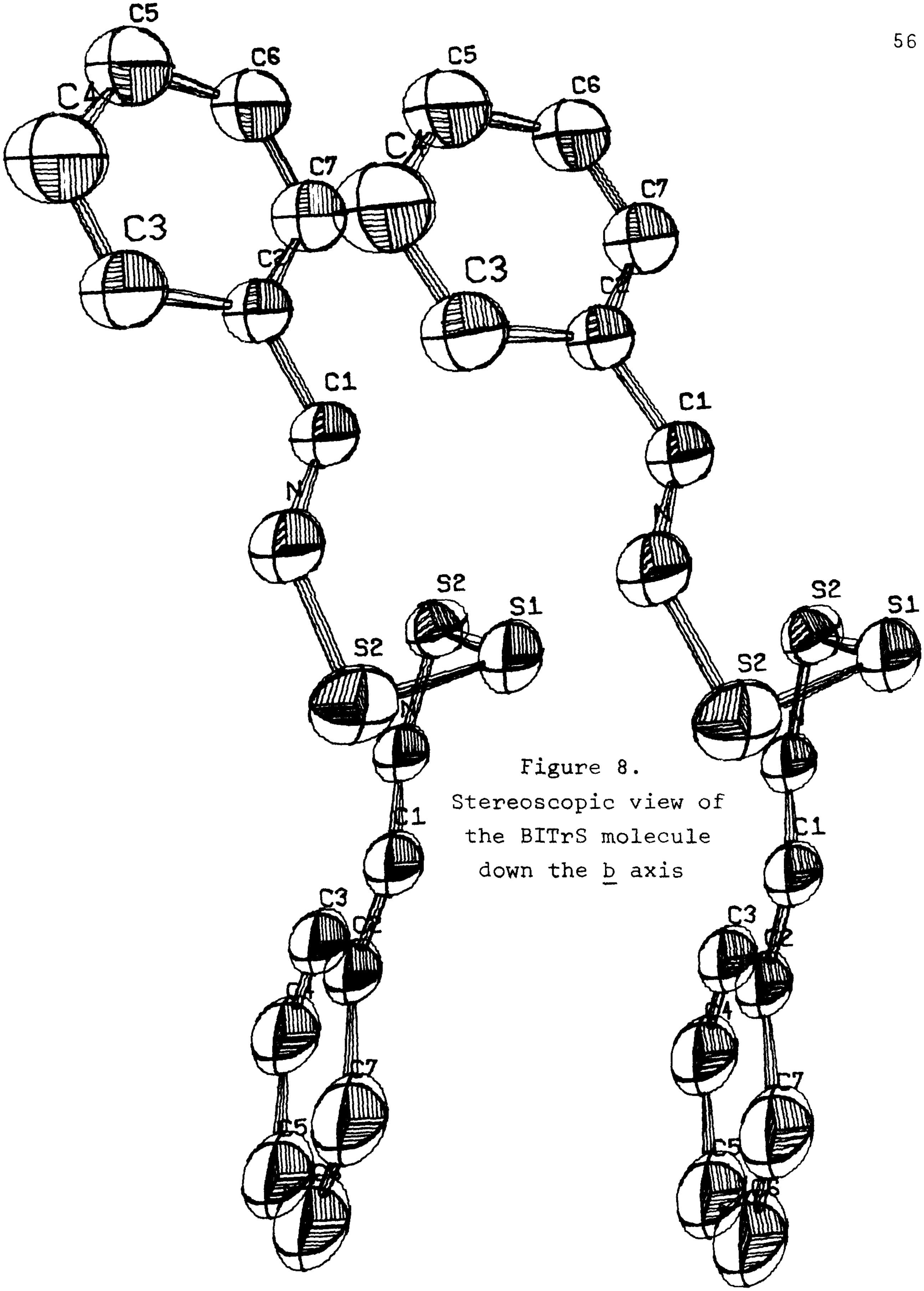


Figure 8.
Stereoscopic view of
the BITrS molecule
down the b axis

Figure 9.

BITrS contents of two unit cells

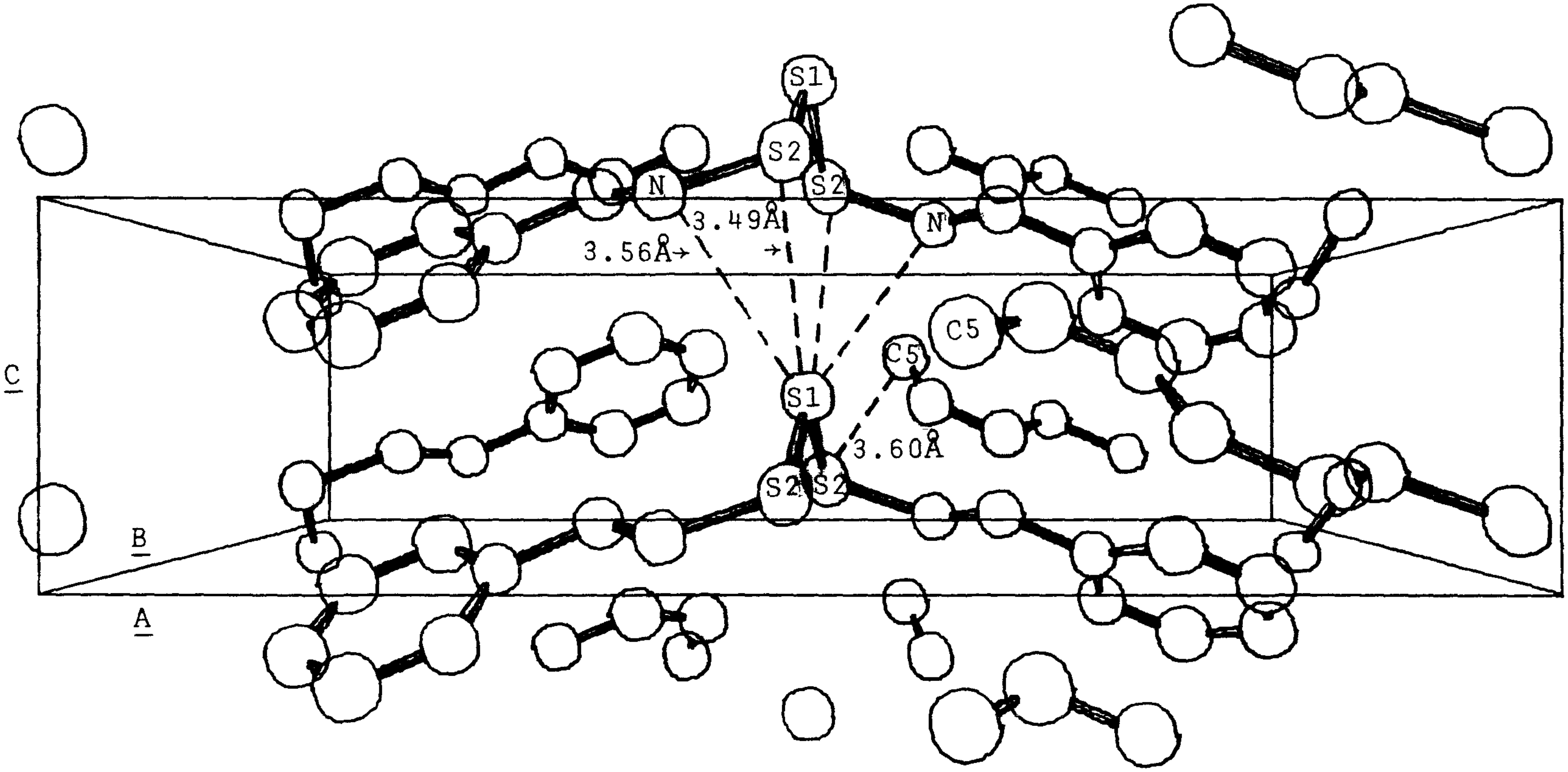


Table 8: Molecular Geometry of Benzylidenimine Trisulfide

Bond distances in Å

S_1-S_2	2.049(6)	C_3-C_4	1.350(21)
S_2-N	1.666(10)	C_4-C_5	1.386(20)
N-C_1	1.249(16)	C_5-C_6	1.342(23)
C_1-C_2	1.453(17)	C_6-C_7	1.364(21)
C_2-C_3	1.390(21)	C_7-C_2	1.390(20)

Bond angles in degrees

$S_2S_1S'_2$	107.4(3)	$C_3C_2C_7$	119.1(12)
S_1S_2N	110.2(4)	$C_2C_3C_4$	118.9(13)
S_2NC_1	127.7(10)	$C_3C_4C_5$	122.9(15)
NC_1C_2	123.8(12)	$C_4C_5C_6$	116.8(14)
$C_1C_2C_3$	120.5(12)	$C_5C_6C_7$	123.2(15)
$C_1C_2C_7$	120.4(13)	$C_6C_7C_2$	119.0(15)

Table 9: BITrS Molecular Geometry

Selected intermolecular contact distances (Å)

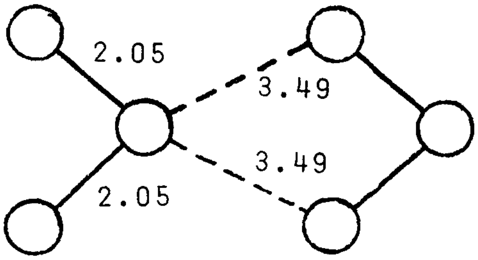
$S_1 \ldots S_2$	3.490(7)	$C_2 \ldots C_4$	3.57(2)
$S_1 \ldots N$	3.561(12)	$C_5 \ldots C_7$	3.58(3)
$S_2 \ldots C_5$	3.597(16)	$C_3 \ldots C_7$	3.63(2)
$C_4 \ldots C_7$	3.56(2)	$C_5 \ldots C_6$	3.67(3)

Dihedral angle $N\text{-}S_2\text{-}S_1\text{-}S_2'$ 81.85°

Selected least squares planes

Atoms in plane		Direction cosines of planes			Deviation from plane (|Å|)	
Determining	Relative	α	β	γ	Maximum	Average
C_2-C_7		.37116	.24933	.59514	.015	.007
	S_2				.022	
	N				.095	
	C_1				.014	
C_1-C_7		.37408	.24943	.59437	.016	.007
N_1,C_1-C_7		.38718	.24654	.59377	.040	.019
S_1,N_1,C_1-C_7		.38087	.24717	.59474	.059	.018

The average carbon-carbon bond length in the benzene ring is 1.37Å; the maximum and average deviations from the mean are 0.028Å and 0.018Å, respectively. The average C-C-C angle for the ring is 120.0°; the maximum and average deviations from this value are 3.2° and 2.1°, respectively. All the bond lengths and angles are chemically reasonable, as discussed in Chapter 6. The three sulfur atoms form a vee pointing up the c axis and being nearly perpendicular to the a axis; these vees stack closely on top of one another forming an arrow pointing through the structure up the c axis, alternating with screw-related arrows distant by 1/2, 1/2, 0 and pointing down through the structure. The screw-related benzylidene groups lie side-by-side in the b direction; the cell is one molecule thick in c.



$S_1 \ldots S_2$ non-bonding distance of 3.49Å is somewhat less than the sum of Van der Waals radii (3.70Å), indicating a possible strong interaction; the next closest contacts ($S_1 \ldots N$ and $C_4 \ldots C_7$, both at 3.56Å; see Figure 9) are well outside of Van der Waals contact distances.

Observations of crystal decomposition may provide evidence of some intermolecular sulfur-sulfur interaction.

On standing over a period of months a yellow streak develops down the middle of the crystal in the c direction. Eventually the whole crystal becomes covered with a powdery-yellow excrescence. It is suggested that decomposition proceeds by sulfur chain growth in the direction of the non-bonding interaction; the observation may bear further investigation.

CHAPTER 5: CRYSTAL AND MOLECULAR STRUCTURE OF BENZYLIDENIMINE DISULFIDE (BIDS)

A. Solution of the Structure

The compound was obtained from the reaction of sulfur with benzylamine, in the presence of lead oxide as a sulfide scavenger:[14]

$5S + 2C_6H_5CH_2NH_2 + 3PbO \rightarrow 3PbS + C_6H_5CHNS_2NCHC_6H_5 + 3H_2O$.

The product was purified by chromatography on a silica gel column, followed by fractional crystallization from methanol, and further recrystallization from benzene, to give white needles melting at 100-100.5°C.[14c]

$h0\ell$ and $h1\ell$ Weissenberg photographs showed that the crystal class was monoclinic. The space group was established to be $P2_1/c$ with the help of an hk0 precession photograph. These films and all subsequent ones were only consistent with systematic absences of type $h0\ell$ for ℓ odd and 0k0 for k odd. Accurate unit cell parameters were determined by least squares refinement of a,b,c and β to the diffractometer-measured 2θ angles of 38 reflections to be a= 12.91(2), b= 5.557(9), c= 20.48(6)Å and β= 112.53(18)°. Intensity data was initially obtained from integrated Weissenberg and precession photographs. $Hn\ell$, n= 0-4, intensity data were recorded with CuKα radiation using an integrating Weissenberg camera from a crystal measuring 0.09x0.15x1.0 mm mounted in the needle direction (010). Integrated precession photographs were obtained for the hk0, 0kℓ, 1kℓ, 2kℓ, and 3kℓ layers on a crystal measuring 0.4 mm (001)x0.64 mm (100)x0.95(010) using MoKα radiation. The intensities were measured with a Joyce-Loebl microdensitometer. Two of the Weissenberg layers were somewhat darkened in the upper and lower quarters, due to misplacement of the beam stop. For these areas, on the h2ℓ and h4ℓ film sets, the unobserved limit was set 5-10 times higher than usual.

No absorption corrections were made. The maximum variations in the transmission factors for the two crystals were ±9% (first crystal, CuKα,$\mu = 32.9\ cm^{-1}$) and ±4% (second crystal, MoKα,$\mu = 3.68\ cm^{-1}$).

The structure factors from the 0kℓ, hk0, h0ℓ, h1ℓ, h2ℓ, h3ℓ, and h4ℓ layers were scaled together by a least squares adjustment of common reflections. The XRAY67 program DATFIX* was then used to estimate the overall temperature factor and scale factor and to calculate quasi-normalized structure factors (E's). The XRAY67 programs SIGMA2 and PHASE were applied to the resulting E's to obtain phases (signs); PHASE determined 140 signs to be positive and seven negative. The Fourier electron density map calculated using these signed E's showed only a single large peak at the origin. Attempts were made to force new solutions to the Sayre equation, having a more even distribution of

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*See pages 21-23 for the use of direct methods programs.

positive and negative signs, by changing the signs of some E's; the only significant effect was to move the large peak from the origin (in some cases) by 1/2 along one or more axes.

An explanation for the failure to find a solution became apparent upon consideration of the high "less-than" limit assigned to a number of reflections due to high backgrounds in the outer quarters of the h2ℓ and h4ℓ layers. The direct methods programs were giving high weight to these high theta "unobserved" reflections. By including only those reflections with $\sin\theta/\lambda$ less than 0.45, a limited set of data was obtained of 873 reflections (654 observed). Using this limited set, DATFIX gave a much higher temperature factor than before (5.0 vs. 3.66), and one more in agreement with that previously obtained for BITS (5.0). The statistics on the E's calculated by DATFIX for the limited subset was also in better agreement with the theoretical distribution of intensities expected for a centric structure. Using this subset, only one cycle of SIGMA2 and PHASE was required to yield a solution in which the signs of 115 reflections were determined, 54 as positive and 61 negative. Careful inspection of the Fourier (E) map calculated from these 115 signed E's yielded the positions of the two sulfurs, two carbons and a nitrogen. An electron density map and a difference synthesis using the structure factors of the limited subset and the phases calculated from the positions of the five atoms from the E-map yielded the positions of three more carbon atoms.

Assumptions were made concerning molecular configurations derived from the structural studies of BITS and BITrS, namely that the SNC_7 moieties were planar, with 120° angles at carbon and nitrogen, and that twelve of the 14 carbon atoms were present as benzene rings. Alternate least squares refinement and electron density and difference maps progressively yielded the remaining atoms other than hydrogen. Further least squares cycles were carried out using the full range of data, refining the scales for the $0k\ell$, $hk0$, $h0\ell$, $h1\ell$, $h2\ell$, $h3\ell$, and $h4\ell$ layers separately. Eventually temperature factors were allowed to vary anisotropically for all non-hydrogen atoms, but the R-factor came down only to 0.145.

At this point it appeared that the refinement was limited by the quality of the data, so a new data set was collected on the Syntex automatic diffractometer. The crystal measured 0.6x0.6x0.35 mm. MoKα radiation was used with a graphite monochromator set at 12°. No absorption corrections were made; the maximum variation in transmission factors would be ±4.5%. The data were collected by the θ-2θ technique at scan rates which varied according to a 2-second read of peak intensity within a range from 2° per minute to 24° per minute. Scan width was adjusted to add one degree on either side of the separation between $K\alpha_1$ and $K\alpha_2$. Stationary-counter background counts were taken at each end of the 2θ scan range such that the duration of each background measurement was equal to 1/2 the duration of the scan. Every 50th scan was that of a standard reflection, so that the standard reflection (-2,1,3) was measured 53 times; the maximum and average deviations from the mean were 7% and 1.8% respectively.

A total of 2478 reflections were measured in one asymmetric zone. The intensities of 1999 symmetry independent non-zero reflections were obtained after averaging, 1619 of which were larger than three standard deviations in the intensity. Standard deviations were obtained from:

$$\sigma(F_o^2)=(\sigma^2\text{counting} + (0.025F_o^2)^2)^{1/2}.$$

Beginning with the structure obtained from the film data, two cycles of refinement brought the R-factor down to 0.07. Because most of the strongest structure factors calculated higher than they measured, secondary extinction was suspected, and a correction applied, according to the equation:[31]

$$F_{corr} = KF_o(1 + \beta'_{(2\theta)}CLpF_o^2)$$

$\beta'(2\theta)$ for each reflection was calculated from[32]

$$\beta'(2\theta) = \frac{(1 + \cos^2 2\theta_o)(1 + \cos^2 2\theta_o \cos^4 2\theta)}{(1 + \cos^2 2\theta_o \cos^2 2\theta)^2},$$

where θ_o was taken as 12^o, the setting angle of the graphite monochromator. C, the extinction correction term, was refined by the least squares program, but was never larger than the least squares error in it, and had negligible effect on the R-factor. A weighting scheme was applied where

$$w = 1/(A + BF_o + CF_o^2 + D(\sigma_F/F_o)^2)$$

The effect of D was to take account of the imprecision of measurement of the weakest reflections, including those measuring less than three standard deviations in the intensities, which were treated as "unobserved." Hydrogen atoms were added in their calculated positions, assuming sp^2-hybridized carbon atoms and a C-H bond distance of 0.97Å (although most of the hydrogen atom positions were visible in a difference electron density map). Positions and isotropic temperature factors of the hydrogen atoms were refined along with the other atoms by full-matrix least squares to R= 0.035 ("observed" reflections only). At this point it was noted that a number (~20) of structure factor of high h and ℓ were calculating considerably higher than they had measured. Consequently 837 reflections, including those which were suspect, were remeasured on a new crystal. The dimensions of this second crystal (an irregular chunk) were 0.21x0.45x0.49 mm, leading to a maximum possible variation in transmission factor of ±5%. Similar conditions of measurement on the Syntex automatic diffractometer were employed, except that the standard reflection chosen was the 104. While most of the new structure factors were in good agreement with those from the previous set (after scaling together to F_c's), there were a number of discrepancies. The new set was in much better agreement with the calculated structure factors in the several regions of reciprocal space where the structure factors had previously calculated too high. Sixty-nine reflections from the first set were therefore removed, and the R-factor refined after two more cycles to 2.94%.

Common reflections between the first and second Syntex data set generally had very similar σ_F's after scaling together on the basis of least squares fit to the F_c's, with the exception of a few of the weakest reflections. With these exceptions, therefore, the scaled F_o's were averaged directly resulting in 2304 unique non-zero reflections (1807 "observed"). (In cases where the standard deviations differed substantially, the structure factor with the smaller σ, i.e. the larger structure factor was chosen.) Full-matrix least-squares refinement was continued (2 more cycles) until the maximum shift/error was 0.28; the average shift/error at this point was 0.052. The final unweighted R-factor (all "observed" reflections only) was 2.91%; the weighted R-factor (all reflections) was 3.63%. Final weighting scheme coefficients were A= 0.07, B= 0.0015, C= 0.00045, D= 22.5.* Here

$$\left\{\frac{w(F_o-F_c)^2}{m-n}\right\}^{1/2} = 0.97$$

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*See page 26.

for this weighting scheme, where m= N_{used}= 1977, including 170 out of 397 "unobserved" reflections which calculated higher than measured, and n= $N_{variables}$= 212.

B. Description of the Structure

The final values of the refined positional and thermal parameters of all atoms are given in Table 10. Table 11 lists observed structure factors and those calculated using the final positional and thermal parameters of the refinement. Figure 10 shows the numbering system used in a perspective view of the molecule. Table 12 gives bond lengths and angles together with their e.s.d.'s; Table 13 gives some intermolecular contact distances, least squares planes, and dihedral angles.

The benzylidenimine groups are planar, as expected, the largest deviation of any atom in the C_7N groups being 0.033Å (for N_2). The average C-C distances for the two rings are 1.381A for C_2-C_7 and 1.383Å for C_9-C_{14}. These are approximately 2 1/2 standard deviations from the value of 1.392(4)Å found by Cox, Cruickshank and Smith[33] for crystalline benzene. Correction for translational and librational effects as discussed by Cruickshank[34] would increase some or all of these lengths, probably bringing these results closer to those for benzene. The average C-C-C angles for both rings are 120.0°. The maximum deviation of any ring angle from 120° is 1.6°; the average, 0.48°. The average C-H bond distance as refined is 0.94Å. The maximum deviation of any C-H bond distance from 0.94Å was 0.06Å; the average deviation

Table 10: BIDS Positional and Thermal Parameters

Atom	x/a	v/b	z/c	U11	U22	U33	U12	U13	U23	RMSDI	RMSD2	RMSD3	Atom
S1	.25984(4)	.99957(10)	.63918(2)	578(3)	760(4)	550(3)	101(3)	254(2)	10(2)	.284	.239	.219	S1
S2	.28072(4)	1.22889(9)	.55856(3)	554(3)	580(3)	647(3)	-24(2)	168(2)	-5(2)	.268	.243	.230	S2
N1	.3942(1)	.7866(3)	.64809(8)	537(9)	680(10)	503(8)	49(8)	177(7)	-13(7)	.266	.232	.223	N1
N2	.1820(1)	1.1329(3)	.48163(8)	519(9)	558(9)	598(9)	11(7)	181(7)	40(7)	.254	.234	.225	N2
C1	.4512(1)	.7754(3)	.60985(9)	539(10)	599(11)	461(9)	-22(9)	170(8)	-27(9)	.246	.236	.213	C1
C2	.5370(1)	.5891(3)	.62149(9)	471(9)	558(10)	461(9)	-35(8)	129(7)	-65(8)	.244	.231	.201	C2
C3	.6015(2)	.5931(4)	.58084(11)	756(13)	637(12)	653(12)	91(11)	353(10)	77(10)	.288	.243	.235	C3
C4	.6813(2)	.4165(4)	.58948(13)	785(15)	944(14)	852(15)	149(12)	467(12)	58(12)	.315	.270	.228	C4
C5	.6974(2)	.2370(4)	.63810(12)	618(13)	631(13)	798(14)	94(11)	234(11)	-10(11)	.291	.266	.230	C5
C6	.6348(2)	.2340(4)	.67983(11)	601(12)	655(13)	635(12)	37(10)	138(9)	90(10)	.283	.259	.225	C6
C7	.5553(2)	.4090(4)	.67155(10)	512(11)	676(12)	496(10)	-26(9)	152(8)	-3(9)	.261	.238	.217	C7
C8	.1272(2)	.9380(3)	.47399(10)	550(10)	512(11)	609(11)	77(8)	272(9)	51(9)	.257	.228	.211	C8
C9	.0393(1)	.8736(3)	.40572(9)	478(10)	483(10)	619(10)	50(8)	251(8)	-20(8)	.249	.230	.198	C9
C10	-.0219(2)	.6632(4)	.39841(12)	701(13,	522(11)	789(14)	9(10)	335(11)	34(11)	.283	.255	.227	C10
C11	-.1080(2)	.6066(4)	.33457(13)	680(13)	586(12)	951(17)	-109(11)	341(12)	-217(12)	.324	.257	.218	C11
C12	-.1323(2)	.7574(4)	.27765(12)	583(12)	741(14)	721(13)	4(11)	230(11)	-185(12)	.307	.243	.232	C12
C13	-.0702(2)	.9635(4)	.28339(11)	607(12)	705(14)	630(12)	72(10)	218(9)	-3(11)	.275	.252	.238	C13
C14	.0149(2)	1.0024(4)	.34674(10)	533(10)	529(11)	648(11)	23(9)	238(9)	21(9)	.255	.233	.225	C14

H1	.437(1)	.882(3)	.571(1)	30(5)	H8	.140(2)	.829(4)	.513(1)	31(5)
H3	.588(2)	.711(4)	.548(1)	38(6)	H10	-.001(2)	.566(4)	.437(1)	39(6)
H4	.725(2)	.425(4)	.559(1)	52(6)	H11	-.147(2)	.469(4)	.330(1)	55(7)
H5	.752(2)	.118(4)	.646(1)	48(6)	H12	-.190(2)	.720(4)	.235(1)	58(7)
H6	.648(2)	.112(4)	.714(1)	45(6)	H13	-.087(2)	1.068(4)	.244(1)	46(6)
H7	.512(2)	.412(4)	.698(1)	36(5)	H14	.058(2)	1.171(4)	.352(1)	33(5)

Table 11: BIDS Observed and Calculated Structure Factors (x10), * = unobserved

			FOBS	FCLC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 11. (continued)

			FOBS	FCLC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Figure 10.

Perspective view of the BIDS molecule

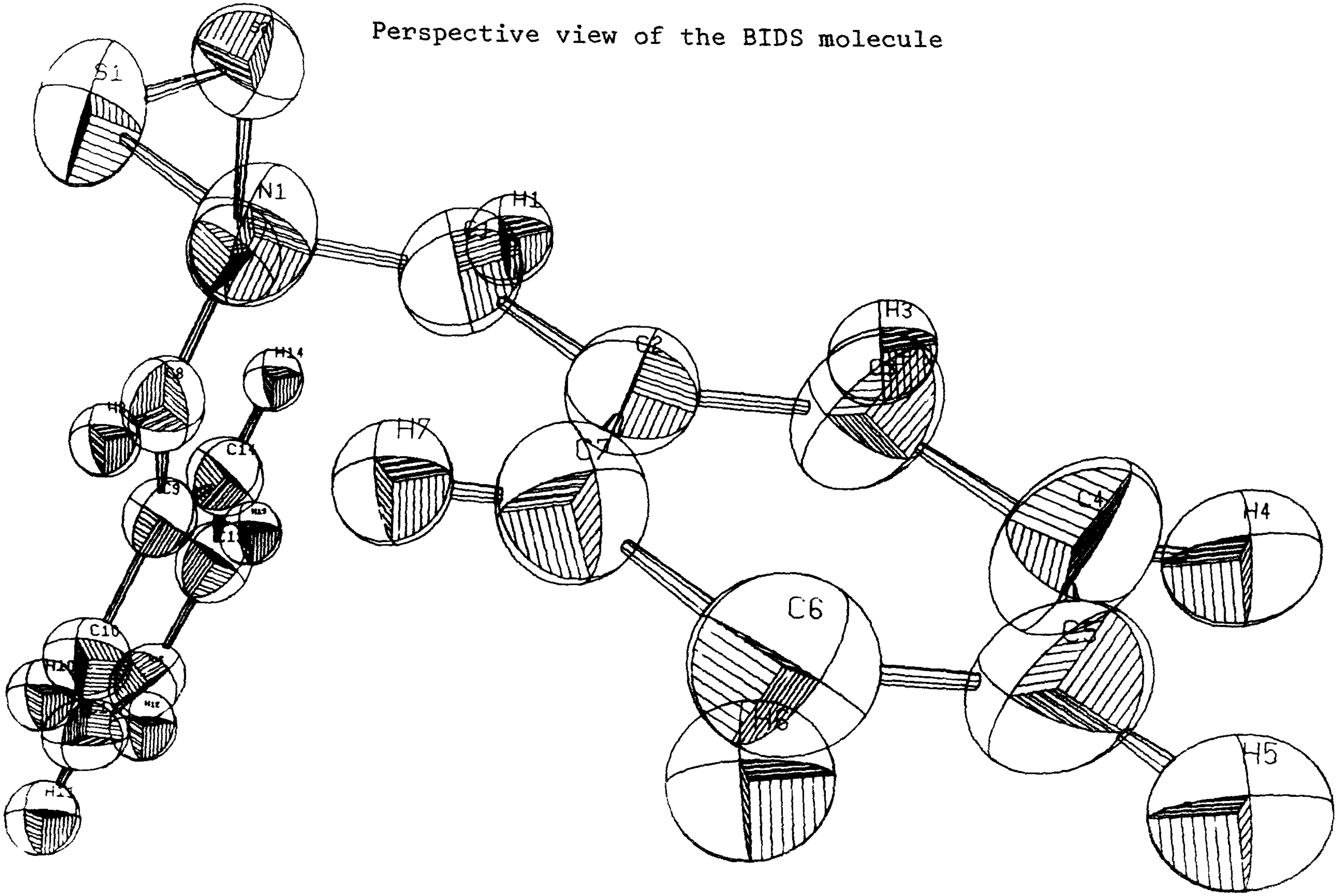


Table 12

Molecular geometry of benzylidenimine disulfide (BIDS)

Bond distances in Å

S_1-S_2	2.035(4)	C_7-C_2	1.387(4)	C_4-H_4	1.00(3)
S_1-N_1	1.693(3)	C_8-C_9	1.468(5)	C_5-H_5	0.93(2)
S_2-N_2	1.686(5)	C_9-C_{10}	1.387(3)	C_6-H_6	0.95(2)
N_1-C_1	1.265(4)	$C_{10}-C_{11}$	1.389(5)	C_7-H_7	0.91(3)
N_2-C_8	1.270(3)	$C_{11}-C_{12}$	1.371(4)	C_8-H_8	0.96(2)
C_1-C_2	1.467(3)	$C_{12}-C_{13}$	1.377(4)	$C_{10}-H_{10}$	0.90(2)
C_2-C_3	1.468(5)	$C_{13}-C_{14}$	1.380(5)	$C_{11}-H_{11}$	0.90(3)
C_3-C_4	1.384(4)	$C_{14}-C_9$	1.397(4)	$C_{12}-H_{12}$	0.93(2)
C_4-C_5	1.368(4)	C_1-H_1	0.96(2)	$C_{13}-H_{13}$	0.95(2)
C_5-C_6	1.384(5)	C_3-H_3	0.91(2)	$C_{14}-H_{14}$	0.98(2)
C_6-C_7	1.377(3)				

Bond angles in degrees

$S_1-S_2-N_2$	111.2(5)	$C_{10}-C_{11}-C_{12}$	120.1(6)	$C_7-C_6-H_6$	121(1)
$S_2-S_1-N_1$	111.1(3)	$C_{11}-C_{12}-C_{13}$	120.0(4)	$C_6-C_7-H_7$	122(1)
$S_1-N_1-C_1$	123.9(3)	$C_{12}-C_{13}-C_{14}$	120.3(5)	$C_2-C_7-H_7$	117(1)
$S_2-N_2-C_8$	125.0(3)	$C_{13}-C_{14}-C_9$	120.5(7)	$N_2-C_8-H_8$	121(1)
$N_1-C_1-C_2$	121.1(3)	$C_{14}-C_9-C_{10}$	118.4(4)	$C_9-C_8-H_8$	117(1)
$N_2-C_8-C_9$	121.2(5)	$C_{14}-C_9-C_8$	121.0(6)	$C_9-C_{10}-H_{10}$	116(1)
$C_1-C_2-C_3$	118.8(4)	$N_1-C_1-H_1$	121(1)	$C_{11}-C_{10}-H_{10}$	123(1)
$C_2-C_3-C_4$	120.1(4)	$C_2-C_1-H_1$	118(1)	$C_{10}-C_{11}-H_{11}$	121(1)
$C_3-C_4-C_5$	120.6(4)	$C_2-C_3-H_3$	118(1)	$C_{12}-C_{11}-H_{11}$	119(1)
$C_4-C_5-C_6$	119.8(5)	$C_4-C_3-H_3$	121(1)	$C_{11}-C_{12}-H_{12}$	120(1)
$C_5-C_6-C_7$	120.0(4)	$C_3-C_4-H_4$	117(1)	$C_{13}-C_{12}-H_{12}$	120(1)
$C_6-C_7-C_2$	120.6(4)	$C_5-C_4-H_4$	122(1)	$C_{12}-C_{13}-H_{13}$	120(1)
$C_7-C_2-C_3$	119.0(5)	$C_4-C_5-H_5$	123(1)	$C_{14}-C_{13}-H_{13}$	120(1)
$C_7-C_2-C_1$	122.3(4)	$C_6-C_5-H_5$	118(1)	$C_{13}-C_{14}-H_{14}$	121(1)
$C_8-C_9-C_{10}$	120.6(3)	$C_5-C_6-H_6$	119(1)	$C_9-C_{14}-H_{14}$	118(1)
$C_9-C_{10}-C_{11}$	120.7(5)				

Table 13: BIDS Molecular Geometry

Selected intermolecular contact distances (Å)

$S_1...C_{12}$	3.457(4)	$S_2...H_3$	3.24(3)	$N_2...H_4$	2.98(3)
$S_1...C_{11}$	3.459(4)	$N_1...C_7$	3.562(4)	$N_1...H_7$	2.99(3)
$S_2...C_7$	3.555(4)	$C_1...C_6$	3.400(4)	$C_5...H_{13}$	3.00(2)
$S_2...N_1$	3.613(4)	$C_3...C_3$	3.501(4)	$H_5...H_{12}$	2.52(3)

Dihedral angle N -S -S -N 80.7

Selected least squares planes

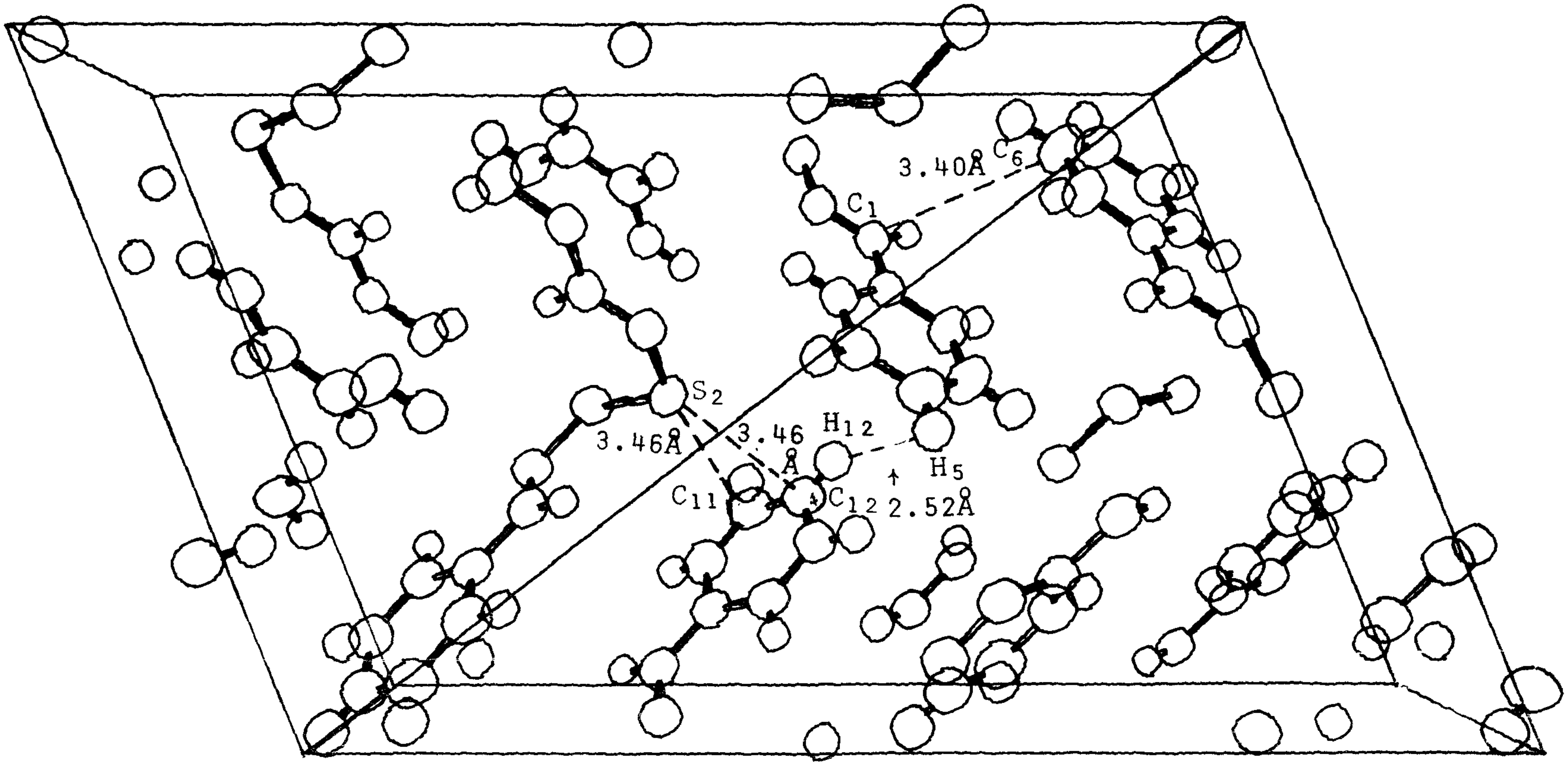
Atoms in plane		Direction cosines of plane			Deviation from plane (|Å|)	
Determining	Relative	α	β	γ	Maximum	Average
C_2-C_7		.45848	.56462	.68629	.009	.005
	C_1				.041	
	N_1				.016	
	S_1				.019	
	H_1,H_3-H_7				.153	.041
C_9-C_{14}		.82015	-.50054	-.77717	.013	.008
	C_8				.058	
	N_2				.112	
	S_2				.229	
	H_8,H_{10}-H_{14}				.075	.031
C_1-C_7		.45301	.57023	.68528	.016	.009
C_8-C_{14}		.82496	-.49794	-.26739	.023	.013
N_1,C_1-C_7		.45904	.56815	.68301	.032	.012
N_2,C_8-C_{14}		.83060	-.49086	-.26297	.033	.022
S_1,N_1,C_1-C_7		.46144	.56652	.68274	.040	.011
S_2,N_2,C_8-C_{14}		.83669	-.48480	-.25479	.057	.030

was 0.026Å. A correction[35] for the effect of hydrogen "riding" on carbon in the refinement gave an average C-H length of 0.97Å, closer to the usually accepted value, but a hardly significant difference in view of the precision of the measurements.

The average N-S, C=N, and benzylidene C-C bond distances are respectively 1.689(3)Å, 1.267(3)Å, and 1.467(3)Å. The average SSN, SNC, and NCC angles are respectively 111.17(22)°, 124.43(20)°, and 121.1(3)°. These bond lengths and angles, and the thermal parameters, are reasonable in comparison with known structures, as discussed in Chapter 6. The closest intermolecular contact distance is $H_5 \ldots H_{12}$ at 2.52Å (Van der Waals contact distance 2.4Å); the closest non-hydrogen distance is $C_1 \ldots C_6$ at 3.40Å (Van der Waals contact distance 3.4Å); and the closest involving sulfur are $S_1 \ldots C_{11}$ and $S_1 \ldots C_{12}$, both at 3.46Å (Van der Waals contact sum 3.55Å).

Unlike the structures of BITS and BITrS, wherein the packing along the short axis is determined primarily by sulfur-sulfur and sulfur-nitrogen Van der Waals contact, the short axis distance in BIDS depends on ring-ring contact. The cant of the rings with respect to the <u>b</u> axis of 56° and 60° accounts for the thickness of the cell relative to the thinnest dimension of a benzene ring (3.4Å)[30]. Figure 11 shows the orientation of the molecule in the unit cell.

Figure 11. BIDS Unit Cell Contents



CHAPTER 6: DISCUSSION

A. Bond Lengths and Angles - The Empirical Evidence

The crystal structures of the three compounds studied have confirmed their formulation[14] as benzylidenimine moieties joined by chains of dicovalent sulfur atoms.

Table 14 shows some comparative bond lengths and bond angles, including dihedral angles, in BITS, BITrS, and BIDS. The errors listed are calculated by the FORTRAN program MOLG from the combined least-squares errors in the refinements of the structures and the unit cell dimensions. In the case of BITS, these least-squares errors have been increased by a factor of $\sqrt{2}$ (see p. 34). No thermal corrections have been made.

The large anisotropic temperature factors found for all atoms, including sulfur, imply potentially large corrections to the bond lengths arising from thermal motion. However, inspection of the Figures 3, 8, and 10 showing the 50% probability ellipsoids and comparison with their rms displacements, in Tables 1, 7, and 10, shows that the thermal displacements in the directions of the bonds are similar in all cases and thus will not likely change the interatomic distances very much. The sulfur atoms are also most likely to move independently of the other atoms in the structure. This is true since they are the heaviest atoms in the

Table 14: Selected bond lengths (Å)

	BITS		BITrS	BIDS
S-S	2.024(4)	}outer	2.049(6)	2.035(4)
	2.028(4)			
	2.084(4)(inner)			
S-N	1.691(9)		1.666(10)	1.693(3)
	1.686(9)			1.686(5)
N-C	1.260(13)		1.249(16)	1.265(4)
	1.232(13)			1.270(3)
exocyclic C-C	1.467(14)		1.453(17)	1.467(3)
	1.469(13)			1.468(5)

Selected bond angles (°)

SSS	106.4(3)	107.4(3)	-------
	106.3(3)		
SSN	111.2(4)	110.2(5)	111.1(3)
	110.5(4)		111.2(5)
SNC	125.1(6)	127.7(10)	123.9(3)
	124.0(6)		125.0(3)
NCC	121.0(11)	123.8(13)	121.1(3)
	122.8(11)		121.1(3)

Selected dihedral angles (°)

SSSS	105.0	------	-------
NSSS	93.8	81.85	80.7(NSSN)
	89.8		

structure and also because they are not constrained by steric hindrance or ring strain. The sulfur atom positions are of primary interest in the present study, and corrections based on thermal motion would involve a number of questionable assumptions about the ways in which vibrations coupled atoms together,* so they were not made. Nevertheless calculations of the type performed by Busing and Levy[35] were carried out using the program MOLG in order to get some idea of at least the magnitudes that these corrections could have. In all cases except those bonds involving hydrogen, the minimum "corrected" distance so calculated, for correlated parallel motion, was within 0.002Å of the uncorrected distance. The maximum, for correlated anti-parallel motion, was always greater than the uncorrected distance, corrections varying from as little as 0.12Å for S-S bonds to as much as 0.35Å for C-C bonds. (Carbon-hydrogen bond corrections were larger, and the assumptions simpler, so corrections may be justified; see pp. 69&76.) In view of the magnitude of

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*Busing and Levy[35]: "While it is clear that errors introduced by neglect of thermal effects will frequently be appreciable, it is seldom possible, on the basis of available information, to make the rigorously appropriate corrections. Specifically, a knowledge of the correlation in thermal displacements of the two atoms, that is their joint distribution, is needed, and this in general would require a detailed analysis of the dynamics of the atomic system. However, it frequently happens that useful estimates can be made from simplified models of the vibrating system, and these estimates may serve as acceptable approximations to the actual system; it is also possible to place rigorous upper and lower bounds upon the corrections."

these corrections, and the inability to calculate accurate corrections, improved accuracy could be best obtained by refinement of low-temperature intensity data. This is a step that would be well advised if further work were done on these compounds.

The similarity of these three compounds, differing only in numbers of sulfur atoms, suggests that systematic error corrections would likely tend to be in the same direction. In other words, differences between atom positions among the compounds would likely remain constant even though absolute atom positions might change by systematic error corrections.

For purposes of comparing two bond lengths,

$$\sigma_{\Delta}{}^{2} = \sigma_{1}{}^{2} + \sigma_{2}{}^{2}$$

assuming no correlation between the atom positions in the two bonds. If the two bonds originate from a common atom, (see p. 28):

$$\sigma_{\Delta}{}^{2} = \sigma_{AB}{}^{2} + \sigma_{AC}{}^{2} + 2\sigma_{A}{}^{2}\cos\theta \qquad (3)$$

In BITS, the outer two sulfur bond lengths (S_1-S_2 and S_3-S_4) differ by 0.004(6)Å. Hence the two outer S-S bond lengths do not differ significantly; the mean outer S-S bond length is thus 2.026(3)Å. The bond angles S_1-S_2-S_3 and S_2-S_3-S_4 differ by 0.1(4)°, again an insignificant difference. θ in equation 3 is then 106.3(2)° for purposes of comparison of the inner and outer bonds; $\sigma_A = 0.003$Å (Table 1--pooled e.s.d. from errors on S_2 and S_3). The difference between the inner and outer S-S bonds is then 0.058(6)Å, i.e. 10 pooled standard deviations, a highly significant difference. Clearly alternation of S-S bond lengths occurs in BITS.

The inner S-S distance in BITS is significantly longer than any other bond in any of the three structures. The next longest bond, the sulfur-sulfur distance in BITrS, is less by 0.035(7)Å, or 4.8 standard deviations. The BITrS S-S bond is in turn longer than the outer S-S bonds in BITS by 0.023(7)Å, or 3.4 standard deviations; the probability that the latter two types of bonds are equivalent is thus less than 0.1%.[36] On the other hand, the difference between the S-S distance in BIDS and that in BITrS, and the difference between the S-S distance in BIDS and the outer S-S bond length in BITS, are much less significant. The difference between the BIDS and BITrS S-S lengths is 0.014(7)Å, or 1.9 standard deviations; the probability that the bonds are equivalent is therefore at least 5%. The difference between the S-S bond in BIDS and the outer bonds in BITS is 0.009(5)Å, or 1.8σ; the probability of equivalence is at least 7.5%. Thus the four unique S-S bond distances are in decreasing order of length:

inner BITS >> BITrS > BIDS > outer BITS, where >> indicates significantly greater than and > indicates probably greater than.

Among the four sulfur-nitrogen distances in BITS and BIDS, the maximum difference between any two is 0.007(6)Å; the "best value"[*], then, is

$$x = \frac{\sum_i (x_i/\sigma_i^2)}{\sum_i (1/\sigma_i^2)} = \frac{30.246\text{x}10^4}{17.889\text{x}10^4} = 1.691\text{Å}$$

$$\sigma^2(\bar{x}) = \frac{1}{1.7889\text{x}10^5} = 5.59\text{x}10^{-6};\ \sigma(\bar{x}) = 0.0024$$

The S-N distance in BITrS, however, is 0.025(10)Å less than this "best value"; the probability that the S-N bond in BITrS is equivalent to those in BITS and BIDS is thus only about 1%. If all five are included together anyway, however, the "best value" becomes 1.689(2)Å, in fair agreement with the value of 1.66Å predicted by Sasaki[†] from the infrared spectra of the benzylidenimine polysulfides on the basis of the empirical formula:[37]

$$r_{SN} = 0.0483(\mu_{SN}) + 1.099$$

where r_{SN} = bond length in Å, and μ_{SN} = wave length of stretching frequency in $\mu\,(\text{cm}^{-1})$. The S-N distance is

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[*] See pp. 27-28; Reference 29a.

[†] Reference 17, p. 38.

substantially shorter than the "normal" single N-S bond length of 1.76Å (sulfamic acid, $H_3\overset{+}{N}-SO_3^-$), or the single bond radii sum[30] of 1.74Å, suggesting some double bond character. The empirical plot of Chapman and Waddington[38] relating bond length to bond order implies a bond order of about 1.4. Shortening of N-S single bonds is more the rule then the exception whenever a lone pair resides on nitrogen.[10] The average value of 1.69Å found in these three compounds is not to be construed in any way as an "unusual" N-S bond length. Presumably dπ-pπ bonding between sulfur and nitrogen provides the explanation.

The combined "best value" for the five carbon-nitrogen distances is

$$\bar{x} = \frac{240435}{189863} = 1.267\text{Å}.$$

$$\sigma^2(\bar{x}) = \frac{1}{189863} = 5.73\text{x}10^{-6};\ \sigma(\bar{x}) = 0.0024\text{Å}.$$

The maximum deviation from this combined value is the N_2-C_8 distance in BITS, differing by .035(13)Å--possibly significant (i.e. a 1% confidence level). This distance is typical of carbon-nitrogen double bonds.[10]

The combined "best value" for the five exocyclic carbon-carbon distances is

$$\bar{x} = \frac{243,141}{165,745} = 1.467\text{Å} \quad \sigma^2(\bar{x}) = 6.033\text{x}10^{-6};\ \sigma(\bar{x}) = 0.0025\text{Å}.$$

The maximum deviation from this combined value is the C_1-C_2 distance in BITrS, differing by 0.014(17)Å. This distance is significantly less than the carbon-phenyl average distance of 1.506(5)Å normally quoted suggesting increased double bond character. This is to be expected due to overlap of the $p\pi$ orbitals of the C-N double bond with the $p\pi$ orbitals of the aromatic ring. The coplanarity of the exocyclic carbon, nitrogen, and sulfur atoms with the ring in each case (Tables 4, 9, and 13) substantiates $p\pi$-orbital overlap from the ring through the chain.

The average sulfur-sulfur-sulfur included angle in BITS, at 106.3(3)°, differs from the S-S-S angle in BITrS by 1.1(4)°, or 2.6 standard deviations, significantly different at the 1% confidence level; the angles were therefore not averaged. On the other hand, precision is not high enough in the NSS included angles to attribute significance to the 1.0(6)° maximum difference (between the $N_1S_1S_2$ angles in BITS and the NS_2S_1 angle in BITrS); the combined "best value" for the five angles is

$\bar{x} = 110.92^\circ$; $\sigma^2(\bar{x}) = 1/38.521 = .02596$; $\sigma(\bar{x}) = 0.16^\circ$. The maximum deviation then from this combined value is the NS_2S_1 angle in BITrS, differing by 0.7(5)°.

BITrS deviates significantly from BITS and BIDS in the SNC angles. The combined "best value" for the 4 SNC angles in BITS and BIDS is:

$$\bar{x} = \frac{3829.05}{30.759} = 124.5(2)^{\circ};$$

The maximum deviation among the four angles from this combined value is the $S_1N_1C_1$ in BIDS, differing by 0.61(35)°; the difference of this best value from the SNC angle in BITrS is 3.2(10)°, or 3.2 standard deviations, significantly different at the 0.1% confidence level.

The "best value" for the five NCC angles is

$$\bar{x} = \frac{1764.1}{14.538} = 121.34^{\circ}. \quad \sigma^2(\bar{x}) = 0.06877; \ \sigma(\bar{x}) = 0.26^{\circ}.$$

The maximum deviation from this value is the NC_1C_2 angle in BITrS, differing by 2.5(σ=1.25)°.

To be successful, any explanations should account for the following facts (priorities being in the order listed):

(1) The substantial sulfur-sulfur bond length alternation in BITS,

(2) The order of S-S bond lengths:

inner BITS >> BITrS > BIDS > outer BITS,

(3) The near orthogonality of bond angles involving sulfur, including dihedral angles,

(4) The similarity between BITrS and BIDS and difference from BITS in SSSN dihedral angles (Tables 4, 9 and 13),

(5) The suggestion of difference of BITrS from BITS

and BIDS, noted in the S-N bond length and NCC angle especially.

B. Bond Lengths - Possible Explanations

The compound studied by Ricci and Bernal[9] contains two chains of four sulfur atoms each. They found that in each chain, the outer two sulfur-sulfur bonds (2.026(2), 2.025(2), 2.040(2) 2.020(2)Å, "best value" 2.028(1)Å) were shorter than the inner sulfur-sulfur bond (2.065(2), 2.066(2)Å, "best value" 2.0655(14)Å), the difference between inner and outer bonds being 0.0375(17)Å. Their suggested explanation is that the π-systems of the two phenyl rings are linked by "butadiene-like" S_4 chains. However, in addition at least four other possible explanations seem worthy of consideration.

(1) There was the short sulfur-oxygen non-bonded distance (2.77Å) in their compound. While it is not clear just what effect this should have, it is certainly possible that it might have some effect on the electron density distribution around the sulfur and therefore on the bonding electrons between the sulfurs, and thus on the outer S-S bond length.

(2) It is also conceivable that inductive effects might account for the observed bond length alternation. Withdrawal of electron density from the N-S-S bonding region might affect mainly the central S-S bond, making it anomalously long, and implying that the outer two bonds are more like true single bonds.

It would be useful to be able to refer for comparison to a standard sulfur-sulfur single bond length, but the value for that length is uncertain. The S-S bond length in S_8 is 2.048Å[39], and formally single bond lengths have been reported ranging from 1.999(5)Å[40] to 2.39(1)Å.[41] Huggins[42] calculated a value of 2.053(2)Å on the basis of a bond energy-bond length relationship; the Pauling[30] sum of covalent radii is 2.08Å, based on an empirical averaging over a wide range of lengths.[43] The value of 2.11(2)Å from Cs_2S_6[44] has been taken as a true single bond length,[45] but that determination is highly uncertain (see p. 105). In short, the sulfur-sulfur single bond is not known well enough to rule out any hypothesis solely on the basis of comparison to an absolute standard.

(3) On the other hand, the nitrogen atoms might polarize the d-orbitals on the adjacent sulfur atoms, with resonance contributions from such structures as

$$\mathrm{R{-}\overset{-}{N}{-}\overset{\delta+}{S}{=}\overset{\delta'+}{S}{-}\overset{\delta'+}{S}{=}\overset{\delta+}{S}{-}\overset{-}{N}{-}R}$$

(4) Hyperconjugation has been suggested to account for bond lengths in disulfides;[46] by extension, contributions to ground electronic states might be expected from resonance structures such as

$$\mathrm{\overset{-}{R}\quad S{=}\overset{+}{S}{-}S{-}S{-}R}$$

(5) The tetrasulfur chain itself might be internally stabilized by redistribution of electron density from that of pure single bonds: contributions from resonance structures such as

$$R-\overset{+}{S}=\overset{-}{S}-\overset{-}{S}=\overset{+}{S}-R,\quad R-\overset{-}{S}=\overset{+}{S}-\overset{+}{S}=\overset{-}{S}-R,$$

and/or

$$R-\overset{+}{S}=\overset{-}{S}-\overset{+}{S}=\overset{-}{S}-R.$$

This hypothesis would predict the occurrence of bond-length alternation in almost any tetrasulfur chain, regardless of what it was attached to.

While consideration of the compound of Ricci and Bernal does not permit resolution in favor of one or another of these explanations, the compounds studied here might. Aromatic π-systems are joined by 2-, 3-, and 4-sulfur chains and the extraneous influences of non-bonding interaction are largely avoided.

The idea that the sulfur-oxygen non-bonded interaction in Ricci and Bernal's compound was a significant contributor to the S-S bond-length alternation that they observed can be eliminated in respect of this study, since a similar alternation was found in the absence of any possibility of such a non-bonded interaction (See Table 4 in Chapter 3 for nearest neighbor distances).

The five remaining plausible explanations for the behavior (i.e. alternation) of the tetrasulfur chain each permits predictions about the behavior of trisulfide and disulfide chains, which can then be compared with the empirical data. In combination with other information, then, perhaps some conclusions about the nature of the bonding in polysulfur chains could be drawn.

The inductive explanation predicts that withdrawal of electron density from the polysulfur chain would affect the chain in the same way, though not necessarily to the same extent, regardless of the number of sulfur atoms in the chain. With only a certain amount of electron density available to donate from the two benzylidenimine substituents to the sulfur chain in each case, and differing numbers of sulfur atoms to share it among, the greatest bond-shortening effect would be expected in BIDS, an intermediate amount in BITrS, and the least shortening in BITS. This trend is not observed.

Further evidence against a simple inductive effect comes from ^{19}F-nmr data on m- and p- fluorine substituted benzylidenimine polysulfides. Taft, et. al.,[47] have studied a large number of meta- and para-substituted fluorobenzenes, and correlated the ^{19}F chemical shifts with accepted inductive and resonance parameters (σ_I and σ_Ro derived from kinetic data) for the substituents. They conclude that the chemical shift of a meta-substituted fluorobenzene is a linear function of the inductive ability of the substituent to donate or withdraw electron density to or from the ring, i.e.:

$$\int_{H}^{m-x} = (-7.10)\sigma_I + 0.60 \qquad (4)$$

where $\int_{H}^{m-x}$ represents the chemical shift with respect to unsubstituted fluorobenzene. The shift with respect to unsubstituted fluorobenzene of a para-substituted fluorobenzene was shown to be a linear function of both the resonance and the inductive electron donating or withdrawing power of the substituent. Thus the resonance effect can be isolated by subtracting the meta shift from the para shift:

$$-29.5\sigma_R{}^{o} = \int_{H}^{p-x} - \int_{H}^{m-x} \qquad (5)$$

The constants -7.10, 0.60, and -29.5 are parameters obtained from a least-squares fit to a line of

$$\sigma_I \text{ vs. } \int_{H}^{m-x}$$

for the first two constants, and

$$\int_{H}^{p-x} \text{ vs. } (m\sigma_R{}^{o} - 7.1\sigma_I + 0.60)$$

for the third constant (=m) for a large number of substituents.

The difluoro derivatives of BITS, BITrS, and BIDS were prepared from meta- and para-fluorobenzylamine and the ^{19}F-nmr's studied.[48] The results are summarized in Table 15. The ^{19}F shifts of the tetrasulfide are slightly anomalous.

Table 15

^{19}F-nmr (@ 56.4 MHz) chemical shifts of meta- and para-disubstituted benzylidenimine polysulfides[47]

Compound	Chemical shift (ppm)	Relative to:	σ_I
m-fluoro BITS	-0.05(2)	fluorobenzene	0.092
m-fluoro BITrS	-0.76(5)	fluorobenzene	0.192
m-fluoro BIDS	-0.78(2)	fluorobenzene	0.194
p-fluoro BITS	-4.42(2)	fluorobenzene	
p-fluoro BITrS	-4.52(2)	fluorobenzene	
p-fluoro BIDS	-4.63(2)	fluorobenzene	
			$\sigma_R{}^{o}$
p-fluoro BITS	-4.39(3)	m-fluoro BITS	0.149
p-fluoro BITrS	-3.75(6)	m-fluoro BITrS	0.127
p-fluoro BIDS	-3.85(3)	m-fluoro BIDS	0.130

^{1}H-nmr (@ 60.0 MHz) chemical shifts (ppm) benzylidene proton (relative to TMS)[14]

BITS	-7.87(5)*
BITrS	-8.42(5)
BIDS	-8.14(5)

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*Absolute error estimates (private communication from F. P. Olsen); relative to each other the precisions are estimated at ±0.02 ppm.

In particular, the inductive effect is smaller in BITS than for either of the other two. A smooth trend expected from the inductive hypothesis in going from four to three to two sulfurs in the chain is not found, either in bond lengths or in the effect measured from the ^{19}F-nmr spectra. Thus, while the absolute lengths found in the sulfur chains are indubitably affected by inductive donation from or to the attached organic moieties, the explanation for the differences in sulfur-sulfur distances must be sought elsewhere.

The sulfur-sulfur bond lengths in BITS alternate markedly, implying greater, then lesser, then greater bond order in the bonds in moving across the chain. Such an alternation is not possible in the trisulfide chain, and indeed, the bond length found here is intermediate between the extremes found in BITS. In BIDS it is again possible to "conjugate" from one benzene ring to the other. The slight shortening of the S-S bond in BIDS relative to that in BITrS may be indicative of such an effect.

In other ways also BIDS seems to be more like BITS than like BITrS. The sulfur-nitrogen distance in BITrS is less than those in BITS and BIDS (which are all similar), as would be expected if the electron density in the S-N bonds in BITS and BIDS had been sacrificed to the π systems in the neighboring S-S bonds. The larger SNC included angle in BITrS, implying greater s character in the σ-bonds,[49a] also is consistent with a greater π-bond character in the S-N bond, as indicated by its shortness with respect to the S-N bonds in BITS and BIDS. The ^{1}H-nmr spectra[14] for the benzylidene protons in the three compounds also suggest greater similarity between BIDS and BITS than between either and BITrS (Table 15).

According to Ricci and Bernal,[9b] "...the consistency in the alternation of long and short bonds {in compound I*} suggests an electronic interaction between the two phenyl rings across the chains much in the manner expected if the S_4 fragments were butadiene linkages." Overlap between pπ orbitals as in butadiene requires coplanarity of the bonds, i.e. 0° dihedral angles, whereas what they found were dihedral angles of 89° in both chains. Thus effective pπ-pπ overlap in the sulfur chain can be ruled out by the geometry. From the benzene ring up to the first sulfur atom in the chain, conditions obtain for pπ-pπ overlap for all three molecules of this study, i.e. planarity and bond angles near the 120° required for sp^2 hybridization. After that point the dihedral angles change abruptly from being near 0° (planar) to being near 90°, so that a p orbital which is perpendicular to a plane of three atoms is parallel to a fourth, and cannot effectively form π-molecular orbitals with any atomic orbitals on the fourth atom. Either pπ-dπ or pπ-pπ conjugation can extend indefinitely over a planar system, but where dihedral angles in a chain deviate substantially from 0°, molecular

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*See page 4.

orbitals are limited in extent to three atoms. Thus one ring should have no appreciable resonance effect upon the other.

Some direct evidence concerning the amount of π-bond character conducted from one ring to another across the polysulfur chain might be expected from the $\sigma_R o$'s obtained from the ^{19}F-nmr's (see page 91).

Strictly speaking, the substituents on the m- and p-fluorobenzenes are not identical, since at the far end of the large substituent $CHNS_xNCHC_6H_5F$ for each homologue, the fluorine is meta for measurement of $\int_{H}^{m-x}$ and para for measurement of $\int_{H}^{p-x}$. This difference has no effect on σ_I, which is measured from $\int_{H}^{m-x}$ alone, but in the expression

$$-29.5\sigma_R o = \int_{H}^{p-x} - \int_{H}^{m-x},$$

the x's are different, and thus true $\sigma_R o$'s are not obtained.* The effect which this difference has may be thought of as arising from the resonance contribution from a para-fluorine atom. The maximum error this difference could cause may be estimated by considering the resonance contribution from a fluorine atom attached directly to the ring, i.e. for p-difluorobenzene[47]

$$\sigma_R o = \frac{6.80+3.03}{-29.5} = -0.333.$$

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*The measurement should be for the mixed m-fluorobenzylidenimine p-fluorobenzylidenimine polysulfides.

Thus, the resonance donation of π-electron density into the ring will measure higher than it should if in p-x the x substituent had a meta-fluorine atom to make it strictly comparable to m-x. The extent of the error will depend upon the efficiency of conduction of π-electron density from the one benzylidenimine through the polysulfur chain, and into the other benzylidenimine. Thus, the error could conceivably lie between $\sigma_R o$ for m- and p-difluorobenzene for perfectly efficient conduction, and zero for an insulating polysulfur chain; the resonance electron density donation which is measured is probably higher than the true value according to this efficiency. The positive $\sigma_R o$'s measured for the substituted benzylidenimine polysulfides indicate electron withdrawal from the ring, and maximum withdrawal in BITS. If the true $\sigma_R o$'s were all equal for the three compounds, this "greatest withdrawal" measured for BITS would indicate that conduction across the sulfur chain of the resonance contribution from the p-fluorine was least for the tetrasulfide. That is a rather optimistic assumption, however, considering the small differences in $\sigma_R o$'s found among the three benzylidenimine polysulfides (maximum difference calculated from[47] $\Delta q_{(c)} = 0.133 \Delta \sigma_R o = 0.003$ π-electrons at a ring carbon atom), and considering the unknown magnitude of the error introduced by the difference in x between m-x and p-x. True $\sigma_R o$'s are needed to make this distinction.

Polarization of the d-orbitals on sulfur by the nitrogen (suggested explanation number 3, page 88) implies resonance contribution in BITrS from

$$R—\overset{-}{N}—\overset{\delta+}{S}—S—\overset{\delta+}{S}—\overset{-}{N}—R$$

and in BIDS from

$$R—\overset{-}{N}—\overset{\delta+}{S}—\overset{\delta+}{S}—\overset{-}{N}—R.$$

The greater proximity of the positive charges in BIDS would result in a longer S-S bond than the one in BITrS; such is not found.

Some suggestion of contribution from the polarization effect has been inferred from the structure of 1,3-hexasulfurdiimide (Figure 12) by Postma, van Bolhuis, and Vos.[50]

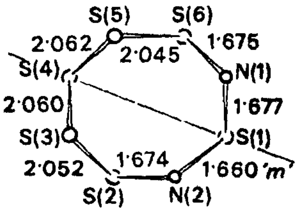
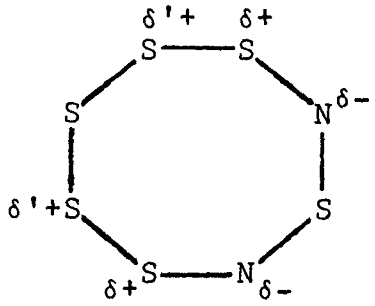


Figure 12. 1,3-hexasulfurdiimide

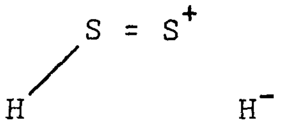
Although the estimated standard deviations on their bond lengths may be optimistic due to their use of the block-diagonal least-squares approximation[27a], the difference between the two inner and two outer sulfur-sulfur bonds in the pentasulfur chain of the molecule is probably still significant. Employing their error estimates, the average of the two S-S bonds next to the N-S bonds is 2.0485(11)Å, and the average of the other two (inner) S-S bonds is 2.061(1)Å, the difference being 0.0125(18)Å, or 7σ (incorporating shared-atom correlation in the pooled e.s.d., see page 28) so that even if their e.s.d.'s are optimistic by a factor of two the difference between the two types of bonds is significant at at least the 0.1% confidence level.

There is no possibility of contribution to this observed effect from an attached aromatic system, and so it may be that the effect is due, as the authors ascribe it, to "an increase of the double bond character because of a polarization of the sulfur d-orbitals by the nitrogen atoms[51,52]," i.e. resonance contributions from structures such as

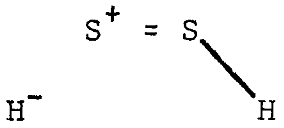


This difference of 1/80Å, then, may indicate the order of magnitude of the contribution to the BITS alternation from the inductive (or polarization) effect. Thus, this effect might account for the difference between the degree of alternation of 0.038Å in the compound of Ricci and Bernal (Compound I) and the degree of alternation in BITS of 0.058Å, since the electronegativity difference is greater between N and S than between C and S.

The hyperconjugation explanation for the relative S-S bond lengths found in the three compounds of this study derives from some considerations by Winnewisser, et. al.[46] They studied the rotational spectrum of H_2S_2 and found an HSS bond angle of $91.3(5)^\circ$ and a dihedral angle of $90^\circ 36(3)'$. They also found a much higher barrier to rotation around the S-S bond than had been found in H_2O_2. They suggest that the orthogonal bond angle implies nearly pure p bonding orbitals from sulfur, and state: "Because of orthogonalities, an unshared pair on each sulfur will be in a p orbital which is in the plane of the S-H bond of the other. As a result, there will be a strong hyperconjugative interaction which will contribute π-bond character to the S-S bond." Qualitatively, there will be a contribution to the ground electronic states from structures such as



and



This contribution to double bond character is their explanation for the difference between 2.08Å, the sum of the covalent radii for sulfur, and 2.055(1)Å, the value found from electron diffraction for the S-S bond in H_2S_2. The electronegativities of sulfur and hydrogen are not very different, permitting small contributions from a configuration with a hydrogen negative with respect to sulfur, whereas in H_2O_2 the much greater electronegativity of oxygen does not permit much hydridic character for the hydrogen, and the O-O bond is therefore not less than the sum of the covalent radii. On the other hand, they attribute the S-S bond shortening (to 1.98(4)Å, 1.97(3)Å, and 1.888(1)Å, respectively) in S_2Br_2,S_2Cl_2 and FSSF to increasing degrees of hyperconjugation, allowed by the increasing electronegativities of the halogens. (The dihedral angles in all three cases are not significantly different from orthogonality: 83.5°(11°), 82.5°(12°), and 87.9°(1.5°).)

Similarly, the SSSN (and NSSN) dihedral angles in the benzylidenimine polysulfides are not appreciably different from orthogonality, at 91.8° (average) for BITS, 81.9° for BITrS, and 80.7° for BIDS. The resonance structures from hyperconjugation for BITS could include

$$\mathrm{R{-}\overset{-}{N}\quad S{=}\overset{+}{S}{-}S{-}S{-}N{-}R}$$

and

$$\mathrm{R{-}N{-}\overset{+}{S}{=}S\quad \overset{-}{S}{-}S{-}N{-}R}$$

the latter accounting for the long inner bond of BITS. (The latter might be expected to contribute slightly less than the former because the SSSS dihedral angle, at 105.0°, differs somewhat from 90°. Pauling[30] gives the variation in energy with dihedral angle as a function of form $A\cos\delta + B\cos^2\delta$; thus, the loss of overlap lies between 3.4% and 6.7%.) For BITrS the resonance forms

$$\mathrm{R{-}\overset{-}{N}\quad S{=}\overset{+}{S}{-}S{-}N{-}R}$$

and

$$\mathrm{R{-}N{-}\overset{+}{S}{=}S\quad \overset{-}{S}{-}N{-}R}$$

affect both sides equally, predicting a bond intermediate in strength between the inner and outer lengths in BITS. For BIDS the resonance forms

$$\mathrm{R{-}\overset{-}{N}\quad S{=}\overset{+}{S}{-}N{-}R}$$

and

$$\mathrm{R{-}N{-}\overset{+}{S}{=}S\quad \overset{-}{N}{-}R}$$

lead again to a shorter length than is found in BITrS; the apparent shortness of the BIDS S-S bond with respect to that in BITrS might indicate this effect. With the greater electronegativity of nitrogen than sulfur, however, the disulfide bond would also be expected to be shorter than the outer bond in BITS, and this is not found.

Further evidence against this hypothesis is the sulfur-nitrogen bonds. With contributions from zero-bond-order resonance forms they would be expected to show anomalous length; instead they show the usual shortening with respect to pure single bonds that is found in N-S bonds where there is a lone pair on the nitrogen atom. It appears necessary to seek further.

The fifth hypothesis, of internal stabilization of tetrasulfur chains, accounts for the alternation of bond length found in tetrasulfur chains by invoking dπ-pπ overlap within the chain, permitted by resonance structures of the type

$$R-\overset{+}{S}=\overset{-}{S}-\overset{-}{S}=\overset{+}{S}-R$$

$$R-\overset{-}{S}=\overset{+}{S}-\overset{+}{S}=\overset{-}{S}-R$$

and

$$R-\overset{-}{S}=\overset{+}{S}-\overset{-}{S}=\overset{+}{S}-R$$

The former two account for the lengthening of the central bond, since they have like charges residing on adjacent atoms. Thus, bond length alternation is predicted generally in tetrasulfur chains, aromatic or not. No particular prediction about the tri- and disulfides results from this hypothesis of a peculiar stability for tetrasulfur chains, except that they be more like each other than like BITS. Some of the evidence is in support of this likeness between BITrS and BIDS as opposed to BITS. In the ^{19}F-nmr, both σ_I'd and σ_R's were more similar between BIDS and BITrS than between either and BITS, and the similarity between BIDS and BITrS is also greater for SSSN (and NSSN) dihedral angles.

There is a considerable variety of other data which provides "circumstantial evidence" in support of some special stability for tetrasulfur chains. Firstly, preparative work: as noted earlier*, BITS can be prepared in a wide variety of different ways. In many cases it is the only member of the homologous series which is isolated; e.g. the spontaneous decomposition of initially solid N-benzylheptasulfurimide results in good yield of BITS, and negligible amounts of other benzylidenimine polysulfides. Homologues with chains of more than four sulfur atoms have not been found.

Thermal decomposition studies on non-aromatic compounds containing polysulfide chains have also indicated a pattern of strong-weak-strong bonds in tetrasulfides.[53,54]

Tobolsky, et. al.[54] have found from mass spectroscopic and kinetic studies (see Table 16) that the central bond in dimethyltetrasulfide is considerably weaker than the S-S bond in dimethyltrisulfide, which in turn is weaker than that in dimethyldisulfide. Furthermore they have found that the MeS_2. radical is much less reactive than the MeS. radical. (While MeS. and other RS. radicals readily abstract hydrogen from triphenylmethane and add to double bonds, heating dimethyltetrasulfide in CCl_4 solution with triphenylmethane and with cyclohexene {i.e. under conditions known from esr studies to produce radicals, specifically the MeS_2. radical} produced no hydrogen abstraction or double-bond addition over

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*Page 4; Reference 14.

Table 16 from Reference 53, p. 1908

Data collected by Muller and Hyne[53] from data originally published by Tobolsky, et. al.,[54] and Pryor[55]

Compound	Bond dissociation energy, kcal/mol
MeS-SMe	69[*]
HS-SH	72[†]
HO-OH	48[†]
MeS-S-SMe	(46)[*]
HS-S-S-SH	64[†]
MeS_2-S_2Me	37[*]
$S_8^{ring} \rightleftarrows S_8^{chain}$	33[*]
HS-H	89[†]

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[*] From Tobolsky, et. al.[54] [†] From Pryor[55].

periods greater than 100 hours.) Tobolsky, et. al.,[54] have extended the studies to other organic RS· and RS_2· fragments, and found a consistant pattern of stability. Muller and Hyne[53] similarly found the HS_2· fragment to be less reactive than the HS· radical. Assuming an inverse correlation between bond dissociation energy and bond length, then, the studies of Hyne, et. al., and Tobolsky, et. al., are rather suggestive of an unusually long central bond in tetrasulfur linkages in general. (Note that the substituents here are alkyl groups rather than conjugating aromatic species.)

Some crystallographic evidence suggests bond length alternation in non-aromatic polysulfides.

Abrahams and Grison[44] studied the structure of cesium hexasulfide in 1953, and found alternation in the sulfur-sulfur bond lengths.

Table 17: Reported bond lengths in Cs_2S_6[44]

S_1-S_2 = 1.99(3)Å

S_2-S_3 = 2.10(3)Å

S_3-S_4 = 2.03(3)Å

S_4-S_5 = 2.12(3)Å

S_5-S_6 = 2.03(3)Å

The first, third, and fifth bonds, with a maximum deviation of 0.03(4)Å from the "best value" of 2.02(2)Å, are clearly not significantly different; the second and fourth bonds, each deviating by 0.01(4) from the mean of 2.11(2), are also not significantly different. In comparing the two means, correlation should be taken into account, so that the pooled standard deviations become

$$\sigma_L = \sigma^2_{1,3,5}+\sigma^2_{2,4}+2\sigma_c^2\cos\theta,$$

where σ_c is the positional error in the shared atoms = 0.021Å, and θ = average bond angle = 108°48'. σ_L then equals 0.032Å, and the difference, 0.09Å, between the two types of bonds is 2.9 standard deviations--an apparently significant difference.

The structure was refined at the time by the double Fourier technique, using an overall temperature factor for a total of 26 variables and over 400 independent observed reflections. The refinement had been only carried to R= 0.194 and it seemed likely that further refinement by full-matrix least squares might be possible. This was carried out using the published parameters and structure factors. At first an overall temperature factor was refined, then isotropic temperature factors on all atoms, and finally with anisotropic components on the cesium atoms. Refinement in each case was continued until maximum shift/error<0.5. An attempted refinement with anisotropic temperature components on the sulfurs resulted in non-positive-definite components on several sulfur atoms, i.e. physically meaningless rms amplitudes of thermal vibration. Hamilton's R-test[35b] showed that anisotropic temperature factors on cesium and isotropic temperature factors on the sulfur atoms were an improvement over the overall temperature factor model at (at least) the 10% confidence level. (The R-test was based on the weighted R-factor, in turn based on Cruickshank weighting schemes which were fairly successful in normalizing the curve of F_o vs $w\Delta^2$.) The unweighted R-factor refined finally to 0.170. The final sulfur-sulfur bond lengths are shown in Table 18.

Table 18: Refined bond lengths in Cs_2S_6

S_1-S_2 = 2.025(26)
S_2-S_3 = 2.028(24)
S_3-S_4 = 1.998(25)
S_4-S_5 = 2.116(26)
S_5-S_6 = 2.025(26)

The changes are not significant with respect to the errors in them, yet virtually all semblance of bond-length alternation has vanished, though the bonds appear no more equivalent than ever. The limiting quantity in the least squares refinement is the quality of the data and recollection is clearly necessary before any conclusions could be drawn from Cs_2S_6 that would have any relevance to the present study. This leaves little crystallographic data to support alternation in non-aromatic polysulfides.

In evidence against S-S bond length alternation in non-aromatic systems are several crystal structure determinations involving chains of dicovalent sulfur between non-aromatic systems which do not show significant bond length alternation (Table 19). In many cases the structures have not been determined with sufficient precision to identify S-S bond differences of the order of 0.05Å, such as found in BITS and compound I. Among those which might have had sufficient precision to find such alternation are tetrathiadecalin[56] (Figure 13), in which no significant

Table 19

Bond lengths in chains of four or more dicovalent sulfur atoms (in order of decreasing apparent difference between inner and outer bonds)

Entry No.	Compound	Bonds				References
		Innermost	Inner	Outer	Outermost	
1.	Cs_2S_6	2.03(3)	2.10(3)		1.99(3)	44
			2.12(3)		2.03(3)	
2.	$S_8C_{20}O_4H_{28}$		2.065(2)	2.026(2)		9
			2.066(2)	2.025(2)		
				2.040(2)		
				2.020(2)		
3.	$BaS_4.H_2O$ (see also #10)		2.07(4)	2.03(4)		6
				2.02(4)		
4.	$Cl_2en_2Co^{III}$-$S_6O_6.2H_2O$		2.054(10)	2.025(15)		58
5.	$S_6N_2H_2$-1,3		2.060(2)	2.045(2)		50
			2.062(2)	2.052(2)		
6.	$S_6N_2H_2$-1,4		2.047(6)	2.037(4)		57
7.	BaS_6O_6		2.05(2)	2.04(2)		59
				2.04(2)		
8.	$S_4C_6H_{12}$ (tetrathia-decalin)		2.060(8)	2.058(8)		56
				2.053(8)		
9.	$(C_5H_5)_2TiS_5$		range of lengths 2.051 -	2.059		60
10.	$BaS_4.H_2O$		2.0633(38)	2.0793(33)		7
			2.0690(35)	2.0624(36)		
11.	$(NH_4)_2PtS_{15}$ ring 1{		2.026(12)	2.040(10)		61
			2.059(13)	2.021(10)		
	ring 2{		2.074(12)	2.064(13)		
			2.066(14)	2.042(1)(sic)		
	ring 3{		2.054(11)	2.033(11)		
			2.082(11)	2.025(11)		
(with average deviation from mean) {	average		2.060(14)	2.038(11)		
	overall average		2.049(17)			

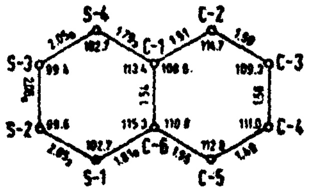


Figure 13.

alternation was found (Δinner-outer = 0.005(9)Å), and 1,4-hexasulfur diimide[57], where the inner bond was found to be greater than the outer bonds in the tetrasulfur chain by only 0.010(7)Å. Foss and Marøy[58] found an inner S-S distance of 2.054(10)Å and an outer distance of 2.025(15)Å for the dicovalent tetrasulfur chain in $Cl_2en_2Co^{III}S_6O_6.2H_2O$ with a bond angle of 105.8(7)°. This is a difference of 0.029(20)Å, significant only at the 15% confidence level and therefore not acceptable. (The difference is of interest, however, in the light of this study since it is as consistent with a larger distance as with a smaller one--i.e. a difference of 0.058Å is as likely as one of 0.000Å. The determination is only precise enough to be tantalizing)

Abrahams and Bernstein[7] obtained two inner and two outer independent S-S distances in their careful redetermination of the structure of $BaS_4.H_2O$: 2.0633(38), 2.0690(35)Å (inner) and 2.0793(33), 2.0624(36)Å (outer). They discuss the statistical implications in detail. Although they did not conclude definitely that the differences were not significant, the probability that the inner bond in $BaS_4.H_2O$ is longer than the outer bond by more than 0.01Å is less than 0.5%.

The observation of substantial tetrasulfide bond length alternation in two aromatic compounds and in virtually no non-aromatic compounds implies that the π-orbitals of attached substituents directly influence the bond order in the terminal sulfur-sulfur bonds. Contribution to the observed effect from internal redistribution of electron density in the chain is apparently small.

Apparently there must be more than one contributing factor to account for the observed sulfur-sulfur bond lengths in the three compounds. These observations can probably be interpreted in terms of some conbination of effects, including hyperconjugation, internal redistribution of π-electron density within the sulfur chain, and d-orbital polarization by the adjacent nitrogen atoms, no one of which hypotheses is adequate by itself.

CHAPTER 7: SUMMARY OF CONCLUSIONS

(1) The crystal and molecular structures of benzylidenimine tetra-, tri-, and disulfides have been determined.

(2) The S-S bonds in BITS alternate in length--short-long-short--by an amount judged to be "significant".

(3) A cis-cis orientation of the benzylidenimine substituents with respect to the SSS planes was found in BITS.

(4) Molecular configurations of the three molecules appear to be dictated by the requirement that SSSS dihedral angles be near 90° rather than by packing considerations.

(5) S...O non-bonded interaction as a possible explanation for the observation of Ricci and Bernal[9] is rejected.

(6) An explanation for the amount of S-S bond length alternation found, based solely on differences in the inductive effect at different distances from the benzylidenimine substituents, has been rejected.

(7) Hyperconjugation as a possible explanation is inadequate.

(8) The hypothesis of a peculiar uniqueness of the tetrasulfur chain cannot be completely ruled out, but is inadequate in itself.

(9) A "butadiene-like" conjugative explanation ($p\pi$-$p\pi$) has been ruled out.

(10) Conduction of π-electron density from one benzene ring to the other is unlikely.

(11) Polarization of the d-orbitals by the adjacent nitrogen atoms probably accounts for some, but not all, of the observed bond length alternation.

(12) A combination of effects involving $d\pi$-$p\pi$ orbital overlap to produce multiple bond character in the outer sulfur-sulfur bonds of BITS appears necessary to explain the observations.

APPENDIX: CRYSTAL AND MOLECULAR STRUCTURE OF o-CHLOROBENZYLIDENIMINE DISULFIDE (o-CLBIDS)

Solution of the structure of o-ChloroBenzylidenImine DiSulfide was undertaken at a time when the structure of the unsubstituted disulfide (BIDS) was defying solution, in the hope that its molecular configuration might provide clues to the solution of the structure of BIDS. It was not used for this purpose, however, since the structure of BIDS was solved independently (see Chapter 5) at about the same time that the structure of o-ClBIDS was solved. Because the compound was not exactly homologous with the series of unsubstituted benzylidenimine polysulfides, and because the precision of the determination was too poor for comparisons with the other compounds to be of general utility, it has not been included in the main body of the thesis.

A. Solution of the Structure

The compound was obtained from the reaction of sulfur with benzylamine in the presence of lead oxide as a sulfide scavenger:

$$5S + 2o\text{-}ClC_6H_4CH_2NH_2 + 3PbO \rightarrow 3PbS + (o\text{-}ClC_6H_4CHN)_2S_2 + 3H_2O.$$

The product was purified by fractional crystallization from methanol and further recrystallization from benzene to give white needles melting at 130-1°.

Weissenberg 0kℓ and 1kℓ photographs showed that the crystal class was monoclinic and confirmed the space groups as $P2_1/c$; these films and all subsequent measured intensities were only consistent with systematic absences of type h0ℓ for ℓ odd and 0k0 for k odd. Accurate cell parameters were determined by least squares refinement of a, b, c, and β to the diffractometer-measured 2θ angles of 20 reflections to be a= 4.867(2), b= 25.773(6), c= 12.404(3)Å and β= 104.95(3)Å. Intensity data were collected on the Syntex automatic diffractometer (conditions as specified pp. 65-6) from a crystal measuring 0.033x0.04x0.27 mm. No absorption corrections were made; the maximum variation in transmission factor would be ±7.5% (μ = 6.72 cm^{-1} for MoKα radiation). A total of 936 reflections were measured in one asymmetric zone. The intensities of 818 symmetry independent non-zero reflections were obtained after averaging, 505 of which were larger than three standard deviations in the intensity. Standard deviations were obtained from:

$$\sigma_I{}^2 = \sigma^2_{\text{counting}} + (0.025F_o{}^2)^2$$

The XRAY67 program DATFIX was used to estimate an overall temperature factor and absolute scale factor and to calculate quasi-normalized structure factors (E's). The XRAY67 programs SIGMA2 and PHASE were applied to the resulting E's to obtain phases (signs); PHASE determined 71 signs to be positive and 71 negative. The positions of the two sulfur atoms and the two chlorine atoms were determined from the Fourier (E) map calculated from the 142 signed E's.

The rest of the structure was gradually elucidated using electron density and difference Fourier maps calculated using the full data set and phases calculated from the atoms already discovered. The assumption was made that the two SNC_7Cl moieties were each planar with 120° angles at carbon and nitrogen. Least squares refinement cycles were carried out first allowing all atoms to vary isotropically. Eventually the sulfur and chlorine atoms were varied with anisotropic temperature factors, for a total of 101 variables. The final ratio of observed reflections to variables was 5.0:1. A Cruickshank weighting scheme (p.67) was applied with final coefficients A= 0.7, B= 0.01, C= 0.001, D= 1000. The final unweighted R-factor ("observed" reflections only) was 0.0605 at a maximum shift/error of 0.43; the average shift/error at this point was 0.10. The final weighted R-factor (all reflections) was 0.067.

B. Description of the Structure

The final refined atomic positional and thermal parameters are given in Table 20. Table 21 lists observed structure factors and those calculated using the final positional and thermal parameters of the refinement. Figure 14 shows the numbering system used in a stereoscopic view of the molecule. Bond lengths and angles are in Table 22.

Table 20

o-ClBIDS positional and thermal parameters

	x/a	y/b	z/b	B(Åx10^3)
S$_1$	.2692(10)	.1190(2)	.3244(4)	-----
S$_2$	.3681(10)	.1930(2)	.2956(4)	-----
Cl$_1$	.2576(11)	.1799(2)	.6041(4)	-----
Cl$_2$	.8058(12)	.0533(2)	.0581(4)	-----
N$_1$	.527(3)	.0910(5)	.4276(10)	44(4)
N$_2$	.546(2)	.1943(5)	.1926(10)	36(4)
C$_1$	.746(4)	.1180(6)	.4787(12)	43(5)
C$_2$	.953(4)	.0893(7)	.5670(13)	45(5)
C$_3$	.191(4)	.1135(6)	.5288(13)	46(5)
C$_4$	.409(4)	.0917(7)	.7133(13)	50(5)
C$_5$	.364(4)	.0394(6)	.7356(13)	51(5)
C$_6$	.120(4)	.0106(6)	.6792(13)	50(5)
C$_7$	.914(4)	.0364(6)	.5947(13)	49(5)
C$_8$	.615(3)	.1525(6)	.1514(12)	37(5)
C$_9$	.761(3)	.1595(6)	.0602(12)	40(5)
C$_{10}$	.863(3)	.1155(6)	.0143(12)	39(5)
C$_{11}$	.016(3)	.1194(6)	.9316(12)	39(5)
C$_{12}$	.054(3)	.1675(6)	.8926(13)	44(5)
C$_{13}$	.960(4)	.2127(7)	.9325(13)	51(5)
C$_{14}$	.803(3)	.2084(6)	.0149(13)	43(5)

Anisotropic thermal parameters $\underline{\underline{U}}$ (Åx10^3)

	U$_{11}$	U$_{22}$	U$_{33}$	U$_{12}$	U$_{13}$	U$_{23}$
S$_1$	46(4)	94(5)	47(3)	-13(4)	15(3)	5(3)
S$_2$	51(4)	72(4)	41(3)	12(3)	15(3)	-2(3)
Cl$_1$	69(4)	51(4)	66(4)	-15(3)	17(3)	-4(3)
Cl$_2$	126(6)	48(3)	68(4)	15(4)	38(4)	-0(3)

Figure 14. Stereoscopic View of the o-ClBIDS Molecule down the a Axis

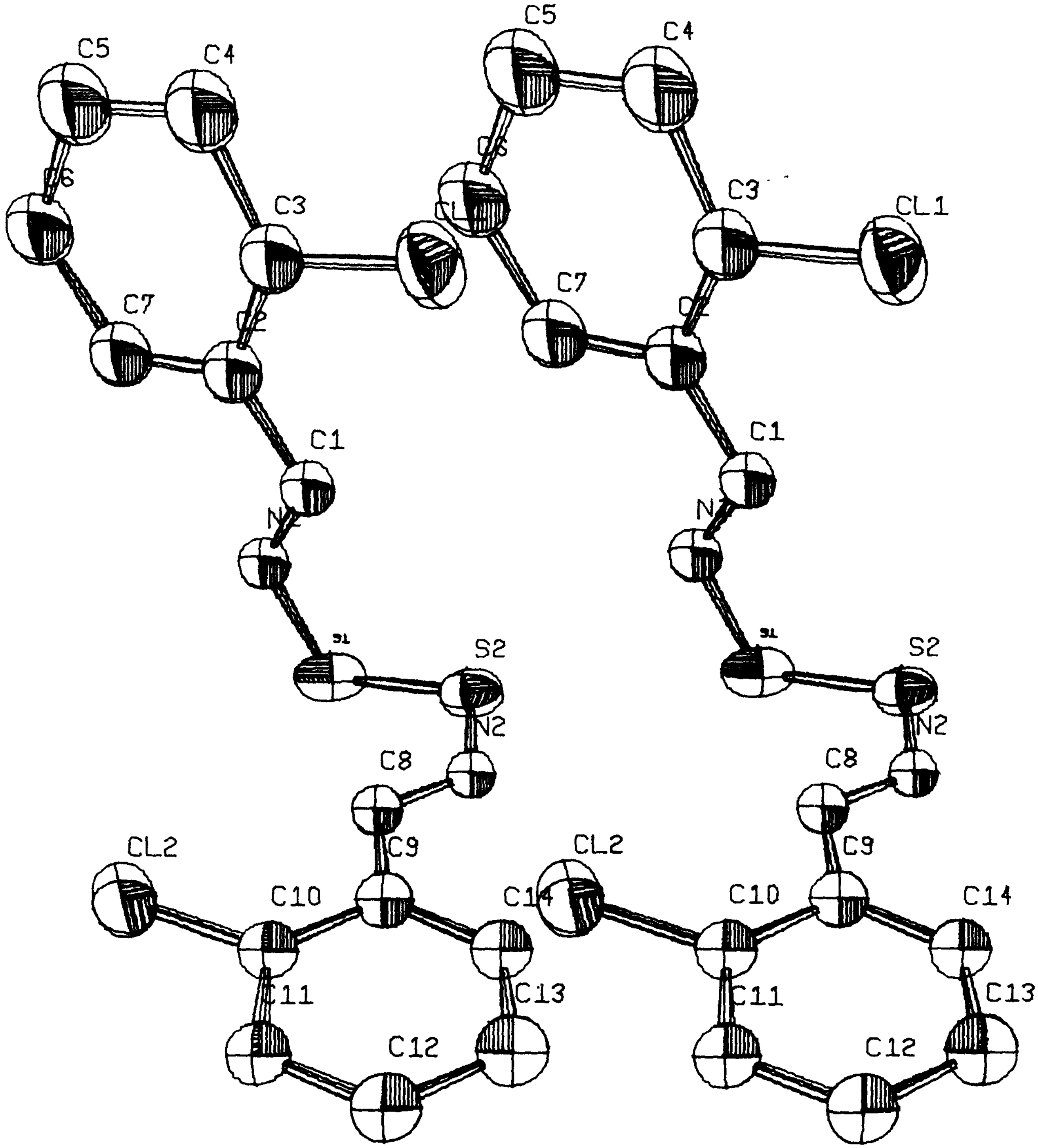


Table 21: o-ClBIDS Observed and Calculated Structure Factors (x10), Unobserved Reflections Indicated by *

K	L		FOBS	FCLC
			H = 0	
0	2		461	453
0	4		270	-268
0	6		252	-208
0	8		625	-626
0	10	*	122	238
1	1		293	-180
1	2		273	-311
1	3		1038	1125
1	4		524	-547
1	5		230	-243
1	6		359	364
1	7		167	68
1	8	*	125	-45
1	9		223	-176
1	10	*	104	-148
2	0		260	-190
2	1		417	-452
2	2		141	231
2	3		411	439
2	4		136	130
2	5	*	106	-41
2	6		203	-182
2	7		983	-979
2	8		143	-92
2	9	*	90	71
2	10		210	-301
3	2		303	-319
3	3		369	-397
3	4		303	-317
3	5	*	21	23
3	6		224	-240
3	7		216	-185
3	8		197	193
3	9	*	68	104
3	10	*	131	-156
4	0		1373	-1417
4	1		593	604
4	2		289	-313
4	3		1389	-1440
4	4		292	296
4	5	*	79	-173
4	6		227	-231
4	7		287	309
4	8	*	103	79
4	9	*	130	-77
5	1		377	420
5	2		371	-384
5	4	*	72	-58
5	5		151	143
5	6		489	-483
5	7	*	116	137
5	8	*	83	5
5	9		331	-314
6	0		454	452
6	1		133	117
6	2		530	-497
6	3		142	144
6	4		434	-451
6	5		347	-359
6	6	*	76	60
6	7	*	93	-116
6	8		138	131
6	9		192	108
7	1		233	-202
7	2		1063	-1060
7	3		177	-156
7	4		537	-533
7	5		180	-166
7	7		178	-166
7	8	*	92	-82
7	9		203	193
8	0		750	-785
8	1		287	273
8	2	*	57	-33
8	3		211	-196
8	5		173	-153
8	6		655	642
8	7		141	-127
8	8	*	107	129
8	9	*	144	-73
9	1		446	-466
9	2	*	59	-10
9	3		377	382
9	4	*	58	81
9	5		203	-200
9	6		158	-180
9	7	*	120	69
9	8	*	90	95
9	9		370	384
10	0		744	765
10	1	*	48	-48
10	2		402	-404
10	3		134	-145
10	4		200	163
10	5		270	280
10	6		310	255
10	7	*	34	23
10	8	*	117	-141
10	9	*	149	-85
11	1		687	-689
11	2		417	476
11	3	*	60	1
11	5		213	195
11	6		362	374
11	7		400	407
12	0		611	-614
12	1	*	59	61
12	2	*	32	-52
12	3		721	716
12	4		389	-370
12	5	*	100	30
12	6		257	-252
12	7		290	-292
12	8	*	125	130
13	1		239	261
13	2		212	-203
13	3		617	-574
13	4		209	220
13	5	*	59	120
13	7	*	77	11
13	8	*	193	125
14	0		771	-717
14	1		615	602
14	2	*	49	55
14	3		165	-160
14	4		159	139
14	5		156	87
14	6	*	106	165
14	7		393	387
15	1		241	226
15	2		124	123
15	3		183	145
15	4		600	590
15	5		182	-175
15	6		224	-213
15	7	*	124	-70
16	0		339	384
16	1		149	-196
16	2		142	-127
16	3	*	79	30
16	5		182	159
16	6		188	195
17	1	*	86	12
17	2	*	120	114
17	3		318	321
17	4	*	69	-3
17	5	*	100	-62
17	6	*	81	222
18	0		209	224
18	2		405	418
18	3		352	351
18	4	*	118	-101
19	1		511	544
19	2	*	159	69
19	3	*	94	58
19	5		187	-138
20	0	*	152	126
20	2	*	42	-52
20	3	*	124	-146
21	4		214	176
K	L		H = 1	
0	0		151	150
0	2		1713	1634
0	-2		864	816
0	4		465	-488
0	-4		206	-125
0	6		404	402
0	-6		1148	-1145
0	8		296	273
0	-8		198	-201
0	-10	*	102	173
1	0		467	-518
1	1		771	692
1	2		1054	1046
1	-2		941	921
1	3		821	776
1	-3		447	-476
1	4		496	500
1	-4		584	578
1	5		469	479
1	-5		474	-465
1	6	*	128	-117
1	-6		276	245
1	7		320	-301
1	-7		169	-171
1	8	*	130	61
1	-8	*	66	17
1	9		194	185
1	-9	*	129	-149
1	-10		268	-252
2	0		433	450
2	1		1810	1636
2	-1		464	520
2	-2		530	-528
2	3		256	-289
2	-3		1528	-1438
2	4		601	590
2	-4		903	-891
2	5	*	142	198
2	-5		305	282
2	6	*	127	-89
2	-6		465	446
2	7	*	114	-82
2	-7		246	-244
2	8	*	152	-187
2	-8		231	-207
2	9		238	-263
2	-9	*	149	159
2	-10		227	230
3	0		242	235
3	1		305	-292
3	-1		676	-699
3	2		310	302
3	-2		1240	1288
3	3		770	-762
3	-3		1003	976
3	4		323	-348
3	-4		754	718
3	5	*	103	20
3	-5	*	94	-11
3	6		300	-295
3	-6		392	-383
3	7		559	543
3	-7		232	-275
3	-8	*	26	-9
3	9		258	-248
3	-9	*	120	84
3	-10	*	184	-185
4	0	*	141	100
4	1		1139	-1079
4	-1		307	291
4	2		374	-356
4	3		677	676
4	-3	*	137	-105
4	4		303	302
4	-4		676	-652
4	5	*	72	31
4	-5		171	210
4	-7		152	191
4	8		219	-215
4	-8	*	104	89
4	9	*	136	-129
4	-9		416	-428
4	-10		301	-298
5	0		778	769
5	1	*	105	116
5	-1		399	-372
5	2		221	-256
5	-2		785	760
5	3		265	301
5	-3		198	-253
5	4		618	-619
5	-4	*	96	-90
5	5		310	-312
5	-5		230	234
5	-6		271	-267
5	7	*	14	-22
5	-7	*	112	-8
5	8	*	72	-140
5	-8		237	-231
5	-9	*	135	199
6	0	*	130	-115
6	1		585	698
6	-1		264	268
6	2		220	-183
6	-2		177	203
6	3		210	174
6	-3		789	780
6	4		302	-306
6	-4		204	184
6	5	*	112	-60
6	-5	*	111	90
6	6	*	127	80
6	-6		260	-279
6	7		257	-240
6	-7		504	-504
6	8	*	120	73
6	-8	*	68	58
6	-9		370	348
6	-10	*	90	-39
7	1		207	-199
7	-1		278	-279
7	-2	*	84	-85
7	3	*	93	47
7	-3		266	248
7	4	*	63	-41
7	-4		233	-211
7	5		179	-182
7	-6		388	398
7	7	*	142	40
7	-7		227	223
7	8		251	-161
7	-8		439	-456
8	0		409	441
8	-1		302	307
8	2		267	-300
8	-2		442	-448
8	3	*	29	-55
8	-3		317	300
8	4	*	86	28
8	-4		358	365
8	5		519	-512
8	-5	*	30	69
8	6		223	-251
8	-6		582	609
8	7		199	-149
8	8	*	135	-100
8	-8	*	78	-114
8	-9		281	-277
9	0		421	393
9	1		397	-367
9	-1		627	636
9	2	*	133	127
9	-2	*	78	-86
9	3		258	-278
9	-3		628	596
9	-4		255	-248
9	-5		205	192
9	6		163	-66
9	-6		355	-338
9	7	*	99	-38
9	8	*	105	-28
9	-9		220	-237
10	0		277	-292
10	1		214	-204
10	2	*	113	-119
10	-2		656	633
10	-3		272	-291
10	4		538	-556
10	-4		574	569
10	5		259	281
10	-5		356	350
10	6	*	140	177
10	-6	*	16	-38
10	7		205	177
10	-7	*	146	213
10	8	*	151	112
10	-8		282	269
10	-9	*	190	-178
11	0		518	-507
11	1	*	115	73
11	-1	*	107	-125
11	2		232	276
11	-2		579	590
11	3	*	89	28
11	-3		336	-350
11	4		423	411
11	-4	*	48	-41
11	5		319	-302
11	-5		383	351
11	6	*	84	46
11	-6	*	144	-153
11	7	*	157	-210
11	-7		227	233
11	-8		357	360
11	-9		220	236
12	0	*	110	-164
12	1		381	397
12	-1		283	-271
12	2		715	-739
12	3		421	-406
12	-3		617	-607
12	4	*	113	159
12	-4	*	59	-75
12	5		218	216
12	-5	*	74	48
12	6	*	77	-27
12	-6		308	299
12	-7	*	47	-134
13	0		575	-583
13	1	*	113	122
13	-1		339	-347
13	2		296	-322
13	-2		185	-198
13	3		261	-252
13	-3		292	331
13	-4		212	185
13	5		356	-380
13	-5	*	67	14
13	6	*	132	82
13	-6		218	198
13	7		246	248
13	-7		215	-201
13	-8	*	112	9
14	1		517	-481
14	-1		248	-230
14	-2		277	-292
14	3		451	475
14	-3		184	-200
14	4		265	309
14	-4	*	73	-82
14	5	*	155	-57
14	-5		210	-205
14	6		197	-173
14	-6		272	216
14	-7		228	239
14	-8	*	71	-34
15	0		367	371
15	1		193	-199
15	-1		302	272
15	2		231	-226
15	-2		345	-342
15	4		371	-367
15	-4		235	-237
15	5	*	133	22
15	-6	*	134	13
16	1	*	138	-87
16	-1		433	-425
16	2	*	107	67
16	-2	*	67	113
16	3	*	54	-31
16	-3	*	151	93
16	4		263	-252
16	-4		271	289
16	5		262	263
16	-5	*	149	137
16	-6		341	-342
16	-7	*	124	-52
17	0		379	-410
17	1	*	29	210
17	2	*	107	-150
17	3		400	415
17	-3		364	-395
17	4	*	127	133
17	-4	*	136	-99
17	5	*	90	76
17	-5		300	-290
17	-6	*	57	72
18	1	*	144	95
18	-1	*	125	44
18	2	*	112	0
18	-2	*	144	-119
18	3		403	-408
18	-3		206	-91
18	4		245	241
18	-4	*	176	-162
19	1	*	145	213
19	-1	*	113	22
19	-2	*	89	-96
19	-3		222	36
19	-4	*	154	86
19	-5		219	-217
20	-1	*	110	142
20	2		279	316
20	-2	*	110	-126
21	0		316	294
K	L		H = 2	
0	0		611	-636
0	2		228	-191
0	-2	*	145	-41
0	4		730	748
0	-4		909	-909
0	6		339	-301
0	-6		298	-284
1	0		478	510
1	1	*	74	49
1	-1	*	67	-57
1	2		251	244
1	-2		463	-474
1	3		302	-319
1	-3		620	-628
1	4		912	912
1	-4		496	-467
1	5	*	140	68
1	-5		212	215
1	6	*	138	-168
1	-6		180	229
1	7		294	322
1	-9	*	67	152
1	-10	*	180	92
2	0	*	130	76
2	1		238	260
2	-1		299	-280
2	2		352	389
2	-2		258	-257
2	3		602	568
2	-3		558	560
2	4		183	-132
2	-4		168	-101
2	-5		546	-499
2	6	*	120	166
2	-6		469	-470
2	7		494	497
2	-7		346	-314
2	-8		408	418
2	-10	*	99	132
3	0		157	221
3	1		790	-816
3	-1		451	-463
3	2	*	79	-9
3	-2		194	191
3	3		554	551
3	-3		316	316
3	4		293	311
3	-4		154	-207
3	-5		355	336
3	-6		154	-131
3	-7	*	69	25
3	-10	*	132	-86
4	0		362	346
4	1		522	516
4	-1	*	102	-84
4	2		205	-186
4	-2		197	-216
4	3	*	111	-119
4	-3		564	-568
4	4		163	-130
4	5	*	77	123
4	-5		246	224
4	6	*	114	119
4	-6		616	566
4	7		230	-137
4	-7	*	123	-170
4	-8	*	66	-121
4	-9	*	151	101
4	-10	*	145	48
5	0		416	400
5	1		366	365
5	-1	*	127	-136
5	2	*	92	13
5	-2	*	111	158
5	3		221	-239
5	-3		263	242
5	4		300	-263
5	5		204	-218
5	-5		504	-508
5	6	*	115	72
5	-6		594	-572
5	7		233	-145
5	-7		477	-424
5	-8		257	-258
5	-9		394	366
6	0		334	-307
6	1		297	-267
6	-1		364	366
6	2		435	-433
6	3		311	226
6	4		291	276
6	-4	*	91	-84
6	-5		491	-510
6	6	*	157	6
6	-6		734	730
6	7	*	184	-37
6	-7		272	267
6	-8	*	86	19
6	-9		426	-447
7	0		280	242
7	1		274	288
7	-1		374	368
7	2		379	337
7	-2		541	-552
7	-3	*	85	7
7	4	*	42	111
7	-6		341	-331
7	-9	*	116	-71
8	1		177	-186
8	-1	*	145	-147
8	2		183	199
8	-2		516	509
8	-3		233	-214
8	4		294	-269
8	-4		212	214
8	5		222	212
8	-5	*	102	160
8	6	*	176	-159
8	-6		689	-712
8	-7	*	73	-170
8	-8		225	218
9	0		324	-297
9	1		371	370
9	-1		157	113
9	2	*	49	-2
9	-2		434	434
9	3	*	90	-82
9	-3	*	130	152
9	4	*	129	-153
9	5	*	21	-13
9	-5		480	462
9	6	*	145	34
9	-6		328	-328
9	-7	*	39	-142
9	-8	*	152	138
9	-9		499	-504
10	0		174	188
10	1		487	465
10	-1	*	140	-182
10	2	*	94	-145
10	-2		457	471
10	3	*	116	138
10	-3		330	-358
10	4		195	215
10	-4	*	86	-54
10	-5		229	223
10	6		348	-337
10	-6	*	10	-13
10	-7	*	132	-65
10	-8		515	-530
11	0		250	265
11	1		314	307
11	-1	*	116	-9
11	2		280	-309
11	-2		190	144
11	3	*	128	-220
11	-3	*	152	160
11	4		184	243
11	5		209	-221
11	-5	*	84	-53
11	-6		223	269
11	-7	*	72	19
11	-8	*	130	105
12	0		246	275
12	1		240	-230
12	2	*	79	100
12	3	*	143	-150
12	-3		481	452
12	-4		214	219
12	5		207	-186
12	-5	*	40	-67
12	-6		179	218
12	-7		212	222
12	-8	*	130	74
13	0		179	-162
13	1		533	-513
13	-1	*	131	-127
13	-2		322	-299
13	3		252	212
13	-3		191	248
13	4	*	18	-57
13	-4	*	98	70
13	5	*	84	-35
13	-5	*	142	-118
13	-6		244	288
13	-7		235	245
14	0		294	307
14	1		243	-208
14	-1	*	77	-82
14	-2	*	71	72
14	3		239	-287
14	-3		158	-120
14	4		218	-202
14	-4	*	58	-85
14	-5		364	342
15	0		280	-279
15	1		244	288
15	-1	*	106	-197
15	2	*	50	-33
15	-2	*	109	184
15	-3	*	46	5
15	4		276	-255
15	-4		312	274
15	-5	*	30	-59
15	-6		243	-246
16	0		376	-407
16	1	*	142	-106
16	2	*	139	-179
16	-2	*	84	70
16	3	*	33	-5
16	-3	*	50	-23
16	-5	*	90	2
16	-6	*	178	202
17	1		441	519
17	-1	*	152	122
17	2	*	175	-201
17	-3		265	-310
17	-4	*	109	26
17	-5	*	158	-148
18	0		252	-308
18	-2	*	142	-167
18	-3		188	119
18	-4	*	91	-13
19	-1		212	-218
K	L		H = 3	
0	0	*	100	119
0	2	*	136	-139
0	-2		570	-560
0	4	*	114	83
0	-4		169	-178
0	-6		196	216
0	-8		239	199
1	0		237	206
1	1	*	137	66
1	-1		268	-256
1	2		195	210
1	-2		308	-301
1	3		242	-259
1	-3		335	300
1	4		380	-358
1	-4		236	-243
1	-5	*	106	30
1	-6		256	-240
1	-8	*	112	33
2	0	*	138	-220
2	1		322	-338
2	-1		282	-264
2	2	*	155	-210
2	-2		261	265
2	3		381	364
2	-3		179	-211
2	4		261	241
2	-4		189	-161
2	-5	*	105	6
2	-6		173	182
2	-7	*	69	109
2	-8	*	164	50
3	0	*	158	134
3	1	*	64	57
3	-1	*	60	-21
3	2	*	74	-49
3	-2	*	91	-116
3	3	*	46	-59
3	-3		250	-240
3	4	*	93	-41
3	-4		174	-188
3	-5		170	196
3	-6		277	270
3	-7	*	138	121
3	-8		236	-234
4	0	*	61	-103
4	1		231	167
4	-1		182	-166
4	2	*	57	72
4	-2	*	33	3
4	3	*	135	40
4	-3	*	141	151
4	4	*	147	-137
4	-4		385	367
4	-5		447	-471
4	-6		189	-177
4	-7	*	77	108
4	-8		234	184
5	0		269	-201
5	1		372	-377
5	-1		242	265
5	2	*	120	129
5	-2		264	195
5	-3	*	149	187
5	4	*	73	120
5	-4	*	58	-58
5	-5	*	63	-74
5	-7		154	191
5	-8	*	60	-67
6	0	*	100	186
6	1	*	84	3
6	-1	*	159	-142
6	2		305	274
6	-2		289	-274
6	3		278	-260
6	-3		540	-537
6	4	*	32	-110
6	-5		338	333
6	-6	*	69	-12
6	-7		200	-190
6	-8		260	223
7	0	*	156	-147
7	1		306	319
7	-1	*	103	-76
7	2	*	154	153
7	-2	*	87	57
7	-3	*	67	-158
7	4	*	17	-96
7	-4	*	148	-140
7	-5	*	167	233
7	-6		357	-396
7	-7		238	-219
7	-8		372	379
8	1		151	-84
8	-1		189	-185
8	2		177	-171
8	-2		530	555
8	-3	*	34	76
8	-4		400	-417
8	-5	*	135	146
8	-6	*	125	-54
8	-7		221	258
9	0	*	60	-21
9	1		307	301
9	-1	*	14	-94
9	2		269	-220
9	-2		264	-194
9	3	*	144	69
9	-3	*	108	-110
9	-4		175	-188
9	-5	*	161	-163
9	-6		373	356
9	-7		321	-351
10	0	*	135	44
10	1	*	126	107
10	-1		150	201
10	-2	*	100	-73
10	3	*	113	85
10	-3		355	336
10	-4	*	146	-36
10	-5		366	-357
10	-6		247	-265
11	0	*	146	109
11	1	*	180	-64
11	-1	*	117	133
11	2	*	145	229
11	-2		222	-217
11	-3	*	176	162
11	-4	*	142	29
11	-5		279	-224
11	-6	*	61	-101
12	1	*	115	-107
12	-1		203	64
12	-2	*	102	10
12	-3	*	153	30
12	-4	*	56	-331
12	-5		273	324
12	-6	*	137	168
13	-2		247	295
13	-3	*	102	-290
13	-4	*	175	198
13	-5		250	278
14	0	*	102	-107
14	-1	*	109	-109
14	-2		263	265
14	-4	*	62	134
K	L		H = 4	
1	-4	*	57	-146
1	-2	*	114	48

Table 22

Molecular geometry of o-chlorobenzylidenimine disulfide (o-ClBIDS)

Bond distances in Å

S_1-S_2	2.022(7)	C_1-C_2	1.480(21)	C_8-C_9	1.496(25)
S_1-N_1	1.704(2)	C_2-C_3	1.367(22)	C_9-C_{10}	1.413(23)
S_2-N_2	1.719(14)	C_3-C_4	1.401(21)	C_{10}-C_{11}	1.418(24)
Cl_1-C_3	1.785(17)	C_4-C_5	1.404(24)	C_{11}-C_{12}	1.360(23)
Cl_2-C_{10}	1.741(17)	C_5-C_6	1.423(23)	C_{12}-C_{13}	1.388(25)
N_1-C_1	1.294(20)	C_6-C_7	1.415(22)	C_{13}-C_{14}	1.430(26)
N_2-C_8	1.274(21)	C_7-C_2	1.429(24)	C_{14}-C_9	1.415(22)

Bond angles in degrees

$S_2S_1N_1$	111.7(5)	$Cl_2C_{10}C_{11}$	116.7(12)	$C_8C_9C_{10}$	119.4(14)
$S_1S_2N_2$	109.7(5)	$C_1C_2C_3$	120.3(15)	$C_8C_9C_{14}$	123.5(15)
$S_1N_1C_1$	119.7(11)	$C_1C_2C_7$	123.3(14)	$C_{10}C_9C_{14}$	117.1(16)
$S_2N_2C_8$	121.4(12)	$C_3C_2C_7$	116.4(14)	$C_9C_{10}C_{11}$	122.6(15)
$N_1C_1C_2$	114.2(14)	$C_2C_3C_4$	127.3(16)	$C_{10}C_{11}C_{12}$	117.8(15)
$N_2C_8C_9$	115.3(14)	$C_3C_4C_5$	114.0(15)	$C_{11}C_{12}C_{13}$	123.4(17)
$Cl_1C_3C_2$	120.4(12)	$C_4C_5C_6$	123.8(14)	$C_{12}C_{13}C_{14}$	118.5(16)
$Cl_1C_3C_4$	112.9(12)	$C_5C_6C_7$	117.5(15)	$C_{13}C_{11}C_9$	120.5(15)
$Cl_2C_{10}C_9$	120.7(13)	$C_6C_7C_2$	121.0(15)		

Selected intermolecular contact distances

$S_1 \ldots C_8$	3.46(2)	$Cl_1 \ldots C_{13}$	3.56(2)	$C_4 \ldots C_7$	3.48(3)
$Cl_1 \ldots C_1$	3.54(2)	$Cl_1 \ldots N_2$	3.59(1)	$C_4 \ldots C_{11}$	3.52(2)

The average C-C distances for the two rings are 1.406Å and 1.404Å respectively; the maximum and average deviations from the overall mean of 1.405Å are 0.045 and 0.016Å. The average C-C-C angles for the two rings are each 120.0°; the maximum deviation of any ring angle from 120° is 7.4°, the average deviation 3.3°.

The "best value" N-S, C-Cl, C=N and exocyclic C-C distances are respectively 1.712(9), 1.763(12), 1.282(14) and 1.484(16)Å. For the SSN, SNC, and NCC angles the "best values" are respectively $110.8(4)^\circ$, $120.1(8)^\circ$, and $114.5(9)^\circ$. The sum of the angles around the carbon atoms to which the chlorine atoms are attached is in each case 360 . The chlorine atoms bend away from the exocyclic carbon atoms, however (contact distances $Cl_1...C_1$ 3.03(2)Å and $Cl_2...C_8$ 3.05(2)Å), so that the four ClCC angles are not equivalent, the inner one being $120.4(9)^\circ$ and the outer one $114.2(9)^\circ$.

The difference between the sulfur-sulfur bond length in o-ClBIDS and the inner distance in BITS is definitely significant at 0.062(8)Å. The difference from the S-S bond in BITrS, at 0.027(9), is also probably significant, but the differences from the BIDS S-S bond and the outer S-S bonds in BITS, at 0.013(8) and 0.004(8) respectively, are not significant. Thus, the S-S bond in o-ClBIDS is consistent with expectations based on the number of sulfur atoms in the chain, but provides no new information.

The difference of the average S-N bond length at 1.712(9)Å from the weighted average of the other three compounds {1.689(2)Å} is 0.023(10)Å, possibly significant. The difference from the S-N bond in BITrS {1.666(10)} is more definitely significant ($\Delta/\sigma = 3.4$).

The carbon-chlorine bond is significantly longer than the 1.70(1)Å quoted in Interatomic Distances Supplement[10] for the aromatic C-Cl average distance ($\Delta/\sigma = 4.0$), and is quite close to the value quoted therein {1.767(5)Å} for the paraffinic C-Cl bond ($\Delta/\sigma = 0.3$).

The nitrogen-carbon and exocyclic C-C distances do not deviate significantly from those found in the other three benzylidenimine polysulfides studied {$\Delta_{NC} = 0.017(14)$ and $\Delta_{c-c} = 0.021(16)$}.

The SSN angle average is not significantly different from the value from the other three structures {$\Delta = 0.2(4)^\circ$}. The SNC and NCC angles {$120.6(8)^\circ$ and $114.8(10)^\circ$ respectively} are both less than those found in the unsubstituted compounds, however: $\Delta_{SNC} = 3.9(8)^\circ$ and $\Delta_{NCC} = 6.6(10)^\circ$.

The general molecular configuration is similar to that in BIDS in that, unlike BITS and BITrS, the packing along the short axis is determined by phenyl ring contacts rather than sulfur-sulfur contacts. The cant of the rings with respect to the short axis (in this case a) is less than in BIDS, accounting for the relatively shorter short axis. The shortest intermolecular contact distance is $S_1 \ldots C_8$ at 3.46(2)Å (Van der Waal's sum 3.55Å[30], but see p. 76); there are no other unusually short contact distances.

REFERENCES AND BIBLIOGRAPHY

1. Rahman, R., Safe, S., and Taylor, A., Quart. Rev., *24*, 208 (1970).

2. Chem. Eng. News, *47* (48), 40 (1969).

3. Nickless, G., Ed., "Inorganic Sulfur Chemistry," Elsevier Publishing Company, New York, 1968, p. 353.

4. Lindqvist, I., J. Inorg. Nucl. Chem., *6*, 159 (1968).

5. (a) Foss, O. and Tjomsland, O., Acta Chem. Scand., *10*, 424 (1956).

   (b) *idem*., *ibid*., *12*, 44 (1958).

6. Abrahams, S. C., Acta Cryst., *7*, 423 (1954).

7. Abrahams, S. C., and Bernstein, J. L., *ibid*., *B25*, 2365 (1969).

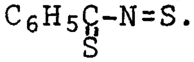
8. *ibid*., p. 2369.

9. (a) Ricci, J. C., Jr. and Bernal, I., Chem. Comm., 1453 (1969).

   (b) *idem*., J. Chem. Soc. B, 1928 (1971).

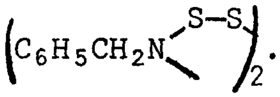
10. "Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956-1959," Sutton, L. E., Ed., The Chemical Society, London, 1965.

11. Schenck, R., Ann., *290*, 171 (1896). Formulated as

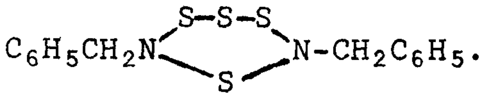


$C_6H_5\underset{\underset{S}{\|}}{C}\text{-}N{=}S$.

12. Levi, T. G., Gazz. Chim. Ital., *61*, 294 (1931). Proposed $(C_6H_5C\text{-}NH\text{-}S)_2$

or 

13. Pond, J. S., Ph.D. Thesis, University of Minnesota, Minneapolis, Minnesota, 1964. Proposed



14\. (a) Sasaki, Y., and Olsen, F. P., Can. J. Chem., 49, 271 (1971).

(b) *ibid.*, p. 283.

(c) *ibid.*, p. 278.

15\. Olsen, B. A., and Olsen, F. P., Inorg. Chem., 8, 1736 (1969).

16\. Sasaki, Y., Ph.D. Thesis, McMaster University, Hamilton, Ont., 1970.

17\. (a) Becke-Goehring, M., and Jenne, H., Chem. Ber., 92, 1149 (1959).

(b) *idem.*, Angew. Chem., 70, 399 (1958).

18\. Zachariasen, W. H., "Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945.

(a) *ibid.*, pp. 85-89.

19\. "International Tables for X-Ray Crystallography, Vol. II," Kynoch Press, Birmingham, England, 1967.

20\. Buerger, M. J. "Crystal Structure Analysis," John Wiley and Sons, New York, 1960.

21\. Stout, G. H., and Jensen, L. H., "X-Ray Structure Determination--A Practical Guide," Macmillan Co., New York, 1968.

(a) *ibid.*, Chapter 5.

(b) *ibid.*, pp. 171-3.

(c) *ibid.*, pp. 178-194.

(d) *ibid.*, pp. 222-6.

(e) *ibid.*, Chapter 13.

(f) *ibid.*, p. 406.

(g) *ibid.*, Chapter 18.

(h) *ibid.*, pp. 423-424.

(i) *ibid.*, p. 192.

22. Buerger, M. J., "The Precession Method," Wiley, New York, 1964.

23. Woolfson, M. M., "Direct Methods in Crystallography," Oxford University Press, New York, 1961.

24. (a) Hauptman, H., and Karle, J., Acta Cryst., 15, 451 (1962).

    (b) Karle, J., and Hauptman, H., ibid., 9, 635 (1956).

25. Cochran, W., and Woolfson, M. M., Acta Cryst., 8,1 (1955).

26. Cruickshank, D. W. J., J. Chem. Soc., 5486 (1961).

27. idem. in "Computing Methods in Crystallography," Rollett, J. S., Ed., Pergamon Press, Oxford, 1965, Chapter 14.

    (a) ibid., p. 116.

28. Rogers, D., ibid., Chapter 16.

29. (a) Hamilton, W. C., "Statistics in Physical Science," The Ronald Press Company, New York, 1964, p. 43.

    (b) ibid., pp. 117-122, 139.

30. Pauling, L., "The Nature of the Chemical Bond, 3rd Edition," Cornell University Press, Ithaca, New York, 1960.

31. Stephens, J. S. and Cruickshank, D. W. J., Acta Cryst., B26, 223 (1970).

32. Zachariasen, W. H., ibid., 16, 1142 (1963).

33. Cox, E. G., Cruickshank, D. W. J., and Smith, J. A. S., Proc. Royal Soc., A247, 1 (1958).

34. Cruickshank, D. W. J., Acta Cryst., 18, 958 (1965).

35. Busing, W. R. and Levy, H. A., ibid., 17, 142 (1964).

36. "Handbook of Chemistry and Physics, 48th Edition," Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p. A-157: Table of Probability of Occurrence of Deviations.

37. Bannister, A. J., Moore, L. F., and Padley, J. S., Spectrochim. Acta, 23A, 2705 (1967).

38. Chapman, D. and Waddington, T. C., Trans. Faraday Soc., 58, 1679 (1962).

39. Caron, A. and Donohue, J., Acta Cryst., 18, 562 (1965).

40. Karle, I. L., Estlin, J. A., and Britts, K., *ibid.*, 22, 273 (1967).

41. Dunitz, J. D., *ibid.*, 9, 579 (1956).

42. Huggins, M. L. J., Am. Chem. Soc., 75, 4123, 4126 (1956).

43. Abrahams, S. C., Quart. Rev. 10, 407 (1956).

44. Abrahams, S. C., and Grison, E., Acta Cryst., 6, 206 (1953).

45. Ricci, J. S., Jr., and Bernal, I., J. Chem. Soc. B, 806 (1970).

46. Winnewisser, G., Winnewisser, M., and Gordy, W., J. Chem. Phys., 49, 3465 (1968).

47. Taft, R. W., Price, E., Fox, I. R., Lewis, I. C., Anderson, K. K., and Davis, G. T., J. Am. Chem. Soc. 85, 709 (meta), 3146 (para) (1963).

48. Ram, P., and Olsen, F. P., unpublished results.

49. Mitchell, K. A. R., Chem. Rev., 69, 157 (1969).

(a) *ibid.*, p. 165.

50. Postma, H. J., van Bolhuis, F., and Vos, A., Acta Cryst., B27, 2480 (1971).

51. Hordvik, A., Acta Chem. Scand., 20, 1885 (1966).

52. Craig, D. P., and Zauli, C., J. Chem. Phys., 37, 609 (1962).

53. Muller, E. and Hyne, J. B., J. Am. Chem. Soc., 91, 1907(1969).

54. Pickering, T. L., Saunders, K. J., and Tobolsky, A. V. in "The Chemistry of Sulfides," Tobolsky, A. V., Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 5.

55. Pryor, W. A., "Mechanisms of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., p. 17.

56. Feher, F., Klaeren, A., and Linke, K.-H., Angew. Chem. Int. Ed. Eng., 9, 895 (1970).

57. Van de Grampel, J. C. and Vos, A., Acta Cryst., B25, 611 (1969).

58. Foss, O., and Marøy, K., Acta Chem. Scand., 19, 2219 (1965).

59. Foss, O., and Johnsen, K., *ibid.*, 2207.

60. Epstein, E. F., and Bernal, I., Chem. Comm., 1454 (1969).

61. Jones, P. E., and Katz, L., Acta Cryst., B25, 611 (1969).