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THE CRYSTAL STRUCTURE OF
DIBENZOTHIOPHENE SULFONE

by

Louis Roberts Kronfeld

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Thesis Director's signature:

A handwritten signature, likely "Harold A. Levy", is written in dark ink over a horizontal line.

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INTRODUCTION

This work describes the determination of the crystal structure of dibenzothiophene 5,5-dioxide (dibenzothiophene sulfone). The study of this particular molecule was prompted in part by the results of another study in this laboratory. In determining the structure of cis-2-butene episulfone, Desiderato and Sass found that the ring closing carbon-carbon bond was uncommonly long ($1.58 \text{ \AA}$ vs. the expected $1.47\text{--}1.49 \text{ \AA}$ normally observed in similar three-membered rings).¹ A search of the literature for similar results revealed that few structural studies have been made of heterocyclic sulfur systems. This is somewhat surprising since in 1951 Jeffery indicated in the discussion of the structure of β -isoprene sulfone that such compounds would prove worthy of study.²

Jeffery's work had revealed anomalies similar to that found in the episulfone. The sulfur-carbon and carbon-carbon bond distances appeared shorter than expected (1.74 and $1.75 \text{ \AA}$ vs. $1.81 \text{ \AA}$ in the case of normally observed sulfur-carbon bond; approximately 1.47 instead of 1.54 for the carbon-carbon bond). To partially account for these figures Jeffery uses the arguments of "hyperconjugation." In ending his discussion he states, "While the chemical evidence definitely shows that unsaturated hydrocarbons containing sulfone groups undergo reactions which support their possessing some unusual features in their molecular structures, isoprene sulfone, thiophen, and thiophthen are the only heterocyclic sulfur compounds whose molecular dimension have hitherto been investigated in detail, and the present requirement seems to be for further studies of molecules of a similar type."³

From that time till the present, however, almost no work on these systems has been reported.

OBTAINING CRYSTALS

Crystals of dibenzothiophene sulfone are commercially available from a variety of sources. Those used for this study, obtained from Aldrich Chemical Co., proved suitable for X-ray crystallographic studies after recrystallization.

Recrystallization from various solvents including water, ethanol and diethyl ether was tried but proved unsuccessful. The crystals were imperfect and poorly shaped.

Suitable crystals were finally prepared from the melt by sublimation onto a cool surface. The solid was placed in a small 35 ml pear-shaped flask. This was immersed in a sand bath. The temperature was raised to the region of the melting point, 236-238°C. Crystals immediately began to grow as the hot vapor contacted the cool neck of the flask protruding from the bath. The crystals were colorless translucent needles of varying size. They appeared well formed and of good quality under 25 power magnification.

Crystal chunks with well developed faces but rather poor quality were later obtained by very slow evaporation of a dilute diethyl ether-dibenzothiophene sulfone solution. They were of such poor quality that they were not used.

COLLECTION OF DATA

A crystal of approximately .75 cm length, .2-.3 mm diameter was selected and mounted on a glass rod along the needle axis. This needle axis was subsequently chosen to be the crystallographic $\vec{c}$ axis.

Preliminary rotation and Weissenberg photographs were taken using $\text{Cu}\cdot\text{K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The Laue symmetry was observed to be monoclinic. The following systematic absences were observed:

$$hk\ell \text{ absent when } h + k = 2n + 1$$

$$h0\ell \text{ absent when } \ell = 2n + 1$$

Two space groups are possible on the basis of these absences. They are the noncentric Cc (C_s^4 group) and the centric C2/c (C_{2h}^6). (Fig. 1a,b, Fig. 2a,b)⁴

Unit cell dimensions were precisely measured using standard sodium chloride (NaCl ; $a = 3.56907 \text{ \AA}$) powder lines superimposed on the various photographs. Again $\text{Cu}\cdot\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) was used. The cell constants are:

$$a = 10.090 \pm .015 \text{ \AA}$$

$$b = 13.894 \pm .03 \text{ \AA}$$

$$c = 7.219 \pm .013 \text{ \AA}$$

$$\beta = 93^\circ 30'' \pm 25'' (.4^\circ)$$

The β angle was determined using the method of angular lag.⁵

Flotation density measurements were made and indicated

$\rho \cong 1.5 \text{ gm/cc}$. Compared with theoretical density calculations of 1.35 gm/cc for four molecules per unit cell and 2.712 gm/cc for eight molecules per unit cell, this indicated that the unit cell contained four molecules per unit cell.⁶

EQUIVALENT POSITIONS SPACE GROUPS C_c AND $C_{2/c}$

Figure 1a

Figure 1b

(After: International Tables for X-Ray Crystallography, Vol. I)

SYMMETRY ELEMENTS

SPACE GROUPS C_c AND $C_{2/c}$

C_c

Figure 2a

$C_{2/c}$

Figure 2b

(After: International Tables for X-Ray Crystallography, Vol. I)

General positions in the space group Cc exhibit fourfold multiplicity. If the molecule were to be in this symmetry group, no restriction would be placed on the molecular position. In the case of the C2/c space group, the general positions are eightfold. This means that if this space group is the correct one, the four sulfur atoms must occupy special positions having fourfold multiplicity. In this group, the only such positions which would not induce additional systematic absences were those which place the sulfur atom on the twofold axes $0, y, 1/4$; $0, \bar{y}, 3/4$; $1/2, 1/2+y, 1/4$; $1/2, 1/2-y, 3/4$. This was not unexpected since the molecule has a twofold axis which would thereby lie coincident with a twofold axis in the space group (Fig. 2b).^{7,8}

Multiple film equi-inclination Weissenberg intensity photographs were made of the $\ell = 0, 1, 2$, and 3 layers (CuK α radiation $\lambda = 1.5418 \text{ \AA}$). The relative intensities of the various reflections ($hk\ell$) were estimated visually by comparison with a standard intensity strip. This standard strip was prepared in the usual manner by repeated exposure of a suitable reflection (in this case the (040) reflection). Again multiple film techniques were used.⁹

TREATMENT OF DATA

At this point much of the following was going on simultaneously with the various stages of refinement. As the respective layers of data were collected, the relative intensities were corrected by applying appropriate Lorentz, polarization and Tunnel factors calculated in the usual manner.¹⁰ Absorption was neglected.

As in all studies using film techniques, each layer was observed on a separate set of films. Data for each layer is thus on a separate

scale depending in part on the length of time the pictures were taken. There are several techniques for placing all layers of data on the same scale. The one which is considered most reliable and advantageous is the collection of data with the crystal mounted around another crystallographic axis.¹¹ While this is sometimes complicated by experimental problems, the advantages so far outweigh the difficulties that it is deemed necessary. The advantages are manyfold. First, the two independently measured sets of data can be used to place all the data on the same scale. This is of great importance in the least square refinement stages.¹² Second, the more observations one makes for each particular piece of data, the more reliable the data should be. Third, a more complete set of data is available improving accuracy and resolution. This is especially important for use of the data for Fourier synthesis because it helps to minimize the termination of series error which is present with a partial set of data.¹³

As mentioned above, this procedure is sometimes experimentally difficult. This case was no exception. One would like crystals of approximately uniform cross section thus minimizing absorption effects. Since the crystals were rather long needles, attempts were made to cut some crystals with a razor blade, thus obtaining a small crystal of almost equal size in all directions. A small piece of crystal was finally selected and mounted with the glass rod attached to a face parallel to what was formerly the needle axis. This crystal was not perfectly uniform but was the best that could be found.¹⁴

Normally, one encounters a problem in the alignment of such a small piece of crystal. The technique usually required is to take a series of systematic oscillation pictures until one locates a suitable

axis. Adjustment is then made to align this axis for the collection of data.

In this case, the crystal as mounted on the rod was very close to alignment. After one slight adjustment, the pictures appeared suitable for intensity work.

Rotation photographs indicated that the rotation axis was approximately $8.1 \text{ \AA}$ long. Although this does not correspond to a principle crystallographic axis as previously determined, a close examination revealed that this corresponds to either

$$\frac{\vec{a} + \vec{b}}{2} \text{ or } \frac{\vec{a} - \vec{b}}{2} . \quad \left[\text{Note: } \sqrt{\frac{a^2 + b^2}{2}} = 8.116 \text{ \AA} \right]$$

This would indicate that the crystal is mounted around an axis of the (hh0) zone. (Fig. 3)

While alignment along a non-crystallographic axis complicates the treatment of data, it was decided that this was the best crystal available to collect and analyze the data. There were no insurmountable problems since when one knows the operations necessary to transform the first axial coordinate system into that of the second, then one also knows the transformation for the indices. The indices of the reflections will transform by the same operations as the axes.¹⁵

Measurements from preliminary Weissenberg photographs indicated approximate cell dimensions for the 2nd axial coordinate system;

$$a' = 8.1 \text{ \AA}$$

$$b' = 8.1 \text{ \AA}$$

$$c' = 7.2 \text{ \AA}$$

$$\alpha' \cong \beta' \cong 90^\circ$$

$$\gamma' \cong 100^\circ$$

FIGURE 3

This figure shows a representation of the two axial sets as they appear in the reciprocal lattice. The first set of axes is designated as a and b. The second set of axes is designated as a' and b'.

THE RECIPROCAL LATTICE: THE RELATIONSHIP BETWEEN THE TWO AXIAL SETS.

Figure 3

Comparison with the cell constants determined for the 1st axial system indicated that suitable transformations would relate the coordinate systems in the following manner:

Either

$$a' = \pm \frac{\vec{a} + \vec{b}}{2} \quad \text{and} \quad b' = \pm \frac{\vec{a} - \vec{b}}{2}$$

or

$$a' = \pm \frac{\vec{a} - \vec{b}}{2} \quad \text{and} \quad b' = \pm \frac{\vec{a} + \vec{b}}{2}$$

and

$$c' = \pm c.$$

In accordance with this the indices (HKL) for the 2nd axial system would be related to the (hkl) for the first axial system by the same types of relationship.

Either

$$H = \pm \frac{h + k}{2} \quad \text{and} \quad K = \pm \frac{h - k}{2}$$

or

$$H = \pm \frac{h - k}{2} \quad \text{and} \quad K = \pm \frac{h + k}{2}$$

and

$$L = \pm l.$$

The Laue symmetry of this new cell appeared to be triclinic even though α' and β' were approximately 90° . (The space group is probably $P\bar{1}$.) Since determination of cell constants is considerably more difficult and less accurate for a triclinic group than for a monoclinic case, cell dimensions were determined by calculating analytically from the previously determined constants.¹⁶ (See Appendix I)

These dimensions are

$$a' = 8.116 \text{ \AA}$$

$$b' = 8.116 \text{ \AA}$$

$$c' = 7.219 \text{ \AA}$$

$$\alpha' \cong \beta' \cong 90^\circ \quad (\cos \alpha' = \cos \beta' = .0032)$$

$$\gamma' = 108^\circ 28''$$

These values were used to calculate the Lorentz, polarization and Tunnel factors for the (HKL) reflections. Before they could be applied, however, it was necessary to ascertain the unambiguous relationship of the first and second axial systems.

Ambiguity arises from the choice of transformations. The problem was surmounted empirically by a systematic examination of the data. The various possible combinations of (hk ℓ) were compared with the various corresponding possibilities for (HKL). For example, the initial comparison was made by looking at the (OKL), (OK $\bar{L}$), (HOL), (HO $\bar{L}$) data. (These signs were designated by convention on the film. The rotation axis was designated $\vec{a}'$; thus, the $\vec{b}'$ axis and the $\vec{c}'$ axis could be assigned according to normal convention of a right handed system.) The only possible combinations corresponding to these reflections were the (h=K, k=K, $\pm\ell$) called (K, K, $\pm\ell$) or (h=H, k=H, $\pm\ell$) called (H, H, $\pm\ell$) reflections from the first set of data. Looking at the respective pairs which showed a large disparity in the two intensities, one could assign the correspondence without applying L p and Tunnel factors. This then resolved part of the ambiguity and indicated that the (OKL) reflections transformed into (KK ℓ) and (OK $\bar{L}$) transformed into (KK $\bar{\ell}$). Thus, L was equated with ℓ .

For the other reflections (HKL) there is a fourfold ambiguity. (HKL), (HKL), (HKL) and (HKL) are all different. By extending the previous arguments and looking again at corresponding sets (HKL) and (hk~~l~~), assignment could be made. For example, the only possible combinations in the case of the 1, $\pm K$, $\pm L$ type reflections are:

$$h = 1 + K, h = 1 - K, \pm l \text{ and } h = 1 - K, k = 1 + K, \pm l.$$

Again looking at the cases where one member was large and the other small, a suitable one to one correspondence was made.

Knowing the index correlation, the various combinations of Lorentz, polarization and Tunnel factors were examined for the sets which indicated the best correlation.

With the index correspondence determined and all necessary corrections made, the correlation of the data was straightforward. Since each layer of data contained reflections which appeared on a number of films, the cross correlation of the data was easy. The ratio necessary to scale each layer to the scale of the 1st axial zero layer (hk0) data was calculated. Final agreement between the scale factors of the respective layers indicated that this scaling method was satisfactory and the resulting scale factors were essentially correct. (Table 1)

STRUCTURE DETERMINATION

The assumption of C2/c symmetry was made. Because of the similarity of the molecule in the Cc and C2/c groups, this choice caused no real complication and would have to be resolved only in the final stages of refinement. (Fig. 4) Final refinement indicated that C2/c was indeed the correct space group.

TABLE 1

SCALE FACTORS

Index	Scale Factor (σ)
hK0	.36868 (.004)
hK1	.35563 (.005)
hK2	.35124 (.005)
hK3	.315832 (.005)
hK l (l =4, 5, 6, 7)	.25801 (.006)

MOLECULAR PLACEMENT SPACE GROUPS C_c AND $C_{2/c}$

FIGURE 4

A Patterson projection $P(u,v)$ was synthesized down the short ($\vec{c}$) axis using the 72 observed pieces of (hk0) data. (Fig. 5) The largest non-origin peaks which occurred at ($u = 0.0, v = .40$) and ($u = .50, v = .10$) were assigned to the sulfur-sulfur interaction. According to the form of the Patterson function, these Harker peaks were consistent with $y = \pm .300$ or $y = \pm .200$, for the sulfur atom. These two sets of positions were identical and would transform by a shift of origin.¹⁷

Restricted to the special positions of the C2/c space group, the sulfur atoms were fixed at (.00, .300, .250); (0.0, .700, .750); (.500, .800, .250); (.500, .200, .750).¹⁸

The Patterson map also contained a moderately well resolved image of the undistorted molecule around both the origin peaks and those peaks assigned as the sulfur-sulfur Harker Peaks. (Fig. 5)

The plane of the molecule appeared from the Patterson projection to lie almost parallel to the plane of projection. A trial structure was assigned on the basis of these images. There was some slight ambiguity of tilt in the molecule but this was later resolved. At this point, it was sufficient to fix the z parameters for all atoms except the oxygens as either .250 or .750. The z parameters for the oxygen atoms were assigned on the basis of a sulfur-oxygen bond of 1.45 Å and an oxygen-sulfur-oxygen bond angle of 120°. Preliminary least square refinement indicated that the proposed structure was essentially correct in projection. The "reliability factor" (R) decreased from 31 to 25 in these early stages.²⁰ This high value was not surprising since the proposed structure had considerable overlap in projection which would hinder refinement.²¹

PATTERSON PROJECTION $P(U,V)$

FIGURE 5

An electron density projection $\rho(x,y)$ using signs fixed by the least square calculations, showed an image of the molecule with the oxygen peak slightly skewed from the $\vec{y}$ axis. On the basis of this, the molecule was tilted so that the new oxygen x coordinate was $x = .970$. The direction of tilt was chosen to conform with the tilt of the axis due to the β angle. Having assigned this degree of tilt, the z parameters for the other atoms were assigned. The thought here was to tilt the molecule slightly from the $z = .250$ or $z = .750$ planes and allow the least square refinement program to shift the atoms into the correct positions.

At this time, a full matrix, three dimensional least square refinement was attempted with the isotropic temperature factors frozen and equal weights assigned to each reflection. The "reliability factor" for the approximately 600 reflections improved from 35 to 28. At this point, further attempts to refine produced little change. A full matrix isotropic refinement using the Busing-Levy program (ORFLS) was tried but produced little change.²²

A number of sources of disagreement seemed possible. First, the molecular tilt as assigned might be incorrect in direction and magnitude. Second, the molecule might be in the non-centric space group. Third and last, the molecular orientation as assigned might be incorrect.

To discount the first possible source of disagreement, a three-dimensional electron density map $\rho(x,y,z)$ was synthesized using signs fixed by the least square program. The parameters as determined from this map were very similar to those already obtained from the least square refinement. The molecular tilt as already assigned appeared to be essentially correct. If this were not the case the peaks on the

electron density map would have indicated that some shifting was necessary.²³

In addition a least square refinement was attempted with the molecule tilted in the opposite direction to that assigned. The agreement was quite poor.

To resolve the second possible source of disagreement, an attempt was made to refine the molecule in the non-centric, Cc, space group. Using the identical molecular parameters changed to the format necessary for the non-centric case, a refinement was attempted again using ORFLS. This refinement failed at first because the program was not able to calculate the correct parameter changes necessary to move the molecule from the centric position to the non-centric position. The parameters were shifted slightly into a non-centric orientation and the refinement was repeated. There was no improvement, and the molecule shifted back toward the centric position. (Fig. 4)

Finally, to resolve the third source of disagreement, the molecular orientation was changed to a structure which would have no overlap in projection. (Fig. 6) Such a structure would give a Patterson map somewhat different from that already obtained. When the parameters for such a model were tried, the two-dimensional least square refinement indicated that this structure was incorrect. The "reliability factor" increased to 58.

At this time a systematic examination of the work done to this point seemed imperative. The data being used at this point was considered to be reliable and of somewhat better quality than that which had been used in the earlier stages of refinement. The reason for confidence in the data was that it had been collected by two individuals

POSSIBLE MOLECULAR ORIENTATIONS:
SPACE GROUP $C_{2/c}$.

POSSIBLE STRUCTURE: NO OVERLAP

POSSIBLE STRUCTURE: WITH OVERLAP

FIGURE 6

from separate sets of films. The agreement of the sets of data seemed good. Also, multiple independent readings were available for reflections which appear on both sets of data collected around the separate axes. The internal agreement between readings from the different films indicated that the data was reliable. Using this set of data, the Patterson projection was again synthesized. This time, however, the appearance was somewhat different from that obtained earlier. The sulfur-sulfur and sulfur-oxygen peaks were drastically changed. (Fig. 7)

Concern over the proper sulfur atom position prompted the synthesis of a three-dimensional Patterson map using all the available data. Using some 650 pieces of data, this map was generated. Examination revealed that this map was in close agreement with the original Patterson projection. The sulfur atom positions were the same. Again the image of the molecule around both the origin peaks and sulfur-sulfur peaks was resolved. This time, the tilt was also indicated. Although some slight parameter differences were noted, the model indicated was essentially the same as that being used.

The agreement between the three-dimensional and the original two-dimensional Patterson maps indicated that there must be some problem with the data which was used in the second Patterson projection. The data was examined layer by layer. Using the parameters indicated by the Patterson function, a least square refinement was tried using the (hk0) data. The "reliability factor" improved from 27 to 22. A significant difference was noticed. The scale factor which had previously been 3.25 now calculated as 2.95, a significant change. Agreement of F_{obs} with F_{calc} appeared generally good. No great disparities were observed. There was, however, one noticeable trend. The poorest

PATTERSON PROJECTION $P(U,V)$
RERUN

(NOTE: DIFFERENCES FROM FIGURE 5)

FIGURE 7

agreement of the observed vs. calculated values occurred for those structure factors which observed quite large. In almost every such case, the value calculated on the basis of the model was considerably larger than the observed. Those structure factors of moderate magnitude agreed quite well.

At this stage, a re-evaluation of the scaling factors and some specific pieces of data was carried out. The scaling factor for each layer of data was determined by exercising an option available in the least square program used on the Rice Computer. New Weissenberg photographs were taken of the $\ell = 0,1,2,3$, layers. These photographs were specifically made to determine the intensities of the very dark reflections which, as mentioned above, seemed the key to the solution of the problem. Earlier photographs had been taken for periods of approximately 25 hours. The new pictures were taken for only two to three hours. The intensities of all reflections which appeared on these films were estimated. Noticeable changes were observed for the relative intensities of those reflections in question, the very intense ones. This data was corrected by the appropriate factors. Scaling factors were determined by cross correlation. The values of the structure factors as observed in this set were substituted into the data list.

A least square refinement with isotropic B's fixed was carried out using ORFLS including data for the $\ell = 0,1,2,3$, layers. Separate scale factors for each layer were entered as variables under the option in this program. Equal weights were used. The "reliability factor" (R) calculated 19.9 before the first cycle and reduced to 15.6 after four cycles. A full matrix, isotropic least square again with unit weights was carried out using the $\ell = 0,1,2,3$ layers of data. The R value was

reduced to 13.9. It was also noted that the so called "weighted R"

$$R_w = \frac{\sqrt{\sum w (F_{\text{obs}} - F_{\text{calc}})^2}}{\sqrt{\sum w F_{\text{obs}}^2}}$$

was also 13.9. Normally as a model approaches the correct structure, one expects the two "R" values to approach the same value. Choice of a correct weighting scheme should cause the "weighted R" to be better than the "unweighted R."²⁴

Preliminary to assigning a weighting scheme, an anisotropic least square refinement was carried out. The appropriate temperature factors were determined under an option in ORFLS which converts isotropic temperature factors into anisotropic ones. Both reliability factors were reduced to 11.8.²⁵

At this point, a weighting scheme was introduced. The one used is as follows:

$$\begin{aligned} \text{SIGMA} &= 1/\text{weight} = F & : F > 4 \times F_{\text{min}} \\ \text{SIGMA} &= 1/\text{weight} = 4F_{\text{min}} & : F < 4F_{\text{min}} \end{aligned} \quad ^{26}$$

The effect of such a weighting scheme was to underweight those reflections which observed either very large or very small. This was necessary to minimize the influence of the high degree of inaccuracy of measurement in these regions. This was quite important if the least square procedure was to converge to the correct structure.²⁷

Isotropic refinement was tried using this weighting scheme. A full matrix least square refinement with the scale factors as variables and using 605 observed reflections was carried out again using the ORFLS routine. This refinement used all the available reflections including some data with $\ell = 4, 5, 6, 7$. The results were an "unweighted R" of 16.3

and a "weighted R" of 15.3. This value for the "weighted R" indicated that the weighting scheme was essentially correct.

The scale factors were fixed, and a full matrix anisotropic refinement was attempted using the same data. The "weighted" and "unweighted R" factors were 11.9 and 14.1, respectively.

At this point the structure appeared correct. The bond distances and angles were reasonable. All that remained was the inclusion of the hydrogen atoms. Using the equation of a plane passing through the molecule, the hydrogen atom positions were calculated assigning a carbon-hydrogen bond distance of $.90 \text{ \AA}$ and a carbon-carbon-hydrogen bond angle of 120° . These atoms were frozen in position and a full matrix least square carried out. The "weighted" and "unweighted R" values were 11.0 and 13.2, respectively.

On the basis of the reasonable molecular dimensions (Table 2) and the values for the reliability factors, the structure was presumed to be correctly determined.²⁸

DISCUSSION

The molecule is pictures in Figure 8. Table 2 lists the bond distances and angles, and Table 3 lists the final atomic parameters including isotropic temperature factors. The anisotropic temperature factors are shown in Table 4. The standard deviations were estimated from the least square results.²⁹

Various views of the cell are presented in Figures 9, 10, and 11. The packing is quite reasonable. The intermolecular distances are as expected for molecules containing benzene rings. No distances are shorter than the sum of the normally accepted Van der Waals radii.

FIGURE 8. DIBENZOTHIOPHENE SULFONE

FIGURE 9. b AXIS PROJECTION

FIGURE 10. c AXIS PROJECTION

FIGURE II. UNIT CELL PACKING IN PERSPECTIVE

Values for the observed and calculated structure factors are listed in Appendix III. In the least square refinement routine the quantity $\sum_w (|F_o| - |F_c|)^2$ was minimized. The final stages of refinement reduced this quantity to 4.875. The scattering factors for the various atoms were taken from Volume III of International Tables for X-Ray Crystallography.³⁰

As mentioned in the introduction, the reactions of heterocyclic sulfone systems indicate that these molecules possess interesting features. Sulfur atoms may form more than four covalent bonds. The 3d orbitals in sulfur are available for bond formation by expansion of the outer octet. When this occurs, certain characteristics may be induced into the molecule.

While electrophilic substitution of dibenzothiophene normally occurs in the 2 position, substitution of the sulfone analog, dibenzothiophene sulfone, occurs in the 3 position. It is possible that the sulfone group acts like a metadirecting group in withdrawing electrons from the ring. This would cause ring stabilization. In accordance with the following types of resonance systems, the 1,3-positions would be least deactivated:

These structures, however, show only a displacement of π electrons caused by the inductive effect of the sulfone group.³¹

Another effect would also be conceivable. New bonds may be formed by some mechanism which would lead to an expanded valence shell for the sulfur atom. As before, the 2 and 4 positions are deactivated preferentially with the 3 position favored for substitution. In this case, structures of the type:

would become important.³² The effect of this would be apparent. The sulfur-carbon bond would not be a pure single bond but would exhibit double bond character. The resulting bond would be considerably shorter than the $1.8 \text{ \AA}$ observed in many compounds. The bond length should approach that of a sulfur-carbon double bond ($1.71 \text{ \AA}$). (Table 5)

The sulfur-carbon bond distances reported herein are $1.74 \text{ \AA}$. This value is in good agreement with those observed by Jeffrey in β -isoprene sulfone and those observed by Desiderato and Sass in cis-2-butene episulfone (Table 5). In both of these structures, the bond length was attributed to 3d character of the bond.

Jeffrey accounts for this value with structures of the type:

Although Jeffery indicates dissatisfaction with such structures in completely accounting for his observations, he could offer no alternatives.³³ Since that time, such "hyperconjugation" has been discounted as a significant contributor to organic molecules. These structures are, however, similar to the structures drawn for dibenzothiophene sulfone.

Desiderato and Sass report that their sulfur-carbon bond would be in agreement with a structure placing some sulfur-carbon double bond character in the ring.³⁴

On the basis of these three reports, there is support for a sulfone sulfur-carbon bond length of 1.72-1.75 Å. This is somewhat different from the value reported by Sutton in tabulating selected bond lengths.³⁵ As mentioned earlier, this would be a sulfur-carbon with a significant amount of 3d character. While one can draw acceptable contributing structures to represent the dibenzothiophene sulfone, as yet no completeing satisfactory model will account for the two other compounds.

In the remainder of the structure, the bond distances and angles are in good agreement with those observed in other compounds. The ring closing carbon-carbon bond (C(6)-C(7)) length of 1.46 Å is in good agreement with a value of 1.48 Å in fluorene.³⁶

The sulfur-oxygen bond (1.49 Å) is slightly longer than that normally observed (Table 5). This is actually in good agreement with a value predicted from the sum of the double bond covalent radii. The short sulfur-oxygen bonds normally observed are accounted for by placing two formal positive charges on the sulfur. Interaction between the negative oxygen and positive sulfur would be observed in such semipolar structures for sulfones, sulfates, and sulfonates. The result would be

a shortened bond.³⁷ In dibenzothiophene sulfone, the amount of positive charge of the sulfur atom is less than two formal charge units. The force of interaction is thus smaller than normally expected. This might account for a longer sulfur-oxygen bond.

Except for the C(1)-C(2)-C(3) bond angle of 115.6° , the benzene rings appear normal within the precision attributed to the values for atomic parameters. Such an anomolous bond length is not unusual. In fluorene, one carbon-carbon-carbon angle observed as $116^\circ 47'$.³⁸

A plane passed through the structure indicates that it is planar (Appendix II). Although some atoms are off the plane by slightly more than the deviation assigned to the atomic parameters, these deviations are of no consequence.

TABLE 2
BOND DISTANCES AND ANGLES IN
DIBENZOTHIOPHENE SULFONE

A. Bond Distances		Standard Deviation
S-C(1)	1.74 Å ^o	.012
S-O(1)	1.49	.01
C(6)-C(12)	1.46	.015
C(1)-C(2)	1.40	.018
C(2)-C(3)	1.40	.021
C(3)-C(4)	1.40	.022
C(4)-C(5)	1.38	.021
C(5)-C(6)	1.37	.017
C(6)-C(1)	1.40	.021
B. Bonding Angles		Standard Deviation
O-S-O	120.4°	1.0°
C ₁ -S-C ₁	91.6°	.8°
S-C ₁ -C ₆	112.7°	.9°
C ₁ -C ₆ -C ₁₂	111.1°	1.1°
C ₆ -C ₁ -C ₂	122.5°	1.1°
C ₁ -C ₂ -C ₃	115.6°	1.1°
C ₂ -C ₃ -C ₄	122.1°	1.2°
C ₃ -C ₄ -C ₅	120.5°	1.2°
C ₄ -C ₅ -C ₆	119.3°	1.1°
C ₅ -C ₆ -C ₁	120.0°	1.1°

TABLE 3
FINAL PARAMETERS AND ESTIMATED STANDARD OF DEVIATIONS
FOR ATOMS IN THE ASYMMETRIC UNIT

	x	y	z	b ^b
S ^a	0.0000	.2958 (2)	.2500	3.12 (12)
O(2)	.9771 (6)	.2429 (4)	.4240 (1)	5.33 (23)
C(1)	.1218 (8)	.3824 (5)	.2897 (1)	3.34 (23)
C(2)	.2566 (8)	.3631 (7)	.3342 (17)	5.24 (30)
C(3)	.3371 (10)	.4432 (10)	.3691 (18)	6.09 (37)
C(4)	.2873 (1)	.5363 (8)	.3546 (16)	6.91 (39)
C(5)	.1545 (10)	.5522 (7)	.3043 (15)	5.99 (36)
C(6)	.0716 (7)	.4757 (5)	.2736 (11)	3.74 (23)
H(1)	.2874	.3075	.3653	
H(2)	.4162	.4362	.3963	
H(3)	.3369	.5792	.3681	
H(4) ^c	.1189	.6007	.2919	

^a x and z parameters for sulfur were frozen at values shown.

^b Refers to isotropic temperature factors.

^c All parameters for hydrogen were frozen.

TABLE 4

FINAL VALUES (ERRORS) FOR ANISOTROPIC TEMPERATURE FACTORS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	.0076	.0035(2)	.0147	0.0	.0006	0.0
O(2)	.0144(8)	.0061(4)	.0208(2)	-.0022(5)	-.0049(10)	.0053(8)
C(1)	.0089(8)	.0041(4)	.0099(28)	-.0013(4)	-.0034(12)	-.0012(8)
C(2)	.0108(10)	.0080(6)	.0213(40)	-.0001(7)	-.0030(16)	.0026(12)
C(3)	.0111(11)	.0115(10)	.0240(40)	-.0040(8)	-.0043(17)	.0024(15)
C(4)	.0222(17)	.0089(9)	.0108(38)	-.0071(10)	-.0006(19)	.0018(12)
C(5)	.0177(15)	.0061(6)	.0158(36)	-.0031(7)	.0001(10)	.0006(10)
C(6)	.0106(7)	.0043(4)	.0022(23)	-.0023(5)	.0009(11)	.0007
H(1)	*.0145	.0075	.0282	0.0	.0012	0.0
H(2)	.0145	.0075	.0282	0.0	.0012	0.0
H(3)	.0145	.0075	.0282	0.0	.0012	0.0
H(4)	.0145	.0075	.0282	0.0	.0012	0.0

* All Hydrogen β 's fixed at the same value.

TABLE 5
DIMENSIONS OF SELECTED MOLECULES CONTAINING SULFUR*

Molecule	C-S (Å)	S-O (Å)
SO		1.493
SO ₂		1.432
SO ₂ Cl ₂		1.43
(CH ₃) ₂ SO ₂	1.80	1.43
(CH ₃) ₂ SO	1.82	1.47
(CH ₃) ₂ S	1.802	
<i>β</i> -isoprene sulfone	1.75	1.44
<u>cis</u> -2-butene episulfone	1.75	1.43
C ₃ H ₆ N ₂ S (double bond C=S)	1.71	
C ₆ H ₄ S ₂ (1:4 thiophthen)	1.73	
C ₄ H ₄ S (thiophen)	1.74	

* All values from Sutton (1958) except those for *β*-isoprene sulfone (Jeffrey, 1951) and cis-2-butene episulfone (Desiderato and Sass, 1967).

APPENDIX I

UNIT CELL DIMENSIONS: SECOND AXIAL SET

The unit cell dimensions for the second axial set (a' , b' , c') can be calculated using the previously determined values for the first axial set.

$$a' = b' = \sqrt{\frac{a^2 + b^2}{2}} = 8.116 \text{ \AA}$$

$$c' = c = 7.219 \text{ \AA}$$

From Fig. 3 one notes

$$\tan^{-1} \gamma_{1/2} = b/a = 13.894/10.090$$

$$= 1.3770$$

$$\gamma = 180^\circ 28''$$

Finally, from the way the unit cell is drawn, $\alpha' = \beta'$. In the case of the second set the volume of the cell is equal to one-half the volume of the original cell.

$$\text{Vol}(2\text{ed}) = 1/2 \text{ Vol (original)}$$

$$\text{Vol} = a \cdot b \cdot c \sin \alpha \sin \beta \sin \gamma$$

so

$$\begin{aligned} \sin \alpha' \sin \beta' &= \sin^2 \alpha' = \frac{abc \sin \gamma}{a' b' c' \sin \beta'} \\ &= \frac{(7.224) (13.894) (10.090) (.99812)}{(7.224) (8.616)^2 (.9485)} \\ &= .9999 \end{aligned}$$

$$\sin \alpha' = \sin \beta' = .9999$$

$$\cos \alpha' = \cos \beta' = .0032$$

$$\alpha' = \beta' \cong 90^\circ$$

APPENDIX II

PLANARITY OF THE MOLECULE

The equation of a plane containing the molecule is:

$$.348939 x + 0.0 y - z = .2500$$

The distances by which the atoms in the asymmetric unit lie off the plane are as follows:

Atom	Distance off the Plane
Sulfur	0.0
C(1)	-.020 Å ^o
C(2)	-.037
C(3)	-.010
C(4)	-.030
C(5)	-.002
C(6)	-.009

APPENDIX III

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	Y(Obs)	Y(Calc)
0	2	0	12.8400	14.0222
0	4	0	19.0500	20.4347
0	6	0	-11.7900	-10.2918
0	8	0	3.0200*	1.4785
0	10	0	-3.2400	-2.963
0	12	0	-11.2300	-10.8038
0	14	0	-1.9500*	-0.7412
0	16	0	1.6100	1.3446
1	1	0	-21.5300	-22.4510
1	3	0	8.9700	8.7945
1	5	0	-11.1600	-11.2567
1	7	0	2.7200	3.1896
1	9	0	6.2700	5.8569
1	11	0	-1.9000*	-0.6620
1	13	0	7.7000	7.4897
1	15	0	-4.0600	-4.2077
1	17	0	3.1600	3.4148
2	0	0	9.9000	8.8431
2	2	0	-32.1000	-39.4126
2	4	0	27.1400	27.1992
2	6	0	-7.5900	-6.7896
2	8	0	1.5800*	2.1366
2	10	0	8.2000	8.9199
2	12	0	-2.0000*	-0.6440
2	14	0	1.9300*	0.6816
3	1	0	-8.9000	-9.8412
3	3	0	1.1100*	0.8198
3	5	0	-15.2600	-17.2353
3	7	0	7.6400	7.3493
3	9	0	-1.5500*	-0.3267
3	11	0	-3.6800	-2.9566
3	13	0	2.5200	2.7827
3	15	0	3.1800	2.7827
3	17	0	4.3700	5.0653

* = Unobserved

4	0	0	17.0200	14.5794
4	2	0	-26.6200	-30.1345
4	4	0	15.9200	13.0548
4	6	0	2.8900	2.3333
4	8	0	-1.8000*	-0.5114
4	10	0	2.5700	2.2290
4	12	0	-2.6200	-2.5877
4	14	0	2.3400	2.9299
4	16	0	-1.2600*	-1.1414
5	1	0	13.6700	12.1871
5	3	0	9.7900	10.0357
5	5	0	-8.6200	-7.9380
5	7	0	9.2700	8.3398
5	9	0	-1.9400*	-0.5726
5	11	0	-3.2500	-2.9496
5	13	0	1.8500*	0.9153
5	15	0	-4.3200	-4.6255
6	0	0	11.1700	11.9703
6	2	0	-10.4000	-10.0627
6	4	0	10.9000	10.0917
6	6	0	-6.3900	-5.3578
6	8	0	-7.5200	-7.5201
7	1	0	-4.5600	-3.1529
7	3	0	8.7000	8.8819
7	5	0	-3.5400	-3.4005
7	7	0	4.9000	4.3823
7	9	0	-2.0000*	-1.6137
7	11	0	3.3200*	1.1132
7	13	0	3.3200	3.8296
8	0	0	9.1900	10.2968
8	2	0	-10.3900	-10.7545
8	4	0	-5.2600	-4.6730
8	6	0	-2.9300	-2.3348
8	8	0	-1.9900*	-0.6659
8	10	0	1.8300*	3.6552
8	12	0	-2.9000	-3.8585
8	14	0	1.7800	2.3641
9	1	0	-1.6000*	-1.2755
9	3	0	5.2300	5.5152
9	5	0	-1.9900*	-2.1758
9	7	0	5.3600	4.3357
9	9	0	-1.7300*	-2.6994
9	11	0	-1.3300	-1.2643
9	13	0	0.6300	1.8575

10 2 0	-3.6400	-4.9573
10 4 0	2.5200	2.9319
10 10 0	3.3000	4.3050
11 3 0	2.2400	2.5967
11 5 0	2.0700	3.4521
11 7 0	2.0700	2.6060
12 0 0	2.5300	4.0337

0 2 1	29.7500	33.0152
0 4 1	-17.4200	-19.4067
0 6 1	-2.6100	-2.1170
0 8 1	-5.6700	-4.8846
0 10 1	8.0800	8.0213
0 12 1	7.1200	6.5668
0 14 1	-4.0400	-4.1323
0 16 1	6.2300	5.6205

1 1 1	-25.3000	-27.1965
1 3 1	19.9200	22.7550
1 5 1	-13.5700	-12.9546
1 7 1	-3.7200	-2.7205
1 9 1	1.2300*	0.4893
1 11 1	-11.9900	-12.1072
1 13 1	-1.4800*	0.3774
1 15 1	1.7700	1.5404

2 2 1	8.3700	8.3630
2 4 1	6.5200	5.9591
2 6 1	24.7100	27.4152
2 8 1	-1.8700	-1.8306
2 10 1	1.3700*	0.0260
2 12 1	4.6000	4.1126
2 14 1	-5.2000	-4.2097
2 16 1	3.6100	3.5124

3 1 1	-26.4000	-31.5652
3 3 1	18.3200	17.4604
3 5 1	-16.0100	-13.4831
3 7 1	-3.5900	-3.3579
3 9 1	5.3000	4.3002
3 11 1	1.3700	1.0162
3 13 1	5.6900	4.9657

4	2	1	2.1700	1.7410
4	4	1	-17.5600	-16.3084
4	6	1	6.6200	6.9820
4	8	1	-3.7500	-3.4739
4	10	1	-1.4300*	-1.9220
4	12	1	1.4300*	0.3501
4	14	1	-3.2400	-3.1577
4	16	1	4.5200	4.9707
5	1	1	-15.3400	-13.4717
5	3	1	19.0800	18.1501
5	5	1	-11.4200	-11.8938
5	7	1	-1.3300*	-0.5967
5	9	1	6.3600	6.3492
5	11	1	-1.4800*	0.0412
5	13	1	2.6500	2.8409
6	2	1	-1.2300*	-0.2994
6	4	1	-10.7300	-10.4030
6	6	1	4.7300	3.8705
6	8	1	-8.8600	-8.2979
6	10	1	-2.9200	-2.7274
6	12	1	1.3600*	0.6836
6	14	1	-3.8300	-4.5136
7	1	1	-14.2400	-14.5246
7	3	1	13.6000	12.9324
7	5	1	5.8000	5.8846
7	7	1	7.3300	7.5918
7	9	1	2.7300	2.5962
7	11	1	-1.7000	-3.8708
7	13	1	2.2700	2.7980
7	15	1	0.9600	0.2796
8	2	1	8.7000	8.8182
8	4	1	-4.4500	-4.4468
8	6	1	1.9900	1.3177
8	8	1	-3.0900	-3.6377
8	10	1	1.8400	1.8806
8	12	1	1.0500*	1.2391
9	1	1	-8.1300	-8.4274
9	3	1	3.0100	3.6304
9	5	1	-5.9500	-5.1555
9	7	1	-1.4100*	-0.2580
9	9	1	2.1900	2.8622
9	11	1	-1.2800	-2.4182

10	2	1	1.4100*	0.3079
10	4	1	-4.3200	-4.4730
10	6	1	2.3200*	3.2387
10	8	1	-2.9300	-3.4389
10	10	1	1.4000*	0.3777
11	1	1	1.2900*	
11	3	1	2.5300	
11	5	1	1.1700*	
11	7	1	-1.4500	-1.3783
12	2	1	0.9300*	1.1527
12	4	1	-1.3100	-2.0185
1	1	-1	31.7100	37.8243
1	3	-1	-11.8300*	-12.9777
1	5	-1	-3.8000	-4.7716
1	7	-1	-2.5800	-1.7723
1	9	-1	1.2300*	0.4893
1	11	-1	13.4100	13.4386
1	13	-1	-1.4800*	-1.5388
1	15	-1	3.2500	2.2618
1	17	-1	2.2800	2.0196
2	2	-1	-1.6000	-1.5712
2	4	-1	3.8500	4.9034
2	6	-1	-19.9000	-19.3248
2	8	-1	1.1700*	2.3311
2	10	-1	-5.5500	-5.6945
2	12	-1	-8.6300	-8.0170
2	14	-1	3.2900	2.6966
2	16	-1	-3.8900	-3.8548
3	1	-1	15.0600	17.0207
3	3	-1	-2.6000	-1.1240
3	5	-1	16.7300	18.3448
3	7	-1	14.0600	13.4007
3	9	-1	-7.7900	-8.1185
3	11	-1	4.5300	4.6355
3	13	-1	-5.8900	-5.3444
3	15	-1	3.2100	1.5488

4 2 -1	-18.2200	-18.1939
4 4 -1	-13.6300	-13.0615
4 6 -1	-10.7100	-10.5190
4 8 -1	3.8000	3.5059
4 10 -1	2.8200	1.7614
4 12 -1	1.3700	1.2095
4 14 -1	4.3800	3.8569
4 16 -1	-4.3200	-4.3838
5 1 -1	6.4500	5.9384
5 3 -1	-11.4200	-10.7399
5 5 -1	-3.9700	-2.3708
5 7 -1	5.0400	5.5014
5 9 -1	-8.7200	-8.5793
5 11 -1	4.9400	4.2553
5 13 -1	-4.0900	-4.5624
5 15 -1	3.3800	3.1155
6 2 -1	-1.1700*	-0.3005
6 4 -1	6.4700	6.5896
6 6 -1	-10.6000	-9.9690
6 8 -1	6.9700	7.4837
6 10 -1	3.1700	2.9741
6 12 -1	1.3500*	0.0971
6 14 -1	2.5100	3.4653
7 1 -1	4.7500	4.4375
7 3 -1	-7.0200	-7.0533
7 5 -1	-6.7500	-6.3898
7 7 -1	-1.4800*	-0.5888
7 9 -1	-8.7200	-8.5616
7 11 -1	4.5900	4.3893
7 13 -1	-4.2300	-4.7733
8 2 -1	-6.1200	-5.8539
8 4 -1	10.8000	10.7881
8 6 -1	4.1900	2.0514
8 8 -1	5.8700	5.8974
8 10 -1	-3.0600	-2.3715
8 12 -1	-1.5700	-1.1738
9 1 -1	6.0700	6.2921
9 3 -1	2.5700	1.3127
9 5 -1	-0.8600	-0.3716
9 7 -1	2.6700	2.0749
9 9 -1	-3.1200	-4.0285
9 11 -1	3.7800	4.4014

10 2 -1	-1.5000	-2.1923
10 4 -1	1.8000	2.9639
10 6 -1	-4.5800	-5.0264
10 8 -1	2.9700	3.4133
10 10 -1	-0.9200*	-0.2915

11 1 -1	1.2900*	2.3686
11 3 -1	-2.5800	-2.4953
11 5 -1	-1.1700*	-0.8118
11 7 -1	1.2200	1.6225
11 9 -1	-2.9800	-3.6034
11 11 -1	1.4100*	2.3137

12 2 -1	-2.3700	-2.1968
12 4 -1	1.0000	2.1414
12 6 -1	-2.4700	-3.6230

0 2 2	-13.7100	-16.0841
0 4 2	4.8000	4.0186
0 6 2	-9.5400	-8.5831
0 8 2	6.3000	6.3324
0 10 2	-8.8800	-8.2774
0 12 2	11.5600	11.6807
0 14 2	-2.5600	-1.9937

1 1 2	-11.0500	-13.1315
1 3 2	-11.1400	-10.4095
1 5 2	15.4900	15.0529
1 7 2	-6.9000	-7.0875
1 9 2	9.3400	9.5744
1 11 2	3.9800	3.5243
1 13 2	-3.4500	-3.1987
1 15 2	2.7000	2.3476
1 17 2	-2.3600	-2.9197

2 0 2	-9.0500	-9.3960
2 4 2	-12.2900	-10.7106
2 6 2	-5.8300	-4.8851
2 8 2	11.2900	10.2092
2 10 2	-10.7500	-9.7251
2 12 2	4.1200	4.4089
2 14 2	-3.5900	-3.1397
2 16 2	1.8900	2.0103

3	1	2	2.1200	0.9321
3	3	2	-11.9000	-10.0803
3	5	2	16.5700	16.6537
3	7	2	-6.9300	-4.6610
3	9	2	2.9000	2.1058
3	11	2	-1.2500*	-0.1829
3	13	2	-1.2000*	-1.1271
3	15	2	2.9600	2.9960
4	0	2	8.0700	8.1239
4	2	2	20.8500	20.8511
4	4	2	-3.2800	-2.8196
4	6	2	-3.4300	-3.5516
4	8	2	6.0400	6.3633
4	10	2	-6.1800	-5.4376
4	12	2	3.5200	2.3775
4	14	2	-3.5700	-4.4157
5	1	2	-3.2300	-1.7350
5	3	2	-4.5100	-3.4121
5	5	2	8.5500	7.8722
5	7	2	-13.0000	-12.7424
5	9	2	-1.2400*	-0.8240
5	11	2	2.1600	0.8866
5	13	2	-1.2900	-1.1449
5	15	2	3.3900	3.6721
6	0	2	-14.5000	-12.2254
6	2	2	8.0700	7.4628
6	4	2	-4.6400	-3.2654
6	6	2	2.3000	1.8649
6	8	2	4.3300	4.6741
6	10	2	-3.4400	-2.7168
6	12	2	5.1000	-1.4963
6	14	2	-1.1100	-1.4963
7	1	2	2.4000	2.0949
7	3	2	-14.1100	-13.5016
7	7	2	-3.7400	-3.1157
7	9	2	3.5300	3.8811
7	11	2	-1.1100*	-0.9163
7	13	2	-1.9700	-2.5394
8	0	2	-9.9200	-9.7366
8	2	2	7.9000	8.2106
8	4	2	2.0600	1.7094
8	6	2	3.5000	3.2104
8	8	2	1.5200	0.9247
8	10	2	-3.4600	-3.9125

9 1 2	-1.2500*	-0.9163
9 3 2	-2.0900	-3.1837
9 5 2	4.4300	4.4683
9 7 2	-2.7400	-3.5257
9 9 2	3.7000	3.2924
9 11 2	0.7500*	1.5296
10 2 2	6.3000	5.3610
10 4 2	-1.1200*	-3.2679
10 6 2	1.0400*	0.0939
10 8 2	2.2900	1.2320
10 10 2	-0.6100*	-2.4125
11 1 2	1.1000	2.4227
11 3 2	-2.3100	-1.5359
11 5 2	0.8100*	3.3677
11 7 2	-2.7200	-2.7469
12 0 2	-0.7300*	-2.6290
12 2 2	-0.7100*	2.4928
12 4 2	-3.2600	-3.6540

1 1 -2	52.7800	63.2882
1 3 -2	-1.6500	-1.1900
1 5 -2	10.0400	10.2214
1 7 -2	-7.4900	-8.0172
1 9 -2	3.3300	3.4262
1 11 -2	-7.1900	-6.9173
1 13 -2	-6.8900	-7.1793

2 2 -2	4.3600	2.7097
2 4 -2	0.7200*	1.0295
2 6 -2	-9.8000	-9.2178
2 8 -2	6.9300	6.8503
2 10 -2	-13.4800	-13.1226
2 12 -2	7.9600	8.1244
2 14 -2	-2.8200	-2.8158
2 16 -2	1.1700	1.1076

3 1 -2	-4.5500	-4.2410
3 3 -2	-4.3800	-5.4246
3 5 -2	16.4500	15.0478
3 7 -2	-10.1700	-9.9498
3 9 -2	6.9600	6.8236
3 11 -2	4.0000	3.3886
3 13 -2	-1.2200*	-1.0083
3 15 -2	2.2200	2.4959

4 0 -2	-5.8000	-7.1123
4 2 -2	1.6900	0.2383
4 4 -2	-3.7700	-2.7830
4 6 -2	-11.8700	-11.4781
4 8 -2	9.1100	9.8078
4 10 -2	-6.7300	-7.6138
4 12 -2	5.0600	5.7309
4 14 -2	-4.1200	-4.2598
4 16 -2	2.3600	2.4649
5 1 -2	-7.6300	-7.0156
5 3 -2	-12.1600	-12.2349
5 5 -2	11.9800	12.0142
5 7 -2	-5.1500	-5.8111
5 9 -2	3.1600	3.2363
5 11 -2	-1.2500*	-0.2667
5 13 -2	-1.1400*	-0.2871
5 15 -2	2.0500	2.6290
6 0 -2	7.3700	5.8825
6 2 -2	5.6400	5.8752
6 4 -2	1.0900*	0.2871
6 6 -2	-1.8900	-1.8214
6 8 -2	9.6500	10.1201
6 10 -2	-6.2900	-7.0019
6 12 -2	2.9700	3.3719
6 14 -2	-3.2300	-4.1516
7 1 -2	3.2900	2.6377
7 3 -2	-3.2200	-4.6141
7 5 -2	5.7700	6.5918
7 7 -2	-7.9900	-8.7396
7 9 -2	1.5800	1.5293
7 11 -2	-1.5000	-1.2294
7 13 -2	-1.6100	-1.6440
8 0 -2	-8.7000	-5.2250
8 2 -2	4.2700	5.3443
8 4 -2	5.6800	4.6762
8 6 -2	-2.1700	-1.6688
8 8 -2	2.7100	3.4623
8 10 -2	-3.2100	-4.0281
8 12 -2	3.8700	5.1472
9 1 -2	1.2700*	1.6041
9 3 -2	-8.1500	-8.6414
9 5 -2	1.7800	0.7736
9 7 -2	-3.7400	-4.6401
9 9 -2	2.4100	3.3221
9 11 -2	-0.8400*	-0.2465

10 0 -2	-1.2200*	-2.2494
10 2 -2	2.0100	3.1003
10 4 -2	-1.1800*	-0.4619
10 6 -2	-1.3900	-0.4551
10 8 -2	1.8400	2.4498
10 10 -2	-3.0600	-4.1556
11 1 -2	-1.0700*	-0.0359
11 3 -2	-1.2500	-2.6528
11 5 -2	3.3400	4.0588
11 7 -2	-1.4500	-2.5737
11 9 -2	0.4800*	2.0524
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0 4 3	13.8800	10.8562
0 6 3	-8.6700	-8.6305
0 8 3	5.4400	5.1465
0 10 3	-8.4100	-8.3002
0 12 3	-4.8100	-4.0498
0 14 3	1.2200*	1.1102
0 16 3	-2.5300	-2.5144
1 1 3	-4.4700	-2.4350
1 3 3	6.5500	5.5543
1 5 3	5.7900	5.3994
1 7 3	15.4200	15.3794
1 9 3	-8.0300	-7.8103
1 11 3	9.6000	10.2581
1 13 3	-3.1900	-3.0049
1 15 3	2.0400	2.0927
2 2 3	-11.0000	-8.7286
2 4 3	4.0800	3.7821
2 6 3	-15.0400	-16.6982
2 8 3	5.4300	5.2427
2 10 3	1.3200*	0.4703
2 12 3	2.5600	1.5710
2 14 3	2.7200	2.3134
2 16 3	-2.0800	-2.0855

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3	3	3	-3.6500	-2.2512
3	5	3	-7.8900	-8.3371
3	7	3	8.3800	8.9473
3	9	3	-8.4300	-8.5571
3	11	3	4.6700	3.9169
3	13	3	-5.3400	-5.5693
3	15	3	2.8900	3.1223
4	2	3	0.9700*	0.1372
4	4	3	10.5000	8.8236
4	6	3	-10.3600	-10.5058
4	8	3	5.3400	5.1280
4	10	3	1.3500*	0.8545
4	12	3	1.2900*	0.8700
4	14	3	1.4900	1.3830
5	1	3	-3.6500	-1.2922
5	3	3	-4.2800	-3.2787
5	5	3	-2.2100	-2.2531
5	7	3	3.9600	4.0363
5	9	3	-9.3500	-10.3367
5	11	3	3.5000	3.0803
5	13	3	-3.9500	-4.5778
5	15	3	1.0000	0.9357
6	2	3	-3.1700	-2.3050
6	4	3	12.6400	12.7996
6	6	3	1.3200*	2.6334
6	8	3	8.1600	7.8857
6	10	3	-1.3000*	-1.7024
6	12	3	-1.1200*	-0.4602
6	14	3	2.2300	2.7456
7	1	3	7.0200	6.4903
7	3	3	1.3300*	0.9248
7	5	3	-5.0500	-6.1288
7	9	3	-2.3000	-3.2184
7	11	3	4.7200	4.9198
7	13	3	-3.3800	-3.6692
8	2	3	-5.7900	-5.9354
8	4	3	1.3500*	0.9231
8	6	3	-5.0400	-4.9095
8	8	3	2.7300	3.3921
8	10	3	-1.0500*	-1.0438
8	12	3	-0.7200	-0.3439

9	1	3	2.3300	1.8122
9	3	3	-3.9600	-2.8936
9	5	3	-1.2500*	-0.3264
9	7	3	1.1400*	0.6622
9	9	3	-3.5100	-4.1628

10	2	3	1.1800*	1.8497
10	4	3	2.9300	3.0326
10	6	3	-2.5800	-3.1080
10	8	3	1.5000	2.1962

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1	5	-3	15.3400	13.7272
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1	11	-3	-11.2900	-11.8605
1	13	-3	3.2500*	3.8422
1	15	-3	-3.0500	-2.6702

2	2	-3	8.2100	8.2072
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2	8	-3	-4.7700	-5.1538
2	10	-3	9.2600	9.0389
2	12	-3	5.000	4.6278
2	16	-3	2.3200	2.6425

3	1	-3	-1.2100	-1.3742
3	3	-3	-2.9000	-1.2946
3	5	-3	-6.7300	-4.7948
3	7	-3	-12.5900	-11.6711
3	9	-3	6.6500	5.6559
3	11	-3	-8.4600	-8.7567
3	13	-3	1.9100	2.2761
3	15	-3	-1.7300	-1.8091

4	2	-3	8.4500	7.8972
4	6	-3	14.0100	14.7647
4	8	-3	-3.7300	-4.2072
4	10	-3	1.9000*	0.1282
4	12	-3	-2.5900	-2.0877
4	14	-3	-2.0900	-2.0759

5 1 -3	-3.4800	-4.3117
5 3 -3	4.4500	4.7985
5 5 -3	4.7100	3.4461
5 7 -3	-6.7900	-4.9850
5 9 -3	5.3100	5.9222
5 11 -3	-2.3100	-2.6838
5 13 -3	3.4300	3.9527
5 15 -3	-1.5900	-2.0624
6 2 -3	1.8300	0.9360
6 4 -3	-7.1300	-7.8765
6 6 -3	6.3700	7.3909
6 8 -3	-5.1100	-5.9279
6 10 -3	-1.3200*	-0.3873
7 1 -3	-1.9500	-3.0335
7 3 -3	3.8600	4.5011
7 5 -3	3.0000*	
7 7 -3	-1.9100	-1.4334
7 9 -3	5.9300	6.6287
7 11 -3	-1.1800*	-1.8935
8 2 -3	2.1200	2.2386
8 4 -3	-8.3700	-8.7272
8 6 -3	2.0500	0.3459
8 8 -3	-5.1200	-5.7202
8 10 -3	1.1400*	1.0508
8 12 -3	0.8600*	0.1042
9 1 -3	-4.4500	-5.5202
9 3 -3	1.3500*	2.2199
9 5 -3	3.5800	2.7662
9 7 -3	1.8800	1.1318
9 11 -3	-2.2000	-2.8906
10 2 -3	3.0300	3.3672
10 6 -3	3.1000	3.4929
10 8 -3	-1.4800	-2.6254
10 10 -3	0.6400*	0.8161
11 1 -3	-1.0900*	-2.5844
11 3 -3	1.8600	2.2427
11 7 -3	0.4900	0.8083
12 2 -3	0.7900*	1.3715
12 4 -3	-1.4800	-2.2441

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2	0	4	5.6400	4.6709
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2	4	4	3.4200	2.8042
2	6	4	5.4800	5.0688
3	1	4	6.1900	5.9731
3	5	4	-8.7800	-8.2556
3	7	4	2.8100	4.1765
4	2	4	-4.4500	-7.9230
4	8	4	-6.5400	-7.9230
5	1	4	-3.6700	-2.4090
5	3	4	2.8500	2.9395
6	0	4	2.1400	2.7201
6	2	4	-5.1600	-3.3253
6	4	4	-5.1400	-5.7611
6	10	4	2.6100	3.3724
7	3	4	11.4000	7.7827
8	0	4	2.0000	0.7295
9	5	4	-5.6500	-3.2729
10	2	4	1.3500	-0.3742
10	6	4	0.9200	1.0658
11	3	4	0.9200	0.3268
1	1	-4	-25.3900	-22.5849
1	3	-4	2.3600	2.1226
1	5	-4	-8.0600	-6.9320
3	3	-4	5.6400	4.8675
3	9	-4	-5.2600	-5.2252
3	11	-4	-1.8900	-1.0888

4	0	-4	4.8400	5.4130
4	2	-4	-3.8800	-5.4028
4	4	-4	6.7600	5.8744
4	8	-4	-2.6300	-2.2040
4	10	-4	3.3900	4.0484
5	1	-4	-1.4200	-1.2412
5	3	-4	3.5400	4.0119
6	2	-4	-8.2800	-8.5726
7	1	-4	1.7800	1.1582
7	3	-4	1.9600	3.3071
8	2	-4	-2.5200	-4.2102
8	4	-4	1.3500	1.3884
9	1	-4	-0.8900	-0.6540
9	3	-4	4.8400	5.0204
9	5	-4	-0.8600	-0.7245
10	2	-4	-2.5600	-3.5010
10	6	-4	-1.6200	-1.1952
11	3	-4	0.5700	1.6306
1	5	5	-7.9900	-8.1369
2	2	5	4.3300	2.4485
2	4	5	-6.1600	-5.9709
2	6	5	4.8200	5.4384
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3	7	5	-2.7700	-2.4208
4	4	5	-4.9800	-4.5216
4	8	5	-3.9300	-4.3429
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6	2	5	4.9400	4.1277
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7	3	5	-2.0600	-1.5712
7	9	5	2.1100	1.7908

8 4 5	-2.8900	-1.9662
9 1 5	-1.5900	-0.9718
9 7 5	-2.4200	-0.7961
10 2 5	2.5000	1.3838

1 1 -5	-9.8500	-11.6476
1 3 -5	2.4900	3.9299
3 1 -5	7.5000	7.7226
3 3 -5	-5.7800	-5.8780
3 11 -5	4.9800	5.3416
4 2 -5	-2.3300	-2.7748
4 4 -5	0.8800	0.7066
4 6 -5	-7.7000	-8.1511
4 12 -5	-1.2500	-1.5413
5 1 -5	5.2700	6.6641
5 3 -5	-2.3200	-4.2250
5 13 -5	-1.4700	-1.9830
7 1 -5	1.7000	3.4393
7 3 -5	-3.1400	-4.4231
8 4 -5	2.6400	3.4921
9 1 -5	1.7700	3.3068
9 3 -5	-2.2600	-2.9755
9 5 -5	-3.2400	-1.9088
10 2 -5	-1.5500	-1.9525
10 6 -5	-0.2700	-0.5142

0 2 6	5.3600	6.5095
1 5 6	5.3300	5.3325
2 2 6	9.8000	9.0050
2 4 6	-6.7900	-4.4822

3 1 6	-4.1500	-4.4656
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4 2 6	2.9000	5.1553
4 4 6	-4.3600	-4.1049
4 8 6	2.7400	3.0244
5 3 6	03.9200	-4.5920
6 2 6	6.7400	6.4299
6 4 6	2.6800	2.4390
6 10 6	-1.4700	-1.2812
7 3 6	-3.8800	-3.5472
8 0 6	-0.8800	-1.3669
8 4 6	-2.9200	-1.9704
1 3 -6	-2.5700	-2.0948
1 5 -6	3.1000	3.9318
2 0 -6	-17.3800	-20.0492
3 1 -6	7.4900	6.0365
3 5 -6	3.5800	3.5343
4 2 -6	3.9700	4.8702
4 4 -6	-3.2100	-3.5004
4 10 -6	-1.9700	-3.6366
5 1 -6	2.8900	0.9242
6 2 -6	2.5500	4.0486
7 1 -6	2.1500	2.0264
7 3 -6	-2.0800	-3.0136
9 3 -6	-1.3600	-2.6704

3 1 7	1.7700	2.6408
4 4 7	3.8100	4.3676
4 8 7	2.6000	3.5494
5 3 7	-3.9200	-3.7670
6 4 7	2.6800	1.1425
6 10 7	-1.4700	-0.5976
7 3 7	-3.8800	-1.2023

2 10 -7	1.7500	2.4200
3 1 -7	3.3400	4.0061
3 5 -7	1.4100	0.8975
4 4 -7	-0.8600	-1.2059
5 1 -7	-3.9000	-2.4622
7 1 -7	-1.8800	-1.2522
7 3 -7	1.2900	2.2891
8 4 -7	-0.4300	-2.1147

3 1 -8	-6.5700	-7.2169
3 5 -8	-1.0100	-3.0777
4 0 -8	1.5500	3.6486

REFERENCES

1. R. Desiderato and R.L. Sass, Acta Cryst., to be published (1967).
2. G.A. Jeffrey, Acta Cryst., 4, 58 (1951).
3. Ibid., pp. 62-63.
4. M.J. Buerger, "X-Ray Crystallography," John Wiley and Sons, New York, 1942, p. 83.
5. Ibid., pp. 377-383.
6. M.J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, New York, 1960, pp. 242-249.
7. Ibid., pp. 249-258.
8. Norman F.M. Henry and Kathleen Lonsdale, "International Tables for X Ray Crystallography," Vol. I, Kynoch Press, Birmingham, 1952, pp. 86-89.
9. M.J. Buerger, "Crystal Structure Analysis," pp. 86-89.
10. Ibid., pp. 152-185.
11. Ibid., pp. 138-146.
12. E.W. Hughes, J. Am. Chem. Soc., 63, 1742 (1941).
13. M.J. Buerger, "Crystal Structure Analysis," pp. 617-618.
14. Ibid., pp. 204-219.
15. M.J. Buerger, "X-Ray Crystallography," pp. 4-28.
16. Ibid., pp. 383-385.
17. M.J. Buerger, "Vector Space and Its Application in Crystal Structure Investigation," John Wiley and Sons, New York, 1959, pp. 5-29, 132-138.
18. Henry and Lonsdale, op. cit., p. 101.
19. Buerger, "Vector Space," pp. 35-37.
20. Buerger, "Crystal Structure Analysis," pp. 586-589.
21. Hughes, op cit., p. 1742.

22. W.R. Busing, H.A. Levy, and K.O. Martin, "ORFLS, A Fortran Crystallographic Least Square Program," Oak Ridge National Laboratory Publication, ORNL-TM-305, Aug. 1962.
23. Buerger, "Crystal Structure Analysis," pp. 590-592.
24. Busing and Levy, op. cit.
25. D.W.J. Cruickshank, Acta Cryst., 9, 747 (1956).
26. R.L. Sass, Ph.D. Thesis, University of Southern California, 1957.
27. Hughes, op. cit., pp. 1741-1742.
28. Buerger, "Crystal Structure Analysis," p. 586.
29. Buerger, "Crystal Structure Analysis," pp. 629-634.
30. C.H. Macgillavry and G.D. Rieck, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1962, p. 202.
31. H.D. Hartough and S.L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers Inc., New York, 1954, p. 13.
32. Ibid., p. 14.
33. Jeffrey, op. cit., p. 62.
34. Desiderato and Sass, op. cit.
35. L.E. Sutton, "Tables of Interatomic Distances," London: The Chemical Society (1958), p. s,18.
36. D.M. Burns and J. Iball, Proceedings of the Royal Society: Series A, Vol. 227, p. 200, 1955.
37. C.C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, 1962, pp. 65-66.
38. Burns and Iball, op. cit., p. 200.