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# The Crystal Structure of Diphenyl Sulfoxide*


BY S. C. ABRAHAMS†

*Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.*


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Diphenyl sulfoxide forms monoclinic crystals, space group $P2_1/n$, in a cell with $a = 8{\cdot}90 \pm 0{\cdot}02$, $b = 14{\cdot}08 \pm 0{\cdot}03$, $c = 8{\cdot}32 \pm 0{\cdot}02$ Å, $\beta = 101° 7' \pm 10'$, containing four molecules. The crystal structure has been solved by a combination of isomorphous-replacement and trial-and-error methods. Refinement of the atomic parameters was effected by the use of double Fourier series, followed by least-squares analysis of a set of 664 independent structure factors. This partially complete set of three-dimensional structure factors was derived by visual intensity measurement. The final coordinates lead to the bond lengths: S–O, $1{\cdot}47 \pm 0{\cdot}016$ Å; S–C, $1{\cdot}76 \pm 0{\cdot}015$ Å; C–C, $1{\cdot}40 \pm 0{\cdot}008$ Å; and the bond angles: C–S–O, $106° 10' \pm 40'$; C–S–C, $97° 19' \pm 58'$; S–C–C, $119° 27' \pm 34'$, corresponding to a pyramidal arrangement of the three bonds about the sulfur atom. The dihedral angle between the normals to the planes of the aromatic rings is $75° 50' \pm 68'$, and between the plane of each ring and the common C–S–C plane is $81° 57' \pm 49'$.


## Introduction

In considering the stereochemistry of subgroup VI*b* of the periodic table, there is a special importance in a study of these atoms when chemically linked to three other atoms. The early debates on the possibility of planarity in the three sulfur bonds in the sulfoxide group were largely ended by the optical resolution of unsymmetrical sulfoxides by Harrison, Kenyon & Phillips (1926). This work clearly demonstrated that the three bonds could not be coplanar, but left the precise arrangement undetermined. Recent studies of the molecular constants of several simple sulfoxides have entirely confirmed the pyramidal form of these bonds. The present study of the simplest aromatic sulfoxide was undertaken in order to throw further light on the stereochemistry of the sulfoxide group.

A survey of the general stereochemistry of oxygen, sulfur, selenium, tellurium and polonium has now been given (Abrahams, 1956).

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† Present address: Bell Telephone Laboratories Incorporated, Murray Hill, New Jersey, U.S.A.

## Crystal data

Diphenyl sulfoxide, $(C_6H_5)_2SO$; m.p., 70·5° C.; $D_m = 1{\cdot}276$ g.cm.$^{-3}$, $D_x = 1{\cdot}313$ g.cm.$^{-3}$. Monoclinic, with $a = 8{\cdot}90 \pm 0{\cdot}02$, $b = 14{\cdot}08 \pm 0{\cdot}03$, $c = 8{\cdot}32 \pm 0{\cdot}02$ Å, $\beta = 101° 7' \pm 10'$. Four molecules per unit cell; (*hkl*) present in all orders; (*h*0*l*) present only when $h+l=2n$ and (0*k*0) only when $k = 2n$. Space group $C_{2h}^5$–$P2_1/n$. No molecular symmetry required. Absorption coefficient for Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), 3·1cm.$^{-1}$. Volume of the unit cell, 1023·3 Å$^3$. Total number of electrons per cell, $F(000) = 424$. Dipole moment, 4·44D (Jensen, 1943). The magnetic anisotropy, measured through the courtesy of Dame Kathleen Lonsdale (Toor, 1952) is $\chi_1 = -69 \times 10^{-6}$, $\chi_2 = -117 \times 10^{-6}$ and $\chi_3 = -126 \times 10^{-6}$ c.g.s.e.s.u., where $\chi_1$ is about 30° to $a$ in acute $\beta$, $\chi_2$ is about 60° to $a$ in obtuse $\beta$ and $\chi_3$ is along $b$.

## Analysis of the structure

The position of the sulfur atom in diphenyl sulfoxide was not apparent from an examination of the Patterson function projected along the crystal axes. A model based upon a poorly resolved peak taken as the

sulfur–sulfur vector, and erroneously assumed consistent with the magnetic measurements, was obtained, but this did not, on refinement, give a value for the reliability factor $R$ less than 0·48. Attempts at sign determination by comparison of the diphenyl sulfoxide intensities with those of the isomorphous diphenyl selenoxide ($a = 8{\cdot}95$, $b = 14{\cdot}1$, $c = 8{\cdot}35$ Å, $\beta = 102° 20'$, space group $P2_1/n$, $Z = 4$), placed upon an absolute scale by the method of Wilson (1942) and Harker (1948), proved to be inconclusive. This failure was probably caused by an error of about 10% in the two scale factors.

At this stage, interpretation of the Patterson projections for diphenyl selenoxide along the two shorter axes immediately gave the coordinates of the selenium atom. Double Fourier series computed for the selenoxide, utilizing signs depending only on the position of the selenium atom, gave excellent resolution for one benzene ring in the $c$-axis projection, but an unidentifiable projection along the $a$ axis. A consideration of both projections together, however, led to a feasible structure.

The atomic coordinates obtained from the selenoxide data were used to provide signs for the diphenyl sulfoxide structure factors, and the resulting double Fourier series were evaluated on XRAC. The projection along the $a$ axis (Fig. 1) was entirely consistent

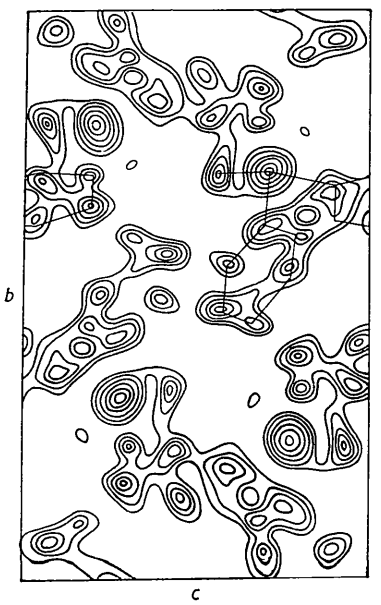


Fig. 1. Projection of one unit cell of diphenyl sulfoxide along the $a$ axis, as computed on XRAC. The outline of one molecule is shown.

with that along the $c$ axis. The most important difference between the correct model and the first model used was the reversal of the original sign of $F(031)$.

The reliability factors at this stage were 0·28 for $R(hk0)$, 0·32 for $R(0kl)$, and 0·29 for $R(h0l)$. Double Fourier series refinement reduced $R(h0l)$ to 0·17. The collection of new intensity data resulted in an increase from 48 to 91 reflections in the $0kl$ layer, and from 39 to 102 reflections in the $hk0$ layer. The corresponding $R(0kl)$ rose to 0·341, which figure was reduced to 0·265 by three successive Fourier series iterations. These reliability factors were computed with structure factors calculated using James & Brindley's (1931) atomic form factors and a value of $B = 4{\cdot}2$ Å$^2$ in the expression $\exp[-B(\sin\theta/\lambda)^2]$ for oxygen and carbon, and Abrahams's (1955) atomic form factor for sulfur, modified by a temperature factor $\exp[-3{\cdot}2(\sin\theta/\lambda)^2]$. A new empirical atomic form factor was then derived for carbon from the measured intensity data, retaining the previous form factor for sulfur (Table 4). This empirical carbon form factor closely resembles the McWeeny (1951) curve with $B = 4{\cdot}2$ Å$^2$. The factor for oxygen was taken as 8/6 of the corresponding value of the carbon curve. The new form factors resulted in sign changes for several small-magnitude structure factors. A final double Fourier series led to no further $F(0kl)$ sign changes, and the corresponding electron-density map is given in Fig. 2. The coordinates from Fig. 2, in which the benzene rings were assumed to

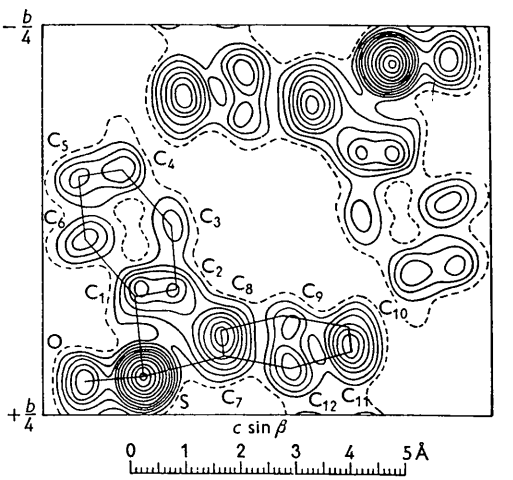


Fig. 2. Electron density of diphenyl sulfoxide viewed along the $a$ axis. The contours are at intervals of 1 e.Å$^{-2}$, the 3 e.Å$^{-2}$ being broken. Above the 8 e.Å$^{-2}$ line for sulfur, the interval is 2 e.Å$^{-2}$.

be regular planar hexagons, yielded a value of $R(0kl)$ of 0·210.

The $y$ coordinates from Fig. 2 were then combined with the $x$ coordinates corresponding to $R(h0l) = 0{\cdot}17$, and, using the new $hk0$ intensities, one double Fourier series sufficed to ensure convergence. The value of $R(hk0)$ was then 0·182, and the final electron-density map projected along the $c$ axis is shown in Fig. 3.

Further refinement of the atomic coordinates was obtained by the use of the method of least squares. In this process, all the reflections observable in the $0kl$, $h0l$, $hk0$, $hk1$, $hk2$, $hk3$ and $hk4$ layers were used, so that a total of 664 different observational equations were available. The only parameters varied were the

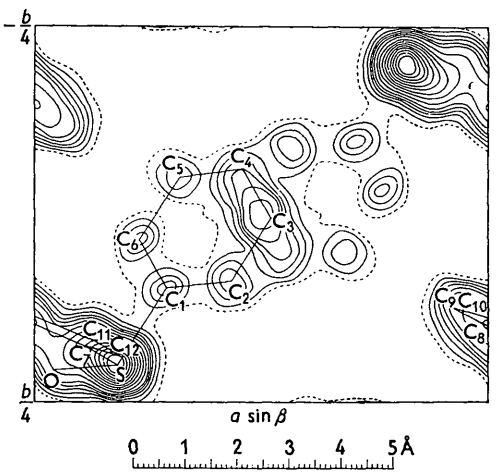


Fig. 3. Electron density of diphenyl sulfoxide viewed along the *c* axis. Contour scale as in Fig. 2.

coordinates of each atom in the molecule, exclusive of hydrogen atoms (which comprise 9·5% of the total scattering power), resulting in 42 unknowns, together with the scale factor which was evaluated separately after each least-squares cycle was computed. The empirical form factors of Table 4 were used throughout. All observations were initially allotted a weight of unity, and only the diagonal elements of the final determinant were evaluated. The cycle of structure-factor calculations followed by least-squares analysis to give a new set of atomic coordinates was carried out four times. On completion of the fourth cycle, it was observed that the magnitude of the correction for every coordinate was less than the standard deviation in that correction.

The weights of unity hitherto used were now replaced by a set found to be more satisfactory (Abrahams, 1955). The standard errors in $F(hkl)$ were taken as $\sigma F(hkl) = 0{\cdot}07|F(hkl)|$, except for magnitudes less than 17, the value of $|F(hkl)|$ at half-height on the normal distribution curve of the magnitudes of the structure factors. For structure factors less than or equal to 17, the standard error was taken to be 1·2. The weights were derived from the standard errors in the usual way, $\omega(hkl) \propto 1/[\sigma F(hkl)]^2$. A final cycle of least squares did not change the condition of convergency previously reached.

The course of refinement in the least-squares process may be followed by the values of $R(hkl)$ at each stage. For the three-dimensional work $F_{calc.}$ was not evaluated if $F(hkl)$ was unobserved. The $z$ coordinates from Fig. 2, combined with the $x$, $y$ coordinates from Fig. 3, gave $R = 0{\cdot}233$, which became successively 0·187, 0·177, 0·176 and 0·174. The value of $R(hkl) = 0{\cdot}174$ did not change on using the new set of weights. In the least-squares process, the signs of 19 structure factors changed, including 9 zero-layer terms.

It is possible that a large part of this residual disagreement among the observed and calculated structure factors is due to anisotropic thermal vibrations, which were not evaluated, all atoms having been assumed to possess an equal and isotropic thermal motion in the least-squares analysis. In addition, part of this residual could be the result of neglecting the hydrogen-atom contributions as well. It may be noted that in the least-squares treatment, only 11% of all the structure factors used have $\sin\theta/\lambda \leq 0{\cdot}4$, at which limit the maximum hydrogen contribution to a structure factor is only about 2·3.

## Atomic coordinates

The final set of coordinates obtained from the least-squares analysis, using the second set of weights, is collected in Table 1. The atomic coordinates in Table 1

Table 1. *Atomic coordinates of diphenyl sulfoxide*

| | $x$ | $x'$ (Å) | $y$ | $y'$ (Å) | $z$ | $z'$ (Å) |
|---|---|---|---|---|---|---|
| S | 0·1813 | 1·255 | 0·2047 | 2·882 | 0·2240 | 1·829 |
| O | 0·0481 | 0·286 | 0·2010 | 2·830 | 0·0883 | 0·721 |
| $C_1$ | 0·2854 | 2·202 | 0·0999 | 1·407 | 0·2106 | 1·719 |
| $C_2$ | 0·4349 | 3·390 | 0·0923 | 1·299 | 0·2996 | 2·446 |
| $C_3$ | 0·5187 | 4·152 | 0·0085 | 0·120 | 0·2893 | 2·362 |
| $C_4$ | 0·5429 | 3·787 | 0·9378 | −0·876 | 0·8246 | 1·432 |
| $C_5$ | 0·6945 | 2·597 | 0·9458 | −0·763 | 0·9237 | 0·623 |
| $C_6$ | 0·2255 | 1·849 | 0·0302 | 0·425 | 0·0984 | 0·804 |
| $C_7$ | 0·1127 | 0·357 | 0·1750 | 2·464 | 0·4026 | 3·287 |
| $C_8$ | 0·9652 | −0·936 | 0·1376 | 1·937 | 0·3904 | 3·187 |
| $C_9$ | 0·9101 | −1·658 | 0·1224 | 1·723 | 0·5351 | 4·368 |
| $C_{10}$ | 0·9999 | −1·113 | 0·1397 | 1·967 | 0·6931 | 5·658 |
| $C_{11}$ | 0·1424 | 0·159 | 0·1762 | 2·481 | 0·6910 | 5·641 |
| $C_{12}$ | 0·2031 | 0·923 | 0·1949 | 2·744 | 0·5519 | 4·506 |

are also given in Ångström units, referred to an orthogonal set of axes, in which $z'$ is normal to $x$ in the original $xz$ plane, and $x' = x - 0{\cdot}1928z$, $y' = y$ and $z' = 0{\cdot}9812z$.

## Molecular dimensions

The coordinates of Table 1 correspond to a molecule with the dimensions given in Table 2.

Table 2. *Bond lengths and angles in diphenyl sulfoxide*

| | | | |
|---|---|---|---|
| S–O | = $1{\cdot}47_3$ Å | $C_1$–S–O | = 106° 9′ |
| S–$C_1$ | = $1{\cdot}75_6$ | $C_7$–S–O | = 106° 11′ |
| S–$C_7$ | = $1{\cdot}76_3$ | $C_1$–S–$C_7$ | = 97° 19′ |
| Av. C–C | = $1{\cdot}40_0$ | S–$C_1$–$C_2$ | = 119° 24′ |
| | | S–$C_1$–$C_6$ | = 119° 53′ |
| | | S–$C_7$–$C_8$ | = 120° 2′ |
| | | S–$C_7$–$C_{12}$ | = 118° 27′ |

The least-squares-derived equation of benzene ring $C_1$–$C_6$ is

$$x' + 0{\cdot}833y' - 1{\cdot}344z' - 1{\cdot}119 = 0 \qquad (1)$$

and of ring $C_7$–$C_{12}$ is

$$x'-2\cdot517y'+0\cdot102z'+5\cdot513 = 0\,. \qquad (2)$$

The r.m.s. deviation of atoms $C_1$–$C_6$ from Plane 1 is 0·021 Å with a maximum deviation of 0·035 Å, and of atoms $C_7$–$C_{12}$ from Plane 2 is 0·008 Å with a maximum deviation of 0·012 Å. The dihedral angle between these two planes is 75° 50′, between Plane 1 and the common C–S–C plane it is 80° 36′ and between Plane 2 and the common C–S–C plane it is 83° 18′.

## Intermolecular distances

There is only one intermolecular contact in the present crystal worthy of mention. This lies between $O_B$ and $C_{12}$, where the *B* molecule is related to the molecule in Table 1 by the glide-plane relation $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$, and is of length 3·36 Å. In principle, this length is indistinguishable from a normal van der Waals contact. However, the geometrical arrangement of this oxygen–carbon vector suggests that it might be an example of a C–H · · · O bond. The angle $O_B$–$C_{12}$–$C_9$ is 175·4°, and the oxygen atom lies 0·07 Å from the plane of the $C_7$–$C_{12}$ ring, indicating that this oxygen atom is situated on the extended diagonal of the benzene ring, within the experimental error. Further, the angle $S_B$–$O_B$–$C_{12}$ is 111·1°, which is a reasonable value for the oxygen valency bond angle. This 3·36 Å contact links molecules in endless chains running through the structure, with one C–H · · · O bond per molecule.

Along the *b*-axis direction, there are parallel pairs of $C_1$–$C_6$ benzene rings, interleaved by parallel pairs of $C_7$–$C_{12}$ benzene rings. These pairs are separated by distances of 3·6 and 3·8 Å respectively, across alternate centers of symmetry.

## Accuracy of the determination

The least-squares method of refining the atomic coordinates offers a reliable means for the determination of the errors to be feared in those coordinates. A discussion of this method has often been given (e.g. Abrahams, 1955), and in the present study the usual diagonal approximation treatment has been adopted. The standard deviations in the positions of the three kinds of atoms are given in Table 3. The actual standard deviations for the twelve individual carbon atoms are within ±0·001 Å of the average values given in Table 3.

Table 3. *Standard deviations in the atomic positions*

| | $x$ (Å) | $y$ (Å) | $z$ (Å) |
|---|---|---|---|
| S | 0·005 | 0·005 | 0·006 |
| O | 0·014 | 0·016 | 0·016 |
| C | 0·019 | 0·020 | 0·021 |

From this table, it is apparent that the standard deviations are spherically symmetrical for each atom, and the radii of these spheres can be taken as $\sigma r_S$ = 0·005 Å, $\sigma r_O$ = 0·015 Å, $\sigma r_C$ = 0·020 Å. The standard deviation in the length of the S–O bond is thus 0·016 Å, in the S–C bond it is 0·021 Å and in the C–C bond it is 0·028 Å. The standard deviation in the O–S–C and C–S–C bond angles is 58′ and in the S–C–C bond angle it is 68′.

Since the S–C bond has been measured twice, the standard error in the average S–C bond length is $0\cdot021\div\sqrt{2} = 0\cdot015$ Å. Similarly, the standard deviation in the average C–C bond length is 0·008 Å, in the average O–S–C bond angle it is 40′, and in the average S–C–C bond angle it is 34′.

The standard deviation in the dihedral angles is also about 68′, and hence in the average dihedral angle between the plane of a benzene ring and the common C–S–C plane it is 49′.

It may be noted that the atomic coordinates in Table 1 form a completely regular hexagon for *neither* benzene ring. Nevertheless, within the limits of accuracy in this determination, these departures from regularity are not significant.

## Discussion

The present study has confirmed that the three bonds formed by the sulfur atom in the sulfoxide group are non-coplanar, and instead form a pyramid. A discussion of the molecular dimensions of those sulfoxides which have been measured has already been given (Abrahams, 1956).

The nature of the orbitals used by sulfur in the diaryl sulfoxides has not yet been elucidated. In the case of diphenyl sulfone, Koch & Moffitt (1951) have proposed that the sulfur 3*d* and the carbon 2*p* orbital overlap is sufficient for the two benzene rings to be perpendicular to the common C–S–C plane. The corresponding angle in diphenyl sulfoxide is 81·9°, so that a similar mechanism could apply in this molecule. The great similarity in the molecular shapes of diphenyl sulfoxide and diphenyl sulfone has already been pointed out by Abrahams & Silverton (1956). They demonstrated that in the sulfoxide the lone pair of electrons on the sulfur atom probably occupies the same direction and effective volume as one of the sulfur–oxygen bonds in the sulfone.

Table 4. *Atomic form factors for diphenyl sulfoxide*

| $2\sin\theta_{\mathrm{Mo}\,K\alpha}$ | $f_S$ | $f_C$ |
|---|---|---|
| 0 | 16 | 6 |
| 0·1 | 15·1 | 5·5 |
| 0·2 | 13·1 | 4·4 |
| 0·3 | 10·3 | 3·1 |
| 0·4 | 7·4 | 1·8 |
| 0·5 | 4·8 | 1·0 |
| 0·6 | 2·9 | 0·7 |
| 0·7 | 1·7 | 0·5 |
| 0·8 | 1·0 | 0·4 |
| 0·9 | 0·5 | 0·3 |
| 1·0 | 0·3 | 0·2 |

## Table 5. *Measured and calculated values of the diphenyl sulfoxide structure factors*

| hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ | hkl | $F_{meas}$ | $F_{calc}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 002 | 61 | - 69 | 310 | 18 | -21 | $22\bar{3}$ | 41 | + 46 | 141 | 35 | +31 | $75\bar{2}$ | 15 | +11 | $47\bar{3}$ | 17 | -19 | 0, 10, 4 | 16 | +15 |
| 004 | 11 | + 15 | 311 | 4 | +10 | $22\bar{4}$ | 43 | + 46 | 142 | 15 | -19 | $75\bar{3}$ | 9 | -10 | $47\bar{4}$ | 19 | +18 | 0, 10, 6 | 5 | - 6 |
| 006 | 20 | - 19 | 312 | 34 | +34 | $32\bar{1}$ | 18 | - 13 | 143 | 14 | -15 | $85\bar{4}$ | 4 | + 7 | $57\bar{2}$ | 11 | +11 | 1, 10, 3 | 5 | + 5 |
| 008 | 12* | - 8 | 313 | 54 | -53 | $32\bar{3}$ | 55 | - 52 | 144 | 11 | +14 | 060 | 28 | +31 | $57\bar{4}$ | 14 | -16 | 2, 10, 0 | 11 | -11 |
| 0, 0, 10 | 9 | + 10 | 314 | 4 | - 2 | $42\bar{1}$ | 23 | - 21 | 240 | 36 | -36 | 061 | 28 | -34 | $67\bar{3}$ | 7 | +10 | 2, 10, 2 | 4 | + 3 |
| 101 | 110 | -135 | 410 | 35 | +47 | $42\bar{2}$ | 13 | - 13 | 241 | 22 | -26 | 062 | 4 | + 3 | 080 | 31 | -32 | 3, 10, 0 | 11 | +12 |
| 103 | 11 | + 14 | 411 | 24 | +21 | $42\bar{3}$ | 7 | + 9 | 242 | 8 | -11 | 063 | 12 | +19 | 081 | 30 | +34 | 3, 10, 3 | 5 | -11 |
| 105 | 14 | - 14 | 412 | 25 | -25 | $42\bar{4}$ | 10 | - 9 | 243 | 31 | +32 | 064 | 4 | - 4 | 082 | 4 | + 8 | 4, 10, 3 | 8 | -11 |
| 107 | 5 | + 3 | 413 | 10 | - 8 | $52\bar{1}$ | 9 | + 11 | 340 | 12 | +16 | 065 | 11 | -13 | 083 | 26 | -26 | 5, 10, 0 | 4 | - 1 |
| 109 | 8 | + 7 | 414 | 10 | +12 | $52\bar{2}$ | 5 | + 3 | 341 | 12 | +14 | 066 | 5 | - 5 | 084 | 7 | - 1 | 5, 10, 3 | 6 | - 8 |
| 200 | 14 | + 12 | 510 | 3 | - 4 | $62\bar{1}$ | 18 | - 13 | 342 | 9 | - 4 | 067 | 5 | + 5 | 085 | 7 | + 6 | 5, 10, 4 | 6 | + 7 |
| 202 | 17 | - 15 | 511 | 27 | -26 | $62\bar{3}$ | 4 | + 7 | 344 | 12 | +11 | 160 | 51 | -53 | 086 | 5 | + 6 | 6, 10, 0 | 5 | + 2 |
| 206 | 6 | + 1 | 512 | 8 | -12 | $62\bar{4}$ | 7 | - 8 | 440 | 3 | + 5 | 161 | 16 | + 9 | 180 | 22 | +24 | 6, 10, 2 | 5 | - 7 |
| 208 | 7 | + 3 | 513 | 10 | + 9 | $72\bar{1}$ | 7 | - 10 | 441 | 6 | + 8 | 162 | 12 | -11 | 181 | 10 | +10 | 8, 10, 0 | 4 | - 6 |
| 301 | 23 | + 26 | 514 | 5 | - 4 | $72\bar{3}$ | 5 | + 6 | 442 | 12 | +16 | 163 | 4 | - 3 | 182 | 13 | -11 | 9, 10, 0‡ | 4 | + 1 |
| 303 | 7 | - 3 | 610 | 4 | -11 | $72\bar{4}$ | 22 | - 21 | 443 | 15 | +14 | 164 | 12 | -12 | 183 | 4 | - 9 | 1, 10, $\bar{1}$ | 28 | +27 |
| 305 | 13 | - 9 | 611 | 5 | + 4 | $82\bar{1}$ | 11 | - 10 | 444 | 8 | - 9 | 260 | 14 | + 8 | 184 | 18 | +15 | 1, 10, $\bar{3}$ | 30 | -30 |
| 307 | 6 | - 7 | 612 | 6 | - 6 | $82\bar{2}$ | 12 | - 12 | 540 | 14 | -15 | 262 | 9 | - 9 | 280 | 20 | +24 | 2, 10, $\bar{1}$ | 17 | -14 |
| 309 | 7 | - 3 | 613 | 5 | + 7 | $82\bar{3}$ | 18 | + 14 | 541 | 5 | + 9 | 264 | 4 | + 2 | 281 | 5 | - 5 | 2, 10, $\bar{2}$ | 21 | +20 |
| 400 | 29 | + 26 | 614 | 6 | + 6 | $82\bar{4}$ | 8 | + 8 | 542 | 24 | +18 | 360 | 3 | - 4 | 283 | 4 | + 4 | 2, 10, $\bar{4}$ | 8 | - 9 |
| 402 | 8 | - 3 | 710 | 2 | + 3 | $92\bar{1}$ | 6 | + 7 | 543 | 25 | -24 | 361 | 14 | +10 | 382 | 4 | + 4 | 3, 10, $\bar{1}$ | 5 | + 3 |
| 404 | 15 | - 15 | 712 | 15 | -13 | $92\bar{2}$ | 7 | - 7 | 544 | 11 | -10 | 461 | 5 | + 7 | 480 | 10 | + 8 | 3, 10, $\bar{3}$ | 7 | + 9 |
| 406 | 8 | + 8 | 713 | 5 | + 4 | 10, 2, $\bar{1}$ | 7 | + 1 | 640 | 5 | + 9 | 462 | 10 | + 7 | 481 | 5 | + 4 | 4, 10, $\bar{1}$ | 5 | + 1 |
| 501 | 6 | - 2 | 810 | 3 | - 4 | 031 | 66 | + 64 | 641 | 12 | +10 | 463 | 5 | - 6 | 482 | 16 | -13 | 4, 10, $\bar{2}$ | 4 | - 1 |
| 503 | 9 | - 10 | 812 | 7 | + 6 | 032 | 47 | + 43 | 643 | 12 | -10 | 561 | 19 | +11 | 484 | 4 | + 7 | 6, 10, $\bar{4}$ | 4 | + 6 |
| 505 | 8 | + 6 | 813 | 6 | + 7 | 033 | 4- | + 2 | 644 | 8 | + 7 | 562 | 28 | -29 | 582 | 4 | - 4 | 0, 11, 1 | 6 | - 4 |
| 507 | 7 | - 5 | $11\bar{1}$ | 25 | +29 | 034 | 6 | - 11 | 740 | 14 | +16 | 563 | 7 | - 8 | 680 | 5 | - 5 | 0, 11, 2 | 16 | -15 |
| 509 | 7 | + 7 | $11\bar{2}$ | 62* | +85 | 035 | 17 | - 16 | $14\bar{1}$ | 43 | +53 | 564 | 8 | + 5 | 780 | 15 | +12 | 0, 11, 6 | 5 | - 5 |
| 600 | 14 | + 17 | $21\bar{1}$ | 55 | -55 | 036 | 9 | + 8 | $14\bar{2}$ | 7 | -10 | 660 | 11 | + 8 | 781 | 6 | + 8 | 0, 11, 8 | 5 | + 3 |
| 602 | 34 | - 27 | $21\bar{2}$ | 4 | +10 | 037 | 5 | + 5 | $14\bar{3}$ | 13 | -14 | 661 | 19 | -16 | 880 | 9 | + 7 | 1, 11, 0 | 4 | - 7 |
| 604 | 5 | - 3 | $21\bar{3}$ | 36 | +31 | 038 | 7 | - 5 | $14\bar{4}$ | 13 | +15 | 662 | 16 | -12 | 980 | 4 | - 4 | 1, 11, 1 | 11 | -10 |
| 701 | 9 | - 11 | $21\bar{4}$ | 16 | +13 | 039 | 5 | - 5 | $24\bar{1}$ | 22 | -20 | 663 | 18 | +18 | $18\bar{1}$ | 16 | -22 | 1, 11, 2 | 6 | + 7 |
| 703 | 20 | + 15 | $31\bar{1}$ | 38 | -45 | 130 | 142 | - 134 | $24\bar{2}$ | 4 | + 1 | 760 | 8 | - 7 | $18\bar{2}$ | 17 | -30 | 1, 11, 3 | 12 | +10 |
| 705 | 6 | - 1 | $31\bar{2}$ | 5 | + 6 | 131 | 19 | + 24 | $24\bar{3}$ | 36 | -37 | 762 | 13 | +11 | $18\bar{4}$ | 9 | +11 | 2, 11, 0 | 4 | - 6 |
| 800 | 12 | - 11 | $31\bar{3}$ | 22 | +14 | 132 | 17 | + 22 | $24\bar{4}$ | 14 | +11 | 860 | 9 | + 7 | $28\bar{1}$ | 15 | +15 | 2, 11, 1 | 5 | + 8 |
| 802 | 5 | - 1 | $41\bar{1}$ | 4 | + 4 | 133 | 23 | - 27 | $34\bar{1}$ | 4 | - 2 | 960 | 4 | + 2 | $28\bar{2}$ | 8 | -11 | 2, 11, 2 | 12 | +10 |
| 804 | 8 | - 6 | $41\bar{2}$ | 18 | -18 | 134 | 21 | - 21 | $34\bar{2}$ | 6 | +12 | $16\bar{1}$ | 22 | -21 | $28\bar{3}$ | 21 | -23 | 2, 11, 4 | 6 | - 6 |
| 901 | 6 | + 4 | $41\bar{3}$ | 11 | +16 | 230 | 56 | + 56 | $34\bar{4}$ | 49 | -46 | $16\bar{2}$ | 29 | +37 | $28\bar{4}$ | 13 | +14 | 3, 11, 0 | 8 | -11 |
| 903 | 6 | - 2 | $41\bar{4}$ | 30 | +31 | 233 | 12 | - 14 | $44\bar{1}$ | 23 | +20 | $16\bar{3}$ | 13 | +11 | $38\bar{1}$ | 25 | -14 | 3, 11, 3 | 12 | -13 |
| 10, 0, 0 | 6 | + 4 | $51\bar{1}$ | 6 | + 3 | 234 | 7 | + 11 | $44\bar{3}$ | 25 | +23 | $16\bar{4}$ | 11 | -13 | $38\bar{2}$ | 4 | + 3 | 4, 11, 0 | 11 | +10 |
| 12, 0, 0 | 4 | - 4 | $51\bar{2}$ | 6 | + 5 | 330 | 12 | + 13 | $44\bar{4}$ | 19 | +14 | $26\bar{1}$ | 8 | -10 | $38\bar{3}$ | 10 | -11 | 4, 11, 2 | 5 | - 8 |
| $10\bar{1}$ | 52 | + 54 | $51\bar{3}$ | 14 | -19 | 331 | 12 | - 14 | $54\bar{1}$ | 5 | - 8 | $26\bar{2}$ | 3 | + 2 | $38\bar{4}$ | 12 | -14 | 5, 11, 0 | 4 | - 4 |
| $10\bar{3}$ | 21 | + 26 | $61\bar{1}$ | 7 | - 3 | 332 | 7 | - 6 | $64\bar{1}$ | 10 | -11 | $26\bar{3}$ | 28 | +33 | $48\bar{1}$ | 7 | + 8 | 5, 11, 1 | 9 | - 7 |
| $10\bar{7}$ | 24 | - 17 | $61\bar{2}$ | 4 | + 7 | 333 | 5 | + 11 | $64\bar{4}$ | 5 | + 7 | $26\bar{4}$ | 5 | - 3 | $48\bar{2}$ | 4 | - 6 | 5, 11, 2 | 5 | + 7 |
| $20\bar{2}$ | 12 | + 14 | $61\bar{3}$ | 4 | - 1 | 334 | 16 | + 19 | $74\bar{2}$ | 13 | -12 | $36\bar{2}$ | 23 | -26 | $48\bar{4}$ | 8 | -10 | 5, 11, 4 | 5 | - 1 |
| $20\bar{4}$ | 45 | - 48 | $61\bar{4}$ | 21 | -21 | 431 | 16 | - 16 | $74\bar{4}$ | 13 | +11 | $36\bar{3}$ | 10 | + 7 | $58\bar{2}$ | 4 | + 5 | 6, 11, 0 | 5 | - 6 |
| $20\bar{6}$ | 27 | + 24 | $71\bar{1}$ | 5 | - 8 | 432 | 24 | + 28 | $84\bar{1}$ | 14 | +15 | $36\bar{4}$ | 18 | +18 | $68\bar{1}$ | 11 | -10 | 1, 11, $\bar{4}$ | 6 | - 7 |
| $20\bar{8}$ | 10 | - 10 | $71\bar{3}$ | 10 | +11 | 433 | 18 | + 22 | 051 | 11 | +15 | $46\bar{1}$ | 4 | + 7 | $68\bar{4}$ | 6 | - 6 | 2, 11, $\bar{3}$ | 5 | + 7 |
| 2, 0, $\bar{10}$ | 6 | + 5 | $81\bar{4}$ | 6 | - 7 | 434 | 5 | - 6 | 052 | 3 | + 9 | $46\bar{3}$ | 11 | -11 | $78\bar{1}$ | 6 | - 9 | 3, 11, $\bar{1}$ | 17 | -15 |
| $30\bar{1}$ | 16 | + 15 | $91\bar{2}$ | 5 | + 4 | 530 | 17 | - 22 | 054 | 15 | -14 | $46\bar{4}$ | 3 | + 6 | $88\bar{1}$ | 6 | + 7 | 3, 11, $\bar{3}$ | 7 | +10 |
| $30\bar{3}$ | 50 | + 47 | $91\bar{4}$ | 4 | - 5 | 531 | 15 | + 12 | 056 | 12 | +11 | $56\bar{4}$ | 12 | +15 | 092 | 6 | + 8 | 4, 11, $\bar{1}$ | 6 | + 5 |
| $30\bar{5}$ | 12 | - 14 | 020 | 37 | -34 | 532 | 13 | + 15 | 057 | 7 | - 4 | $66\bar{3}$ | 10 | -11 | 093 | 7 | - 6 | 4, 11, $\bar{4}$ | 4 | + 6 |
| $30\bar{7}$ | 7 | + 7 | 021 | 44 | -44 | 533 | 19 | - 19 | 058 | 5 | + 4 | $66\bar{4}$ | 8 | +12 | 094 | 3 | - 1 | 0, 12, 0 | 14 | -15 |
| $30\bar{9}$ | 8 | - 3 | 022 | 7 | + 9 | 534 | 4 | + 3 | 059 | 5 | + 4 | $76\bar{1}$ | 6 | - 7 | 096 | 7 | + 4 | 0, 12, 1 | 12 | -14 |
| $40\bar{2}$ | 10 | - 15 | 023 | 8 | +12 | 630 | 10 | + 9 | 150 | 44 | +45 | $76\bar{4}$ | 4 | - 6 | 098 | 5 | - 4 | 0, 12, 6 | 5 | + 5 |
| $40\bar{4}$ | 9 | + 12 | 024 | 12 | -16 | 634 | 6 | + 5 | 151 | 20 | -18 | 071 | 30 | -33 | 099 | 5 | + 3 | 1, 12, 0 | 13 | -16 |
| $40\bar{6}$ | 15 | - 17 | 025 | 8 | - 7 | 730 | 5 | - 4 | 152 | 39 | -38 | 072 | 6 | - 8 | 193 | 9 | - 9 | 1, 12, 1 | 11 | +11 |
| $40\bar{8}$ | 7 | - 4 | 026 | 11 | +10 | 732 | 20 | + 15 | 153 | 10 | +17 | 073 | 25 | +25 | 194 | 4 | + 6 | 2, 12, 0 | 10 | + 7 |
| 4, 0, $\bar{10}$ | 7 | - 1 | 027 | 17 | +18 | 930 | 4 | + 2 | 250 | 13 | -15 | 074 | 5 | + 5 | 290 | 17 | +22 | 3, 12, 0 | 4 | - 1 |
| $50\bar{1}$ | 8 | + 4 | 120 | 72 | -72 | $13\bar{1}$ | 32 | - 36 | 251 | 23 | -27 | 075 | 9 | -10 | 291 | 17 | -12 | 4, 12, 4 | 8 | + 7 |
| $50\bar{3}$ | 9 | + 8 | 121 | 3 | + 5 | $13\bar{2}$ | 16 | + 18 | 253 | 22 | +24 | 076 | 5 | - 2 | 292 | 4 | - 5 | 6, 12, 0 | 5 | - 3 |
| $50\bar{5}$ | 5 | - 2 | 122 | 9 | +13 | $13\bar{4}$ | 24 | + 24 | 254 | 10 | -14 | 077 | 14 | +10 | 293 | 10 | +13 | 8, 12, 0 | 5 | + 4 |
| $50\bar{7}$ | 6 | + 6 | 123 | 42 | -43 | $23\bar{1}$ | 33 | - 34 | 350 | 53 | -60 | 079 | 5 | - 4 | 294 | 14 | +14 | 1, 12, $\bar{1}$ | 11 | -10 |
| $60\bar{2}$ | 10 | - 13 | 124 | 6 | + 7 | $23\bar{2}$ | 45 | - 40 | 351 | 15 | +17 | 172 | 18 | +20 | 390 | 5 | - 7 | 1, 12, $\bar{2}$ | 4 | + 4 |
| $60\bar{4}$ | 25 | + 23 | 220 | 20 | +21 | $23\bar{3}$ | 25 | - 22 | 352 | 24 | +31 | 173 | 4 | - 2 | 393 | 17 | +13 | 1, 12, $\bar{3}$ | 5 | + 6 |
| $60\bar{6}$ | 5 | - 6 | 221 | 4 | + 3 | $23\bar{4}$ | 24 | + 26 | 354 | 9 | -12 | 174 | 11 | -11 | 394 | 13 | -12 | 2, 12, $\bar{2}$ | 6 | -10 |
| $60\bar{8}$ | 8 | - 6 | 222 | 18 | -21 | $33\bar{1}$ | 23 | + 26 | 451 | 16 | +16 | 270 | 54 | -52 | 490 | 8 | - 6 | 3, 12, $\bar{3}$ | 5 | - 9 |
| $70\bar{1}$ | 12 | + 13 | 223 | 36 | -36 | $33\bar{2}$ | 15 | - 11 | 453 | 21 | -21 | 271 | 6 | - 5 | 491 | 5 | + 2 | 5, 12, $\bar{1}$ | 6 | + 5 |
| $70\bar{3}$ | 8 | - 6 | 224 | 16 | +15 | $33\bar{3}$ | 42 | - 50 | 550 | 18 | +21 | 272 | 10 | +10 | 492 | 14 | +12 | 0, 13, 3 | 8 | + 6 |
| $70\bar{5}$ | 8 | + 4 | 320 | 15 | +17 | $33\bar{4}$ | 12 | + 12 | 551 | 5 | - 4 | 273 | 4 | - 9 | 590 | 4 | + 6 | 1, 13, 0 | 5 | - 9 |
| $70\bar{7}$ | 7 | + 1 | 323 | 17 | +12 | $43\bar{1}$ | 6 | + 13 | 552 | 7 | - 8 | 370 | 23 | +25 | 59. | 6 | + 4 | 1, 13, 1 | 6 | + 9 |
| $80\bar{2}$ | 13 | + 9 | 324 | 10 | +11 | $43\bar{2}$ | 29 | + 32 | 553 | 5 | - 8 | 371 | 17 | +14 | 593 | 5 | - 8 | 1, 13, 3 | 6 | - 6 |
| $80\bar{4}$ | 9 | - 5 | 420 | 25 | +28 | $43\bar{3}$ | 27 | - 31 | 554 | 8 | + 1 | 372 | 19 | -20 | 594 | 9 | - 3 | 2, 13, 0 | 7 | + 4 |
| $80\bar{6}$ | 8 | + 6 | 421 | 23 | -19 | $43\bar{4}$ | 28 | - 28 | 650 | 16 | -15 | 374 | 13 | +11 | 691 | 6 | - 3 | 3, 13, 0 | 4 | + 3 |
| $80\bar{8}$ | 6 | - 2 | 422 | 14 | -16 | $53\bar{1}$ | 11 | - 12 | 651 | 26 | -21 | 470 | 7 | + 8 | 692 | 5 | + 5 | 4, 13, 0 | 5 | - 6 |
| $90\bar{1}$ | 15 | - 14 | 424 | 10 | + 7 | $53\bar{2}$ | 21 | + 23 | 652 | 12 | + 5 | 471 | 18 | -20 | 790 | 4 | - 4 | 5, 13, 0 | 4 | - 2 |
| $90\bar{3}$ | 9 | + 7 | 520 | 9 | +11 | $53\bar{3}$ | 23 | + 22 | 654 | 8 | + 3 | 472 | 9 | - 9 | 890 | 4 | + 4 | 6, 13, 0 | 8 | + 8 |
| $90\bar{5}$ | 11 | - 6 | 521 | 14 | -13 | $53\bar{4}$ | 31 | - 29 | 750 | 10 | -10 | 473 | 30 | +24 | 990 | 4 | - 4 | 1, 13, $\bar{1}$ | 6 | - 9 |
| $90\bar{7}$ | 7 | + 6 | 522 | 14 | -13 | $63\bar{1}$ | 5 | - 7 | 950 | 4 | - 4 | 474 | 12 | - 6 | $19\bar{1}$ | 17 | -19 | 2, 13, $\bar{2}$ | 5 | - 9 |
| 10, 0, $\bar{4}$ | 10 | + 12 | 523 | 12 | +13 | $63\bar{2}$ | 15 | - 13 | $15\bar{1}$ | 15 | +19 | 570 | 10 | -11 | $19\bar{4}$ | 3 | - 5 | 3, 13, $\bar{1}$ | 16 | +12 |
| 10, 0, $\bar{6}$ | 7 | - 7 | 620 | 10 | -14 | $63\bar{3}$ | 12 | + 11 | $15\bar{2}$ | 10 | +10 | 571 | 10 | -10 | $29\bar{1}$ | 10 | +11 | 4, 13, $\bar{2}$ | 5 | + 4 |
| 012 | 36 | - 36 | 621 | 7 | - 8 | $63\bar{4}$ | 5 | + 4 | $25\bar{1}$ | 69 | +71 | 572 | 4 | + 5 | $29\bar{2}$ | 4 | - 4 | 5, 13, $\bar{1}$ | 6 | - 5 |
| 014 | 10 | + 19 | 622 | 22 | +20 | $73\bar{1}$ | 11 | + 10 | $25\bar{2}$ | 11 | -14 | 574 | 4 | - 6 | $29\bar{3}$ | 9 | + 5 | 0, 14, 0 | 5 | + 3 |
| 015 | 8 | - 10 | 623 | 10 | +11 | $73\bar{3}$ | 10 | - 12 | $25\bar{4}$ | 14 | +15 | 670 | 12 | -11 | $29\bar{4}$ | 9 | - 7 | 0, 14, 2 | 5 | - 5 |
| 016 | 30 | - 26 | 624 | 4 | - 4 | $83\bar{2}$ | 10 | + 9 | $35\bar{2}$ | 42 | +43 | 673 | 6 | + 8 | $39\bar{2}$ | 4 | + 5 | 0, 14, 3 | 5 | + 3 |
| 018 | 5 | + 5 | 721 | 11 | + 10 | $83\bar{3}$ | 5 | - 5 | $35\bar{3}$ | 12 | -10 | 770‡ | 4 | - 1 | $49\bar{1}$ | 7 | - 9 | 5, 14, 0 | 5 | - 3 |
| 0, 1, 10 | 4 | - 2 | 723 | 11 | - 10 | 040 | 23 | - 21 | $35\bar{4}$ | 28 | -26 | 771 | 6 | + 6 | $49\bar{2}$ | 13 | +14 | 6, 14, 0 | 4 | + 5 |
| 111 | 12 | - 9 | 820 | 8 | + 5 | 041 | 32 | + 34 | $45\bar{1}$ | 4 | -10 | 772 | 5 | + 3 | $49\bar{3}$ | 7 | + 9 | 2, 14, $\bar{3}$ | 8 | - 9 |
| 112 | 2 | - 8 | 823 | 6 | - 3 | 042 | 3 | - 7 | $45\bar{3}$ | 21 | +25 | $17\bar{1}$ | 27 | +31 | $49\bar{4}$ | 16 | -17 | 0, 15, 3 | 5 | - 3 |
| 113 | 11 | - 11 | 11, 2, 2 | 8 | - 2 | 043 | 10 | + 7 | $45\bar{4}$ | 3 | + 6 | $17\bar{2}$ | 12 | -11 | $59\bar{1}$ | 8 | -10 | 0, 15, 5 | 5 | + 1 |
| 114 | 4 | - 6 | $12\bar{1}$ | 14 | -15 | 044 | 4 | + 5 | $55\bar{1}$ | 18 | +16 | $17\bar{3}$ | 8 | + 9 | $59\bar{3}$ | 19 | +18 | 3, 15, 0 | 4 | - 1 |
| 210 | 74 | - 76 | $12\bar{2}$ | 82 | +85 | 045 | 8 | + 11 | $55\bar{4}$ | 22 | +24 | $17\bar{4}$ | 4 | - 4 | $69\bar{1}$ | 6 | + 5 | 5, 15, 0 | 5 | + 4 |
| 211 | 30 | - 25 | $12\bar{3}$ | 49 | +42 | 046 | 12 | - 9 | $65\bar{1}$ | 19 | +17 | $27\bar{1}$ | 25 | -31 | 0, 10, 0 | 25 | +25 | 0, 16, 1 | 5 | - 5 |
| 212 | 44 | + 43 | $12\bar{4}$ | 31 | -39 | 047 | 14 | - 11 | $65\bar{3}$ | 17 | -14 | $27\bar{3}$ | 14 | +16 | 0, 10, 1 | 8 | -11 | 0, 16, 3 | 5 | + 1 |
| 213 | 13 | + 16 | $22\bar{1}$ | 38 | -46 | 048 | 5 | + 2 | $65\bar{4}$ | 4 | + 8 | $37\bar{2}$ | 20 | -22 | 0, 10, 2 | 15 | -17 | 1, 16, 0 | 4 | - 3 |
| 214 | 15 | - 21 | $22\bar{2}$ | 89 | -81 | 140 | 82 | + 80 | $75\bar{1}$ | 5 | + 6 | $47\bar{1}$ | 18 | +16 | 0, 10, 3† | 5 | + 3 | 0, 18, 0 | 5 | - 2 |

* Reflection partly cut off.

† This structure factor was entered in the Fourier series for Fig. 2 with the wrong sign.

‡ This structure factor was entered in the Fourier series for Fig. 3 with the wrong sign.

It is apparent that the hybridization of the sulfur atom in diphenyl sulfoxide and diphenyl sulfone is substantially different from that in di-*p*-tolyl sulfide, taking the dihedral angle between the benzene rings and the central C–S–C plane as the criterion. In the case of the aromatic sulfide (Blackmore & Abrahams, 1955), this angle is 33·8°, resulting in a close approach of 3·19 Å between nearest non-bonded carbon atoms. In the sulfoxide, this angle is 81·9° and the corresponding approach is 3·52 Å. Hence, in the aromatic sulfide, there cannot be the freedom of rotation about the C–S bond present in the sulfoxide.

## Experimental

Small, regular, plate-like crystals were grown from 60–80° petroleum-ether solution, and were cut to suitable size for X-ray photography. The radiation used for all intensity records was Mo $K\alpha$ ($\lambda$=0·7107 Å) to minimize errors due to absorption, except for some *h0l* reflections, which were measured using Cu $K\alpha$ radiation ($\lambda$ = 1·5418 Å). Precession and modified Weissenberg (Abrahams, 1954) cameras were used. Intensity measurements were made visually, using both the multiple-exposure and the multiple-film techniques. For the latter, sheets of 1-mil nickel foil were interleaved between films. Three crystals were used, of which the smallest was 0·08×0·20×0·20 mm. and the largest 0·15×0·60×0·80 mm. The smallest crystal was employed for the majority of the intensity measurements, the larger crystals only for the weaker reflections. The ratio of maximum to minimum intensity was about 4000:1 in *hk*0; 850:1 in 0*kl*; 4000:1 in *h*0*l*; 2300:1 in *hk*1; 2240:1 in *hk*2; 560:1 in *hk*3; and 640:1 in *hk*4. The intensities were converted into structure factors in the usual way, no absorption corrections being made. The Tunell (1939) rotation factor was used for the upper-layer equi-inclination Weissenberg photographs. Common sets of reflections were used to place all 664 structure factors on the same scale, and, where reflections were measured more than once, the mean value was taken. The complete set of observed structure factors are collected in Table 5 under $F_{meas.}$.

The calculated structure factors, based on the final atomic coordinates in Table 1, make use of the atomic form factors given in Table 4, and are listed in Table 5 under $F_{calc.}$.

All structure factors and least-squares calculations were made on International Business Machines. Four-figure accuracy was maintained throughout. The double Fourier series were summed using Beevers–Lipson strips, with the *a*, *b* and *c* axes subdivided into 30, 60 and 30 parts, respectively. The positions of the contour lines in Figs. 2 and 3 were obtained from the summation totals by graphical interpolation.

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