154. *The Structure of Certain Polysulphides and Sulphonyl Sulphides. Part III. The Crystal Structure of Bisphenylsulphonyl Sulphide.*

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A quantitative *X*-ray analysis of the crystal and molecular structure of bisphenylsulphonyl sulphide is described, and projections of the molecule have been made by Fourier series methods from which the atomic positions can be determined with considerable accuracy. The molecule displays an exact two-fold axis of symmetry which passes through the central sulphur atom. The bond lengths (Table IV) are normal, the short sulphur–oxygen distances (1·41 A.) indicating double-bond characteristics rather than co-ordinate links, in agreement with other recent work. The valency angles of the sulphur atoms show considerable deviations from tetrahedral values, and the stereochemistry may be based on a distorted octahedral structure. The oxygen atoms make close approaches to certain aromatic carbon atoms of adjoining molecules (Tables V) and these attractions probably govern the rather compact grouping of the molecules in the crystal.

In Part I (Dawson, Mathieson, and Robertson, *J.*, 1948, **322**) crystallographic data were given for a number of molecules containing groups or chains of sulphur atoms. In many cases these molecules were found to possess an exact two-fold axis of symmetry in the crystalline state, and in all cases the evidence was strongly in favour of extended zigzag sulphur chains rather than structures involving any form of side co-ordination to one or more of the sulphur atoms. Although this generalisation can be made fairly readily from the preliminary data, exact analysis leading to atomic co-ordinates and bond-length measurement is exceedingly difficult in this series owing to the many degrees of freedom possessed by these molecules. One approach by the well-known heavy-atom method has been successful in the case of 2 : 2′-di-iododiethyl trisulphide, and the results are described in Part II (Dawson and Robertson, *J.*, 1948, 1256).

In the present paper, which gives a detailed analysis of bisphenylsulphonyl sulphide, another method is employed, which depends upon a careful comparison of the isomorphous phenyl and *p*-tolyl analogues. This method is to a certain extent direct. Perutz (*Nature*, 1942, **149**, 491) has utilised the variations in intensities of *X*-ray reflections consequent on the gradual variation of cell dimensions due to varying degrees of hydration to determine the relative phase constants of certain reflections in the hæmoglobin crystal. In the present example, gradual variation of dimensions is not possible, but the dimensional changes which result from the insertion of the extra methyl group, combined with a study of the reflections which change in intensity and those which do not change, give a very clear indication of the orientation of the benzene ring in the crystal, and enable a preliminary trial structure to be set up. The work then proceeds by correlation of calculated and observed structure amplitudes, and refinement by double Fourier series methods.

Analysis of the Structure.

Bisphenylsulphonyl sulphide, $C_{12}H_{10}O_4S_3$, and bis-*p*-tolylsulphonyl sulphide, $C_{14}H_{14}O_4S_3$, crystallise in the monoclinic prismatic class, space group C_{2h}^6 $(A2/a)$, with four molecules per unit cell, and the molecules display a two-fold axis of symmetry parallel to the *b* crystal axis. The principal crystal data for the two compounds are summarised in Table I (for further details, see Part I, *J.*, 1948, 322).

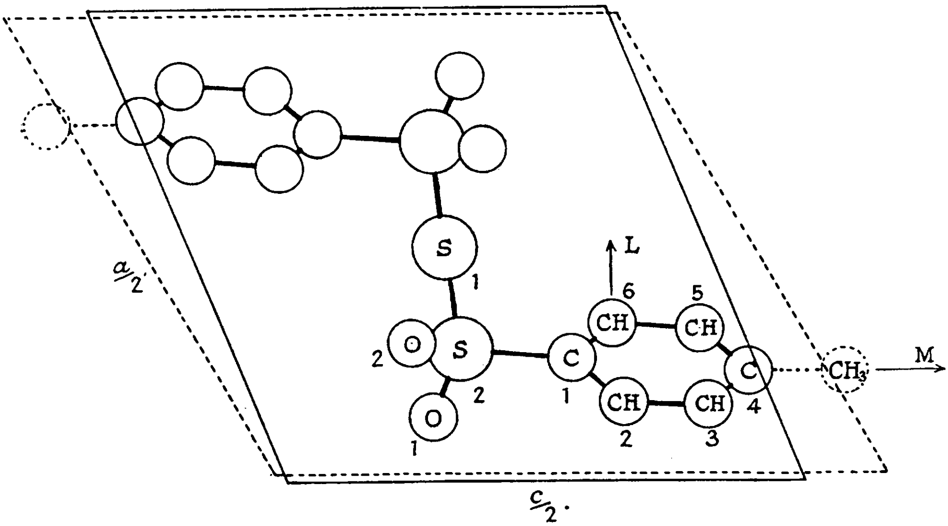
Table I.

	a, A.	*b*, A.	*c*, A.	β.	d_{100}.	Cell vol., A.^{3}.	*d* (calc.).
Bisphenylsulphonyl sulphide ...	15·88	5·52	15·88	112·9°	14·60	1282	1·618
Bis-*p*-tolylsulphonyl sulphide...	16·50	5·85	18·88	119·9°	14·31	1581	1·430

The most important changes in passing from the phenyl to the *p*-tolyl compound are the expansion of 3·0 A. in the length of the *c* axis, and the expansion of 7° in the β angle. Although the *a* axis also increases in length, the corresponding spacing, d_{100}, shows little change. There is a considerable overall expansion in the unit cell volume with a decrease in density, and it is clear that the molecular extension which causes these changes must take place mainly in the direction of the *c* axis. This dimensional evidence is confirmed by the fact that the distribution of intensities in the (*h*00) series of reflections is closely similar for the two compounds.

The trial model which results from the above considerations is shown in Fig. 1, projected on the (010) plane. The sulphur atom S(1) must occupy the special position (*a*/4, *y*, *c*/4), and the very strong (400) indicates that the line S(2)C(1)C(4) must lie close to the direction of the *c* axis, with the benzene rings rather steeply inclined to the (010) plane. The actual orientation can be determined more precisely from a consideration of the more outstanding intensities from the smaller spacing (*h*0*l*) planes, particularly the (20$\bar{4}$), (20$\bar{6}$), (20$\bar{8}$), (60,10) (60,12), and (804). The positions assigned to the oxygen atoms are obtained by assuming a tetrahedral distribution of bonds about the sulphur atom S(2).

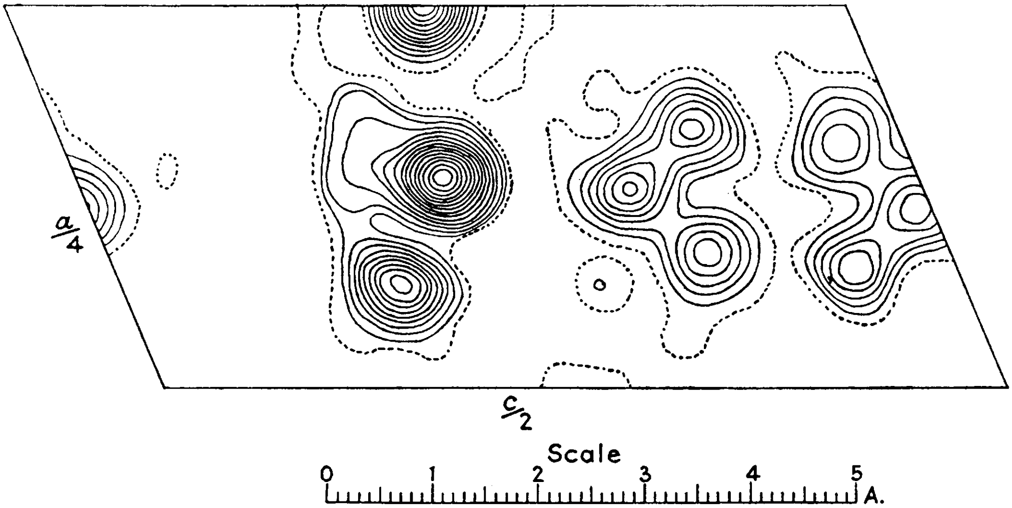
FIG. 1.



*Structural relationship of bisphenylsulphonyl sulphide (full lines) and bis-*p*-tolylsulphonyl sulphide (dotted lines), projected on* (010).

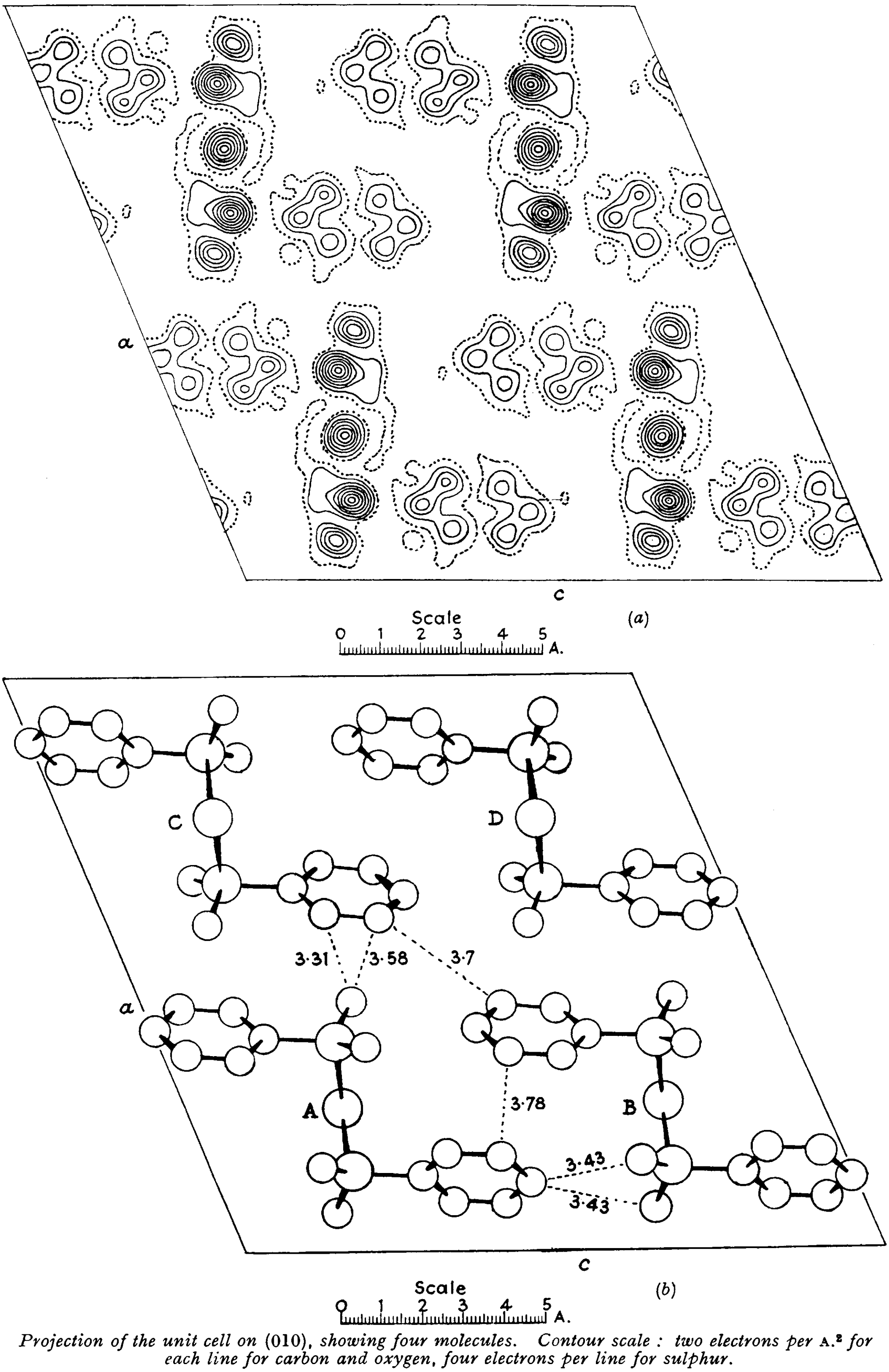
After several minor adjustments, this trial model gave a certain measure of agreement between the observed and calculated structure amplitudes, the average discrepancy, $\Sigma\{|F, \text{obs.}| - |F, \text{calc.}|\}/\Sigma|F, \text{obs.}|$, being 33%. From this stage the work was continued by carrying out three successive double Fourier summations giving projections of the structure on the (010) plane. Recalculation of the structure amplitudes from the co-ordinates derived from

FIG. 2.



Projection of the asymmetric crystal unit (half molecule) on the (010) *plane. Contour scale: one electron per* A.^{2} *for each line on the carbon and oxygen centres, two electrons per line for sulphur. The one-electron line is dotted.*

FIG. 3.

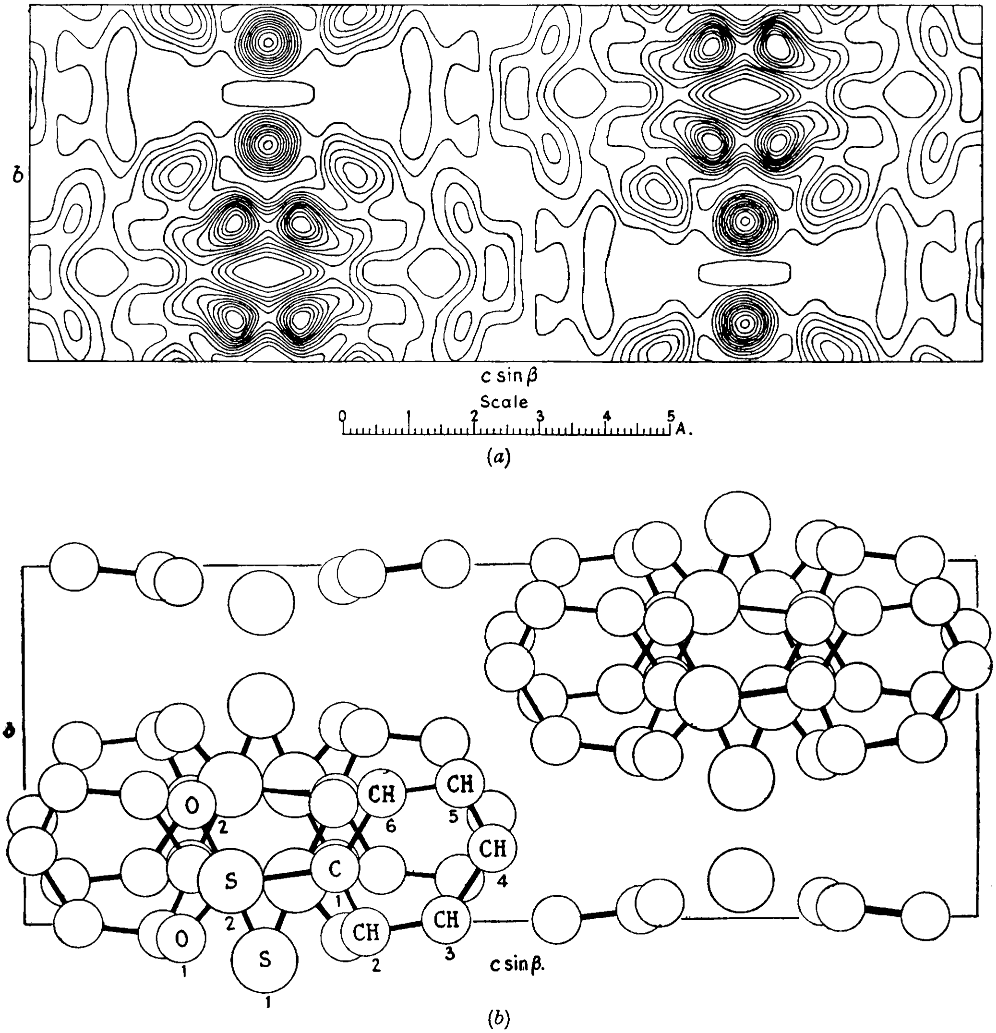


Projection of the unit cell on (010), *showing four molecules. Contour scale : two electrons per* A.^{2} *for each line for carbon and oxygen, four electrons per line for sulphur.*

the last synthesis gave an average discrepancy of 19%, indicating that a considerable degree of refinement had been achieved.

The results of the final synthesis from the ($h0l$) structure amplitudes are shown by the contour map of Fig. 2 which covers the asymmetric crystal unit (half the chemical molecule and one-eighth of the unit cell). In this projection all the atoms except hydrogen and the oxygen atom O(2) are very clearly resolved, and the positions of the centres can be determined with some certainty.

FIG. 4.



Projection of the unit cell along the **a** *axis on the* (100) *plane, showing overlapping molecules.*

The mutual relations of the different molecules in the unit cell are shown in the smaller-scale electron-density map of Fig. 3(a), which covers the complete unit cell. The corresponding line drawing in Fig. 3(b) shows the positions of the atoms. The compact grouping of the molecules and the achievement of a very uniform occupation of the available space in spite of their rather clumsy shapes is well illustrated in these diagrams.

In Fig. 3(b), molecule B is identical with the standard molecule A, but is translated 0, $b/2$, $c/2$, with respect to A. Molecule C is related to A by a reflection in a plane parallel to the plane of the paper at $y = b/4$ and a translation of $a/2$. Molecule D is related to C as B is to A.

The co-ordinates of the atoms perpendicular to these projections may be deduced from certain assumptions regarding the regularity of the molecule. The space-group requirements, however, also permit a free translation along the *b* axis for the molecule as a whole [the special position for the central sulphur atom, S(1), is *a*/4, *y*, *c*/4]. Some adjustment by trial and error methods was therefore necessary before proceeding to the next projection. In this connection the most important reflections are the axial set (020), (040), and (060), and the strong series (04*l*). The outstanding reflection from the (03,17) plane was also a useful guide to the correct position. After small variations to obtain the maximum agreement for these structure factors, it was possible to proceed by Fourier series methods. Two successive syntheses were carried out with the (0*kl*) structure factors as coefficients, and the final projection on the (100) plane is shown in Fig. 4(*a*). All four molecules are shown, but there is considerable overlap of atoms, not only within the molecule but also between adjacent molecules. In the corresponding explanatory diagram, Fig. 4(*b*), the atoms of the asymmetric unit are designated by letters. The sulphur atom S(1) is very clearly resolved, and this helps to determine the position of the molecule with respect to the *b* axis.

Orientation, Co-ordinates, and Dimensions.

The projection shown in Fig. 2 clearly defines the x and z co-ordinates of all the atoms except O(2), and gives some guide as to the disposition perpendicular to this projection plane. The heavy atoms have a certain distorting effect on the others, and so to fix the carbon positions a regular hexagonal benzene ring was assumed. The positions selected are those which give the best fit on the contour map, compatible with this assumption of regularity.

The orientation of the benzene ring in the crystal may be defined by the angles χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; χ_N, ψ_N, ω_N, where these are the angles made by the molecular axes L and M, and their perpendicular N (see Fig. 1) with the axes a', b, and c. For this purpose a' is chosen as the perpendicular to the crystal axes b and c. The orientation deduced from the contour maps is then given by the angles in Table II. It will be noted that the inclination of the benzene ring to the (010) plane, expressed by the angle between the normal to the plane of the ring and the b crystal axis, or ψ_N, is 60·3°.

TABLE II.

Orientation of benzene ring in crystal.

$\chi_L = 59{\cdot}9°$	$\cos\chi_L = 0{\cdot}502$	$\chi_M = 93{\cdot}9°$	$\cos\chi_M = -0{\cdot}068$
$\psi_L = 30{\cdot}4$	$\cos\psi_L = 0{\cdot}862$	$\psi_M = 83{\cdot}7$	$\cos\psi_M = 0{\cdot}110$
$\omega_L = 93{\cdot}8$	$\cos\omega_L = -0{\cdot}065$	$\omega_M = 7{\cdot}4$	$\cos\omega_M = 0{\cdot}992$
	$\chi_N = 149{\cdot}2°$	$\cos\chi_N = -0{\cdot}859$	
	$\psi_N = 60{\cdot}3$	$\cos\psi_N = 0{\cdot}496$	
	$\omega_N = 97{\cdot}1$	$\cos\omega_N = -0{\cdot}124$	

The co-ordinates of the atoms with respect to the crystal axes and centre of symmetry as origin are given in Table III. Most of these values may be obtained in a fairly direct manner from the contour maps, but there is difficulty in the case of O(2) and also in the case of the y co-ordinates of the lighter atoms, as the resolution in Fig. 4(*a*) is poor. In the latter connection reliance is placed on the calculated orientation and assumed regularity of the benzene rings. With regard to the co-ordinates of O(2), diffraction effects due to the sulphur atoms must be considered, but if allowance is made for these effects then a reasonably accurate position can be assigned to this atom.

Only the atoms in the asymmetric crystal unit, or half the molecule, are listed in Table III. The co-ordinates of the other atoms may be derived from these by the operations appropriate to this space-group. The origin is taken at a centre of symmetry, with a two-fold rotation axis at $a/4, y, c/4$. The co-ordinates of the equivalent points, for $A2/a$, then become

$$A\begin{cases}(1)\ x,\ y,\ z\\(2)\ \tfrac{1}{2}-x,\ y,\ \tfrac{1}{2}-z\end{cases}\qquad D\begin{cases}(5)\ -x,\ -y,\ -z\\(6)\ \tfrac{1}{2}+x,\ -y,\ \tfrac{1}{2}+z\end{cases}$$

$$B\begin{cases}(3)\ x,\ \tfrac{1}{2}+y,\ \tfrac{1}{2}+z\\(4)\ \tfrac{1}{2}-x,\ \tfrac{1}{2}+y,\ -z\end{cases}\qquad C\begin{cases}(7)\ -x,\ \tfrac{1}{2}-y,\ \tfrac{1}{2}-z\\(8)\ \tfrac{1}{2}+x,\ \tfrac{1}{2}-y,\ z\end{cases}$$

These values differ from the co-ordinates given in the " International Tables for the Determination of Crystal Structures " because of the change of axes from $C2/c$ to $A2/a$ and because the centre of symmetry chosen as origin lies at (0, $b/4$, $c/4$) with respect to the centre of symmetry used as origin in those tables. These changes have been made in order to bring one complete chemical molecule into the first quarter of the unit cell (Fig. 1).

TABLE III.

Co-ordinates with respect to monoclinic crystal axes. Centre of symmetry as origin.

Atom (cf. Fig. 1).	x, A.	$\frac{2\pi x}{a}$.	y, A.	$\frac{2\pi y}{b}$.	z, A.	$\frac{2\pi z}{c}$.
S(1)	3·97	90·0°	−0·60	− 39·0°	3·97	90·0°
S(2)	2·18	49·5	+0·64	+ 42·0	3·46	78·5
O(1)	1·07	24·2	−0·25	− 16·0	2·63	59·7
O(2)	2·33	53·0	+1·84	+120·0	2·78	63·0
C(1)	2·06	46·7	+0·83	+ 54·0	5·16	117·0
CH(2)	1·34	30·4	−0·14	− 10·0	5·64	128·0
CH(3)	1·26	28·6	+0·02	+ 1·0	6·98	159·0
CH(4)	1·85	42·0	+1·13	+ 74·0	7·82	177·5
CH(5)	2·56	58·0	+2·11	+138·0	7·35	167·0
CH(6)	2·66	60·3	+1·96	+128·0	6·00	136·0

Bond lengths may be obtained by converting the co-ordinates of Table III to the rectangular axes, a', b, and c, where a' is perpendicular to b and c. If x, y, z are the monoclinic crystal co-ordinates, and x', y', z' are the rectangular co-ordinates, the relations are

$$x' = x \sin \beta,\ y' = y,\ z' = z + x \cos \beta$$

The bond lengths and angles within the molecule are listed in Table IV. Two important non-bonded distances, between the sulphonyl oxygen atoms and the carbon atoms of the benzene ring, are included in this table.

TABLE IV.

Bond lengths and angles.

S(1)–S(2) = 2·07 ± 0·02 A.
S(2)–O(1) = 1·41 ± 0·04 A.
S(2)–O(2) = 1·41 ± 0·04 A.
S(2)–C(1) = 1·76 ± 0·02 A.
C–C (average in ring) = 1·39 ± 0·04 A.
O(2) . . . . CH(6) = 3·11 ± 0·05 A.
O(1) . . . . CH(2) = 2·92 ± 0·05 A.
S(2)–$\widehat{\text{S}(1)}$–S(2′) = 106·5° ± 1°
S(1)–$\widehat{\text{S}(2)}$–O(1) = 104·2° ± 3°
S(1)–$\widehat{\text{S}(2)}$–O(2) = 111·9° ± 3°
S(1)–$\widehat{\text{S}(2)}$–C(1) = 101·7° ± 1°
O(1)–$\widehat{\text{S}(2)}$–O(2) = 117·2° ± 4°
O(1)–$\widehat{\text{S}(2)}$–C(1) = 107·5° ± 3°
O(2)–$\widehat{\text{S}(2)}$–C(1) = 115·9° ± 3°

Intermolecular Distances.—The approach distances between the atoms of neighbouring molecules are shown in Fig. 3(*b*) and listed in Table V. Between the carbon atoms these distances are similar to those usually found in crystals of aromatic molecules (3·7—3·8 A.), but between the sulphonyl oxygen atoms and adjacent aromatic carbon atoms the distances are sometimes significantly less, and become as low as 3·3 A. These values indicate certain attractions, probably in the nature of very weak hydrogen bonds, between the sulphonyl oxygen and the aromatic hydrogen atoms.

TABLE V.

Intermolecular distances (A.).

CH(2A) . . . O(1C) = 3·33
CH(3A) . . . O(1C) = 3·58
CH(4A) . . . O(1B) = 3·43
CH(4A) . . . O(2B) = 3·43
CH(5A) . . . CH(5B) = 3·78
CH(3A) . . . CH(3D) = 3·78
CH(2A) . . . CH(6C) = 3·68

Discussion of Results.

In this analysis certain diffraction effects due to the relatively heavy sulphur atoms are clearly visible on the contour maps. These effects tend to diminish the accuracy of the bond-length and bond-angle determinations, but the positions of the sulphur atoms and the relatively distant carbon atoms can be determined with considerable accuracy. The oxygen positions are more difficult to estimate, and the resolution is poor, especially for O(2). Taking account of these factors, the probable limits of error have been estimated and these are given in Table IV.

The length of the sulphur–sulphur bond (2·07 A.) is slightly less than the value of 2·12 A. reported for orthorhombic sulphur (Warren and Burwell, *J. Chem. Physics*, **1935**, **3**, 6) and slightly greater than the value of 2·04 reported both for dimethyl disulphide (Stevenson and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 2872) and for 2 : 2′-di-iododiethyl trisulphide (Dawson and Robertson, *J.*, 1948, 1256). These variations are small, and this bond appears to be a more or less normal single bond.

The sulphur–carbon bond length of 1·76 A. is slightly less than the value of 1·81 A. given by the sum of the single-bond radii, but is in very good agreement with a number of recent measurements, *e.g.*, 1·77 A. in dimethyl disulphide (Stevenson and Beach, *loc. cit.*), 1·75 A. in β-isoprene sulphone (Cox and Jeffrey, *Trans. Faraday Soc.*, 1942, **38**, 241), and 1·76 A. in *pp′*-dibromodiphenyl sulphide (Toussaint, *Bull. Soc. roy. Sci. Liège*, 1944, **13**, 111, 163). It seems probable that this bond is also a normal single bond, although Cox and Jeffrey (*loc. cit.*) have suggested a certain amount of semi-ionic bond character in β-isoprene sulphone.

The sulphur–oxygen bond lengths (1·41 ± 0·04 A.) are not as reliable as the other measurements in this structure, but the result is in quite good agreement with similar determinations, *e.g.*, 1·44 A. in β-isoprene sulphone (Cox and Jeffrey, *loc. cit.*), 1·44 A. in dimethyl sulphone (Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495), 1·45 A. in thionyl chloride, 1·43 A. in sulphonyl chloride, 1·43 A. in sulphur trioxide (Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360), 1·40 A. in α-sulphur trioxide (Westrik and MacGillavry, *Rec. Trav. chim.*, 1941, **60**, 794), and 1·43 A. in potassium sulphamate (Brown and Cox, *J.*, 1940, 1). Although this bond may be formulated as a co-ordinate link, recent work has made it clear that the older formulation as a double bond is probably more correct (Phillips, Hunter, and Sutton, *J.*, 1945, 146). The length is, in fact, rather less than that calculated from the usual double-bond radii.

The stereochemistry of this molecule is interesting, and in the present analysis all the bond angles can be measured with reasonable accuracy. The bond angle of the central sulphur atom (106·5°) is near the expected tetrahedral value. For the other sulphur atom, S(2), the angles deviate considerably from the tetrahedral value. This is perhaps to be expected, as the stereochemistry of sexacovalent sulphur should be based on the regular octahedron. In compounds of the type $R_1R_2SO_2$ the octahedral configuration will be distorted by double-bond formation, and one might expect the angle between the single bonds to approach 90° and that between the double bonds to approach 120° (assuming that the double bonds lie midway between two pairs, not in a plane, of the octahedral bonds). In the present study, the angle found between the single bonds, $\mathrm{S(1)–\widehat{S(2)}–C(1)}$, is 101·7° and that between the double bonds, $\mathrm{O(1)–\widehat{S(2)}–O(2)}$, is about 117°. The other angles are also arranged in rather unequal pairs. On the other hand, electron-diffraction studies on dimethyl sulphone appear to show that the tetrahedral arrangement is more correct (Lister and Sutton, *loc. cit.*).

Interaction of various groups in the crystal is also likely to produce some distortion of the valency angles. In this connection the approach distances of the oxygen atoms to the aromatic carbon atoms in the same molecule and in adjoining molecules are of considerable interest [Fig. 3(*b*) and Tables IV and V]. Within the molecule these approach distances between the oxygen atoms and the *o*-carbon atoms of the benzene ring are 3·11 and 2·92 A. It would appear that this must imply some form of bonding, presumably due to the large partial charge on the oxygen, because the ring could easily rotate about the single bond, S(2)–C(1), so as to increase these distances. Other short distances of 3·3—3·4 A. are found to occur between the oxygen atoms and the carbon atoms of neighbouring molecules. The intermolecular attractions indicated by these approach distances appear to be the dominant factor in maintaining the crystal structure and accounting for the isomorphism between the phenyl and the *p*-tolyl compound.

EXPERIMENTAL.

Crystals of bisphenylsulphonyl sulphide were prepared as described in Part I (*J.*, 1948, 322). By slow cooling from glacial acetic acid solution well-developed specimens were obtained, of a size suitable for *X*-ray work.

All the measurements were carried out with copper *K*α radiation (λ = 1·54 A.). Rotation, oscillation, and zero-layer line moving-film photographs were taken, the first for determining axial lengths, the last two for indexing the general (*hkl*) reflections and for intensity records.

The absent spectra indicate the space-groups *Aa* and *A*2/*a* as possible. Pyroelectric measurements showed no evidence of polarity, and so the space-group of higher symmetry, *A*2/*a*, was assumed for preliminary trials, and subsequently confirmed by the complete analysis described above.

Measurement of Intensities.—The three principal zones, (0*kl*), (*h*0*l*) and *hk*0) were studied in detail by means of moving-film photographs of the zero-layer lines for rotation about the *a*, *b*, and *c* axes. The multiple-film technique was used to correlate the strong and weak reflections and intensities were obtained over a range of about 1000 to 1. Visual estimation was used, and after applying the usual correction factors the observed structure amplitudes, F, were placed on an absolute scale based on the calculated values. The results are collected in Table VI.

TABLE VI.

Measured and calculated values of the structure factor.

hkl.	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.
200	0·105	36	−46
400	0·211	160	−179
600	0·316	<7	−8
800	0·422	63	+63
10,00	0·527	84	+80
12,00	0·633	11	+18
14,00	0·738	32	+29
16,00	0·844	28	+22
18,00	0·949	24	−37
002	0·105	95	−135
004	0·211	53	+52
006	0·316	47	+30
008	0·422	<9	+3
00,10	0·527	28	−27
00,12	0·633	<11	+6
00,14	0·738	<11	+4
00,16	0·844	<10	−7
00,18	0·949	25	+20
020	0·279	54	+40
040	0·558	73	−67
060	0·837	8	+2
$20,\bar{1}\bar{8}$	0·915	<9	+2
$20,\bar{1}\bar{6}$	0·812	21	−18
$20,\bar{1}\bar{4}$	0·705	46	+44
$20,\bar{1}\bar{2}$	0·602	22	−24
$20,\bar{1}\bar{0}$	0·497	14	+21
$20\bar{8}$	0·395	114	−112
$20\bar{6}$	0·295	111	+108
$20\bar{4}$	0·200	176	−203
$20\bar{2}$	0·120	28	+34
202	0·125	56	+77
204	0·267	52	+57
206	0·368	18	−9
208	0·470	31	+29
20,10	0·573	10	−2
20,12	0·676	23	+15
20,14	0·781	<11	−1
20,16	0·885	<9	−5
20,18	0·990	13	+24
$40,\bar{1}\bar{8}$	0·892	35	−40
$40,\bar{1}\bar{6}$	0·791	22	+24
$40,\bar{1}\bar{4}$	0·690	39	−40
$40,\bar{1}\bar{2}$	0·589	67	+58
$40,\bar{1}\bar{0}$	0·490	49	−40
$40\bar{8}$	0·396	88	+72
$40\bar{6}$	0·310	114	−103
$40\bar{4}$	0·240	<6	+4
$40\bar{2}$	0·200	30	+30
402	0·267	15	+19
404	0·349	21	−10
406	0·442	21	−31
408	0·535	<10	+12
40,10	0·635	31	−29
40,12	0·737	12	+15
40,14	0·838	35	−31
40,16	0·942	29	+40
$60,\bar{2}\bar{0}$	0·985	22	−40
$60,\bar{1}\bar{8}$	0·832	23	+33
$60,\bar{1}\bar{6}$	0·786	27	−27
$60,\bar{1}\bar{4}$	0·690	<11	+7
$60,\bar{1}\bar{2}$	0·596	22	−24
$60,\bar{1}\bar{0}$	0·506	13	+12
$60\bar{8}$	0·437	63	+47
$60\bar{6}$	0·360	47	−28
$60\bar{4}$	0·312	27	+31
$60\bar{2}$	0·295	<7	−2
602	0·368	<8	+12
604	0·442	17	−34
606	0·526	52	+46
608	0·614	75	−65
60,10	0·708	72	+58
60,12	0·805	57	−55
60,14	0·904	<8	+10
$80,\bar{2}\bar{0}$	0·980	<7	+11
$80,\bar{1}\bar{8}$	0·885	<9	+4
$80,\bar{1}\bar{6}$	0·795	<11	+3
$80,\bar{1}\bar{4}$	0·702	11	+16
$80,\bar{1}\bar{2}$	0·620	16	−17
$80,\bar{1}\bar{0}$	0·543	25	+19
$80\bar{8}$	0·477	9	+1
$80\bar{6}$	0·427	<8	+7
$80\bar{4}$	0·402	62	+50
$80\bar{2}$	0·400	51	−50
802	0·470	80	−82
804	0·535	112	+99
806	0·615	62	−45
808	0·697	39	+34
80,10	0·786	<11	+2
80,12	0·879	13	+20
80,14	0·975	<7	−5
$10,0,\bar{2}\bar{0}$	0·990	13	+15
$10,0,\bar{1}\bar{8}$	0·900	12	−18
$10,0,\bar{1}\bar{6}$	0·816	<11	+12
$10,0,\bar{1}\bar{4}$	0·736	<11	+3
$10,0,\bar{1}\bar{2}$	0·660	50	−37
$10,0,\bar{1}\bar{0}$	0·596	68	+58
$10,0\bar{8}$	0·542	49	−40
$10,0\bar{6}$	0·507	47	+42
$10,0\bar{4}$	0·492	27	−30
$10,0\bar{2}$	0·500	95	+94
10,02	0·573	47	+38
10,04	0·636	38	−33
10,06	0·708	<11	−4
10,08	0·787	26	+20
10,0,10	0·872	32	−19
10,0,12	0·962	22	+19
$12,0,\bar{1}\bar{8}$	0·929	27	−26
$12,0,\bar{1}\bar{6}$	0·850	34	+33
$12,0,\bar{1}\bar{4}$	0·778	44	−48
$12,0,\bar{1}\bar{2}$	0·715	23	+25
$12,0,\bar{1}\bar{0}$	0·660	71	−65
$12,0\bar{8}$	0·620	38	+38
$12,0\bar{6}$	0·596	57	−49
$12,0\bar{4}$	0·589	26	+28
$12,0\bar{2}$	0·602	22	−19
12,02	0·677	39	+30
12,04	0·736	46	−43
12,06	0·805	<11	+8
12,08	0·880	<9	−1
12,0,10	0·960	<7	−11
$14,0,\bar{1}\bar{8}$	0·965	39	+51
$14,0,\bar{1}\bar{6}$	0·896	30	−39
$14,0,\bar{1}\bar{4}$	0·835	29	+35
$14,0,\bar{1}\bar{2}$	0·778	<11	0
$14,0,\bar{1}\bar{0}$	0·736	16	−8
$14,0\bar{8}$	0·702	32	−31
$14,0\bar{6}$	0·690	<11	+9
$14,0\bar{4}$	0·690	<11	−8
$14,0\bar{2}$	0·705	46	−40
14,02	0·780	<11	−5
14,04	0·838	<11	−5
14,06	0·902	<12	+20
14,08	0·972	23	−33
$16,0,\bar{1}\bar{6}$	0·955	<7	0
$16,0,\bar{1}\bar{4}$	0·896	<9	+6
$16,0,\bar{1}\bar{2}$	0·850	20	+16
$16,0,\bar{1}\bar{0}$	0·816	26	+24
$16,0\bar{8}$	0·795	11	−10

TABLE VI.—*Continued.*

hkl.	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.	*hkl.*	sin θ ($\lambda = 1{\cdot}54$).	F, meas.	F, calc.
16,0$\bar{6}$	0·786	11	+ 15	460	0·862	<16	− 13
16,0$\bar{4}$	0·791	<11	− 2	560	0·877	<16	− 20
16,0$\bar{2}$	0·812	21	− 11	660	0·893	<16	− 2
16,02	0·886	31	− 36	760	0·917	<14	0
16,04	0·942	29	+ 40	860	0·937	<13	− 13
18,0,$\bar{1}\bar{4}$	0·965	< 7	− 12	960	0·967	<10	+ 5
18,0,$\bar{1}\bar{2}$	0·929	7	− 8	10,60	0·990	< 8	+ 10
18,0,$\bar{1}\bar{0}$	0·900	17	+ 16				
18,0$\bar{8}$	0·885	< 9	− 3	011	0·149	100	− 98
18,0$\bar{6}$	0·882	18	+ 23	013	0·210	< 4	0
18,0$\bar{4}$	0·892	20	− 26	015	0·298	5	+ 6
18,0$\bar{2}$	0·915	28	+ 42	017	0·395	36	− 42
18,02	0·987	18	+ 40	019	0·497	22	+ 16
20,0,$\bar{1}\bar{2}$	0·995	8	+ 18	01,11	0·610	43	− 35
20,0,$\bar{1}\bar{0}$	0·990	23	− 42	01,13	0·700	16	+ 16
20,0$\bar{8}$	0·980	26	+ 36	01,15	0·818	18	− 20
20,0$\bar{6}$	0·985	22	− 38	01,17	0·910	17	+ 22
20,0$\bar{4}$	0·995	8	+ 24	022	0·302	21	− 18
				024	0·350	24	− 18
120	0·295	40	+ 22	026	0·422	13	− 17
220	0·302	41	+ 30	028	0·507	< 7	− 9
320	0·317	67	− 60	02,10	0·597	34	− 29
420	0·350	16	+ 12	02,12	0·690	< 9	0
520	0·381	67	+ 65	02,14	0·789	8	+ 6
620	0·422	51	− 50	02,16	0·888	7	− 4
720	0·462	27	+ 18	02,18	0·990	< 4	0
820	0·507	34	+ 30	031	0·422	16	− 12
920	0·550	28	− 26	033	0·447	6	+ 6
10,20	0·597	<19	+ 14	035	0·495	21	− 19
11,20	0·645	54	− 47	037	0·560	< 8	− 7
12,20	0·690	<20	+ 22	039	0·635	25	+ 22
13,20	0·740	59	+ 54	03,11	0·720	31	− 36
14,20	0·789	<19	+ 10	03,13	0·805	42	+ 36
15,20	0·842	<17	− 12	03,15	0·897	19	− 23
16,20	0·888	<16	+ 2	03,17	0·990	26	+ 31
17,20	0·945	17	− 15	042	0·565	66	+ 65
18,20	0·990	< 8	− 11	044	0·595	54	+ 45
140	0·560	<18	+ 10	046	0·640	35	+ 27
240	0·565	57	+ 50	048	0·698	9	− 15
340	0·577	<18	+ 11	04,10	0·769	< 8	0
440	0·595	26	+ 29	04,12	0·840	8	+ 12
540	0·615	30	+ 31	04,14	0·925	< 6	+ 5
640	0·640	34	− 38	051	0·702	36	+ 41
740	0·665	<20	− 16	053	0·715	< 9	− 5
840	0·698	44	− 53	055	0·746	14	− 12
940	0·733	<20	− 9	057	0·790	11	+ 14
10,40	0·769	48	+ 48	059	0·845	< 8	+ 2
11,40	0·802	<19	0	05,11	0·910	< 7	+ 2
12,40	0·840	<17	+ 6	05,13	0·980	< 4	− 5
13,40	0·880	<16	+ 7	062	0·842	7	+ 12
14,40	0·925	<14	− 6	064	0·862	13	− 21
15,40	0·963	<10	− 12	066	0·893	12	+ 18
160	0·840	<17	+ 5	068	0·937	< 6	− 13
260	0·842	<17	+ 9	06,10	0·990	< 4	+ 2
360	0·851	24	+ 32				

The crystal specimens were small, and completely bathed in the *X*-ray beam. For the (*h*0*l*) zone the specimen had a cross-section of 0·26 by 0·24 mm. and a length of 0·65 mm. along the *b* axis. For the (0*kl*) zone a specimen was cut to a cross-section of 0·45 by 0·50 mm., and was 0·25 mm. in length along the *a* axis. For the (*hk*0) series the specimen cross-section was 0·18 mm. by 0·42 mm. and length along *c*, 0·58 mm. The high absorption coefficient ($\mu = 53{\cdot}3$ per cm. for $\lambda = 1{\cdot}54$) makes it difficult to apply accurate corfections, and no attempt in this direction was made. With crystals of the above dimensions it can be shown, however, that intensity errors due to this cause are small.

Structure Analysis.—The final Fourier summation on (010) was made at 900 points on the asymmetric unit (half the chemical molecule). The *a* axis was subdivided into 60ths (interval 0·265 A.) and the *c* axis into 120ths (interval 0·132 A.). Three-figure cosine factors were employed (Robertson, *J. Sci. Instr.*, 1948, **25**, 28), and the position of the contour lines obtained by graphical interpolation from the summation totals.

The orientation of the benzene ring (Table II) was obtained by inscribing the projection of a regular hexagon on the contour map in such a manner as to give the best fit for all the atoms. The orientation angle and co-ordinates may then be deduced in a manner similar to that described for the coronene analysis (Robertson and White, *J.*, 1945, 607, 615).

A recalculation of the structure factors based on the final co-ordinates is given in Table VI. Separate atomic scattering curves for carbon, oxygen, and sulphur were used. For carbon the average scattering curve for hydrocarbons was employed (Robertson, *Proc. Roy. Soc.*, 1935, *A*, **150**, 106) and for oxygen this curve was scaled for the atomic number of oxygen. An empirical scattering curve for sulphur was deduced by correlation between the calculated and observed structure factors.

The average discrepancy for the (*h*0*l*) structure factors, expressed as a sum of the discrepancies divided by the sum of the observed F values, is 19·0%. For all the recorded reflections the average is 18·5%.

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