

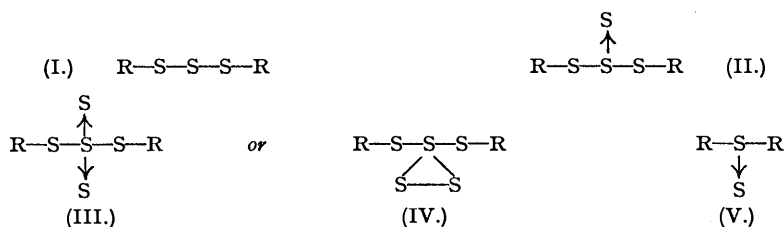
80. The Structure of Certain Polysulphides and Sulphonyl Sulphides.  
Part I. A Preliminary X-Ray Survey.

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A survey of unit cell and space-group data is given for diphenyl and di-*p*-tolyl disulphide, 2:2'-di-iododiethyl trisulphide, 2:2'-dichlorodiethyl trisulphide, diphenyl and di-*p*-tolyl disulphone, bisphenyl- and bis-*p*-tolyl-sulphonyl sulphide, bisphenyl- and bis-*p*-tolyl-sulphonyl trisulphide. At least five, and possibly six of these molecules display a two-fold axis of symmetry in the crystal. This element is present in all the molecules which contain groups of three or more sulphur atoms, from which it is clear that there is no possibility of side co-ordination to a single sulphur atom. In all cases the evidence is in favour of extended zigzag sulphur chains. Preliminary estimates of molecular orientation in the crystal lattice are given for several of the compounds, and those most suitable for further detailed X-ray analyses are indicated.

EXACT knowledge of configuration, bond distances, and valency angles in molecules which involve groups or chains of sulphur atoms is rather meagre. Some of the well-known crystalline modifications of the element itself have received fairly detailed examination. In the stable orthorhombic form the  $S_8$  molecule has a regular, puckered-ring structure, the S-S distance being 2.12 Å. and the S-S-S angle  $105.4^\circ$  (Warren and Burwell, *J. Chem. Physics*, 1935, 3, 6). This configuration appears to hold, although associated with rather large thermal vibrations, in the vapour phase (Lu and Donohue, *J. Amer. Chem. Soc.*, 1944, 66, 818), but an open-chain form has been established for plastic sulphur (Meyer and Go, *Helv. Chim. Acta*, 1934, 17, 1081).

Determination of the molecular configuration of the organic polysulphides by chemical methods has been rendered exceedingly difficult by the instability of these compounds, the higher polysulphides readily decomposing to give free sulphur and a lower polysulphide. In previous structural investigations both parachor and viscosity measurements have been utilized. From the former, Baroni (*Atti R. Accad. Lincei*, 1931, 14, 28) found support for the idea that tri-, tetra-, and penta-sulphides contain 3 sulphur atoms in a linear arrangement (I), with the additional sulphur atoms side-co-ordinated in the case of tetra- and penta-sulphides, (II)—(IV). Bezzi (*Gazzetta*, 1935, 65, 693), on the other hand, obtained viscosity measure-



ments which indicated that in mono-, di-, and tetra-sulphides with the same terminal alkyl groups the molecular length is constant. He concluded, therefore, that in all the polysulphides there is a marked tendency to side-co-ordination and he formulated the disulphides as (V).

It is thus a point of considerable interest to determine whether sulphur does in fact show a tendency to form co-ordinate links in the polysulphides. In the various molecular forms of the element itself there is as yet no evidence of any such tendency. The present work was therefore initiated partly in an effort to resolve the inconsistencies in the reported results from parachor and viscosity measurements given by Baroni and by Bezzi (*loc. cit.*).

With regard to the polythionates, the structures of the dithionate and trithionate ions have been studied by a number of workers in various inorganic salts. In the dithionate ion,  $S_2O_6^{2-}$ , the two sulphur atoms lie on a three-fold symmetry axis, about 2.08 Å. apart, and about each sulphur atom the three oxygen atoms and the other sulphur atom are arranged tetrahedrally, with a sulphur-oxygen distance of about 1.50 Å. (Huggins and Frank, *Amer. Min.*, 1931, 16, 580; Helwig, *Z. Krist.*, 1932, 83, 485; Huggins, *ibid.*, 1933, 86, 384; Barnes and Wendling, *ibid.*, 1938, 99, 153). The metabisulphite (pyrosulphite) ion,  $S_2O_5^{2-}$ , is similar in structure to the dithionate ion, but with one oxygen atom removed (Zachariasen, *Physical Rev.*, 1932, 40, 923). In the trithionate ion,  $S_3O_6^{2-}$ , the terminal  $SO_3$  groups are again approximately tetrahedral and the bonds to the central linking sulphur atom make a S-S-S valency angle of about  $103^\circ$ . The sulphur-oxygen distances are about 1.50 Å., and sulphur-sulphur about 2.15 Å.

(Zachariasen, *Z. Krist.*, 1934, **89**, 529; Ketelaar and Sanders, *J. Chem. Physics*, 1936, **4**, 621). Morphological and space-group data have been given for potassium tetrathionate (Tunell, Merwin, and Ksanda, *Amer. J. Sci.*, 1938, *A*, **35**, 361) but structural details appear to be unknown for the higher polythionates.

Some fairly detailed *X*-ray studies, with Patterson and Fourier projections, have been made by Toussaint (*Bull. Soc. roy. Sci. Liège*, 1944, **13**, 111, 163) of *pp'*-dibromodiphenyl sulphide and *pp'*-dibromodiphenyl sulphone. The results are somewhat obscured by effects due to the heavy atoms, but in the sulphone an approximately tetrahedral distribution of bonds about the central sulphur is established, with a rather uncertain sulphur-oxygen distance of 1.54 Å. The planes of the benzene rings are found to lie at right angles to the plane containing Br . . S . . Br. In both molecules a two-fold axis of symmetry passes through the central sulphur. Further space-group data for di-*p*-tolyl sulphide, phenyl  $\alpha$ -naphthyl sulphide, and nitro-derivatives are given by the same author (*ibid.*, 1943, **12**, 153, 533).

The present paper gives a survey of unit cell and space-group data for several crystalline organic di- and tri-sulphides, two isomorphous disulphones (so-called dithionates), and some sulphonyl sulphides and sulphonyl trisulphides (so-called trithionates and pentathionates). This preliminary work is necessary in order to select the compounds most suitable for the detailed *X*-ray analyses to be described in subsequent papers. There was also a hope that some elements of molecular symmetry might be detected which would limit the possible structural types as well as simplify subsequent calculations. This has proved to be the case, for a two-fold axis of symmetry has been established in five of the molecules and is probably present in a sixth.

*Diphenyl Disulphide*,  $C_{12}H_{10}S_2$ .—*Crystal data.* *M*, 218.3; *m. p.* 59°; *d*, calc. 1.336, found 1.338; orthorhombic hemihedral,  $a = 8.11 \pm 0.02$ ,  $b = 23.67 \pm 0.03$ ,  $c = 5.61 \pm 0.02$  Å. Absent spectra, (*h*00) when *h* is odd, (0*k*0) when *k* is odd, (00*l*) when *l* is odd. Space-group,  $D_2^2$ - $P2_12_12_1$ . Four molecules per unit cell. Molecular symmetry, none required. Volume of the unit cell, 1077 Å.<sup>3</sup>. Absorption coefficient for *X*-rays ( $\lambda = 1.54$ ),  $\mu = 40.7$  per cm. Total number of electrons per unit cell =  $F(000) = 456$ .

Good crystals in the form of long needles or laths, with prominent development of (110) faces, are easily obtained by crystallisation from alcohol. Previous crystallographic studies are recorded by Groth ("Chemische Kristallographie," Leipzig, 1919, **5**, 33), and more recently an *X*-ray investigation has been made by Egartner, Halla, and Schachel (*Z. physikal. Chem.*, 1932, *B*, **18**, 189), whose determination of the unit cell and space-group are in good agreement with our data.

Neither cell dimensions nor space-group data provide any special clue to the molecular arrangement. Molecules of presumably similar shape exist in the stilbene and *trans*-azobenzene crystals (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568; de Lange, Robertson, and Woodward, *ibid.*, 1939, *A*, **171**, 398), but apart from the similarity of the *b* axis in these crystals (5.70 and 5.77 Å.) to the *c* axis in diphenyl disulphide (5.61), there is little to be gained from this comparison.

*Di-p-tolyl Disulphide*,  $C_{14}H_{14}S_2$ .—*Crystal data.* *M*, 246.4; *m. p.* 46°; *d*, calc. 1.240, found 1.246; monoclinic hemihedral,  $a = 7.72 \pm 0.02$ ,  $b = 5.76 \pm 0.02$ ;  $c = 14.81 \pm 0.03$  Å.,  $\beta = 95.4^\circ \pm 0.2^\circ$ . Absent spectra, (0*k*0) when *k* is odd. Space-group,  $C_2^2$ - $P2_1$  (or  $C_{2h}^2$ - $P2_1/m$ ). Two molecules per unit cell. Molecular symmetry, none required (centre in  $P2_1/m$ ). Volume of the unit cell = 656 Å.<sup>3</sup>. Absorption coefficient for *X*-rays ( $\lambda = 1.54$ ),  $\mu = 34.1$  per cm. Total number of electrons per unit cell =  $F(000) = 260$ .

Well-formed, needle-shaped crystals, with (001) prominently developed, and (100) and (011) also present, are readily obtained from alcohol. There is cleavage parallel to (100) and (010). A slight positive pyroelectric effect was noted, indicating the space-group of lower symmetry,  $P2_1$ .

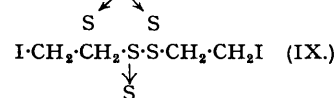
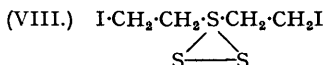
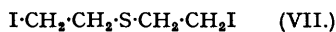
As in the case of diphenyl disulphide, neither cell dimensions nor symmetry provides any obvious clue to the molecular arrangement. A Patterson synthesis of intensity data from the (*h*00) zone of reflections was prepared, and this indicated that the long axes of the molecules lie approximately parallel to the (010) plane and that their distance apart in projection along the *b* axis is about 4 Å. The complexity of the structure made it impossible to recognise the peaks due to the interaction of bonded atoms, and it would appear that further progress must be made by trial and error methods.

*2'-Di-iododiethyl Trisulphide*,  $C_4H_8I_2S_3$ .—*Crystal data.* *M*, 406.1; *m. p.* 110°; *d*, calc. 2.521, found 2.478; tetragonal trapezohedral,  $a = b = 6.01 \pm 0.02$ ,  $c = 29.40 \pm 0.04$  Å. Absent spectra, (*h*00) when *h* is odd, (0*k*0) when *k* is odd, (00*l*) except when  $l = 4n$ . Space-

group  $D_4^4-P4_12_1$  (or  $D_4^8-P4_32_1$ ). Four molecules per unit cell. Molecular symmetry, two-fold axis perpendicular to (110). Volume of the unit cell, 1162 Å.<sup>3</sup>. Absorption coefficient for X-rays ( $\lambda = 1.54$ ),  $\mu = 551.2$  per cm. Total number of electrons per unit cell =  $F(000) = 744$ .

Thin, flat plates are readily obtained from alcohol-benzene, with (001) prominently developed; (011) and (101) are also displayed. A distinct tendency for cleavage parallel to (100) was noted.

The space-group data are free from ambiguity ( $D_4^8$  is merely the enantiomorph of  $D_4^4$ ) and require each molecule to possess an exact two-fold axis of symmetry. This definitely excludes structure (IX) with side co-ordination to a single sulphur atom, and limits the possible molecular



configurations to (VI), (VII), or (VIII). Of these, (VI) appears to be the most probable from dimensional considerations based on the known covalent radii for carbon, sulphur, and iodine. These are in favour of an extended zigzag chain type of structure, lying in the direction of the  $c$  axis. Such a model is supported by a study of the X-ray intensities, particularly the very strong (008) and (106) reflections. These considerations lead to a full analysis of the structure, which will be described in a subsequent paper.

2: 2'-Dichlorodiethyl Trisulphide,  $C_4H_8Cl_2S_3$ .—Crystal data.  $M$ , 223.2; m. p. 27°;  $d$ , calc. 1.491, found 1.494; orthorhombic,  $a = 5.47 \pm 0.03$ ,  $b = 8.01 \pm 0.03$ ,  $c = 22.5 \pm 0.04$  Å. Absent spectra, ( $h00$ ) when  $h$  is odd, ( $00l$ ) except when  $l = 4n$ . No data obtained about ( $0kl$ ), ( $0k0$ ), or ( $hk0$ ). Space-group, possibly  $D_2^2-P2_12_12_1$ . Four molecules per unit cell. Molecular symmetry, none required from space-group considerations, but the quartering of ( $00l$ ) indicates a two-fold axis. Volume of the unit cell, 998 Å.<sup>3</sup>. Total number of electrons per unit cell =  $F(000) = 456$ .

Unfortunately, this compound can only be crystallised with great difficulty, and the high volatility of the few single crystals obtained did not permit of a complete analysis. The cell dimensions show some resemblance to those of the di-iodo-compound, and the apparent quartering of the ( $00l$ ) series of reflections is significant. This in effect indicates an identity of the electron-density distribution in the unit cell over each quarter of the  $c$  axial line projection, and with four molecules in a unit cell of this cross-section implies a two-fold axis of symmetry in the molecule. These results favour the conclusion that the molecular configuration of the dichloro-compound is similar to that of the di-iodo-compound.

Diphenyl Disulphone,  $C_{12}H_{10}O_4S_2$ .—Crystal data.  $M$ , 282.2; m. p. 193°;  $d$ , calc. 1.472, found 1.482; triclinic,  $a = 6.31 \pm 0.02$ ,  $b = 7.90 \pm 0.03$ ,  $c = 8.40 \pm 0.04$  Å.,  $\alpha = 57^\circ 48'$ ,  $\beta = 112^\circ 41'$ ,  $\gamma = 116^\circ 17'$ ;  $d_{100} = 5.54$ ,  $d_{010} = 6.36$ ,  $d_{001} = 6.97$  Å. No absent spectra. Space-group,  $C_2^1-P1$  or  $C_2^1-\overline{P}1$ . One molecule per unit cell. Molecular symmetry, none in  $P1$ , centre in  $\overline{P}1$ . Volume of the unit cell, 316 Å.<sup>3</sup>. Absorption coefficient for X-rays ( $\lambda = 1.54$ ),  $\mu = 38.9$  per cm. Total number of electrons per unit cell =  $F(000) = 146$ .

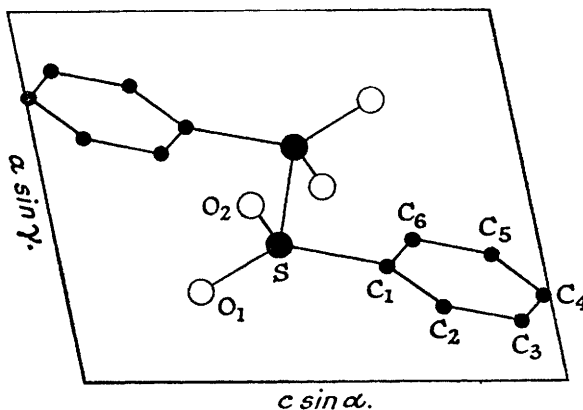
From glacial acetic acid well-formed prisms are obtained, showing (100), (010), (001), and (110) faces. No molecular symmetry can be deduced from space-group data, although a centre of symmetry is possible, and dipole-moment measurements (Oesper and Smyth, *J. Amer. Chem. Soc.*, 1942, 64, 768) suggest a tetrahedral grouping about two sulphur atoms joined by a single bond with the possibility of rotation, which is consistent with a centrosymmetric molecule in the crystal. We have carried out tests for piezo- and pyro-electric effects and have obtained no definitely positive results, which is again in favour of a centrosymmetric structure.

Comparison of dimensions with the isomorphous ditolyl compound, described below, indicates that the benzene rings must lie fairly close to the  $c$  axis. Inspection of the zero layer line moving-film photographs of ( $0kl$ ), ( $h0l$ ) and ( $hk0$ ) supports this conclusion and further indicates that the S-S line is lying at a small angle to the  $b$  axis since (010) is strong, (020) very strong, and (030) medium. The ( $h0l$ ) series more readily defines the general lay-out of the molecule, with (001) very strong, (002) strong, (003) strong, (004) strong, and (100) very strong, (200) weak, (300) weak, (400) strong, (500) strong. The deductions from this intensity distribution are in accordance with the general arrangement shown in Fig. 1. The structure as a whole probably bears a close resemblance to that of the disulphonyl sulphide described below (Fig. 2). It seems likely that the assumption of a centre of symmetry in the molecule is justified and may lead to a fully detailed structure determination.

*Di-p-tolyl Disulphone*,  $C_{14}H_{14}O_4S_2$ .—*Crystal data.*  $M$ , 310.2; m. p. 206° (decomp.);  $d$ , calc. 1.409, found 1.422; triclinic,  $a = 7.21 \pm 0.03$ ,  $b = 8.14 \pm 0.03$ ,  $c = 9.97 \pm 0.04$  Å.,  $\alpha = 56^\circ 2'$ ,  $\beta = 128^\circ 19'$ ,  $\gamma = 122^\circ 56'$ ;  $d_{100} = 5.39$ ,  $d_{010} = 6.43$ ,  $d_{001} = 7.37$  Å. No absent spectra. Space-group,  $C_1^1-P1$  or  $C_1^1-P\bar{1}$ . One molecule per unit cell. Molecular symmetry, none in  $P1$ , centre in  $P\bar{1}$ . Volume of the unit cell = 363 Å.<sup>3</sup>. Absorption coefficient for X-rays ( $\gamma = 1.54$ ),  $\mu = 34.5$  per cm. Total number of electrons per unit cell =  $F(000) = 162$ .

The crystal habit is similar to that of the diphenyl compound, and the data show that they are isomorphous. In the ditolyl crystal the  $c$  axis has expanded from 8.40 to 9.97 Å. and the  $\beta$  angle has increased from  $112^\circ 41'$  to  $128^\circ 19'$ , which is consistent with an orientation of the benzene rings similar to that shown in Fig. 1. There is further a close similarity in the distribution of intensities for the ( $h00$ ) and the ( $0k0$ ) reflections in the two crystals, whereas the ( $00l$ ) reflections are modified by the expansion of the  $c$  axis and the enlargement of the angle  $\beta$ . A complete structure analysis of this crystal again appears to be feasible.

FIG. 1.

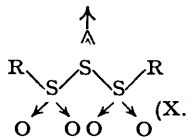


*Approximate orientation of diphenyl disulphone molecule in the unit cell.*

*Bisphenylsulphonyl Sulphide*,  $C_{12}H_{10}O_4S_3$ .—*Crystal data.*  $M$ , 314.3; m.p. 133°;  $d$ , calc. 1.618, found 1.583; monoclinic prismatic,  $a = 15.88 \pm 0.06$ ,  $b = 5.52 \pm 0.01$ ,  $c = 15.88 \pm 0.06$  Å.,  $\beta = 112.9^\circ$ . Absent spectra, ( $hkl$ ) when  $k + l$  is odd, ( $h0l$ ) when  $h$  is odd or when  $l$  is odd. Space-group,  $C_{2h}^2-A2/a$  (or  $C_2^2-Aa$ ). Four molecules per unit cell. Molecular symmetry, two-fold axis (or centre) in  $A2/a$  (none in  $Aa$ ). Volume of the unit cell, 1282 Å.<sup>3</sup>. Absorption coefficient for X-rays ( $\lambda = 1.54$ ),  $\mu = 53.3$  per cm. Total number of electrons per unit cell =  $F(000) = 648$ .

Further crystallographic data are given by Groth (*loc. cit.*, 1919, 5, 38) who describes the crystal as orthorhombic bisphenoidal, and dipole-moment measurements are reported by Christiansen (*Z. Elektrochem.*, 1928, 34, 638). From glacial acetic acid, lath-like crystals elongated along the  $b$  axis are obtained which show (100) and (001) faces. The crystal class appears to be prismatic and the space-group  $C_{2h}^2$ , but it is impossible to exclude the space-group of lower symmetry  $C_2^2$  from a study of the halvings alone.

In the structure analysis the higher symmetry of  $C_{2h}^2$  was first assumed and later justified by a detailed study of the intensities. With four molecules in the unit cell this space-group requires a two-fold element of molecular symmetry which must be either a centre or a two-fold axis parallel to the  $b$  crystal axis. A centre of symmetry is clearly incompatible with any reasonable molecular structure for the group under discussion, while the two-fold axis is consistent with the expected structure (X) with a tetrahedral distribution of bonds about the two outer sulphur atoms. This conclusion has now been confirmed by a more detailed analysis which will be described in a subsequent paper.



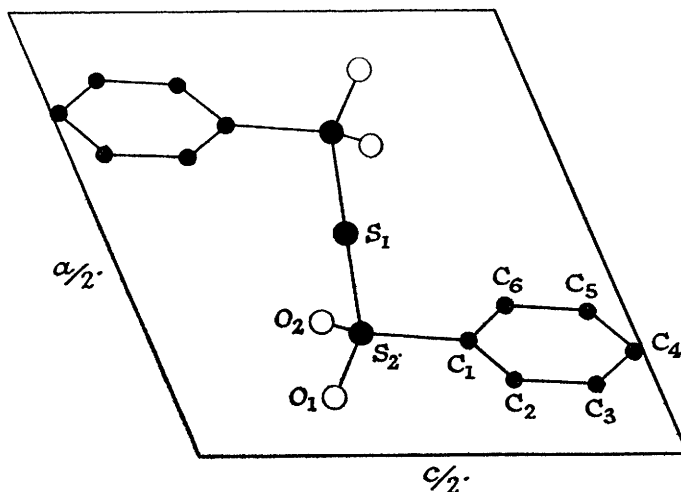
The general disposition of the molecule in the asymmetric crystal unit is shown in Fig. 2, the line  $S_2C_1C_4$  being close to the direction of the  $c$  axis, and giving rise to a very strong (400) reflection. The (204), (206), and (208) are also strong, while the (002) series falls off normally. The two-fold axis of symmetry is normal to the plane of the diagram and passes through the central sulphur atom. The packing of the molecules in the crystal is an interesting

one, and is such that a fairly close approach is made between the oxygen atoms of the  $\text{SO}_2$  groups and the benzene rings of neighbouring molecules.

*Bis-p-tolylsulphonyl Sulphide*,  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2$ .—*Crystal data*.  $M$ , 342.3;  $m. p.$  138°;  $d$ , calc. 1.430, found 1.427; monoclinic prismatic,  $a = 16.50 \pm 0.05$ ,  $b = 5.85 \pm 0.01$ ,  $c = 18.88 \pm 0.03$  Å.,  $\beta = 119.9^\circ$ . Absent spectra,  $(hkl)$  when  $h + l$  is odd,  $(h0l)$  when  $h$  is odd or when  $l$  is odd. Space-group,  $C_{2h}^2-A2/a$  (or  $C_2^h-Aa$ ). Four molecules per unit cell. Molecular symmetry, two-fold axis (or centre) in  $A2/a$  (none in  $Aa$ ). Volume of the unit cell, 1581 Å.<sup>3</sup>. Absorption coefficient for  $X$ -rays ( $\lambda = 1.54$ ),  $\mu = 35.7$  per cm. Total number of electrons per unit cell =  $F(000) = 712$ .

Further crystallographic data are recorded by Groth (*op. cit.*). The crystals are isomorphous with the phenyl analogue and the molecular symmetry is the same, *i.e.*, a two-fold axis parallel to the  $b$  crystal axis. From the expansion of the  $\beta$  angle from  $112.9^\circ$  to  $119.9^\circ$  and the increase in the  $c$  axis from 15.88 to 18.88 Å., it may be concluded that the benzene rings lie closely parallel to the  $c$  axis as in Fig. 2. The  $(h00)$  series of reflections have a distribution of intensities almost the same as those of the diphenyl compound, and the general distribution of

FIG. 2.



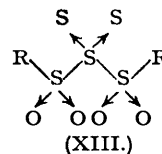
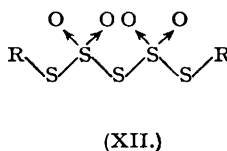
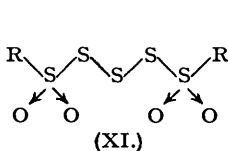
*Approximate orientation of bisphenylsulphonyl sulphide molecule in the unit cell.*

intensities in the  $(h0l)$  zone shows that the structure is very similar to that of that compound as regards its disposition in the unit cell.

*Bisphenylsulphonyl Trisulphide*,  $\text{C}_{12}\text{H}_{10}\text{O}_4\text{S}_3$ .—*Crystal data*.  $M$ , 378.4;  $m. p.$  103°;  $d$ , calc. 1.584, found 1.582; tetragonal trapezohedral,  $a = 7.74 \pm 0.02$ ,  $c = 26.29 \pm 0.05$  Å. Absent spectra,  $(h00)$  when  $h$  is odd,  $(0k0)$  when  $k$  is odd,  $(00l)$  except when  $l = 4n$ . Space-group,  $D_4^2-P4_22_1$  (or  $D_4^2-P4_22_1$ ). Four molecules per unit cell. Molecular symmetry, two-fold axis perpendicular to  $(110)$ . Volume of the unit cell, 1575 Å.<sup>3</sup>. Absorption coefficient for  $X$ -rays ( $\lambda = 1.54$ ),  $\mu = 66.7$  per cm. Total number of electrons per unit cell =  $F(000) = 776$ .

From glacial acetic acid the compound crystallises in small bipyramids showing  $(101)$  and  $(011)$  faces. Further crystallographic measurements are recorded by Groth (*op. cit.*, p. 39) and dipole moment measurements by Christiansen (*loc. cit.*).

The space-group data show clearly that the molecule must possess an exact two-fold axis of symmetry perpendicular to the  $(110)$  crystal plane. This limits the possible structures for the compound to (XI), (XII), or (XIII), and of these (XI) is certainly the most probable on chemical grounds; (XII) would involve the migration of the  $\text{SO}_2$  group in chemical reaction, and does not appear likely. Geometrically, however, all three structures are possible.



The dimensions of the unit cell indicate that the molecule lies approximately along the  $c$  crystal axis, and the data are in general compatible with structure (XI). Comparison of the ( $h0l$ ) series of reflections with those of the di- $p$ -tolyl compound (described below) indicates that, although the crystals are isomorphous, there must be a certain shift in the molecular arrangement in passing from the phenyl to the tolyl compound. Because of this, the comparison is not of immediate assistance in elucidating the detailed structure, and it is necessary to deal with the compounds individually. Patterson and Harker projections have been made, but the large number of parameters (31) renders the interpretation difficult. Further work is in progress.

*Bis-p-tolylsulphonyl Trisulphide*,  $C_{14}H_{14}O_4S_5$ .—*Crystal data.*  $M$ , 406.4;  $m. p.$  180°;  $d$ , calc. 1.528, found 1.547; tetragonal trapezohedral,  $a = 7.70 \pm 0.02$ ,  $c = 29.50 \pm 0.06$  A. Absent spectra, ( $h00$ ) when  $h$  is odd, ( $0k0$ ) when  $k$  is odd, ( $00l$ ) except when  $l = 4n$ . Space-group,  $D_2^4-P4_12_1$  (or  $D_2^5-P4_32_1$ ). Four molecules per unit cell. Molecular symmetry, two-fold axis perpendicular to (110). Volume of the unit cell, 1749 A.<sup>3</sup>. Absorption coefficient for X-rays ( $\lambda = 1.54$ ),  $\mu = 60.3$  per cm. Total number of electrons per unit cell =  $F(000) = 840$ .

The crystal habit is the same as that of the isomorphous diphenyl compounds (see Groth, *op. cit.*), and from the space-group data the same conclusions can be drawn regarding the possible molecular configurations (XI, XII, or XIII). The distribution of intensities in the ( $h0l$ ) zone of reflections is, however, considerably different from that of the diphenyl compound. The additional methyl groups will affect the molecular orientation to some extent, and it is to be expected that the effect on the intensities will be more difficult to interpret than in a space-group of lower symmetry. As the dimensional change is confined almost entirely to a  $c$  axis expansion of 3.2 A. in the di- $p$ -tolyl compound, it is clear that the long axis of the molecule must lie mainly in the direction of the  $c$  axis.

#### Conclusions.

A very interesting fact which emerges from this survey is that at least five, and possibly six out of the ten types of molecule examined display a two-fold axis of symmetry. No other element of molecular symmetry has been detected with certainty, although a centre of inversion is possible in the two disulphones. Further, the two-fold axis of symmetry is present in *all* the molecules which contain groups of three or more sulphur atoms. From this it is immediately clear that there is no possibility of side co-ordination to a single sulphur atom in either the tri- or the penta-sulphides or their sulphones. In all cases the balance of the evidence is in favour of extended zigzag sulphur chains, with other groups attached in approximately tetrahedral positions.

The difficult problem of detailed structure analysis for these complicated types of molecule has been simplified by this survey, and in particular by the dimensional comparisons between the phenyl and the tolyl compounds. It is now easy to select the more promising examples and form a preliminary estimate of the orientation of the molecule in the crystal lattice. In most cases, however, a large number of parameters remain to be determined. The assumption of a centre of symmetry in the triclinic disulphones is likely to be justified and will simplify the problem. In the monoclinic disulphonyl sulphides a preliminary orientation can be deduced from the outstanding intensities and by comparisons between the phenyl and the tolyl compounds. The higher crystal symmetry of the tetragonal disulphonyl trisulphides does not simplify the problem, although the main outlines of these structures can be predicted. In the trisulphides themselves, the iodine atoms in the di-iododiethyl compound (which very curiously belongs to the same space-group as the disulphonyl trisulphides) may be utilised to effect a fairly direct analysis of the atomic positions.

#### EXPERIMENTAL.

The X-ray measurements were in all cases carried out with Cu- $K\alpha$  radiation,  $\lambda = 1.54$  A., except for a few Laue photographs taken with white radiation and used to establish the symmetry of the tetragonal crystals. For axial-length measurements and space-group determinations, rotation, oscillation, and moving-film photographs were taken on small single-crystal specimens. Intensity surveys were carried out on layer line moving-film photographs, by visual estimates on calibrated films, employing the multiple film technique (Robertson, *J. Sci. Instr.*, 1943, 20, 175). The absorption coefficient is high for many of the crystals described, and rough corrections were applied where necessary, but the factors were reduced as far as possible by careful selection or cutting of very small specimens (0.1–0.5 mm.) of nearly square cross-section normal to the rotation axis. Density determinations were made by flotation in suitable liquids.

Diphenyl disulphide was prepared by oxidation of thiophenol with ferric chloride (Zincke and Frohneberg, *Ber.*, 1910, 43, 840). After recrystallisation from ethyl alcohol, long needles,  $m. p.$  59°, suitable for X-ray examination were obtained.

Di-*p*-tolyl disulphide was prepared by oxidation of thio-*p*-cresol with ferric chloride or with iodine (*idem, ibid.*). Recrystallisation from ethyl alcohol gave long needles, m. p. 47°.

2:2'-Di-iododiethyl trisulphide. A pure specimen of this compound was supplied by C.D.E.S., Porton. Recrystallisation from alcohol-benzene yielded flat plates, m. p. 110°, from which sections suitable for X-ray examination were cut.

2:2'-Dichlorodiethyl trisulphide. This compound was also obtained from C.D.E.S., Porton. The low m. p. (27°) made crystallisation difficult. Benzene was found to be the most suitable solvent, and by slow cooling a few specimens suitable for X-ray examination, were obtained.

Diphenyl disulphone was prepared by oxidation of benzenesulphonic acid with powdered potassium permanganate in cold glacial acetic acid (Hilditch, *J.*, 1908, **93**, 1526). Slow crystallisation from glacial acetic acid yielded small crystals, approximately rhombohedral, m. p. 193°.

Di-*p*-tolyl disulphone was prepared by interaction of *p*-toluenesulphonyl chloride and sodium *p*-toluenesulphinat in a mixture of ether and water (Kohler and MacDonald, *Amer. Chem. J.*, 1899, **22**, 222). Slow crystallisation from glacial acetic acid gave small thick prisms, m. p. 210° (decomp.).

Bisphenyl- and bis-*p*-tolyl-sulphonyl sulphide were prepared by treatment of the corresponding sodium sulphinates with sulphur dichloride in dry carbon tetrachloride (Troeger and Hornung, *J. pr. Chem.*, 1899, **60**, 113). Crystallisation from glacial acetic acid yielded lath-like crystals elongated along the *b* crystal axis, m. p. 133° for the phenyl and 138° for the *p*-tolyl compound.

Bisphenyl- and bis-*p*-tolyl-sulphonyl trisulphide were prepared by treatment of the corresponding sodium thiosulphonates with sulphur dichloride in dry carbon tetrachloride (Troeger and Hornung, *loc. cit.*). Crystallisation from glacial acetic acid yielded beautiful bipyramidal crystals, m. p. 102° for the phenyl and 180° for the *p*-tolyl compound.

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