

THE  
CRYSTAL STRUCTURE  
OF  
DIPHENYL DISULPHONYL MONOSULPHIDE  
AND  
RELATED COMPOUNDS.

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T H E S I S

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by

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P R E F A C E.

The work describing the space groups of all the compounds is to be published by the Chemical Society and the complete structure analysis is also to be published in their Journal. The papers are in conjunction with Professor J.M. Robertson.

The author wishes to thank Professor J.M. Robertson for his interest in this work. Thanks are also due to the Carnegie Trustees for a Scholarship and Fellowship held during this work: and to Mr. J. Findlay for aid in preparing reproductions.

## Historical Introduction.

During the 19th century much interest was displayed in the external symmetry of crystals, and classification in terms of symmetry elements was carried out by Hessel and others. The treatment was extended theoretically by Federoff, Schönflies and Barlow, who showed that there are only 230 space groups.

The classical experiment carried out by Friedrich and Knipping (1) in 1912 at the suggestion of von Laue, showed that X-rays were electromagnetic waves and also that the internal structure of crystals was periodic. Application of this method to the determination of the structures of NaCl and KCl by W.L. Bragg (2) quickly followed in 1913. The relation of space group theory to the extinction of X-ray reflections was studied by Niggli (3) and Wycoff (4). Ewald's (5) concept of the reciprocal lattice and Bernal's (6) manipulation to provide a means of graphical indexing made the determination of the space group straightforward.

W.H. Bragg (7) had suggested that Fourier synthesis could, by utilising the spectral components, be applied to give the structure of the crystal. At that time, neither the necessary technical methods nor sufficient information was available although Darwin (8) had showed the relation between the intensity of the diffracted beam and the amplitude of the Fourier component for the two extreme types of

crystals - 'mosaic', and 'perfect'.

This relationship was later deduced independently by Compton (9) and applied for the first time to a complex structure, diopside, by W.L. Bragg (10).

The method of Fourier synthesis combined with an improved technique of estimating large numbers of intensities photographically enabled J.M. Robertson (11) to achieve the complete structure determination of an organic compound - anthracene. All these structures had been based on certain assumptions as to their structure. The determination of platinum phthalocyanine by J.M. Robertson (12) showed the Fourier method at its full power, each phase being fixed by the platinum atom at the centre of symmetry.

In 1935 A.L. Patterson (13) suggested a method of Fourier synthesis utilising only observable data and showed that a Fourier synthesis carried out with  $F^2$  terms gives a density distribution showing vector distances between atoms. This presented the information in a more readily assessable form. P. Harker (14) later modified this method to use the symmetry elements of the particular space group and so use the complete series of  $F^2(hkl)$  for a two-dimensional summation. Much use has been made of this method for structures with a heavy atom to give clearly resolved vector distances (15).

Theoretical Introduction.

1. Diffraction by a three-dimensional lattice.

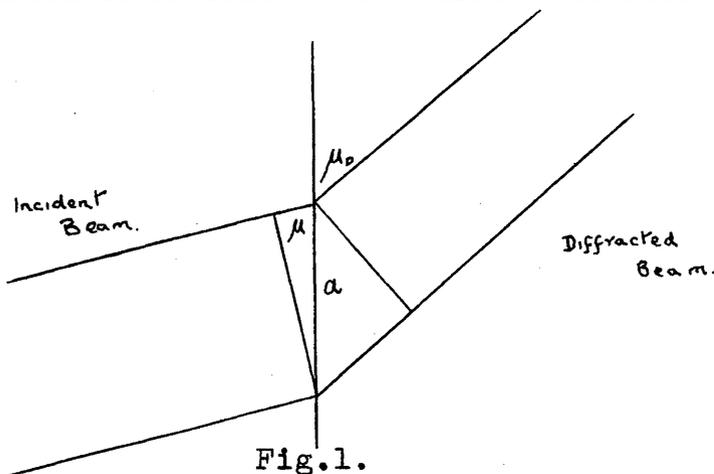


Fig.1.

Friedrich and Knippings (1) experiment had clearly shown that crystals were structure periodic in three dimensions and von Laue (1a) determined the conditions for diffraction by the application of classical wave theory.

If the incident beam makes an angle  $\mu$  with a line of scattering units, repeated periodically with spacing  $a$ , and the diffracted beam an angle  $\mu_D$ , then the condition for a coherent diffracted beam is that the path difference between rays scattered from adjacent units is a multiple of the wavelength

$$a(\cos \mu_D - \cos \mu) = n\lambda.$$

If  $\cos \mu_D = \alpha$  and  $\cos \mu = \alpha_0$ , the condition is

$$a(\alpha - \alpha_0) = h\lambda \quad (1)$$

This is only applicable to a one-dimensional diffraction grating, and since the crystal is a three-dimensional grating, three such conditions must apply and be satisfied simultaneously for a beam to be diffracted.

These are as follows:-

$$a(\alpha - \alpha_0) = h\lambda \quad (2)$$

$$b(\beta - \beta_0) = k\lambda \quad (3)$$

$$c(\gamma - \gamma_0) = l\lambda \quad (4)$$

where  $h$ ,  $k$ ,  $l$  refer to the Miller indices.

## 2. Bragg equation.

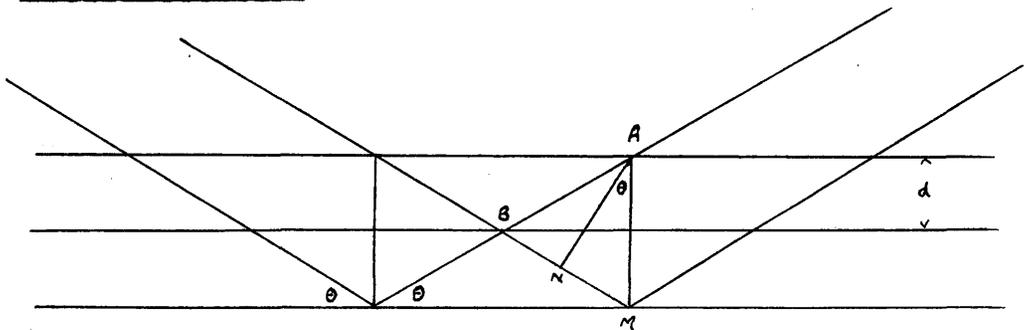


Fig.2.

W.L. Bragg (16) considerably simplified the treatment of diffraction by considering it as reflection from parallel planes in the crystal. The incident beam makes an angle  $\theta$  with the planes, spacing  $d$ , and the path difference between beams reflected from adjacent planes is

$$AB - BN = EM - BN = NM = 2d \sin \theta$$

The Bragg law is thus

$$n\lambda = 2d \sin \theta \quad (5)$$

The modification introduced by Bragg simplifies the relationship since there is only one variable,  $d$ , which is defined by the Miller indices  $(hkl)$  instead of three simultaneous equations to be satisfied. The condition for reflection will be satisfied only when  $\theta$  and  $d$  have such values to satisfy the equation and so an X-ray reflection for monochromatic radiation only occurs for a specific orientation of the crystal. The range of reflection will be limited by the limiting value of  $\theta$  such that  $\sin \theta < 1$ .

### 3. Concept of the Reciprocal Lattice.

The difficulty of visualising the crystal planes in relation to one another and to the observed reflections arising therefrom necessitated a concept which could represent a two-dimensional plane by a one-dimensional quantity. The vector drawn from the origin of the lattice, perpendicular to the plane represents in direction and length the disposition of the plane. Further, postulate a vector from the origin lying in the same direction but whose length is the reciprocal of the length of the direct vector,

$$\text{i.e.,} \quad d^* = \frac{c}{d} \quad \text{where } c \text{ is a constant.} \quad (6)$$

When this is done for all planes in the direct lattice, we have a reciprocal lattice. The properties of the reciprocal lattice were first studied by Bravais (17) and Mallard (18) and later, by vector analysis, by Ewald (5).

The important step in the utilisation of the concept of the reciprocal lattice was by J.D. Bernal (6) for the interpretation of rotation photographs by correlating with the Bragg law.

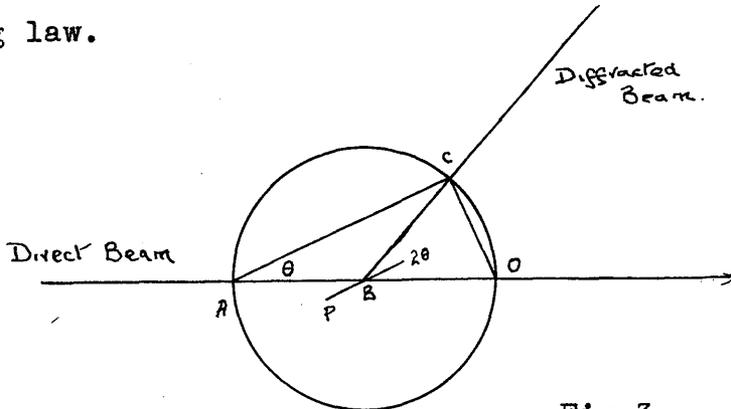


Fig.3.

In the diagram, AO is the direction of the incident X-ray beam, B is the crystal and BC the direction of the reflected beam. A circle is drawn through centre B and radius = 1 passing through the origin O. Then  $CO = 2 \sin \theta$  and CO, passing through the origin, lies perpendicular to the plane PBQ and so represents in dimension and direction the reciprocal vector of the plane PBQ if CO has dimension  $\frac{\lambda}{d}$ . The diagram then indicates the usefulness of the concept if the constant c in equation (6) is  $\lambda$ . Then reflection (the Bragg condition) can only occur if the reciprocal lattice point lies on the circumference of the reflecting circle ACO, of radius 1.

Bernal worked out the graphical result for a rotation camera of a given radius and so enabled the rapid indexing of these films.

The concept has been widely used for the interpretation of photographs from Weissenberg (19), Sauter (20), and Schiebold (21) cameras. De Jong and Bauman (22) and Buerger (23) have constructed cameras to give non-distorted pictures of the reciprocal lattice.

#### 4. Determination of Axial Lengths.

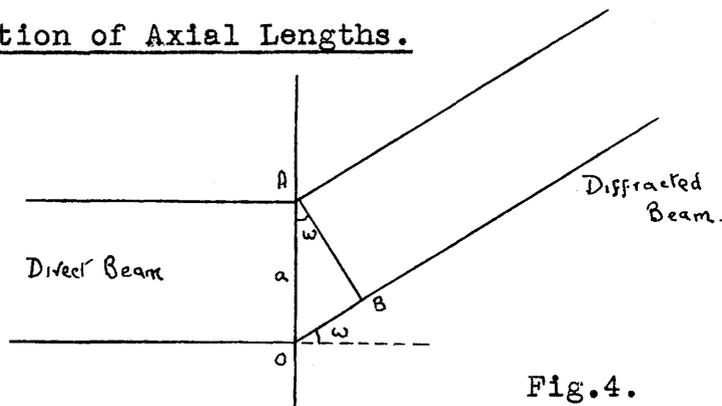


Fig.4.

If a crystal is rotated about a certain axis and an X-ray beam is passed through the crystal normal to this axis, O and A being identical points along this axis of rotation, then the direction of the diffracted beam depends on OA such that the path difference is

$$\begin{aligned} OB &= a \sin \omega = n\lambda \\ \therefore n\lambda &= a \sin \omega. \end{aligned} \quad (7)$$

If OA is the 'a' axis, then all reflections for which h has the same value will have the same angle  $(90 - \omega)$  to the axis and so will lie along a cone with its axis, the axis of rotation. Other  $(nkl)$  reflections will have similar cones of angle dependent on  $\underline{n}$ . If a flat plate is used to record the reflections these groups of cones will meet the plate in hyperbolas, but if a cylindrical film with axis through

the axis of rotation is used, then the cones will intersect the film in circles which become straight lines on the film being opened out. These lines are referred to as layer lines. The dimensions of the inter-line spacings and the radius of the camera gives values corresponding to  $n = 1, 2, 3, 4, \text{etc.}$ , and so the axial length 'a' can be determined.

Other two dimensions 'b' and 'c' may be determined by this means and when a reciprocal lattice is drawn out, Bernal's (6) construction of the reflecting circle can be utilised to index the rotation or oscillation films.

#### 5. Space Groups and Extinctions.

As has been indicated earlier (p.1), the theory of space groups had been fully worked out before the end of the 19th century. It was shown that only certain symmetry elements were permissible in a continuous lattice, and that such as five and seven fold axes are precluded. On this basis of a limited number of symmetry elements allowable, it was deduced that there could be only 230 ways of grouping symmetry elements such as to give different space groups. Any other grouping can be converted to one of the 230 space groups by a suitable choice of axes. A full treatment is given in Hilton (24).

Each symmetry operation involving a translation causes the extinction of a certain class of X-ray

reflections. These extinctions are of extreme importance, for it is by these that the symmetry element is recognised.

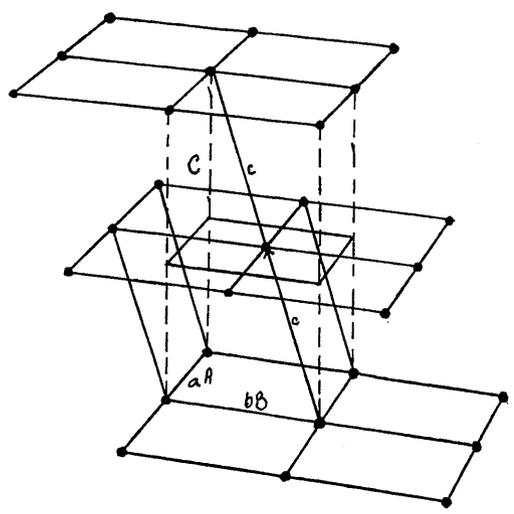


Fig.5.

If we consider a lattice which is body-centred, we may relate it to a primitive lattice as in Fig.5. Then the body-centred lattice axes are related to the primitive lattice axes as follows:-

$$A = a$$

$$B = b$$

$$C = a + b + 2c$$

The indices then become

Body-centred	Primitive
H	h
K	k
L	h+k+2l

$$\text{and } H + K + L = 2(h + k + l).$$

Thus  $H + K + L = 2n$ , where  $n$  is any integer. Therefore

only planes such that  $h + k + l = 2n$  appear. The body-centred lattice cause the most general extinctions in general indices (hkl). Face centred lattices cause extinction in general indices of the type  $h + k = 2n$  for centring on the C face. Glide planes affect only a zone such as (hol) with  $h = 2n$  only appearing. Screw axes only affect axial sets of indices such as (oko) for  $k = 2n$ . This is for a screw axis parallel to the 'b' axis.

It is to be noted that more general extinctions, such as that due to face centring, obscure that due to a more limited symmetry element such as a screw axis. If due to face centring on the C face  $h + k = 2n$ , it cannot be determined if there is a screw axis parallel to the b axis since (oko) will only appear for  $k = 2n$  due to the more general extinction.

The work of correlating space groups and their related extinctions was carried out by Astbury and Yardley (25), Hermann (26) and others, and is to be found complete in the Internationale Tabellen (27). Based on the crystal system, three axes are measured and on these axes the reflections are indexed. The systematic extinctions will determine to which space group or space groups, the crystal can be assigned.

In certain cases, the space group cannot be assigned unequivocally. When rotation axes or reflection planes

are present, these cannot be detected by the X-ray data. In this case the space group can only be assigned to a few possibilities. Thus  $A2/a$  and  $Aa$  cannot be differentiated by the X-ray data. By Friedel's law (28), a centre of symmetry is added on by the diffraction effects. In cases where there may or may not be a centre of symmetry, this can be tested by pyro- or piezo-electric measurements.

## 6. Structure Amplitude.

The amplitude  $\bar{A}$  of the wave scattered by an electron when a wave of amplitude  $A$  falls on it is

$$\bar{A} = \frac{Ae^2}{mrc^2} \quad (8)$$

at a distance  $r$  from the electron. This classical relationship is utilised in the definition of the structure amplitude of a plane as follows. The structure amplitude is the ratio of the amplitude of the reflected by the plane to the amplitude scattered by an electron under the same conditions. The beam scattered by the diffracting unit is compounded from waves radiated by all electrons in this unit. The electrons do not all lie on the plane and so there are phase differences between different atoms. The origin is chosen as reference for fixing the phase. If an atom lies at  $(x, y, z)$ , then the phase difference for the plane  $(hkl)$  will be  $2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$ . The structure amplitude will be a quantity with amplitude and phase dependent on the summation of the amplitudes and phases of

all scattering units in the unit cell and so will be given by

$$F = \sum f \cdot e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \quad (9).$$

$f$  is the scattering due to the individual atom considered. Since the electron distribution of an atom is diffuse, the interference between parts due to phase differences must be considered. The scattering of X-rays by an atom of an element depends on the atomic number and may be calculated as follows:-

$$f = \int_0^{\infty} U(r) \sin \frac{\phi}{r} dr \quad (10)$$

where  $\phi = \frac{4\pi r \sin \theta}{\lambda}$  and  $U(r) \cdot dr$  represents the probability of finding an electron between the limits  $r$  and  $r-dr$ .

The scattering curve for atoms plotted against  $\frac{\sin \theta}{\lambda}$  are given for all atoms in the Internationale Tabellen (27), but these are not modified by a temperature correction which must be applied before use with organic compounds, since such compounds have low melting points and so large thermal movements which cause the electron distribution to be more diffuse. The scattering curve may be corrected by the application of a modifying Debye-Waller function  $e^{-M}$  where  $M = B \left( \frac{\sin \theta}{\lambda} \right)^2$  (11)

The value of  $B$  as given by the Debye-Waller (29), (30) is

$$B = \frac{6h^2}{mk\theta} \left( \frac{\phi(x)}{x} + \frac{1}{4} \right) \quad (12)$$

where  $m$  = mass of the atom,  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $\theta$  is the characteristic

temperature, and  $x = \frac{\theta}{T}$ . Accurate values for certain of these constants is lacking and so an empirical factor may be determined by trial and error.

The scattering curve may be also modified by correlation between calculated and observed structure amplitudes.

Equation (9) may be expressed as

$$F = \sum f \left[ \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) + i \sin 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] \quad (13)$$

and if there is a centre of symmetry and so atoms at  $(x, y, z)$  and  $(\bar{x}, \bar{y}, \bar{z})$ , the sine terms cancel out since

$$\sin 2\pi \left( -\frac{hx}{a} - \frac{ky}{b} - \frac{lz}{c} \right) = -\sin 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)$$

The formula then becomes

$$F(hkl) = \sum f \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \quad (14)$$

When more than one type of atom is present in the unit cell, different scattering curves must be used for the different atoms as denoted by the equation

$$F = \sum f_s. \quad (15)$$

Reference may also be made that the scattering curve is assumed spherically symmetrical but there is evidence (31) that this is in certain cases not sufficiently accurate.

## 7. Geometrical Structure Factors.

In equation (13),  $F(hkl)$  is obtained by summing over all atoms in the unit cell. In a given space group,

however, there is a number of equivalent points dependent on the symmetry operations and one atom occurring is automatically reproduced by the symmetry operations. The complexity of dealing with so many exponential functions for individual atoms can be reduced by combining the functions of all equivalent points into one formula. This will then be the geometrical structure factor for the particular space group

$$S = \sum e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \quad (16)$$

This may be also given as

$$S = \sum \left[ \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) + i \sin 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] \quad (17)$$

and if there is a centre of symmetry

$$S = \sum \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \quad (18)$$

In the space group  $A2/a$ , there are 8 equivalent points

- |     |                    |                    |                    |     |                          |                          |                          |
|-----|--------------------|--------------------|--------------------|-----|--------------------------|--------------------------|--------------------------|
| 1). | $x,$               | $y,$               | $z.$               | 5). | $\bar{x},$               | $\bar{y},$               | $\bar{z}.$               |
| 2). | $x,$               | $\frac{1}{2} - y,$ | $\frac{1}{2} - z.$ | 6). | $\bar{x},$               | $\frac{1}{2} - \bar{y},$ | $\frac{1}{2} - \bar{z}.$ |
| 3). | $\frac{1}{2} - x,$ | $\frac{1}{2} - y,$ | $z.$               | 7). | $\frac{1}{2} - \bar{x},$ | $\frac{1}{2} - \bar{y},$ | $\bar{z}.$               |
| 4). | $\frac{1}{2} - x,$ | $\bar{y},$         | $\frac{1}{2} - z.$ | 8). | $\frac{1}{2} - \bar{x},$ | $y,$                     | $\frac{1}{2} - \bar{z}.$ |

Each point is related by a centre of symmetry to one other and so equation (18) is applicable.

The following are the geometrical structure factors for the principal zones of this space group:

$$S(\text{hol}) = 8 \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \quad (19)$$

If  $l$  is even

$$S(okl) = 8 \cos 2\pi \frac{ky}{b} \cdot \cos 2\pi \frac{lz}{c} \quad (20)$$

If  $l$  is odd

$$S(okl) = -8 \sin 2\pi \frac{ky}{b} \cdot \sin 2\pi \frac{lz}{c} \quad (21)$$

If  $h$  is even

$$S(hko) = 8 \cos 2\pi \frac{hx}{a} \cdot \cos 2\pi \frac{ky}{b} \quad (22)$$

If  $h$  is odd

$$S(hko) = -8 \sin 2\pi \frac{hx}{a} \cdot \sin 2\pi \frac{ky}{b}$$

### 8. Intensity of the X-ray reflection.

The factors  $F(hkl)$  together contain all the information which may be derived from the intensities of the X-ray reflections. The relation of the calculated value to the atomic coordinates and arrangement have been given. It is thus important to find what is the relation of the structure amplitude and the intensity.

The intensity is dependent on the crystal size and perfection. The X-ray reflection is not sharp but takes place over a small angular range in the neighbourhood of  $\theta$  as defined by equation (5). A satisfactory method of determining the total energy reflected, the integrated reflection, was devised by W.H.Bragg (32). If a crystal is rotated with angular velocity  $\omega$ , the total energy received in the ionisation spectrometer or photographic

plate will be inversely proportional to  $\omega$ . If  $I_0$  is the energy in the incident beam, the integrated reflection is measured by

$$I = \frac{E \omega}{I_0} \quad (23)$$

which has been shown to be nearly proportional to the volume of the crystal if that is small (33).

In the case of  $dV$ , the volume being so small that absorption of the X-ray beam is not appreciable, the expression for the integrated reflection of mosaic crystals is as follows:

$$\frac{E \omega}{I_0} = \left[ \frac{N e^2 \cdot F(hkl)}{mc^2} \right]^2 \lambda^3 \cdot \frac{1 + \cos^2 2\theta}{2 \sin \theta} \cdot dV \quad (24)$$

In this expression  $N$  is the number of unit cells per unit volume of the crystal. The  $\frac{e^2}{mc^2}$  comes from equation (8) and  $\frac{1 + \cos^2 2\theta}{2}$  allows for the incident beam being unpolarised. This expression is applicable for very small crystals if absorption corrections are made. The formula indicates that the crystal consists of a mosaic of small perfect crystals and this randomness in the structure spreads the beam over a range about  $\theta$  and also causes the term  $F(hkl)$  to appear as  $F^2$ .

Types of crystal, such as certain diamonds, show very sharp reflections and for these equation (24) cannot be applied. In this case, the equation is as follows:-

$$\frac{E_{\omega}}{I_0} = \frac{8 \cdot N_e^2}{3 \cdot M c^2} \cdot F(hkl) \lambda^2 \frac{1 + \cos 2\theta}{2 \sin 2\theta} \quad (25)$$

These two formulations apply to the two extremes - the 'mosaic' and the 'perfect' crystal. In reality, most crystals approximate to the mosaic type, but if the mosaic units, being perfect, are too large, the beam will give an intensity which is in proportion to a power of  $F$  lying between 1 and 2. This is referred to as primary extinction and can only be corrected for if the crystal is disrupted into smaller mosaic by internal forces due to extreme cold or by powdering the crystal and taking powder photographs.

Secondary extinction occurs when a strong beam suffers internal reflection and the lower part of the crystal is so screened. The effective absorption is increased at a reflecting angle.

For the determination of  $F(hkl)$  values in the general case of organic compounds, the equation (24) applies but the intensities are not usually measured on an ionisation spectrometer or by comparison with a standard crystal (34). The intensity values for a zone of reflection are recorded on films and only the relative  $F$  values are determined. The expression is then

$$\frac{F_1}{F_2} = \sqrt{\frac{I_1 p_1}{I_2 p_2}} \quad (26)$$

where  $p_1$  and  $p_2$  are the combined Lorentz and polarisation factors for the corresponding reflection.

If the intensities are determined from a rotation film or an n-layer moving film, geometrical corrections, as given by Cox and Shaw (35), are also necessary since those planes yielding n-layer reflections are rotating more slowly than the zero layer planes and so their intensity is increased.

Approximate corrections can be made for absorption in the crystal by determining the mean path,  $t$ , through the crystal. If  $\mu$  is the linear absorption coefficient of the substance for the wavelength employed, the absorption is  $e^{-\mu t}$ .

### 9. Fourier Synthesis.

A periodic function of a variable  $x$  repeating when  $x$  is increased by a quantity  $a$  can be expressed as a sum of exponential terms

$$F(x) = \sum F_n e^{\frac{2\pi n x}{a}}$$

In the crystal there is a periodic function which diffracts X-rays and this is the electron distribution which repeats in three dimensions at distances corresponding to the axial lengths determined. This function must therefore be represented by a triple Fourier series

$$\rho(xyz) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A_{pqr} e^{2\pi i \left( \frac{px}{a} + \frac{qy}{b} + \frac{rz}{c} \right)} \quad (27)$$

where  $p$ ,  $q$  and  $r$  are intergers and  $A_{pqr}$  an unknown coefficient. If  $A_{pqr}$  can be determined the electron distribution at all points can be evaluated. By generalising equation (9) for a continuous distribution of scattering matter, we obtain

$$F(hkl) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \rho(xyz) e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} dx dy dz \quad (28)$$

and substituting equation (27)

$$F(hkl) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \left[ \sum_{p=-\infty}^{\infty} \sum_{q=-\infty}^{\infty} \sum_{r=-\infty}^{\infty} A_{pqr} e^{2\pi i \left( \frac{px}{a} + \frac{qy}{b} + \frac{rz}{c} \right)} \right] e^{2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} dx dy dz \quad (29)$$

On integrating, every term is zero but those for which

$p = -h, q = -k$  and  $r = -l$ . This gives

$$F(hkl) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c A_{-h-k-l} dx dy dz = V \cdot A_{-h-k-l} \quad (30)$$

The Fourier series representing the electron density at any point  $x, y, z$ , may then be given as

$$\rho(xyz) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \frac{F(hkl)}{V} e^{-2\pi i \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right)} \quad (31)$$

The zero term in the series  $\frac{F(000)}{V}$  is a constant given by

$$F(000) = \frac{V}{abc} \int_0^a \int_0^b \int_0^c \rho(xyz) dx dy dz = Z \quad (32)$$

where  $Z$  is the total number of electrons in the unit cell.

$F(hkl)$  and  $F(\bar{h}\bar{k}\bar{l})$  are conjugate in agreement with Friedel's law (28) except in the region of an absorption band, when the phase change throughout the parts of the unit cell varies.

The equation (31) may be rephrased

$$\rho(xyz) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} \frac{F(hkl)}{V} \cdot \cos(2\pi hx + 2\pi ky + 2\pi lz - \alpha(hkl)) \quad (33)$$

where  $\alpha(hkl)$  is the phase angle for the structure factor  $F(hkl)$ .

The method can be most readily applied to structures with a centre of symmetry for then  $\alpha = 0$  or  $\pi$ , and the sign of  $F$  is either + or - .

The expression (33) then is written

$$\rho(xyz) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{F(hkl)}{V} \cos 2\pi \left( \frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \quad (34)$$

In general, the three dimensional summation is extremely tedious and a reasonable limit is the two dimensional case.

$$\rho(xz) = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{F(hol)}{A} \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \quad (35)$$

where  $A$  is the area of the projection. This form of Fourier series was first utilised by W.L. Bragg for the structure of diopside (10).

The Fourier method can only be applied when phase angles are known and it is rarely that these are determinable directly as in the case of platinum phthalocyanine (12). In most compounds a trial structure is selected, based on available physical and chemical evidence, which gives adequate agreement between observed and calculated structure amplitudes. By this means the phase of as many as possible  $F$ s are fixed and a Fourier synthesis is carried out from the results of which the phase angles of further terms can be determined. In this way, by approximation, the structure amplitudes can be utilised and the final Fourier projection gives the maximum possible information as to the electron distribution. Positions of the

atoms are assigned and the dimensions of the structure can be calculated. In general two or more plane projections are carried out to determine all three coordinates for each atom.

The representation of the electron density by a Fourier series assumes that the terms are available up to as large a number as possible. However, dependent on the wavelength of the radiation used, the limit of terms recorded is fixed by the Bragg law  $n\lambda = 2d\sin\theta$  and so in each case the Fourier components are terminated abruptly at the limit  $\theta = 90^\circ$ . For most organic compounds this has little effect as the components at this limit are generally small. If, however, they are of appreciable value, spurious effects will appear in the projection which will not greatly affect the peaks, and so the atomic coordinates, but will result in diffraction effects. These may be removed by modifying the observed structure amplitudes by an artificial temperature factor (39), (40).

#### 10. Patterson and Harker Fourier Synthesis.

A.L. Patterson (13) has suggested a method of utilising directly the available information in the form of a Fourier synthesis using  $F^2(hkl)$  terms. He defined a quantity

$$A(uvw) = \frac{1}{V} \int_0^a \int_0^b \int_0^c \rho(xyz)\rho(x+u, y+v, z+w) dz.dy.dz. \quad (36)$$

This expression gives the distribution about  $(xyz)$  as a

function of the parameters (uvw), and this distribution is weighted by the amount of scattering matter between (xyz) and (x + dx, y + dy, z + dz) given by  $\rho(xyz) \cdot dx \cdot dy \cdot dz$ .

$\rho(xyz)$  and  $\rho(x + u, y + v, z + w)$  are expanded by the Fourier series equation ( ) and the expression becomes

$$A(uvw) = \frac{1}{V^2} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F^2(hkl) e^{2\pi i \left( \frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c} \right)} \quad (37)$$

This function  $A(uvw)$  will be large only when  $\rho(xyz)$  and  $\rho(x + u, y + v, z + w)$  are both large. Thus a peak in the function  $A(uvw)$  at  $u_1, v_1, w_1$  gives an interatomic vector in the crystal between peaks in the electron distribution so specified. The possibility of correlating the vectors with the atoms giving these vectors will depend upon the number of atoms. Thus if there are  $N$  atoms,  $N(N-1)$  peaks should appear in the Patterson synthesis. In practice, a large amount of overlap occurs and satisfactory interpretation of atomic positions is only possible if there is a heavy atom in the structure. There is also a very large peak at the origin since each atom has a zero vector with respect to itself. Patterson has shown how this may be removed and he has also indicated how to sharpen up the peaks. This latter device introduces spurious diffraction effects which may be misleading.

In general, two-dimensional Patterson projections are used (15) but Jeffrey (37) has utilised sections at

different levels along an axis.

Harker (14) has modified the two dimensional Patterson method by employing the symmetry elements of the space group to combine all  $F^2(hkl)$  values and yet only carry out a one- or two-dimensional synthesis.

Thus if there is a diad axis, an atom at  $x, y, z$  will be reproduced at  $\bar{x}, \bar{y}, \bar{z}$ , and the interatomic vector in this case is  $2x, 0, 2z$ . There will thus be a peak at  $2x, 0, 2z$  in the function  $A(uvw)$ . The function  $A(uvw)$  need only be evaluated in the plane  $v = 0$ . The series will then be

$$\begin{aligned} A(uvw) &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \frac{F^2(hkl)}{v} \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \\ &= \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \left[ \sum_{-\infty}^{\infty} \frac{F^2(hkl)}{v} \right] \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) \end{aligned} \quad (38)$$

Better resolution than in the ordinary Patterson will be obtained as all  $F^2(hkl)$  terms are included. The number of vectors in a Harker projection are reduced but there is still the possibility that vectors will appear for atoms which are fortuitously related by the necessary symmetry relationship. As above, if two atoms have the same 'y' coordinate, then the interatomic vector will appear in the Harker projection.

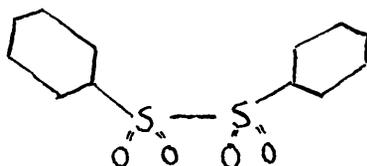
Crystal Structure of Diphenyl Disulphone.

Crystal Data.

Diphenyl disulphone,  $C_{12}H_{10}S_2O_4$ ; M, 282.2; m.p.  $193^\circ$ ; d, calc. 1.472, found 1.482; triclinic (holohedral),  $a = 6.31 \pm 0.03$ ,  $b = 7.90 \pm 0.03$ ,  $c = 8.40 \pm 0.03$ ,  $\alpha = 57^\circ 48'$ ,  $\beta = 112^\circ 41'$ ,  $\gamma = 116^\circ 17'$ : Absent spectra, none. Space group  $P\bar{1}$ . One molecule per unit cell. Molecular symmetry - centre. Volume of the unit cell,  $315.9 \text{ \AA}^3$ . Absorption coefficient for X-rays,  $\lambda = 1.54$ ,  $\mu = 38.9$  per cm. Total number of electrons in the unit cell =  $F(000) = 146$ .

Structure Analysis.

The high stability of this compound to chemical reaction indicates that the formation



is essentially correct and therefore a molecular model of this form will be used as a basis for discussion.

It is, in the general case, often misleading to deduce from the unit cell dimensions some information as to the shape and disposition of the molecule. But in the case of the two isomorphous compounds, diphenyl and ditolyl disulphone, the major part of the molecule is unchanged and only a methyl group is added on in the para

position for the second compound. This addition will cause certain variations in the cell dimensions which may be related to the disposition of the molecule.

Careful comparison of the cell dimensions,  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  for the two compounds can be combined with a comparison of the distribution of intensities of reflections in the zones  $(okl)$ ,  $(hol)$  and  $(hko)$ . For this space group there is no fixed reference position as the triclinic system has no symmetry possible, other than a centre. The change in molecular dimensions may thus cause small variations in all three dimensions so that the tolyl compound may accommodate itself to the closest packing. This will be dependent on the most important intermolecular forces. The important factors to inspect will therefore be large cell changes.

The table below gives the comparison of the dimensions

	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$
phenyl	6.31	7.90	8.40 $^{\circ}$ A	57 $^{\circ}$ 48'	112 $^{\circ}$ 41'	116 $^{\circ}$ 17'
tolyl	7.21	8.14	9.97 $^{\circ}$ A	56 $^{\circ}$ 2'	128 $^{\circ}$ 19'	122 $^{\circ}$ 56'

The principal dimensional change is the expansion of the 'c' axis and the  $\beta$  angle. The other dimensions have altered slightly to maintain, for the tolyl compound, similar packing as in the phenyl compound. The densities are similar although the tolyl isomorph is about 4% lower. The most important molecular expansion which occurs is

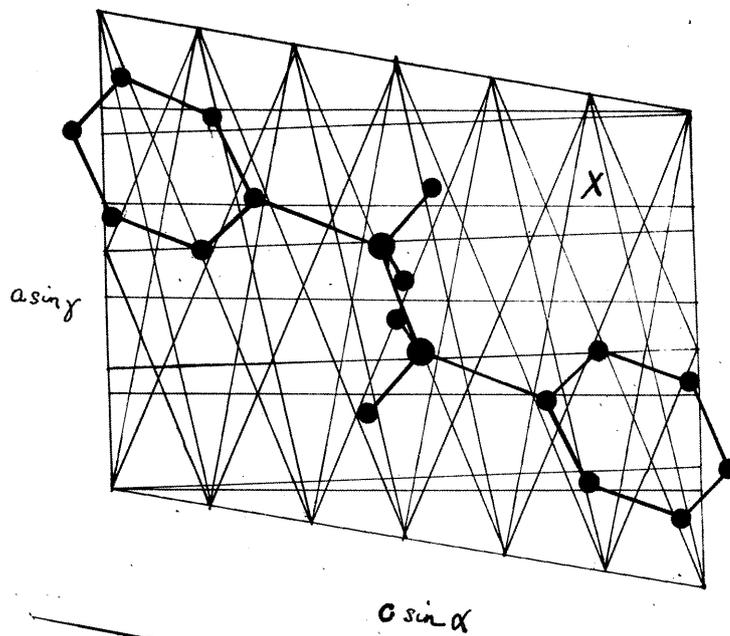


Fig. 1.  
(h0l) projection of diphenyl  
 $\alpha\alpha'$ -disulphone.

along the  $C_1 - C_4$  line (Figs. 1 and 3) due to the para methyl group and must therefore lie approximately parallel to the 'c' axis. The expansion of the angle  $\beta$  indicates that the benzene ring lies close to the 'c' axis and not in position X (Fig.1). The change in  $\alpha^*$  from  $115^\circ 58'$  to  $109^\circ 39'$  in going from the phenyl to the tolyl compound supports this and further indicates that the benzene ring considered lies in the lower part of the unit cell. This position is further supported by consideration of the zone of reflections (hko) for both compounds. Since the axes 'a' and 'b' do not vary greatly for the two compounds the intensity distribution is very similar and the enhancement of the reflections (020), ( $1\bar{1}0$ ), ( $1\bar{2}0$ ) and ( $1\bar{3}0$ ) in both structures indicates that the benzene ring lies in the region of  $y = \frac{b}{4}$  and close to the 'c' axis. This leads to the position of the S-S line which is disposed at a small positive angle with respect to the 'b' axis.

The zones (hol) and (okl) for the two compounds show certain similarities but there are differences due to the expansion of 'c'. It is therefore best to consider each zone for each compound and utilise the distribution of intensities to suggest a reasonable structure consistent with the geometrical deductions.

For the (hol) projection in the diphenyl  $aa^1$  disulphone, the series (001) is (001) vs. (002) s. (003) sm (004) s. (005) w, and the series (hoo) is (100) vs.

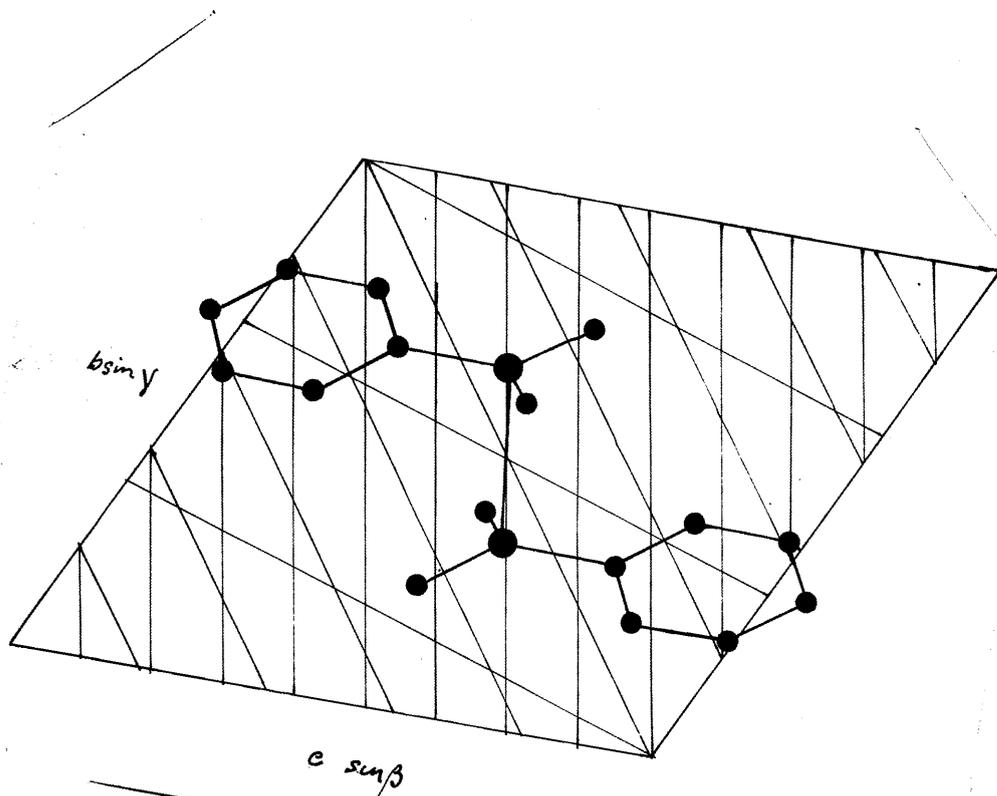


Fig. 2.  
(0kl) projection of diphenyl  
aa'-disulphone.

(200) sm. (300) w. (400) s. (500) sm.

There are several small-spacing planes with high intensities - such as  $(40\bar{1})$ ,  $(50\bar{1})$ ,  $(106)$ ,  $(206)$ ,  $(10\bar{6})$  and  $(20\bar{6})$  which are illustrated in Fig. 1.  $(202)$  is also very strong.

For the  $(okl)$  projection  $(012)$ ,  $(01\bar{1})$ ,  $(02\bar{1})$ , and  $(03\bar{1})$  are very strong. The small spacing planes of high intensity are  $(055)$  and  $(059)$ . These are illustrated in Fig. 2.

The suggested structure satisfactorily correlates the dimensions of the unit cells and the distribution of intensities for the zones  $(okl)$ ,  $(hol)$  and  $(okl)$ .

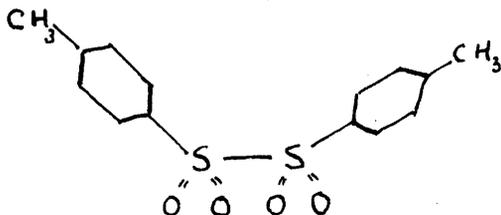
Crystal Structure of Di-p-tolyl      aa'-disulphone.

Crystal Data.

Di-p-tolyl    aa' -disulphone,  $C_{14}H_{14}S_2O_4$  :  $M = 310.2$ ;  
 m.p.  $214^\circ$  (decomp.),  $d$ , calc. 1.410, found 1.422: tri-  
 clinic holohedral,  $a = 7.21 \pm 0.03$ ,  $b = 8.14 \pm 0.04$ ,  $c = 9.965$   
 $\pm 0.04^\circ A$ ,  $\alpha = 56^\circ 2'$ ,  $\beta = 128^\circ 19'$ ,  $\gamma = 122^\circ 56'$ . Absent  
 spectra, none. Space group  $P\bar{1}$ . One molecule per unit  
 cell. Molecular symmetry, centre. Volume of unit cell,  
 $362.8^\circ A^3$ . Absorption coefficient for X-rays,  $\lambda = 1.54$ ,  
 $\mu = 34.5$  per cm. Total number of electrons in the unit  
 cell =  $F(000) = 162$ .

Structure Analysis.

As for the phenyl compound, the only reasonable  
 structure is formulated as shown.



Since the tolyl compound is isomorphous with the phenyl di-  
 sulphone, the general deductions as to the disposition of  
 the molecule in the unit cell apply to this structure. The  
 atomic positions can be more accurately fixed by considera-  
 tion of the intensities of the reflections for the important  
 zones (hol) and (okl).

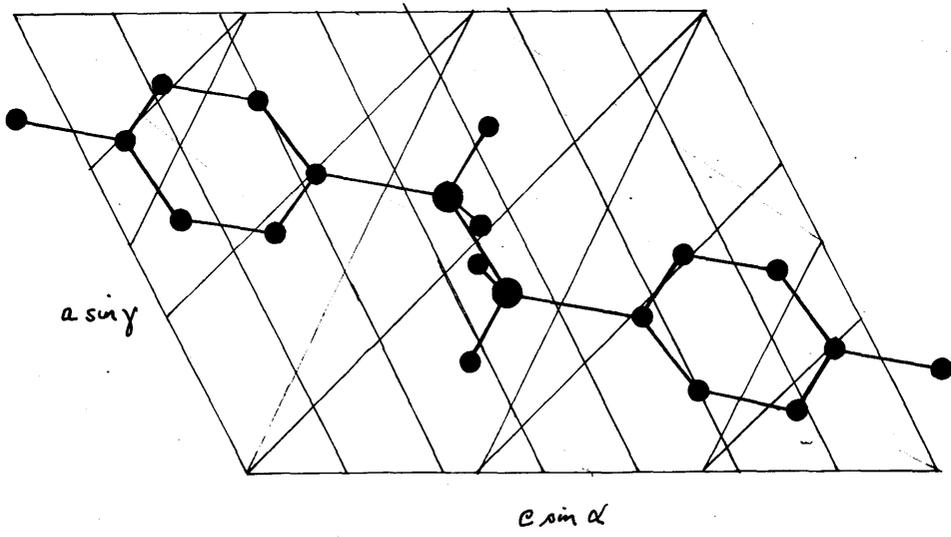


Fig. 3.  
(h0l) projection of di-p-tolyl  
 $\alpha\alpha'$ -disulphone.

For the (hol) zone, such planes as (006), (007), (10 $\bar{7}$ ), (400), (40 $\bar{1}$ ), (50 $\bar{1}$ ), (405), (406) and (407) give strong reflections and are useful guides to fix the atomic positions. In Fig.3 the molecule is illustrated with planes (007), (30 $\bar{3}$ ), (20 $\bar{3}$ ), (102) and (202) which give strong reflections, sketched in.

For the (okl) zone, (01 $\bar{1}$ ), (02 $\bar{1}$ ), and (03 $\bar{1}$ ) are strong as shown in Fig.4. (026) and (036) are two small spacing planes which have high intensities.

The structure proposed gives reasonable agreement in a qualitative manner for the dimensions of the molecule and the distribution of the intensities of the zonal reflections.

### Discussion.

The close correlation between the postulated structures for both compounds and the distribution of the intensities of the X-ray reflections support the experimental evidence for a centrosymmetrical molecule, namely the piezo- and pyro-electric tests, in assigning the structure to the space group  $P\bar{1}$ . This is in agreement with the structure given by Oesper and Smyth (39) on the basis of dipole moment measurements. The arrangement around the sulphur atom is approximately tetrahedral and it would appear that the structure is stabilised in the crystal by intermolecular forces between the hydrogen (of the phenyl

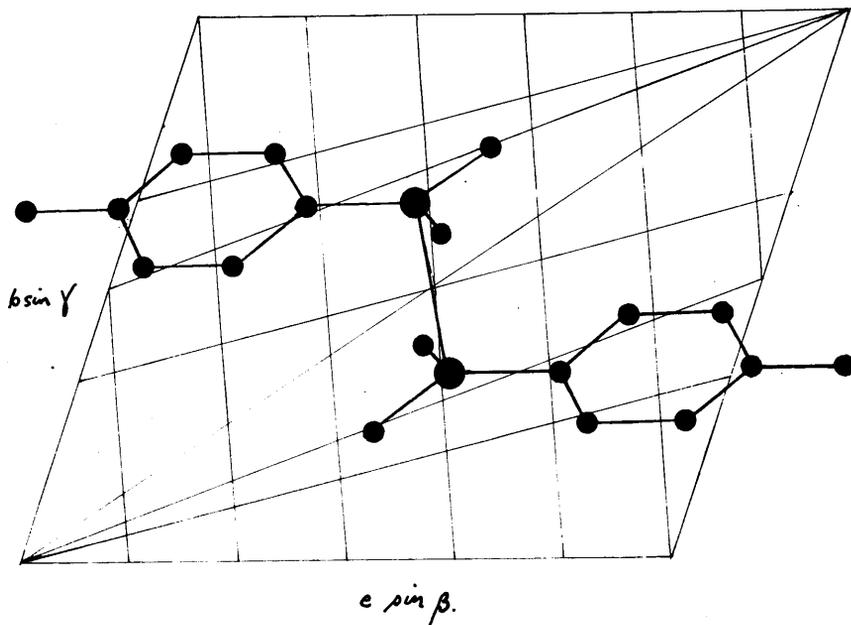


Fig. 4.

(0kl) projection of di-p-tolyl  
 $\alpha, \alpha'$ -disulphone.



Crystal Structure of Diphenyl Disulphonyl Sulphide.

Crystal Data.

Diphenyl disulphonyl sulphide,  $C_{12}H_{10}S_3O_4$ :  $M = 314.3$   
 m.p.  $133^\circ$ , d. calc. 1.587, found 1.588: monoclinic pris-  
 matic,  $c = 15.88 \pm 0.06$ ,  $b = 5.52 \pm 0.02$ ,  $a = 15.88 \pm 0.06$ ,  
 $\beta = 112.9^\circ$ . Absent spectra, (hkl) for  $k+1$  odd, and (hol)  
 for  $h$  odd and  $l$  odd. Molecular symmetry - diad axis.  
 Four molecules per unit cell. Volume of unit cell =  
 $1282^\circ A^3$ . Absorption coefficient for X-rays,  $\lambda = 1.54$ ,  
 $\mu = 53.3$  per cm. Total number of electrons per unit cell  
 $= 648 = F(000)$ .

Structure Analysis.

The compound diphenyl disulphonyl sulphide would be very difficult to analyse by itself, since there are three different types of atoms in the molecule each requiring a different scattering curve. One loaded curve, as used in oxalic acid (4a) would not be sufficiently accurate to determine whether calculated structure amplitudes were in good agreement with the observed values. However, comparison of this compound with the isomorphous p-tolyl compound has been utilised to determine the approximate disposition of the molecule by geometrical considerations. The comparable dimensions are given below.

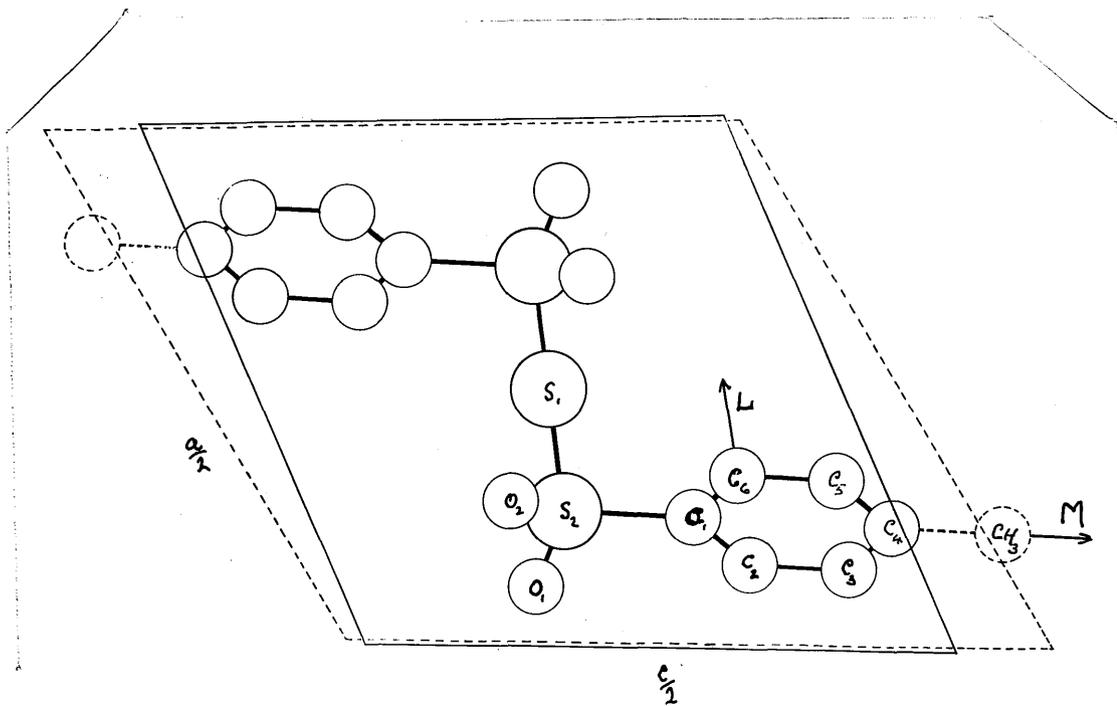


Fig. 5.

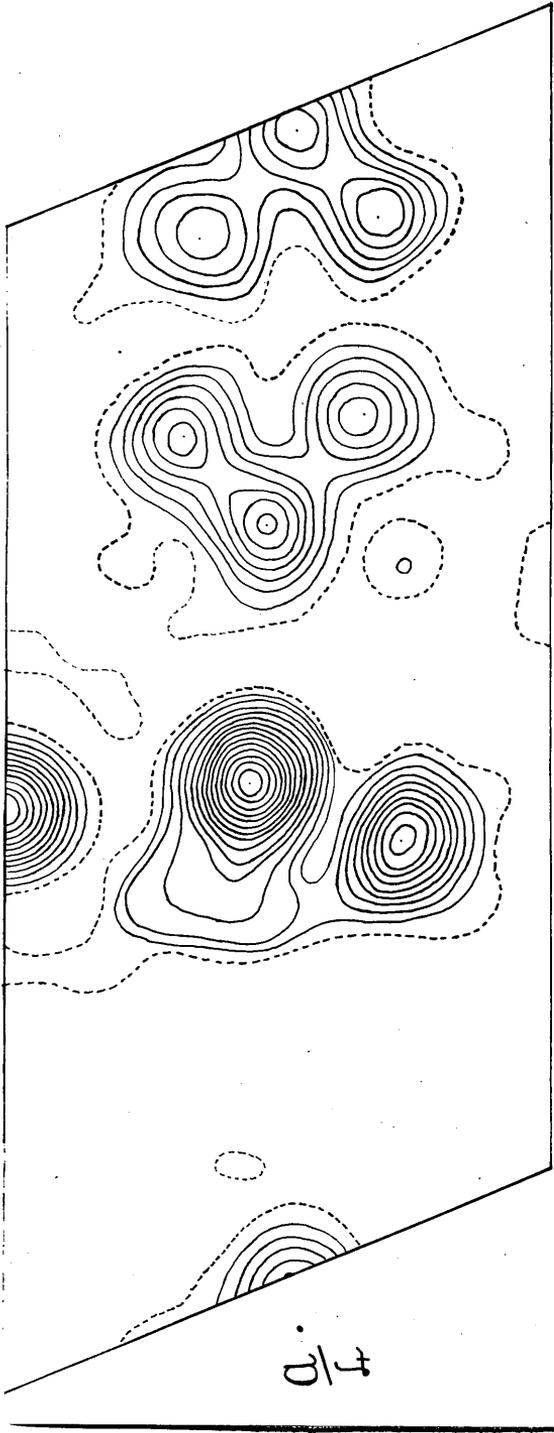
Comparison of (h0l) projections of  
diphenyl and di-p-tolyl sulphonyl  
sulphide.

	a	b	c	$\beta$	d(100)
phenyl	15.88	5.52	15.88	112.9°	14.60
tolyl	16.50	5.85	18.88	119.9°	14.31

The principal changes are the extension of 'c' and the expansion of ' $\beta$ '. The change in 'a' consequent on the expansion of  $\beta$  is not of real importance as we note that the spacing d(100) is almost unchanged. These cell dimension changes may be correlated with the alteration in the molecular dimensions. In the tolyl compound, a methyl group is introduced into the para position and if the general disposition of the molecule is the same in both phenyl and tolyl compounds, this expansion in the molecule should cause a corresponding change in the cell dimension in which the molecular expansion occurs. The deduction from the evidence is that the C<sub>1</sub>-C<sub>4</sub> line lies approximately parallel with the 'c' axis. The expansion of the  $\beta$  angle supports this conclusion and also indicates that the benzene ring must lie in the unit cell in such a position to cause expansion of this angle and not contraction. The similarity of the 'a' axis indicates that the disposition parallel to the (100) face is very similar. The small change in b ( $\Delta b = 0.33^\circ \text{A}$ ) and the change in c ( $\Delta c = 3.00^\circ \text{A}$ ) indicates that the line C<sub>1</sub>-C<sub>4</sub> must be at only a small angle to the plane (010). Fig. 5 will illustrate the relation of the two compounds. The full lines are the 'a' and 'c' axes of the phenyl and the dotted those of the tolyl compound, the

cells being superimposed so that the special position of diad symmetry at  $(\frac{a}{4}, \frac{c}{4})$  coincide. The additional methyl group of the tolyl compound is dotted in.

The most important projection is down the 'b' axis. The molecules here should be clearly resolved. A series of moving films of the (hol) zone was therefore taken and the comparative structure amplitudes determined from the intensities. Inspection of the series (hoo) showed that  $F(200)$  is small but  $F(400)$  very large. Also the series  $F(00l)$  falls off steadily in value for the first four orders. This indicates that there is a large concentration of scattering at  $\frac{a}{8}$  and hence since  $S_1$  in the special position at  $(\frac{a}{4}, y, \frac{c}{4})$  is fixed,  $S_2$  and  $C_1$  and  $C_4$  must lie in this position. The large value of  $F(400)$  indicates that the total tilt of the benzene ring with respect to the (010) plane is large. The actual position of the benzene ring is more accurately fixed by the small spacing planes (60,10) and (60,12). The positions of  $O_1$  and  $O_2$  were determined by constructing a model of this molecule with a tetrahedral disposition around  $S_2$  and hence fixing the coordinates. This model was used to calculate structure amplitudes, using scattering curves obtained from Internationalen Tabellen, and modified by an arbitrary temperature factor. After some small displacements, the modified parameters gave reasonable agreement between observed and calculated



0/2

0/4



Scale.

Fig. 6. Asymmetric portion of (h0l) projection.

structure amplitudes. The discrepancy  $\frac{\sum \Delta F}{\sum F}$  was 33%. Of a total 152 possible terms, 101 were used for the first Fourier and then with the refined coordinates more signs were fixed and 117 terms were introduced. With these structure amplitudes, the scattering curves were modified by correlating observed and calculated values. The new scattering curves, on recalculating structure amplitudes, revealed a few small sign changes and with these the final Fourier was carried out. The reflections were measured visually and brought to approximately absolute values by correlation with the calculated values. The result of the final Fourier synthesis is shown in Fig.6: this is one-eighth of the unit cell. For carbon and oxygen atoms contours are given for each electron level and for the sulphur atoms at each second electron level to clarify the diagrams. Fig.7 shows complete unit cell and Fig.7b is the corresponding diagram with the atoms indicated by circles.

The (hol) projection clearly resolves all atoms except  $O_2$  which is obscured by  $S_2$ . From the atomic coordinates, the tilt of the line  $S_2 - C_1 - C_4$  may be deduced. From the foreshortening of the distance  $C_1 - C_4$  and also from the angle (in projection) which the line  $C_2 - C_6$  makes with the line  $C_1 - C_4$  ( $11.3^\circ$ ), the angle of  $C_1 - C_4$  with respect to the 'b' plane ( $90 - \psi_p$ ) =  $6^\circ 18'$  may be calculated. It can then be calculated from the position of  $O_2$  that if  $S_1$  lies

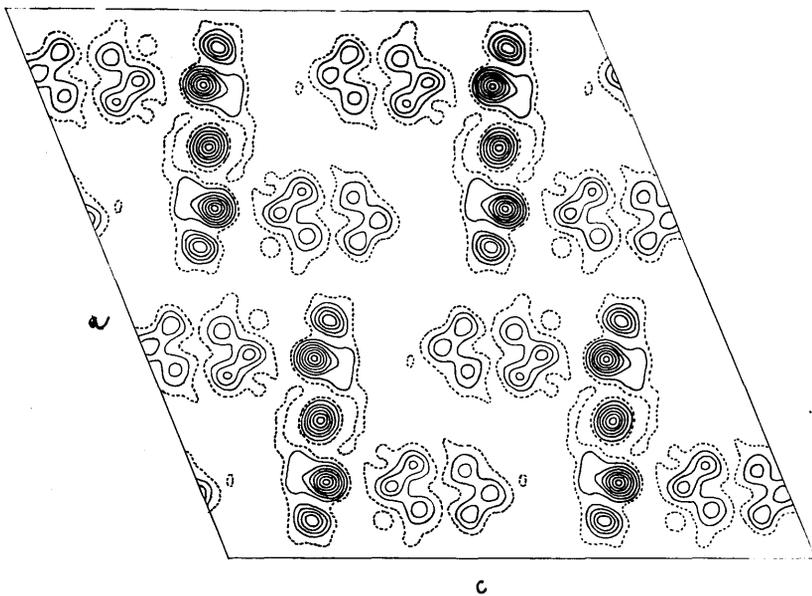


Fig. 7a.  
(h0l) projection of diphenyl  
disulphonyl sulphide.

below  $S_2$  and the disposition around  $S_2$  is approximately tetrahedral, then the line  $S_2-C_1-C_4$  must make an angle of  $+6^\circ 18'$  with respect to the  $b$  plane. Thus, having determined this, it can be deduced that the benzene ring is tilted such that  $C_5$  and  $C_6$  lie above  $C_1$  and  $C_4$  and these above  $C_2$  and  $C_3$ . A model of the molecular structure as viewed down the 'a' axis may then be drawn out. This structure has a free translation  $y$  along the 'b' axis and the position of the model is shifted until satisfactory agreement was obtained for structure amplitudes. The structure amplitudes were put on an approximately absolute scale by correlation with the (001) of the (hol) zone and the important planes utilised were the axial set (020), (040) and (060). These, together with the strong series (041) and the outstanding small spacing plane (03,17) were useful guides to the correct position. After small variations to modify the agreement, most of the signs of the observed reflections were fixed, and a Fourier summation carried out with 40 of the possible 60 terms. This showed a small general movement along the  $y$  axis and with the modified coordinates, structure amplitudes showed three changes of sign. The final Fourier synthesis confirmed the previous coordinates and the discrepancy was then 17.5% for the (okl) projection. The final Fourier drawn out for the whole unit cell is shown in Fig.8a, together with the explanatory diagram in Fig.8b showing the four

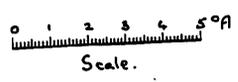
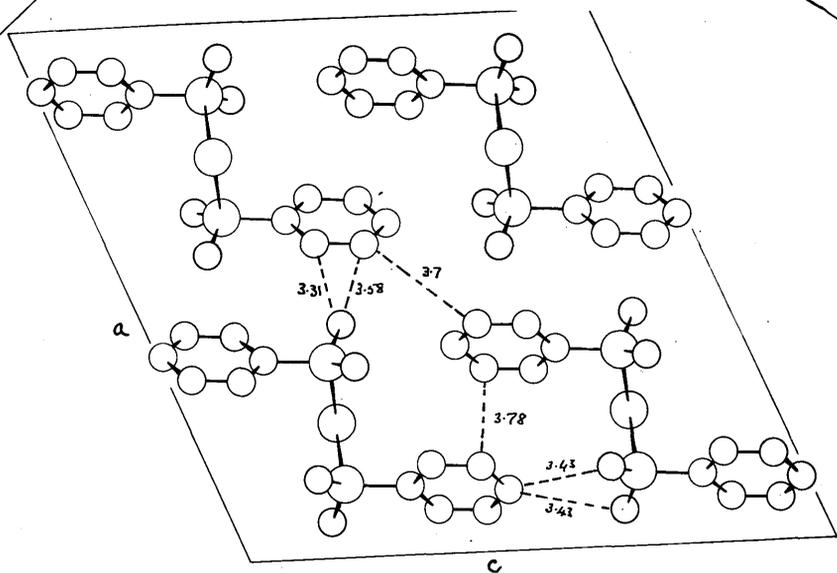


Fig. 7b.

molecules in the unit cell. The atoms of the asymmetric unit are designated by letters and it can be seen that considerable overlap occurs not only between molecules but also within each molecule.

### Orientation and Arrangement of Molecules in the Crystal.

The (hol) projection clearly defines the 'x' and 'z' coordinates for all atoms but O<sub>2</sub> and indicates relative positions of the atoms parallel to the 'y' axis. By correlation with the (okl) projection, the complete disposition can be seen. Fig.9 gives a clear picture of the molecule A in Fig.7b as viewed along the (101) axis. In Fig.7b molecule B is related to molecule A by a shift half along 'c' and half along 'b'. Molecule C is related to A by reflection in a plane at  $y = \frac{b}{4}$  and then a shift half along 'a'. Molecule D is related to C as B is to A. Fig.10 diagrammatically indicates the arrangement as viewed down the 'a' axis.

The atomic coordinates have been obtained from the Fourier projections and the bond dimensions and angles from these. To fix the carbon atom positions in the benzene ring, a regular ring was assumed and the positions selected to give minimum deviation from the observed centres in the contour map for atoms C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub> and C<sub>6</sub>. The orientation of the benzene ring in the crystal can be defined by the angles  $\chi_L, \chi_M, \chi_N, \psi_L, \psi_M, \psi_N, \omega_L, \omega_M$  and  $\omega_N$  where these are the angles made by the molecular axes L, M

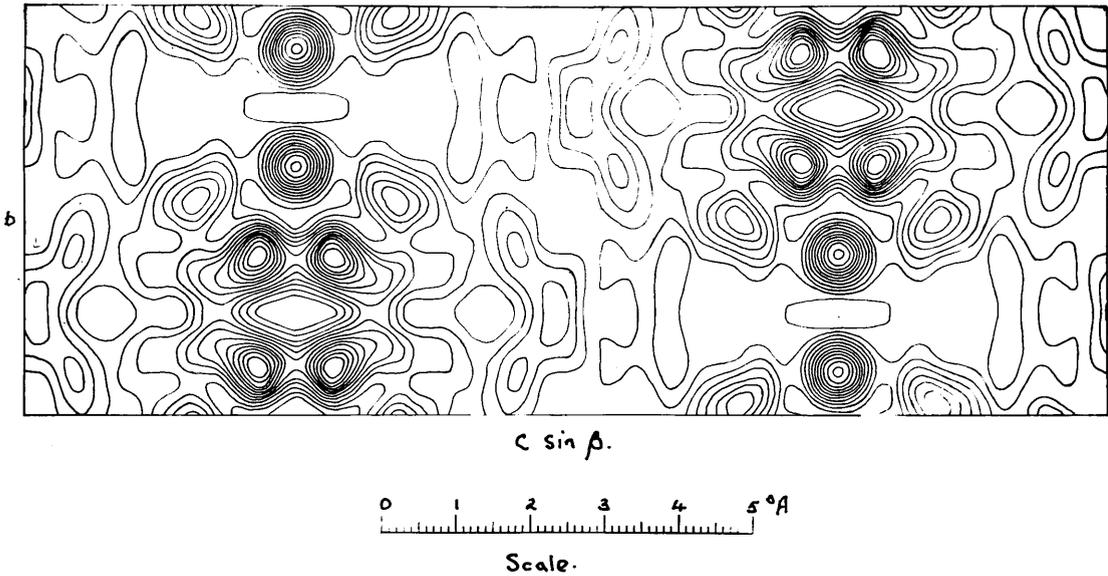


Fig. 8a.  
(0k1) projection of diphenyl  
disulphonyl sulphide.

and their perpendicular N with the crystal axes 'b', 'c' and their perpendicular 'a'. The molecular axes L and M are shown in Fig.5.

Table I.

$\chi_L = 59^\circ 51'$	$\cos \chi_L = 0.5022$
$\psi_L = 30^\circ 24'$	$\cos \psi_L = 0.8625$
$\omega_L = 93^\circ 45'$	$\cos \omega_L = -0.0654$
$\chi_M = 93^\circ 53'$	$\cos \chi_M = -0.0677$
$\psi_M = 84^\circ 42'$	$\cos \psi_M = 0.1097$
$\omega_M = 7^\circ 24'$	$\cos \omega_M = 0.9917$
$\chi_N = 149^\circ 12'$	$\cos \chi_N = -0.8590$
$\psi_N = 60^\circ 18'$	$\cos \psi_N = 0.4955$
$\omega_N = 97^\circ 6'$	$\cos \omega_N = -0.1236$

The total tilt of the benzene ring to the (010) plane given by the angle of the axis N to the b axis,  $\psi_N$  is  $60^\circ 18'$ .

#### Coordinates and Dimensions.

The x and z coordinates can be measured from the (hol) projection for all atoms except  $O_2$ . Diffraction effects between  $S_1$  and  $S_2$  must be considered in fixing the coordinates of  $O_2$ , but if these are allowed a reasonable position can be assigned to it. The y coordinates were determined from the (okl) projection and here the resolution is not very satisfactory due to the overlap of two molecules. The results are given with reference to the crystal axes.

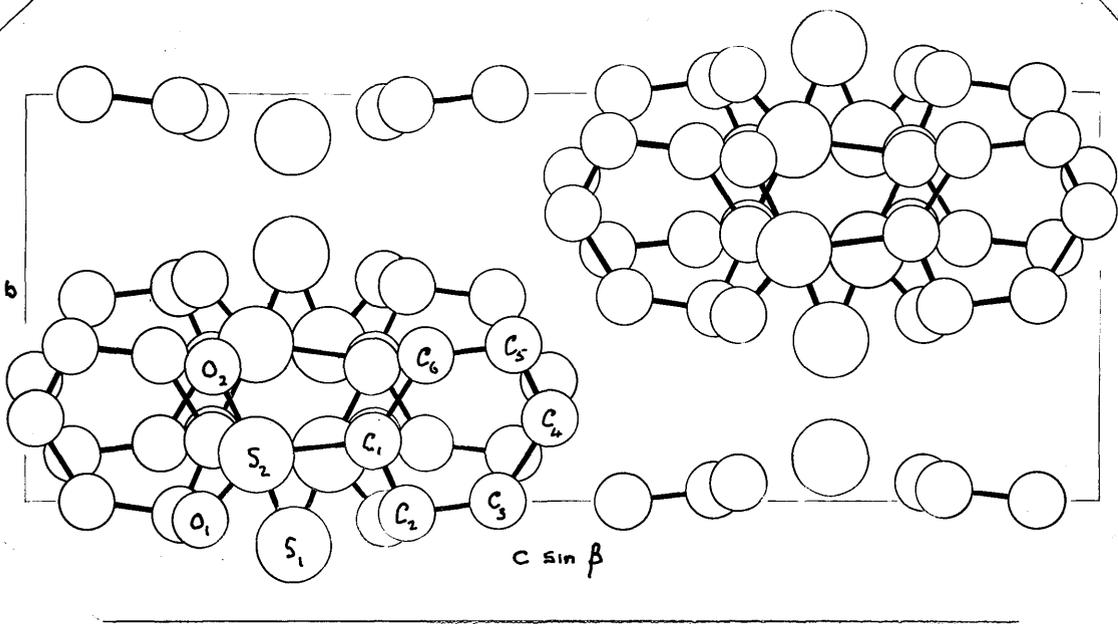


Fig. 8b.

Table II.

Atom	$x^\circ A$	$\frac{2 \pi x^\circ}{a}$	$y^\circ A$	$\frac{2 \pi y^\circ}{b}$	$z^\circ A$	$\frac{2 \pi z^\circ}{c}$
S <sub>1</sub>	3.97	90.0°	-0.60	-39.0°	3.97	90.0°
S <sub>2</sub>	2.18	49.5	+0.64	+42.0	3.46	78.5
O <sub>1</sub>	1.07	24.2	-0.25	-16.0	2.63	59.7
O <sub>2</sub>	2.33	53.0	+1.84	+120.0	2.78	63.0
C <sub>1</sub>	2.06	46.7	+0.83	+54.0	5.16	117.0
C <sub>2</sub>	1.34	30.4	-0.14	-10.0	5.64	128.0
C <sub>3</sub>	1.26	28.6	+0.02	+1.0	6.98	159.0
C <sub>4</sub>	1.85	42.0	+1.13	+74.0	7.82	177.5
C <sub>5</sub>	2.56	58.0	+2.11	+138.0	7.35	167.0
C <sub>6</sub>	2.66	60.3	+1.96	+128.0	6.00	136.0

All other atoms in the unit cell can be reproduced from the coordinates of the asymmetric unit given above by the following operations.

- |    |                    |                    |                    |    |                    |                    |                    |
|----|--------------------|--------------------|--------------------|----|--------------------|--------------------|--------------------|
| 1. | $x,$               | $y,$               | $z.$               | 5. | $\bar{x},$         | $\bar{y},$         | $\bar{z}.$         |
| 2. | $x,$               | $\frac{1}{2} - y,$ | $\frac{1}{2} - z.$ | 6. | $\bar{x},$         | $\frac{1}{2} - y,$ | $\frac{1}{2} - z.$ |
| 3. | $\frac{1}{2} - x,$ | $\frac{1}{2} - y,$ | $z.$               | 7. | $\frac{1}{2} - x,$ | $\frac{1}{2} - y,$ | $\bar{z}.$         |
| 4. | $\frac{1}{2} - x,$ | $\bar{y},$         | $\frac{1}{2} - z.$ | 8. | $\frac{1}{2} - x,$ | $y,$               | $\frac{1}{2} - z.$ |

The bond lengths were determined by converting the crystal coordinates to the rectangular coordinates 'b', 'c' and 'a'. The interatomic distances are listed in Table 3.

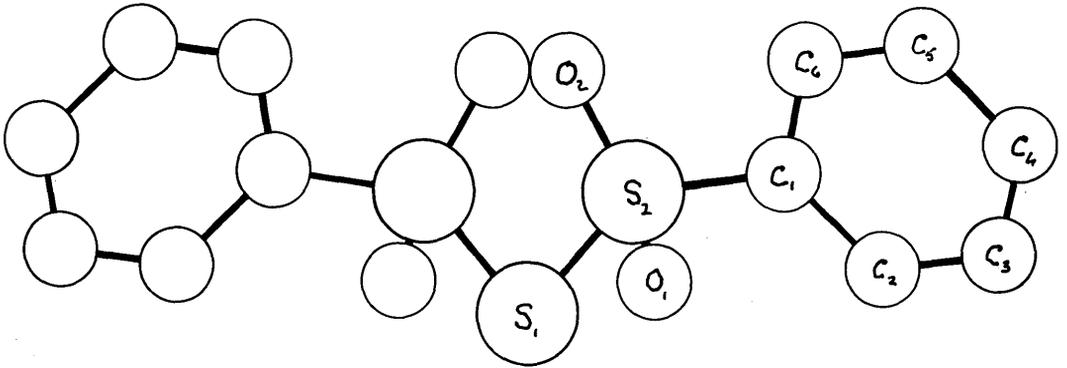


Fig. 9.

Model of the structure as viewed  
along the (101) axis.

Table 3.

$S_1 - S_2$	$2.07 \pm 0.02$	$C_1 - C_2$	1.39
$S_2 - O_1$	$1.41 \pm 0.04$	$C_2 - C_3$	1.38
$S_2 - O_2$	$1.41 \pm 0.04$	$C_3 - C_4$	1.38
$S_2 - C_1$	$1.76 \pm 0.02$	$C_4 - C_5$	1.40
		$C_5 - C_6$	1.39
		$C_6 - C_1$	1.40
		Mean	$1.39 \pm 0.03$

Bond Angles.

$S_1 - S_2 - O_2$	$111.9^\circ$	$O_1 - S_2 - C_1$	$107.5^\circ$
$S_1 - S_2 - O_1$	$104.2^\circ$	$O_2 - S_2 - C_1$	$115.9^\circ$
$O_1 - S_2 - O_2$	$117.2^\circ$	$S_1 - S_2 - C_1$	$101.7^\circ$
$S_2 - S_1 - S_2$	$106.5 \pm 1.0^\circ$		

The S -S -S angle is the most accurate since the sulphur coordinates are accurately fixed in both projections.

The accuracy of the other angles is  $\pm 4.0^\circ$ .

The disposition of the bonds S -S, S =O<sub>1</sub>, S = O<sub>2</sub> and S -C around S<sub>2</sub> is only very approximately tetrahedral and in the crystal due to the close packing of the molecules distortions occur. Mutual repulsions between atoms with large charges, such as the oxygen atoms, will also affect the bond angles. The intra-molecular atomic distances which appear to be of interest are given in Table 4 and in Fig. 7b.

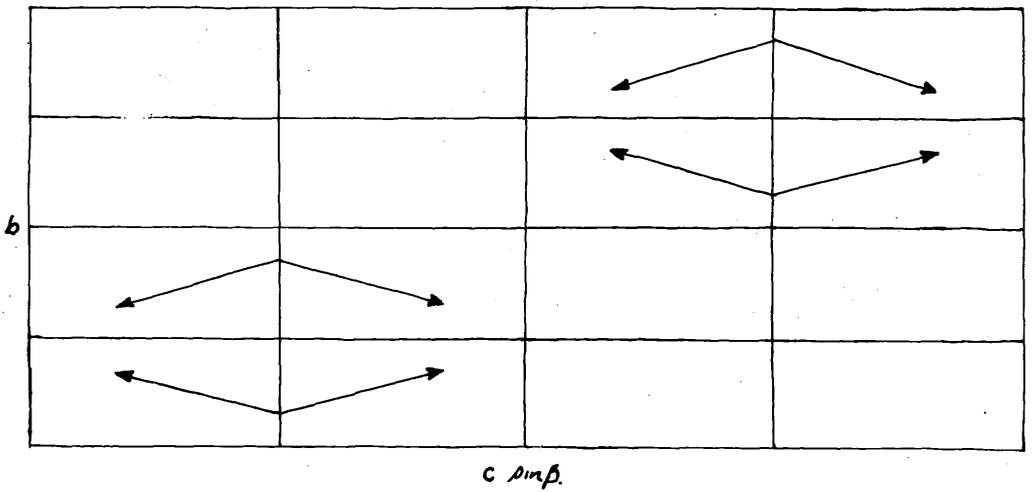


Fig. 10.

Diagrammatic positions of molecules in  
the 'a' axis projection.

### Intermolecular Distances.

The closest approach for the benzene rings, due to the large tilt, is from  $C_6$  to  $C_2$  of the benzene ring with translation b, the distance being  $3.68^{\circ}A$ . A close approach between  $C_5$  and  $C_{5c}$  of  $3.78^{\circ}$  also occurs. A similar distance is observed for  $C_3$  and  $C_{3d}$ . The distances of interest are those observed between the oxygens of the sulphone group and the para-carbon of the benzene ring for  $C_4$  to  $O_{1a}$  and  $C_4$  to  $O_{2a}$  are both  $3.43^{\circ}A$ , a distance somewhat less than the van der Waal approach. The distance  $C_2$  to  $O_{1b}$  is  $3.3^{\circ}A$ .

Table 4.

$O_2 - C_6$	3.11	$C_{4a} - O_{1b}$	3.43
$O_1 - C_2$	2.92	$C_{4a} - O_{2b}$	3.43
$C_{2a} - O_{1c}$	3.33	$C_{5a} - O_{5b}$	3.78
$C_{3a} - O_{1c}$	3.58	$C_{3a} - C_{3d}$	3.78
		$C_{2a} - C_6$	3.68

### Discussion.

For this compound, the range of reflections obtained by the use of Cu K radiation, is not sufficient to give a completely accurate reproduction of the electron density because the Fourier series is terminated at a value which is finite and appreciable. Thus the terms  $F(20, 01)$  lie in the range 20 to 25 units where  $F(000)$  is 648. The result of terminating the series in this manner is to introduce diffraction effects in the Fourier projection and these by mutual interference cause spurious variations of the electron density which must be considered in assigning atomic centres. These interference effects do not alter, to any great extent, the positions of the peaks (41) but modify the lower contour levels and cause difficulty in the case of  $C_2$  which is obscured by  $S_2$  (Fig.6). These diffraction effects would be removed if the range of Fourier terms were extended by the use of a shorter wavelength radiation or by the application of a temperature correction (36). Van Reijen (37) has suggested another method of modifying the Fourier components so that, with limited data, the electron distribution is given sufficiently accurately to study the type of chemical bonding between atoms.

The length of the S-S bond ( $2.07^{\circ}A$ ) is in good agreement with previous determinations (42, 43, 44, 45) and

is a normal single bond. The presence of the grouping around  $S_2$  does not cause any reduction of the formal radius of the sulphur atom which would reduce the  $S_1-S_2$  distance. This reduction of the formal radius of the atom by very short bonds, such as the SO bonds here, has been suggested by Sutton (46) as a possible explanation of bond shortening, but it is clear that this is not the case as the S-S bond is normal and hence short bonds must receive some other explanation. The S-C bond length (1.76) is shorter than the value given by the sum of the single bond radii (47) and consideration of the electronegativity (48) does not alter this value of  $1.81^{\circ}A$ . The value given by Sutton (49) for this bond in  $Me_2SO_2$  (1.90) is probably too large, as recent investigations give measurements in the region 1.75 - 1.77.

Dimethyl Disulphide	1.77 (42)
$\beta$ -Isoprene Sulphone	1.75 (50)
p-p' Dibromdiphenyl Sulphide	1.76 (51).

Cox and Jeffrey (50) suggested that for  $\beta$ -isoprene sulphone this bond implies  $\frac{2}{3}$ rds. single bond and  $\frac{1}{3}$  semi-ionic bond character, but it is difficult to visualise this situation applying to the molecule of diphenyl disulphonyl sulphide. It is probable that the bond is a normal single one.

The accuracy of the SO bond length ( $1.41 \pm 0.04$ ) is

not so great as those for the S-S and S-C bonds due to the obscuring of the oxygen atoms in the projection but the distance is in reasonable agreement with similar measurements.

$\beta$ -Isoprene	$\text{Me}_2\text{SO}_2$	$\text{SOCl}_2$	$\text{S}_2\text{OCl}_2$	$\text{K}\cdot\text{SO}_3\cdot\text{NH}_2$ <del><math>\text{K}\cdot\text{SO}_3</math></del>	$\alpha\text{SO}_3$	$\text{SO}_3$ (g)
-------------------	--------------------------	-----------------	--------------------------	--	---------------------	-------------------

Sulphone

1.44	1.44	1.45	1.43	1.43	1.40	1.43 <sup>o</sup> A
(50)	(49)	(42)	(42)	(52)	(53)	(42)

The normal formulation of the SO bond was  $\text{S} \rightarrow \text{O}$ , as a coordinate or dative bond, following the suggestion of Sidgwick (54) but the fact that the distance is so short, even less than the sum of the double bond radii (1.49), has suggested (55, 56) that this type of bond is best formulated as double. Sutton (46) has shown in a study of the coordinate bond by dipole moment measurements that true coordinate bonds are more rare than had been previously supposed. The evidence both from bond lengths and from heats of formation of the SO bond imply that this bond is very strong and is probably a double bond. The heats of formation of coordinate links are of the order of 20 to 40 kg.cal./g.mol., whereas the value of 103 kg.cal./g.mol. for the SO bond lies far beyond this range and is even greater than the value for the single SO bond (72.4 kg.cal.). Since the coordinate bond is weak, resonance between the coordinate and the double bond will not contribute to stabilise the structure and hence it is most probable that

the bond is double. If these bonds are formulated as double, then sulphur must be hexavalent in compounds of the sulphone type  $R_2SO_2$ . This maximum valency is shown in sulphur hexafluoride. If the oxygen double bond radius is taken as  $0.60^{\circ}A$  and that for S as  $0.94$ , the length for the bond  $S=O$  is  $1.54$ , and taking account of the electronegativity is then  $1.43^{\circ}A$  in good agreement with the observed values. It is to be noted that if the bond were coordinate the bond length would be expected to vary appreciably for such compounds as  $Me_2SO_2$  and  $SO_2Cl_2$  due to the different electronegative character of chlorine and carbon, but within the experimental error the value is the same. The stereochemistry of hexavalent sulphur will be based on the regular octahedron and for compounds of the type  $R_1R_2SO_2$ , the angle between the single bonds will be  $90^{\circ}$  and between the two  $SO$  bonds will be  $120^{\circ}$ . The angles found in this study are, respectively  $101.5^{\circ}$  and  $117.2^{\circ}$ . In  $\beta$ -isoprene sulphone the corresponding angles are  $99^{\circ}$  and  $112^{\circ}$ . The angles show appreciable deviations from the tetrahedral angle  $109^{\circ}38'$  which would be expected if the sulphur atom showed only four-valency. It is probable that the arrangement is due to distortion from the octahedral disposition rather than from the tetrahedral. Sutton attempted a structure of  $Me_2SO_2$  (49) based on a regular octahedron but decided that a tetrahedral arrangement was

more correct. This choice may account for the very long C-S bond length which he finally obtained. The present work would seem to support the contention that sulphur displays hexavalency and that the disposition around the atom is octahedral but distorted by double bond formation and interaction in the crystal.

The benzene ring was assumed regular and on this assumption the average bond distance is normal. The accuracy of determination is not sufficient to decide if any individual variation in bond length within the ring is significant. The most important bond distances are  $C_4-O_1$  and  $C_4-O_2$ . Both these distances are  $3.43^{\circ}A$  which is less than the van der Waal approach and it is noteworthy that the para-hydrogen must therefore approach within  $2.4^{\circ}A$  of the oxygen atoms. It is probable that this close approach is due to the large partial charge on the oxygen,  $0.30e$ , as derived from dipole moment measurements, and the resultant induced charge on the para grouping. In the tolyl compound, the molecular disposition along the 'a' axis is almost the same as that in the phenyl compound and only the 'c' axis has expanded to any extent. The intermolecular bonding perpendicular to the 'c' axis is therefore much weaker than that parallel to this axis and indicates the strength of the O ---- C bonding. That the intermolecular forces of these two isomorphous compounds are very similar

is shown by the fact that the melting points are almost the same,  $133^{\circ}$  (phenyl) and  $138^{\circ}$  (tolyl). Normally the melting point of the corresponding tolyl compound is lower. The density of the p-tolyl compound drops to 1.16 as compared with 1.58 for the phenyl compound, while the disposition as indicated in Fig.5 remains similar, especially with regard to the  $\text{SO}_2\text{---HC}$  grouping. For compounds so closely related, it would be expected that the densities would be very similar, as is apparent in the comparison of the isomorphous disulphones and the disulphonyl trisulphides. It is suggested that this large change is indicative of the important part that the  $\text{SO}_2\text{---HC}$  bonding plays in this compound in determining the crystal structure, which prevents the molecules from orienting themselves to maintain closest packing. This type of link may be considered as weak hydrogen bonding as somewhat similar distances  $\text{NH---O}$  have been recorded in Urea (57) and Glycine (58). In the study of molecular compounds by Huse and Powell (59), the only distances between molecules which indicated bonding of importance in determining the structure were  $\text{N}(\text{NH}_2)\text{---O}(\text{NO}_2)$  lying between 3.1 and  $3.3^{\circ}\text{A}$ .

It is also of interest to note that the orientation of the benzene rings with respect to those above and below (considering the b axis as vertical) is not critical in fixing this structure as it is for the hydrocarbons and yet the tilt is such that the closest approach  $\text{C}_6\text{---O}_2$ ,  $\text{C}_2\text{---O}_1$  is

maintained. These intramolecular distances, 3.11 and 2.92, must imply bonding as the benzene ring could easily rotate around the single bond such as to increase this distance. The distances  $C_2 \cdots O_{1b}$  (3.31) and  $C_3 \cdots O_{1b}$  (3.58) are not critical with respect to the tilt of the benzene ring. In solution, the value of the dipole moment is approximately the same for the compounds  $R_2S_nO_4$  where  $n$  is 2 to 5 (39, 40). For the disulphone, Oesper and Smyth (39) have suggested that the observed value of the dipole moment is in agreement with a structure which has a tetrahedral arrangement of bonds around each sulphur atom, the sulphur atoms being linked by a single bond and rotation around this bond being possible. Because of the similarity in dipole moments, it is probable that the compound diphenyldisulphonyl sulphide in solution displays similar rotation around the S-S single bonds although this may be restricted by the bulkiness of the benzene ring. In the crystal the molecule is orientated with respect to the others so that the bond  $SO_2 \cdots CH$  is important in binding the structure.

The distances of closest approach between carbon atoms of benzene rings situated one another is  $3.68^\circ A$ . Other close approaches are 3.7 and  $3.78^\circ A$  as shown in Fig.7b. These are normal van der Waal approach distances.

Crystal Structure of Di-p-tolyl Disulphonyl Sulphide.

Crystal Data.

Di-p-tolyl disulphonyl sulphide,  $C_{14}H_{14}S_3O_4$ : M, 342.3.  
 m.p.  $138^\circ$ : d. calc. 1.161, found 1.167, monoclinic (prismatic)  
 $a = 16.50 \pm 0.06$ ,  $b = 5.85 \pm 0.02$ ,  $c = 18.88 \pm 0.07^\circ A$ ,  $\beta = 119.9^\circ$ .  
 Absent spectra, (hkl) for  $k+l$  odd, and (hol) for  $h$  odd and  $l$   
 odd. Space group  $A2/a$ . Four molecules per unit cell.  
 Molecular symmetry - diad axis. Volume of the unit cell  
 $= 1581^\circ A^3$ . Absorption coefficient for X-rays,  $\lambda = 1.54^\circ A$ ,  
 $\mu = 35.7$  per cm. Total number of electrons in the unit  
 cell = 712.

The crystal habit is a familiar one, lathe-like  
 crystals elongated in the direction of the  $b$  axis. The  
 (100) and (001) faces are developed but no others are  
 evident.

Analysis of Structure.

The deductions arrived at by a close comparison of  
 the isomorphous phenyl and para-tolyl compounds have been  
 shown to be correct by the complete elucidation of the  
 structure of the phenyl compound. The structure of the p-  
 tolyl disulphonyl sulphide is therefore, in essentials,  
 similar to that shown by the dotted lines in Fig.5. Com-  
 pared with the phenyl compound the distribution of the (hoo)  
 series is almost unchanged, but the (001) distribution is  
 modified and (008), previously zero now becomes medium

strong in intensity. The planes (204), (206), (406), (408) and (40,10) are very strong as previously.

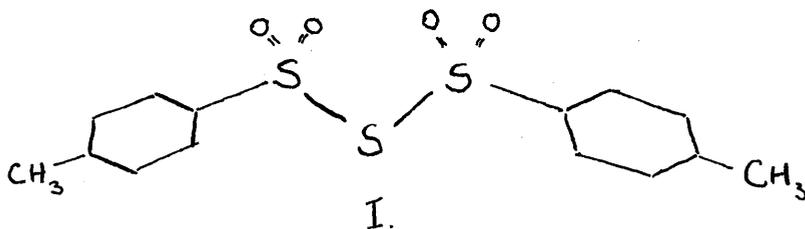
The very great similarity of the (hoo) series for the two compounds indicates that the structures closely resemble one another in their disposition along the 'a' axis.

### Discussion.

The orientation of the benzene ring with respect to the rectangular axes 'b', 'c' and 'a\*' at right angles to the former two will not be greatly altered in the tolyl compound as compared with the phenyl. The angle of tilt to the b axis ( $\psi_N$ ) will therefore be of the order of  $60^\circ$  where L, M and N are as previously designated. All intramolecular bond lengths will be similar to those in the phenyl compound; with the close intramolecular approach of  $O_1-C_2$  and  $O_2-C_6$  causing the plane of the benzene ring to lie approximately parallel with the line  $O_1-O_2$ . The expansion of the 'c' axis and lack of change in disposition along the 'a' axis indicates that the intermolecular bonding between the oxygens of the sulphone group and the carbons (or more likely the hydrogens) of the benzene rings of the adjacent molecule, is very important in the binding forces of these isomorphous crystals. If this bonding did not determine the structure, the tolyl compound would accommodate itself to maintain approximately the same packing and hence, the same density, whereas the density drops from 1.587 for the

phenyl to 1.161 for the tolyl compound, a change of 27%. That the melting point has changed slightly to 138° is also indicative of the importance of this binding between oxygen and hydrogen of the carbon as in the case of most compounds, the introduction of amethyl group in the para position lowers the melting point. The extension of the 'b' axis may also be explicable by the replacement of the para hydrogen by a methyl group. The arrangement of the C-H bonds around the carbon atom will be tetrahedral and hence this will modify the C---O distances and hence the length of the b axis.

The structure of the molecule may thus be given as I.



The SO bonds are formulated as double since the information available indicates that this is more correct than formulation as coordinate bonds.

Crystal Structure of Diphenyldisulphonyl Trisulphide.

Crystal Data.

Diphenyldisulphonyl trisulphide,  $C_{12}H_{10}S_5O_4$ ;  
 M, 378.4, m.p.  $103^\circ$ . d. calc. 1.584, found, 1.582;  
 tetragonal (trapezohedral)  $a = 7.74 \pm 0.02$ ,  $c = 26.29 \pm 0.05$ ;  
 Absent spectra, (hol) for  $h = 2n$ ,  $l = 4n$ . Molecular  
 symmetry - diad axis. Four molecules per unit cell.  
 Volume of unit cell =  $1575 \text{ \AA}^3$ . Absorption coefficient  
 for X-rays,  $\mu = 1.54$ ,  $\mu = 66.7$  per cm. Total number  
 of electrons per unit cell = 776 =  $F(000)$ .

Space Group.

The space group  $P4_12_1$  has no centre of symmetry but  
 due to the diad screw axis it has an apparent centre in  
 projection. To simplify the geometrical structure factors  
 for the (hol) projection which yields most information for  
 this compound, the origin of the unit cell has been altered  
 from that given in the Internationallenen Tabellen (27). The  
 origin is chosen so that a two-fold screw axis along the 'b'  
 axis passes through it and the four-fold screw axis is at  
 the position  $(\frac{a}{4}, \frac{b}{4}, z)$ . The diad axis of symmetry which  
 gives the molecular symmetry then lies at the level  $z = \frac{c}{8}$ ,  
 passing the 'c' axis and at an angle of  $45^\circ$  to both the 'a'  
 and 'b' faces. The coordinates of the equivalent positions  
 are thus as follows†-

- |    |                    |                    |                     |    |                    |                    |                     |
|----|--------------------|--------------------|---------------------|----|--------------------|--------------------|---------------------|
| 1. | $x,$               | $y,$               | $z.$                | 5. | $\bar{y},$         | $\bar{x},$         | $\frac{c}{4} - z.$  |
| 2. | $\frac{a}{2} - y,$ | $x,$               | $\frac{c}{4} + z.$  | 6. | $\frac{a}{2} + x,$ | $\bar{y},$         | $\frac{c}{2} - z.$  |
| 3. | $\frac{a}{2} - x,$ | $\frac{a}{2} - y,$ | $\frac{c}{2} + z.$  | 7. | $\frac{a}{2} + y,$ | $\frac{a}{2} + x,$ | $\frac{3c}{4} - z.$ |
| 4. | $y,$               | $\frac{a}{2} - x,$ | $\frac{3c}{4} + z.$ | 8. | $\bar{x},$         | $\frac{a}{2} + y,$ | $\bar{z}.$          |

and the four special positions lie on the diad axes at the following coordinates

- |    |                    |                    |                 |
|----|--------------------|--------------------|-----------------|
| 1. | $x,$               | $\bar{x},$         | $\frac{c}{8}.$  |
| 2. | $\frac{a}{2} + x,$ | $x,$               | $\frac{3c}{8}.$ |
| 3. | $\frac{a}{2} - x,$ | $\frac{a}{2} + x,$ | $\frac{5c}{8}.$ |
| 4. | $\bar{x},$         | $\frac{a}{2} - x,$ | $\frac{7c}{8}.$ |

For the (hol) planes the geometrical structure factor is

$$S = \sum \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right) + i \sum \sin 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right)$$

and since the projection is centrosymmetric, the sine functions cancel one another and the equation is then

$$S = \sum \cos 2\pi \left( \frac{hx}{a} + \frac{lz}{c} \right)$$

The final equation after combining the trigonometrical functions is

$$S = 4 \left[ \cos \left( \frac{h+1}{2} \cdot \frac{\pi}{2} + l\theta \right) \cdot \cos \left( \frac{h+1}{2} \cdot \frac{\pi}{2} - h\theta \right) \cdot \cos \left( \frac{h+2l}{2} \cdot \frac{\pi}{2} + l\theta \right) \cdot \cos \left( \frac{h-1}{2} \cdot \frac{\pi}{2} - h\theta \right) \right]$$

and for convenience it is best to group these as follows:-

For h odd

1.  $l = 4n + 1.$

$$S = 4(\cos l\theta_3 \cdot \cos h\theta_1 + \sin l\theta_3 \cdot \sin h\theta_2)$$

2.  $l = 4n + 3$

$$S = 4(\cos l\theta_3 \cdot \cos h\theta_1 - \sin l\theta_3 \cdot \sin h\theta_2)$$

3.  $l = 4n + 2$

$$S = -4\sin l\theta_3(\sin h\theta_1 - \sin h\theta_2)$$

4.  $l = 4n$

$$S = -4\sin l\theta_3(\sin h\theta_1 + \sin h\theta_2)$$

For h even.

1.  $l = 4n + 1$

$$S = -4(\sin l\theta_3 \cdot \sin h\theta_1 - \cos l\theta_3 \cdot \sin h\theta_2)$$

2.  $l = 4n + 3$

$$S = -4(\sin l\theta_3 \cdot \sin h\theta_1 + \cos l\theta_3 \cdot \sin h\theta_2)$$

3.  $l = 4n + 2$

$$S = 4\cos l\theta_3(\cos h\theta_1 - \cos h\theta_2)$$

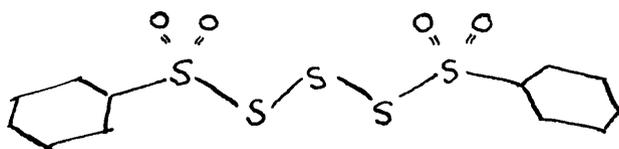
4.  $l = 4n$

$$S = 4\cos l\theta_3(\cos h\theta_1 + \cos h\theta_2)$$

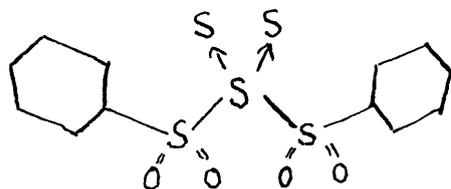
where  $\theta_1 = \frac{2\pi hx}{a}$ ,  $\theta_2 = \frac{2\pi ky}{b}$ , and  $\theta_3 = \frac{2\pi lz}{c}$ . The phase angle is thus 0 or  $180^\circ$  and the sign is + or -.

Structure Analysis.

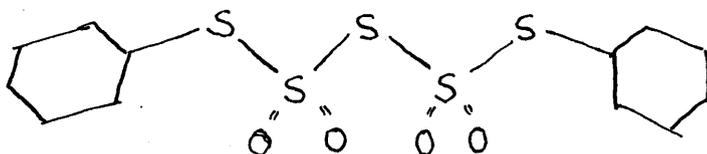
Since there are eight equivalent points in this space group and only four molecules, the molecule must have internal symmetry. It is a diad axis and this symmetry limits the possible structures to the following:



1.



2.



3.

Of these, 3 is the most improbable as it implies a complete movement of the  $\text{SO}_2$  group from the position close to the benzene ring to the second sulphur atom. This is not impossible but should it occur, would more likely lead to a complete breakdown of the initial materials (sodium benzene thiosulphate). Structure 2 will mean two sulphur atoms linked by dative bonds to the central atom and since it is part of the aim of this investigation to determine if this occurs, structures 1 and 2 will be considered as equally probable according to the evidence of space group symmetry.

#### Comparison of Isomorphs.

Since the comparison of the dimensions of the phenyl and p-tolyl isomorphs of the compounds previously studied has been of great use in elucidating the structure, a similar comparison was attempted for the diphenyl and di-p-tolyl disulphonyl trisulphides. From the axial measurements it is noted that the

	a	c
phenyl	7.74	26.3
tolyl	7.70	29.5

only change in the 'c' axis which has expanded 3<sup>o</sup>A. This would indicate that the line through C<sub>1</sub>-C<sub>4</sub> (these atoms being designated as in the benzene rings of previous compounds) most probably lies approximately parallel to the 'c' axis. The length of the 'c' axis would also suggest that the main length of the molecule lies parallel to the 'c' axis.

Further comparison of the zero-layer (hol) moving films of both compounds shows that the two compounds do not bear a close resemblance in their distribution of intensities. This follows from the large number of atoms in the unit cell and the complexity of the geometrical structure factors since the structure amplitude will only be a small proportion of the maximum possible value and any parameter variations will have a corresponding effect on the intensity distribution.

#### Two-crystal Comparison.

Although the intensities of the (hol) planes of the two compounds do not show a close relationship, yet since the extension only occurs along the 'c' axis, it was hoped that by placing the structure amplitudes of the (001) reflections of the two compounds on the same basis, the signs

of some might be fixed. Perutz has used this method for haemoglobin (61) but could have a gradual variation in the axial lengths and so obtain a reasonably smooth curve of variation of  $F$  with change in  $d$  (the plane spacing). For this case there are only two compounds and so only two points in the curve for each plane. The comparable structure factors were obtained from a series of moving films taken on a two-crystal spectrometer which alternately exposed the phenyl and then the tolyl compound to the X-ray beam. The crystals were chosen to be as near as possible the same size. The structure amplitudes were then plotted against  $2 \sin \theta$  and a smooth curve drawn through the points. The points on the curve are, however, too distant to show clearly points of inflection where the continuous function of the structure amplitude crosses the abscissa and changes sign. No evidence was obtained from this comparison.

#### Patterson and Harker Syntheses.

Since comparison of the phenyl and tolyl isomorphs yield little information about the disposition of the molecule, it was necessary to apply to one compound methods which derive the maximum evidence from direct evidence, namely the recorded intensities of the reflections. It is impossible to attempt to deduce this structure by trial and error methods due to the presence of three types of atoms, their number and the complexity of the structure factors.

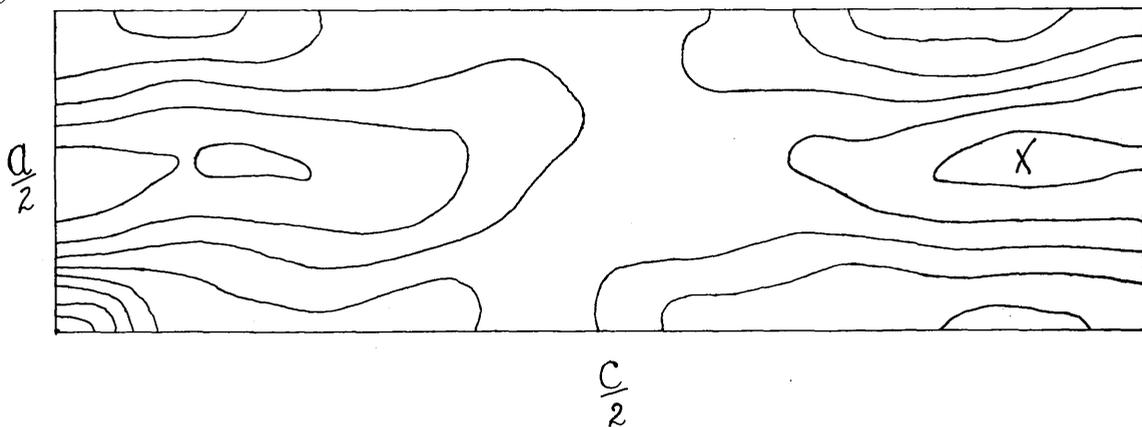


Fig. 11.  
Patterson projection of diphenyl  
disulphonyl trisulphide.

The intensities of the (hol) zero-layer were recorded on a series of moving films and the value of the square of the structure amplitude ( $F^2$ ) obtained. A Fourier synthesis of the  $F^2(\text{hol})$  terms according to Patterson's (13) method was carried out and the result is shown in Fig. 11. Only the portion enclosed by  $\frac{a}{2}$  and  $\frac{c}{2}$  is shown as the other parts are related by planes of symmetry since the crystal system is tetragonal. There will be vectors between sulphur atoms, sulphur and oxygen, and sulphur and carbon. Other vectors will be of very minor importance. Those between sulphur atoms will be largest, being twice the amplitude of sulphur-oxygen and almost three times that due to sulphur-carbon, since the height of the peak (in projection) is proportional to the product of the atomic numbers.

The projection gives no evidence about precise atomic vectors as it is too diffuse, but it shows that the short S-S vectors lie mainly approximately parallel to the 'c' axis and not at a large angle to it as would be the case for structure (2). This is further supported by the ridge at X Fig. 11. which is due to vectors between molecules. There is also a large vector at  $(\frac{a}{2} \frac{c}{20})$  which is probably too large to be intramolecular and is most probably intermolecular. The evidence although not exact enough to fix the molecule in the unit cell does support the chain

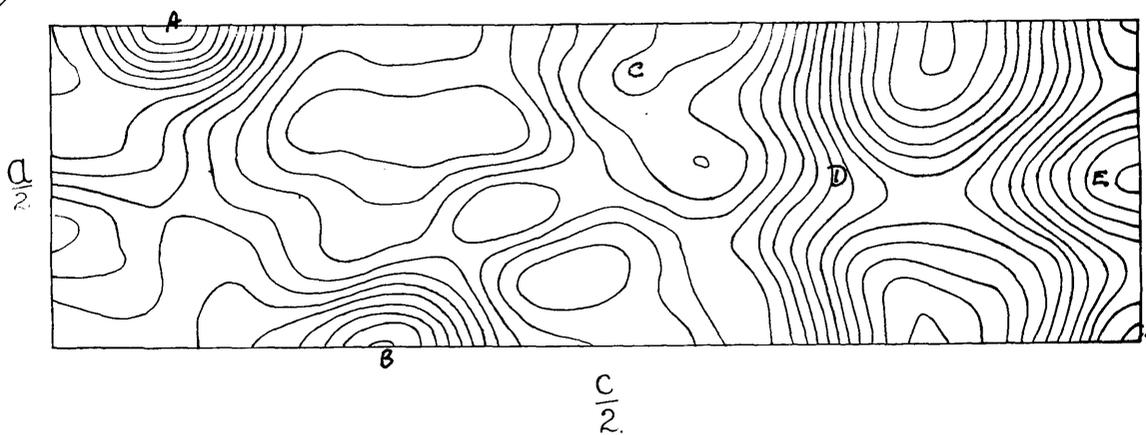


Fig. 12.

Harker projection of diphenyl  
disulphonyl trisulphide.

type of structure (1) and makes structure (2) very unlikely.

To give more precise information as to the disposition of the molecule, mainly the sulphur chain, a Harker (14) synthesis was carried out utilising all  $F^2(hkl)$  terms. These were obtained from intensities of reflections on a series of rotation films. Although the terms are three-dimensional, by using the symmetry of the particular space group, the summation and the projection are two-dimensional. In this case the presence of the diad screw axis along the 'b' axis means that any atom at  $x, y, z$  will be reproduced at  $\bar{x}, \frac{1}{2} + y, \bar{z}$  and the corresponding vector is thus  $2x, \frac{b}{2}, 2z$ . The resultant vector map will therefore show a reproduction of the asymmetric unit, magnified twice, together with other vectors due to positions of high electron density related by the distance  $\frac{b}{2}$  fortuitously. The projection obtained is shown in Fig. 12. There is a basic similarity to the Patterson projection but more detail of vector distribution is revealed.

The important areas of high vector distribution function value are at A, B, C, D and E. The most probable interpretation which has been derived from this projection is that these are due to the S-S vectors produced by the basic space group operations. Since the central S atom

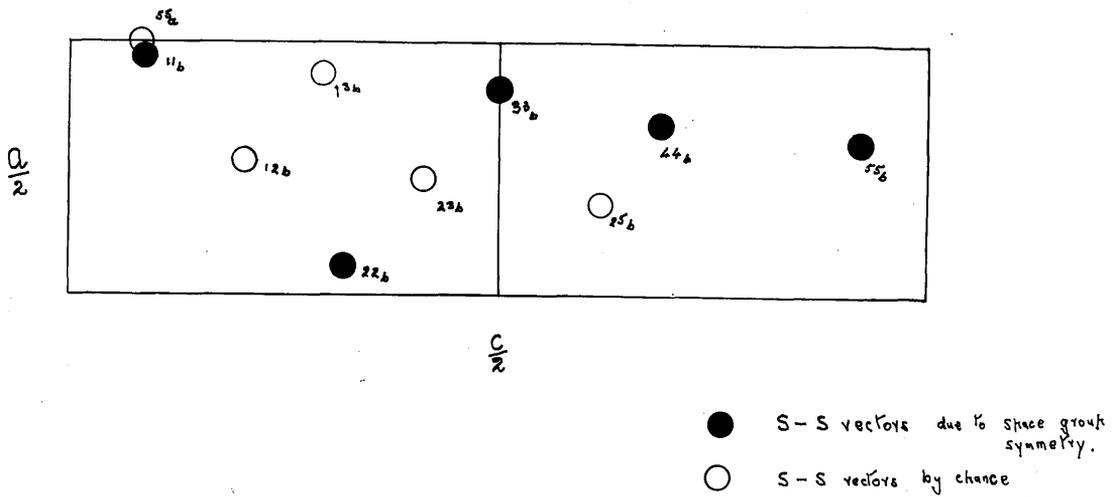


Fig. 13.

Suggested vector map of (h0l) projection  
of diphenyl disulphonyl trisulphide.

has a fixed  $z$  coordinate ( $\frac{c}{8}$ ), there must be a S-S vector at  $\frac{c}{4}$  and although it cannot be precisely located, its most probable position is C. In Fig. 13 is given a reproduction of part of the unit cell with the origin 0, the cell being extended beyond the origin to include the molecule related by the diad axis. In this diagram has been marked the best positions of the sulphur atoms forming the  $S_5$  chain of the compound  $(C_6H_5)_2S_5O_4$  as 1, 2, 3, 4 and 5. Due to the molecular symmetry, 1 and 5, 2 and 4, are related by the diad axis of symmetry which is at  $45^\circ$  to the plane of the paper. Atoms designated  $1_b$  etc. are reproduced by the screw axis through the origin and atoms designated  $1_a$  etc. are produced by the operation of the diad axis at  $\frac{c}{4}$ , lying parallel to the 'a' axis. In Fig. 14 marked by dark circles are shown the vectors  $S_{1.1b}$ ,  $S_{2.2b}$ , etc., these being related by the vector condition  $y = \frac{b}{2}$ , by the space group symmetry. However, in addition, since due to the positions of atom  $S_1$  at  $\frac{a}{4}$  (or very close), atoms  $S_5$  and  $S_{5a}$  will have a vector distance  $y = \frac{b}{2}$  and a vector (shown by a clear circle)  $S_{5.5a}$  will appear. It must be remembered that  $S_1$  and  $S_5$  are related by a diad axis and that the projection down the 'b' axis is similar to that down the 'a' axis with  $S_1$  and  $S_5$  reversed in disposition. Also since  $S_4$  and  $S_5$  have almost the same 'a' coordinate, then  $S_1$  and  $S_2$  will have almost the same  $y$

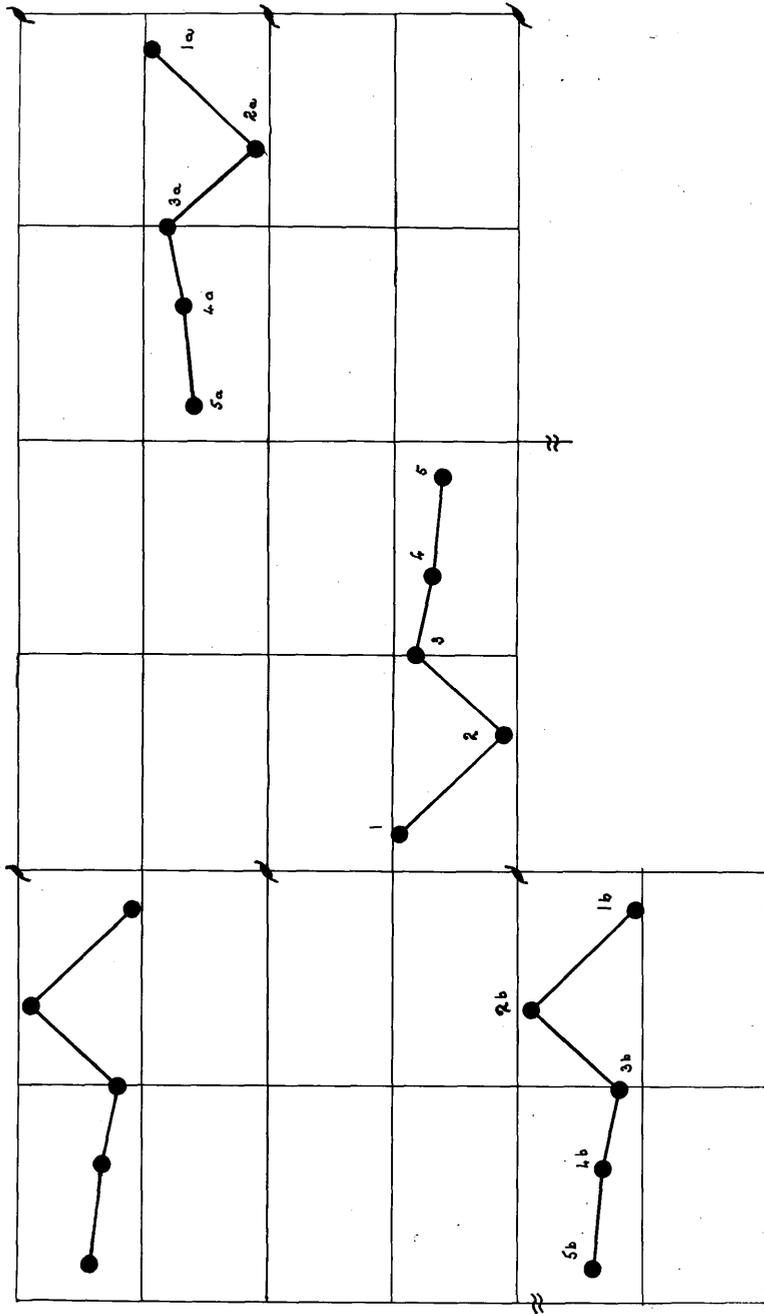


Fig. 14. Proposed position of sulfur chain in (h0l) projection of diphenyl disulphonyl trisulphide.

coordinate and between the portions of high electron density of these two atoms, which are related by the necessary condition, a vector will appear in the Harker projection. This is indicated by the clear circle  $S_{1.2b}$ . Similarly, since  $S_3$  and  $S_4$  have coordinates almost equal, a vector due to  $S_2$  and  $S_{3b}$  appears. Since  $S_3$  and  $S_5$  have also similar x coordinates, there will be electron density sufficiently high and related by the necessary vector condition to yield a vector  $S_{1.3b}$ . And since  $S_1$  and  $S_4$  are similarly related a vector  $S_{2.5b}$ . This interpretation of the Harker projection fits the main distribution of the vector map but does not lead to a decision as to the oxygen positions since these will be determined by O-O vectors which will only have a peak value  $\frac{1}{4}$  of the peak value of a S-S vector. Vectors due to fortuitous relationship of sulphur and oxygen atoms will be of greater importance since the peak value will be only half that of a S-S vector. However, the numbers of chance S-O and S-C vectors are too large to possibly yield a satisfactory interpretation since the major vector peaks have received explanation and other vectors will produce only the minor contour variations. Unfortunately little can be decided as to the position of the benzene ring.

Other interpretations of the vector map were attempted but the above was the only one which yields

reasonable atomic positions and distances, when average S-S bond distances and S-S-S bond angles are used.

### Trial Structure and Fourier.

With the approximate positions of the sulphur atoms, as deduced from the Harker projection, structure amplitudes ( $F$ ) were calculated for various models of structures (1) and (3) with the benzene ring in different dispositions and tilts. A wire model was used as a guide in maintaining the bond angles approximately normal. There are many variables - since the S-SO<sub>2</sub> bond is a single bond, rotation can occur around it, and the tilt of the benzene ring also can take up all positions. Further, the position of the oxygen atoms cannot be determined from the Harker projection. The only limits which were considered, were that the introduction of the p-methyl group in the tolyl isomorph causes expansion along the 'c' axis and not the 'a' axis, and from the analysis of the diphenyldisulphonyl sulphide, large partial charges on the oxygens of the SO<sub>2</sub> group causes induced charges in the benzene ring which seems important in intermolecular binding. The crystals of this compound are harder than those of the monosulphide but have a similar melting point and it is probable that the type of bonding is similar. For the calculation of structure amplitudes, it is to be noted that all three parameters

for each atom of the asymmetric unit have to be used in the calculation of the geometrical structure factor and a separate scattering factor for each type of atom.

To test the correctness of the trial structures attempted, the structure amplitudes (00ℓ), (10ℓ) and (20ℓ) were calculated for each one, but no structure showed sufficient correlation with the observed values to warrant continuation.

Finally, since none showed clear indication of being the correct structure, the signs of the structure factors were fixed using only the sulphur atoms. The Fourier was carried out by the normal summation method but the result was still lacking in clear resolution of the other atoms. The sulphur atoms have not a sufficiently high atomic number ( $5 \times 16 = 80$ ) to outweigh the other atoms

( $4 \times 8 + 12 \times 6 = 104$ ) and hence the signs of important planes are not all fixed by this method. The resultant Fourier unfortunately is not of great use and does not reveal the positions of the oxygen atoms and the benzene ring.

Crystal Structure of Di-p-tolyldisulphonyl Trisulphide.

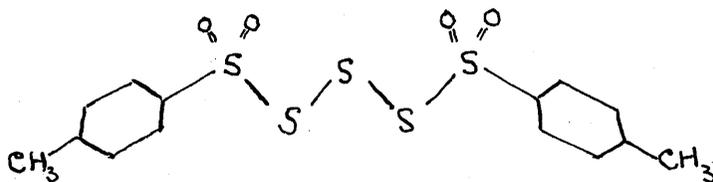
Crystal Data.

Di-p-tolyldisulphonyl trisulphide,  $C_{14}H_{14}S_5O_4$ :  
 M, 406.4. m.p.  $180^\circ$ . d. calc. 1.528, found 1.547:  
 tetragonal (trapezohedral)  $a = 7.70 \pm 0.02$ ,  $c = 29.50 \pm 0.06$ :  
 Absent spectra, (hol) for  $h = 2n$ , (00l) for  $l = 4n$ .  
 Molecular symmetry - diad axis. Four molecules per unit  
 cell. Volume of unit cell =  $1575 \text{ \AA}^3$ . Absorption co-  
 efficient for X-rays,  $\lambda = 1.54$ ,  $\mu = 60.3$  per cm.  
 Total number of electrons per unit cell = 840 =  $F(000)$ .

Structure Analysis.

The conclusions, regarding the phenyl compound, arrived at by a comparison of dimensions of the two isomorphs and the Patterson and Harker projections, apply equally to the tolyl compound. The main length of the molecule lies along the 'c' axis and the sulphur atoms are grouped as a chain, linked by single bonds. However, the distribution of (hol) intensities is modified a great deal and the introduction of the para-methyl group, although it extends the 'c' axis, and does not affect the 'a' axis, does alter markedly the (hoo) as well as the (00l) series. The (200), (400) and (600) intensities are, on an arbitrary scale, 90, 5.5, 4, whereas, on approximately the same scale,

the corresponding values for the phenyl compound are 7, 2, 0. This indicates that the disposition perpendicular to 'a' has been modified and for such a large change the sulphur chain must be assumed to have shifted bodily or changed its general tilt. It is probable that introducing the p-methyl group has reacted on the  $\text{SO}_2$  group and caused a redistribution of relative sulphur dispositions. Since the crystal system is tetragonal, this change has not modified the 'a' axis but within the dimensional limits, the molecule has redispersed itself to maintain similar packing as it may be seen that the densities of the two compounds are very similar. It is the possibility of limited rotation within the sulphur chain which has, for these compounds, prevented the close comparison possible for the simpler members previously discussed. It may be concluded that the structure of the tolyl compound is as the phenyl one.



### Experimental.

#### Diphenyl $\alpha\alpha'$ -Disulphone.

By slow cooling of a solution of glacial acetic acid, good crystals were obtained with the (100), (010), (001), and (110) faces well developed.

#### Determination of Cell Constants and Space Group.

The axial lengths were determined from rotation films, the crystals being set by optical reflections. Oscillation photographs were taken to find out if any symmetry was shown but with negative results. Accordingly the crystal system was assumed triclinic and six parameters had to be obtained to define the unit cell. For each axis measured, a corresponding zero-layer moving film Weissenberg photograph was taken. From the rotation films 'a', 'b' and 'c' were determined and from the moving films, since each zero-layer contains two reciprocal axes, each of which is shown on one of the other films, the values of  $a^*$ ,  $b^*$  and  $c^*$  could be very accurately measured since several orders appear.  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$  were also measured from the moving films. The accuracy of measurement of angles on the moving films is not very high but these angles, having been identified for the crystal, were then accurately measured on an optical goniometer.

The angles of the reciprocal lattice  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$  were utilised to calculate the direct angles  $\alpha$ ,  $\beta$  and  $\gamma$ , using the formula

$$\cot \frac{\alpha}{2} = \sqrt{\frac{\sin(\sigma^* - \beta^*) \times \sin(\sigma^* - \gamma^*)}{\sin \sigma^* \times \sin(\sigma^* - \alpha^*)}}$$

$$\text{where } \sigma^* = \frac{\alpha^* + \beta^* + \gamma^*}{2}$$

As a check  $a^*$ ,  $b^*$  and  $c^*$  were calculated from these direct values 'a', 'b', 'c',  $\alpha$ ,  $\beta$ , and  $\gamma$  with agreement within 0.4%.

The moving films were indexed, using the reciprocal lattice and the reflecting circle, but no regular halvings appear. The space group is therefore P1 or  $P\bar{1}$ .

To determine if the space group is centrosymmetric or not, crystals of diphenyl  $\alpha$ '-disulphone were tested for piezo-electric effect by introducing them into a sensitive electronic circuit prone to oscillation and used as the crystal of an oscillator. However, the result was negative. No sign of polarity in the molecule was apparent. Tests were also carried out for pyro-electric effect by suspending the crystal on a fine thread and dipping slowly below the surface of liquid air and close to a thin sheet of metal also dipping into the liquid air. The temperature gradient so set up in the crystal, if non-centrosymmetrical, should produce a charge distribution which should attract

the crystal to the metal foil. This experiment showed also negative, but is somewhat unsatisfactory due to the surface tension of the liquid air. However, the evidence seems to point to the space group  $P\bar{1}$  and that was provisionally chosen.

The density was measured in a strong solution of potassium iodide and the measured value, 1.482, is in good agreement with that required by one molecule in the unit cell, 1.472.

Di-p-tolyl aa'-Disulphone.

The crystals were grown from a solution in glacial acetic acid by slow cooling. They are well formed small prisms, showing the following faces (100), (010), (001), (101) and (110).

Determination of Cell Constants and Space Group.

Axial lengths were determined from rotation photographs and oscillation films showed no indication of any symmetry. The crystal system was therefore assumed triclinic and six parameters had to be obtained to define the unit cell. For each axial length determined a corresponding zero-layer moving film was taken. Then in each moving film there are two reciprocal axes each of which appears on one other film. The angles  $\alpha^*$ ,  $\beta^*$  and  $\gamma^*$  can also be measured on the Weissenberg films. These angles were more accurately determined by measurement on an optical goniometer and from the reciprocal angles, the direct angles can be calculated by the formula

$$\cot \frac{\alpha}{2} = \sqrt{\frac{\sin(\sigma^* - \beta^*) \times \sin(\sigma^* - \gamma^*)}{\sin \sigma^* \times \sin(\sigma^* - \alpha^*)}}$$

$$\text{where } \sigma^* = \frac{\alpha^* + \beta^* + \gamma^*}{2}$$

The values of the reciprocal axes  $a^*$ ,  $b^*$  and  $c^*$  were calculated accurately by measuring the values of the various axial orders on the moving films. The values of  $a^*$ ,  $b^*$

and  $c^*$  were calculated from 'a', 'b', 'c',  $\alpha$ ,  $\beta$  and  $\gamma$  and corresponded with the calculated values to within 0.4%.

The moving films were indexed using the reciprocal lattice and the reflecting circle and no systematic halvings were found. The space group must be therefore  $P1$  or  $P\bar{1}$ .

The X-ray information cannot decide between these two space groups and further experiment is necessary to determine the choice. Piezo and pyro-electric effects give an indication as to the asymmetry in a space group, but they are not positive in their results. Thus, if no effect is observed, it cannot be concluded that the space group is centrosymmetric, but that it may be. If, however, a positive is obtained, the space group must be non-centrosymmetric.

For di-p-tolyl disulphone, the tests for piezo- and pyro-electro effects were applied as for the phenyl compound but no positive results were obtained for either. It is therefore probable that the compound has a centre of symmetry and the space group is  $P\bar{1}$ .

The density of the compound was obtained by flotation at 20°C in a strong solution of potassium iodide. The measured value, 1.422, is in reasonable agreement with the value, 1.409, calculated for one molecule in the unit cell.

### Diphenyl Disulphonyl Sulphide.

By slow cooling of a solution in glacial acetic acid, crystals were obtained showing well developed (001) and (100) faces.

### Determination of Cell Dimensions and Space Group.

Cu K $\alpha$  radiation was employed for all measurements. Diphenyl disulphonyl sulphide was described by Groth (62) as orthorhombic, but no evidence of symmetry corresponding to this crystal system was found. Oscillation films taken on the long axis of the crystal showed planar symmetry, but there is none in the (hol) zero-layer moving film. The axes 'a' and 'c' are equal within the limit of accuracy  $\pm 0.06^\circ\text{A}$  and this accounts for the interpretation of the earlier crystallographic results. The ratio of axes given by Groth is

$$A : b : C = 2.357 : 1 : 1.564.$$

The results obtained from the X-ray data converting to Groth's axes are

$$\overline{a + c} : b : \overline{a - c} = 2.355 : 1 : 1.562.$$

Rotation, oscillation and zero-layer Weissenberg films were used, the former for determining axial lengths, the latter two for indexing general (hkl) reflections and for intensity records. The reflections were indexed by the use of the corresponding reciprocal lattice and Bernal's construction of the reflecting circle. The missing spectra indicate the

possible space groups  $Aa$  and  $A2/a$ . Pyro-electric measurements showed no evidence of polarity and so the space group of higher symmetry  $A2/a$  was accepted for the preliminary trials for a possible structure. Complete analysis confirmed this space group.

Density measurements were carried out by flotation in a strong solution of silver nitrate at  $20^{\circ}$ . There was no interaction between the compound and the solution. The measured value, 1.583, is in good agreement with the calculated value for 4 molecules in the unit cell, 1.587.

#### Measurement of Intensities.

All three zones (okl), (hol) and (hko) were studied by taking moving films of the zero layers of the rotations about the 'a', 'b' and 'c' axes. The multiple film technique was used to correlate the very strong and weak reflections, and the total range of intensities was about 1,000 to 1. The intensities were estimated visually and, after correction for Lorentz and polarisation factors, the observed structure amplitudes,  $F$ , were placed on an absolute scale with the calculated values.

The crystal specimens were small and completely bathed in the X-ray beam. For the (hol) zone, a crystal was selected of dimensions 0.26 mm. x 0.26 mm. and 0.65 mm. in length along the 'b' axis. The crystal for the (okl) zero-layer was cut from a larger lathe-like crystal. In

cross-section, it was 0.45 mm. x 0.50 mm., and was 0.25 mm. in length along the a axis. The crystal for the (hko) series was also cut to a cross-section of 0.18 mm. x 0.42 mm. and 0.58 mm. long. The crystals were selected and cut so that correction for absorption was not necessary. Since the absorption coefficient is so high,  $\mu = 53.3$  per cm., the approximate method of assessing absorption would not give any greater accuracy of estimating intensities and might well introduce additional errors.

#### Fourier Analysis.

For the preliminary Fourier summation the electron density on the ac plane was computed at 450 points in the asymmetric unit, from the series

$$\rho(x,z) = \frac{1}{ac \sin\beta} \sum_h^{+\infty} \sum_e^{+\infty} F(h0l) \cos 2\pi\left(\frac{hx}{a} + \frac{lz}{c}\right)$$

Both the 'a' and the 'c' axes were subdivided into 60 parts, the intervals along 'a' and 'c' being  $0.265^{\circ}\text{A}$  and the summation was carried out by means of three-figure strips (34). The position of the contour lines was obtained by graphical interpolation from the summation totals by making sections of the rows and columns. 101 of a total possible 154 terms were included and later some small terms were added and a total of 117 were utilised in the final Fourier.

The final Fourier summation was made for 900 points in the asymmetric unit. The 'a' axis was subdivided into 60 parts and the 'c' axis into 120 parts, the intervals

being, along 'a'  $0.265^{\circ}\text{A}$  and along 'c',  $0.132^{\circ}\text{A}$ . The resulting contour map is shown in Fig. . The carbon and oxygen atom contours are for each unit electron level, whereas sulphur is drawn for each two electron level. The two electron level is dotted. The whole molecule Fig. 7a was traced from the Fourier projection but at only 2-electron levels for carbon and oxygen and at each 4-electron level for sulphur.

#### Calculation of Orientation.

The tilt of the line  $C_1-C_4$  to the (010) plane is calculable both from the (x,y,z) coordinates for the two atoms and from the projection angle of the line  $C_1-C_4$  and the line  $C_2-C_6$ . The projection angle of the line  $C_1-C_4$  to the 'c' axis was measured and from the results the orientation of M to 'a', 'b' and 'c' axes  $\chi_M$ ,  $\psi_M$  and  $\omega_M$  can be calculated.

From the tilt of  $C_2-C_6$  to the (010) plane and the projection angle to the a" axis, the orientation of L with respect to the 'a', 'b' and 'c' axes,  $\chi_L$ ,  $\psi_L$  and  $\omega_L$ , can be calculated.

From these six values, the other three quantities may be calculated from the following equations†

$$\begin{array}{l}
 1) \quad \cos^2 \chi_L \quad + \cos^2 \psi_L \quad + \cos^2 \omega_L \quad = 1 \\
 2) \quad \cos^2 \chi_M \quad + \cos^2 \psi_M \quad + \cos^2 \omega_M \quad = 1 \\
 3) \quad \cos^2 \chi_N \quad + \cos^2 \psi_N \quad + \cos^2 \omega_N \quad = 1
 \end{array}$$

$$4) \cos \chi_L \cos \chi_M + \cos \psi_L \cos \psi_M + \cos \omega_L \cos \omega_M = 0$$

$$5) \cos \chi_M \cos \chi_N + \cos \psi_M \cos \psi_N + \cos \omega_M \cos \omega_N = 0$$

$$6) \cos \chi_N \cos \chi_L + \cos \psi_N \cos \psi_L + \cos \omega_N \cos \omega_L = 0.$$

The results of the calculations are shown in Table I.

The complete orientation of the benzene ring is so defined.

The bond distances and angles of the remainder of the molecule were determined by converting the crystal axes to the rectangular axes  $b$ ,  $c$  and ' $a^1$ ' at right angles to these. The bond distances were then calculated by the normal procedure

$$d^2 = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}$$

The bond angles were determined by calculating all three interatomic distances for the three atoms concerned and then calculating the angle.

#### Coordinates of Atoms, Scattering Curves and Structure Factors.

The atomic coordinates were determined from the projection maps for the (hol) and (okl) zones. For the carbon parameters in the (hol) projection, the positions were chosen for a hexagon model which gave the closest fit to the contours of the map. In the case of the  $O_2$  the diffraction effect due to the two sulphur atoms must be taken into consideration since it tends to mislead by shifting the lower contour levels of this atom. Diffraction effects generally are most important here and so the higher levels

are more useful in fixing the atomic positions. The diffraction effect of the sulphur atom probably also produces the lower contour level between  $S_2$  and  $O_1$  and the resulting oval contour of  $O_1$ .

The coordinates of Table II were used for the final calculation of structure factors of zonal planes (hol), (okl) and (hlo). For the calculation of structure factors separate scattering curves for sulphur, oxygen and carbon were used. The carbon curve was that used for anthracene (11) and that for oxygen was obtained by scaling the carbon scattering curve for the atomic number of oxygen. The scattering curve of sulphur was obtained by correlation between the calculated and observed structure factors.

The final discrepancy for the (hol) zone was 19.0% and for all reflections 18.5%.

Table 5.

Measured and calculated values of the structure amplitude for  
diphenyl disulphonyl sulphide.

hkl	sin $\theta$ ( $\lambda = 1.54$ )	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
1400	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
0010	0.527	28	-27
0012	0.633	< 11	+6
0014	0.738	< 11	+4
0016	0.844	< 10	-7
0018	0.949	25	+20
020	0.279	54	+40
040	0.558	73	-67
060	0.837x	8	+2
20 $\overline{18}$	0.915	9	+2
20 $\overline{16}$	0.812	21	-18
20 $\overline{14}$	0.705	46	+44
20 $\overline{12}$	0.602	22	-24
20 $\overline{10}$	0.497	14	+21
20 $\overline{8}$	0.395	114	-112
20 $\overline{6}$	0.295	111	+108
20 $\overline{4}$	0.200	176	-203
20 $\overline{2}$	0.120	28	+34
202	0.125	56	+77
204	0.267	52	+57
206	0.368	18	-9
208	0.470	31	+29
2010	0.573	10	-2
2012	0.676	23	+15
2014	0.781	< 11	-1
2016	0.885	< 9	-5
2018	0.990	13	+24
40 $\overline{18}$	0.892	35	-40
40 $\overline{16}$	0.791	22	+24
40 $\overline{14}$	0.690	39	-40
40 $\overline{12}$	0.589	67	+58
40 $\overline{10}$	0.490	49	-40

hkl	$\sin \theta$ ( $\lambda = 1.54$ )	F, meas.	F, calc.
408	0.396	88	+72
406	0.310	114	-103
404	0.240	< 6	+4
402	0.200	30	+30
402	0.267	15	+19
404	0.349	21	-10
406	0.442	21	-31
408	0.535	< 10	+12
4010	0.635	31	-29
4012	0.737	12	+15
4014	0.838	35	-31
4016	0.942	29	+40
6020	0.985	22	-40
6018	0.832	23	+33
6016	0.786	27	-27
6014	0.690	< 11	+7
6012	0.596	22	-24
6010	0.506	13	+12
608	0.437	63	+47
606	0.360	47	-28
604	0.312	27	+31
602	0.295	< 7	-2
602	0.368	< 8	+12
604	0.442	17	-34
606	0.526	52	+46
608	0.614	75	-65
6010	0.708	72	+58
6012	0.805	57	-55
6014	0.904	< 8	+10
8020	0.980	< 7	+11
8018	0.885	< 9	+4
8016	0.795	< 11	+3
8014	0.702	11	+16
8012	0.620	16	-17
8010	0.543	25	+19
808	0.477	9	+1
806	0.427	< 8	+7
804	0.402	62	+50
802	0.400	51	-50
802	0.470	80	-82
804	0.535	112	+99
806	0.615	62	-45
808	0.697	39	+34
8010	0.786	< 11	+2
8012	0.879	13	+20
8014	0.975	< 7	-5
10,020	0.990	13	+15
10,018	0.900	12	-18
10,016	0.816	< 11	+12
10,014	0.736	< 11	+3

hkl	$\sin \theta (\lambda = 1.54)$	F, meas.	F, calc.
10,0 $\overline{12}$	0.660	50	-37
10,0 $\overline{10}$	0.596	68	+58
10,0 $\overline{8}$	0.542	49	-40
10,0 $\overline{6}$	0.507	47	+42
10,0 $\overline{4}$	0.492	27	-30
10,0 $\overline{2}$	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
10,010	0.872	32	-19
10,0 $\overline{12}$	0.962	22	+19
12,0 $\overline{18}$	0.929	27	-26
12,0 $\overline{16}$	0.850	34	+33
12,0 $\overline{14}$	0.778	44	-48
12,0 $\overline{12}$	0.715	23	+25
12,0 $\overline{10}$	0.660	71	-65
12,0 $\overline{8}$	0.620	38	+38
12,0 $\overline{6}$	0.596	57	-49
12,0 $\overline{4}$	0.589	26	+28
12,0 $\overline{2}$	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
12,010	0.960	<7	-11
14,0 $\overline{18}$	0.965	39	+51
14,0 $\overline{16}$	0.896	30	-39
14,0 $\overline{14}$	0.835	29	+35
14,0 $\overline{12}$	0.778	<11	0
14,0 $\overline{10}$	0.736	16	-8
14,0 $\overline{8}$	0.702	32	-31
14,0 $\overline{6}$	0.690	<11	+9
14,0 $\overline{4}$	0.690	<11	-8
14,0 $\overline{2}$	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 $\overline{16}$	0.955	<7	0
16,0 $\overline{14}$	0.896	<9	+6
16,0 $\overline{12}$	0.850	20	+16
16,0 $\overline{10}$	0.816	26	+24
16,0 $\overline{8}$	0.795	11	-10
16,0 $\overline{6}$	0.786	11	+15
16,0 $\overline{4}$	0.791	<11	-2
16,0 $\overline{2}$	0.812	21	-11
16,02	0.886	31	-36
16,04	0.942	29	+40
18,0 $\overline{14}$	0.965	<7	-12
18,012	0.929	7	-8

hkl	$\sin \theta$ ( $\lambda = 1.54$ )	F, meas.	F, calc.
18,0 $\overline{10}$	0.900	17	+16
18,0 $\overline{8}$	0.885	< 9	-3
18,0 $\overline{6}$	0.882	18	+23
18,0 $\overline{4}$	0.892	20	-26
18,0 $\overline{2}$	0.915	28	+42
18,0 $\overline{2}$	0.987	18	+40
20,0 $\overline{12}$	0.995	8	+18
20,0 $\overline{10}$	0.990	23	-42
20,0 $\overline{8}$	0.980	26	+36
20,0 $\overline{6}$	0.985	22	-38
20,0 $\overline{4}$	0.995	8	+24
120	0.295	40	+22
220	0.302	41	+30
320	0.317	67	-60
420	0.350	16	+12
520	0.381	67	+65
620	0.422	51	-50
720	0.462	27	+18
820	0.507	34	+30
920	0.550	28	-26
10,20	0.597	< 19	+14
11,20	0.645	54	-47
12,20	0.690	< 20	+22
13,20	0.740	59	+54
14,20	0.789	< 19	+10
15,20	0.842	< 17	-12
16,20	0.888	< 16	+2
17,20	0.945	17	-15
18,20	0.990	< 8	-11
140	0.560	< 18	+10
240	0.565	57	+50
340	0.577	< 18	+11
440	0.595	26	+29
540	0.615	30	+31
640	0.640	34	-38
740	0.665	< 20	-16
840	0.698	44	-53
940	0.733	< 20	-9
10,40	0.769	48	+48
11,40	0.802	< 19	0
12,40	0.840	< 17	+6
13,40	0.880	< 16	+7
14,40	0.925	< 14	-6
15,40	0.963	< 10	-12
160	0.840	< 17	+5
260	0.842	< 17	+9
360	0.851	24	+32
460	0.862	< 16	-13
560	0.877	< 16	-20
660	0.893	< 16	-2

hkl	$\sin \theta$ ( = 1.54)	F, meas.	F, calc.
760	0.917	<14	0
860	0.937	<13	-13
960	0.967	<10	+5
10,60	0.990	< 8	+10
011	0.149	100	-98
013	0.210	<4	0
015	0.298	5	+6
017	0.395	36	-42
019	0.497	22	+16
01,11	0.610	43	-35
01,13	0.700	16	+16
01,15	0.818	18	-20
01,17	0.910	17	+22
022	0.302	21	-18
024	0.350	24	-18
026	0.422	13	-17
028	0.507	<7	-9
02,10	0.597	34	-29
02,12	0.690	<9	0
02,14	0.789	8	+6
02,16	0.888	7	-4
02,18	0.990	< 4	0
031	0.422	16	-12
033	0.447	6	+6
035	0.495	21	-19
037	0.560	<8	-7
039	0.635	25	+22
03,11	0.720	31	-36
03,13	0.805	42	+36
03,15	0.897	19	-23
03,17	0.990	26	+31
042	0.565	66	+65
044	0.595	54	+45
046	0.640	35	+27
048	0.698	9	-15
0410	0.769	<8	0
0412	0.840	8	+12
0414	0.925	<6	+5
051	0.702	36	+41
053	0.715	<9	-5
055	0.746	14	-12
057	0.790	11	+14
059	0.845	< 8	+2
0511	0.910	<7	+2
0513	0.980	<4	-5
062	0.842	7	+12
064	0.862	13	-21
066	0.893	12	+18
068	0.937	<6	-13
0610	0.990	<4	+2

Di-p-tolyl Disulphonyl Sulphide.

The crystals were grown from a solution in glacial acetic acid by slow cooling. The (100) and (001) faces are well developed.

Determination of Cell Dimensions and Space Group.

Oscillation films about the 'b' axis displayed a plane of symmetry perpendicular to the 'b' axis but no other symmetry was noted. The crystal therefore belongs to the monoclinic system. The other axes were determined from rotation films, the crystals being set by utilising the available developed faces.

Groth (62) from optical data, gives the axial ratios as

$$a : b : c = 2.8289 : 1 : 3.2212$$

From the values measured from X-ray data, the ratio is

$$a : b : c = 2.820 : 1 : 3.227$$

Moving films were taken for each of the principal zones (hko), (hol) and (okl) and by indexing these with the reciprocal lattice and Bernal's construction of the reflecting circle, the systematic extinctions can be determined.

The extinctions fix the choice of the space group as Aa or A2/a and from piezo- and pyro-electric measurements on the crystals, the results of which were negative, it would appear that the space group is A2/a. That the compound is isomorphous with the phenyl compound is apparent

from the close similarity in the distribution of the intensities of reflections in the principal zones (hol) and (hko). Due to the expansion of the 'c' axis the similarity in the (okl) is not so apparent.

The density of the compound was determined by flotation in a strong solution of potassium iodide at 20° and the observed value 1.167 is in good agreement with that calculated for four molecules in the unit cell 1.161.

Diphenyl Disulphonyl Trisulphide.

The crystals were obtained by slow recrystallisation from glacial acetic acid. They are beautiful small bi-pyramids showing well formed (101) faces.

Determination of Cell Constants and Space Group.

The axial lengths 'a' and 'c' were determined from rotation films and the axial ratio is  $a : c = 1 : 3.3966$ . Groth (62) gives the ratio as  $a : c = 1 : 2.3834$ , but this is because his 'a' axis is the (110) axis in the new unit cell. For this ratio, the X-ray data gives

$$c : (110) = 1 : 2.4008.$$

The agreement is reasonable, but the ratio is probably too large for the determination by optical crystallographic means to be very accurate.

The four-fold symmetry was checked by taking a Laue photograph with the direct beam passing down the 'c' axis. A zero layer (hol) moving film was taken and also a series of  $15^\circ$  oscillation films about the 'c' axis. These, on indexing by Bernal's method showed systematic extinction, namely, quartering on the 'c' axis and halving on the 'a' axis. The space group is therefore  $P4_12_1$ . It could be also  $P4_32_1$ , but these are indistinguishable by the X-ray data and even for a complete analysis would give the same structural dimensions. The only difference would be the disposition around the four-fold axis.

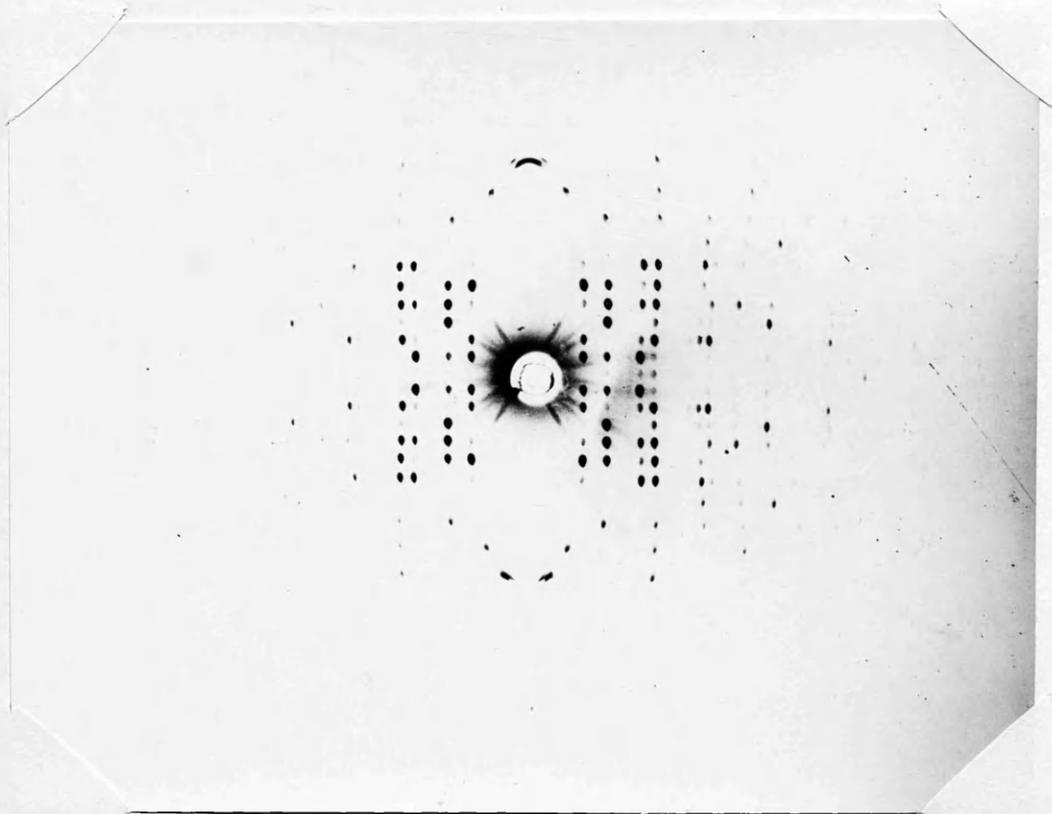


Fig. 15.

'c' rotation film of diphenyl  
disulphonyl trisulphide.

The density of the compound was obtained by flotation in a solution of potassium iodide at  $20^{\circ}$  and the measured value 1.582 agrees well with the value calculated for four molecules 1.584.

#### Measurement of Intensities.

For the (hol) zone, the reflections were recorded on a zero-layer Weissenberg film. The camera in this case was of diameter 4.96 cm, larger than normal, in order to separate clearly the reflections which lie close together because of the long 'c' axis. The strong and very weak intensities were correlated by using the multiple film technique. After correction for Lorentz and polarisation factors the relative structure amplitudes were obtained.

For the (hkl) general structure amplitudes, use was made of the short 'a' and 'b' axes. When a crystal is rotated about the 'c' axis the reflections not only fall into layer lines but also, up to a certain limit, clearly into row lines, as shown in Fig. 15. Thus indices up to a limit of  $2 \sin \theta$  about 1.4 ( $\lambda = 1.54^{\circ}\text{A}$ ) can be easily and correctly assigned from the rotation film. The only overlap occurring is where indices have  $(h_1^2 + k_1^2) = (h_2^2 + k_2^2)$ . However, from correlation with the zero layer (hol) intensities, due allowance can be made and the separate intensities assessed. A small crystal was mounted on the 'c' axis. Three films were loaded simultaneously and exposure was made

in the usual rotation camera. Another set was exposed for a shorter time in the same fashion and from these two sets of multiple films the intensities of all reflections were correlated. As well as Lorentz and polarisation factors, account must be taken both of the geometrical factor (35) which corrects for the slower rotation of planes in the higher layers and the multiplicity of planes giving each reflection. After all these corrections have been applied, the relative structure factors were obtained.

#### Two-crystal Moving Film.

In an attempt to correlate the structure amplitudes for the (001) series of both the diphenyl and the di-p-tolyl disulphonyl trisulphide, a moving film on which was recorded part of the zero-layers (including the (001) series) of both crystals was taken.

A crystal of each of the compounds was selected of approximately the same dimensions and mounted on either arc-holder on two-crystal Weissenberg type camera. Then as the crystals rotate, each is moved into the X-ray beam alternately and under these conditions, the intensities will be proportional to the volume of the crystal and the structure amplitude. Since the crystals were chosen to have approximately the same volume, the intensities will be on the same scale and the structure factors  $F(001)$  can be compared.

Patterson and Harker Synthesis.

The vector distribution of the Patterson function  $A(u,v,w)$  was calculated at 450 points in the asymmetric unit for the series

$$A(u,0,w) = \frac{1}{A^2} \sum_h^{+\infty} \sum_l^{+\infty} F^2(h0l) \cdot \cos 2\pi \left( \frac{hu}{a} + \frac{lw}{c} \right)$$

The 'a' axis was divided into 30 parts, each interval being  $0.257^\circ A$ , the 'c' axis into 60 parts, the intervals being  $0.439^\circ A$ . The summation was carried out using three figure strips (34). The positions of the contour lines were obtained by graphical interpolation from the summation totals by making sections of rows and columns. The contour map is shown in Fig. 11.

Since the Patterson projection yielded little of value, a Harker Fourier summation was carried out using all (hkl) functions  $F^2(hkl)$ . These were obtained from the series of rotation films. In the Harker synthesis, use is made of symmetry elements inherent in the space group to combine all  $F^2(hkl)$  terms and yet only carry out a two dimensional summation. In this projection down the 'b' axis use is made of the  $2_1$  axis down the crystal axis to combine terms such that only vectors between atoms separated by a y coordinate of  $\frac{b}{2}$  appear in the projection.

The function  $A(u, \frac{b}{2}, w)$  was computed at 450 points in the asymmetric unit from the series

$$A(u, \frac{1}{2}, w) = \frac{1}{V^2} \sum_h^{+\infty} \sum_l^{+\infty} \left[ \sum_k^{+\infty} (-1)^k \cdot F(hkl) \right] \cos 2\pi \left( \frac{hu}{a} + \frac{lw}{c} \right)$$

The 'a' axis and the 'c' were divided as for the Patterson projection, the intervals being  $0.257^\circ$  and  $0.438^\circ \text{A}$ . The contour lines were fixed by the same method as given before. The resulting contour diagram is shown in Fig. 12.

### Fourier Analysis.

The electron density on the ac plane was computed at 900 points on the assymmetric unit from the series

$$\rho(x, y) = \frac{1}{ac} \sum_h^{+\infty} \sum_l^{+\infty} F(h0l) \cdot \cos 2\pi \left( \frac{hx}{a} + \frac{ly}{c} \right)$$

The 'a' axis was subdivided into 30 points, the intervals along 'a' being  $0.257^\circ \text{A}$ , along the 'c' axis which was divided into 120 parts, being  $0.2195^\circ \text{A}$ . The summation was carried out with three-figure strips at  $3^\circ$  intervals for the preliminary summation on a new computing device. The positions of the contour lines were obtained by the usual procedure.

### Di-p-tolyl Disulphonyl Trisulphide

The crystals were obtained by slow cooling from a solution in glacial acetic acid. They are very beautiful small bipyramids, showing well formed (101) faces.

### Determination of Cell Constants and Space Group.

The axial lengths and  $c$  were determined from rotation films and the axial ratio is  $a : c = 1 : 3.831$ . Groth (62) gives the axial ratio from optical data as  $a : c = 1 : 2.6905$ . The corresponding axial ratio from the X-ray data is

$$\overline{a + b} : c = 1 : 2.709$$

Fourfold symmetry was shown by taking a Laue photograph with the 'c' axis parallel to the beam. Indexing of rotation films and an (hol) zone from a Weissenberg film by Bernal's reflecting circle and the reciprocal lattice showed only systematic extinction in the 'a' and 'c' axes where reflections appear only for  $h = 2n$  and  $l = 4n$ .

The space group is therefore  $P4_1 2_1 1$ .

The density was determined by flotation in potassium iodide and the value found 1.547 agrees well with the value calculated for four molecules, 1.528.

### Measurement of Intensities.

The intensities of reflections in the (hol) zone were evaluated from a series of moving films. The multiple film technique was used to correlate the intensities which were estimated visually.

Preparations.

Diphenyl  $\alpha\alpha'$ -Disulphone.

Sodium benzene sulphinate was prepared by reacting benzene sulphonyl chloride and a saturated solution of sodium sulphide. The precipitated sulphur was filtered off and the excess benzene sulphonyl chloride removed by extracting with ether. The aqueous solution was concentrated on a water bath, till crystals began to form and then allowed to cool. The crystalline sodium benzene sulphinate was filtered and washed with a little water.

The salt was dissolved in water and the whole cooled down in ice. Sulphuric acid was slowly added with stirring till the solution was slightly acid. The solid benzene sulphinic acid was filtered off and washed with water, then dried in a desiccator.

The benzene sulphinic acid was dissolved in glacial acetic acid as suggested by Hilditch (63) and the solution cooled in iced water. Dry powdered potassium permanganate was added slowly with shaking, until a permanent red colour was produced in the solution. The solution was then poured into cold water and the diphenyl  $\alpha\alpha'$ -disulphone was precipitated. After standing a little time the solid was filtered off and dried. It was crystallised from glacial acetic acid or benzene, m.p.  $193^{\circ}$ . The former solvent gave the best crystals for crystallographic examination.

Di-p-tolyl  $\alpha$ '-Disulphone.

This was prepared by the method of Kohler and McDonald (64). A paste of sodium p-toluene sulphinate and water was made, and to this was added an ether solution of p-toluene sulphonyl chloride, the volume of ether being greater than that of the water. The whole was refluxed for about six hours on a water-bath and the small amount of di-p-tolyl  $\alpha$ -disulphone was filtered off, the remainder being again refluxed with more ether. The final product was recrystallised from glacial acetic acid, m.p.  $214^{\circ}$  (decomp.).

Diphenyl Disulphonyl Sulphide.

Sodium benzene sulphinate was suspended in dry carbon tetrachloride, the whole being cooled in a freezing mixture. An equivalent amount of sulphur dichloride was dissolved in dry carbon tetrachloride and dropped slowly with shaking into the suspension of the salt. The red colour of the sulphur dichloride disappeared on reaction and when all the  $\text{SCl}_2$  was added the carbon tetrachloride was removed by boiling on a water bath. The product was broken up, if necessary, and washed in water to remove  $\text{NaCl}$ . The product on drying can be recrystallised from glacial acetic acid to give fine crystals, m.p.  $133^{\circ}\text{C}$ . (65).

### Di-p-tolyl Disulphonyl Sulphide.

Sodium p-toluene sulphinate was prepared by the reduction of toluene sulphonyl chloride by the method given in Organic Syntheses, vol.2, 89.

The sodium p-toluene sulphinate was powdered and suspended in dry carbon tetrachloride as suggested by Troeger and Hornung (65). To the suspension was added drop by drop a solution of sulphur dichloride in carbon tetrachloride, the whole being shaken and cooled in a freezing mixture. When all the sulphur dichloride was added the carbon tetrachloride was taken off on a water bath. The product was washed in water and finally, after drying, recrystallised from glacial acetic acid, m.p. = 138°C.

### Diphenyl Disulphonyl Trisulphide.

Sodium benzene thiosulphonate was prepared by reacting benzene sulphonyl chloride and a saturated aqueous solution of sodium sulphide. In order to slow down the reaction and prevent the deposition of sulphur and consequent production of sulphinate, the benzene sulphonyl chloride was dissolved in a large volume of benzene and added to the solution of  $\text{Na}_2\text{S}$ . The whole was shaken for four hours and the excess sulphonyl chloride removed by extraction with more benzene. The aqueous solution was then filtered and heated on a water bath till crystals began to appear, when

it was left to cool. The deposited crystals were filtered off, washed with a little water and dried in a desiccator.

The dried and powdered crystalline sodium benzene thiosulphonate was suspended in dry carbon tetrachloride as suggested by Troeger and Horning (65). An equivalent amount of sulphur dichloride was dissolved in dry carbon tetra-chloride and added drop by drop with cooling. The  $\text{CCl}_4$ , when the reaction was finished, was removed by heating on a water bath and the product ground up in water and filtered, washing with plenty of water. It was recrystallised from glacial acetic acid, giving beautiful bipyramidal crystals, m.p. =  $103^\circ\text{C}$ .

#### Di-p-tolyl Disulphonyl Trisulphide.

Sodium p-toluene thiosulphonate was suspended in dry carbon tetrachloride and an equivalent amount of sulphur dichloride in dry  $\text{CCl}_4$  was added drop by drop with cooling and shaking. When the reaction was complete, the product was separated by boiling off the  $\text{CCl}_4$  on a water bath and the solid washed with water thoroughly. When the product was dry, it was recrystallised from glacial acetic acid, giving beautiful bipyramidal crystals, m.p. =  $180^\circ\text{C}$ . (65).

### Conclusion.

The determination of the space groups of the molecules of the type  $R_2S_nO_4$  where R is phenyl or p-tolyl group, has indicated that, in the case of molecules with an odd number of sulphur atoms, the symmetry is a diad axis and for those with an even number the symmetry is a centre. The study has shown that the sulphur atoms are linked by single bonds in chain formation and that no coordinate bonds of the type S-S occur in this series. The complete elucidation of diphenyl disulphonyl sulphide has indicated that bond lengths observed are normal and that the intermolecular bonding  $SO_2 \cdots CH(CH_3)$  gives an unusual change in density for the tolyl compound. This latter information has been useful in deciding the suggested structure for the disulphones but has not been of great help in the attempt to elucidate the structure of diphenyldisulphonyl trisulphide, due to the large number of atoms and the complexity of the arrangement.

Because of the similarity between the constitutions of the inorganic polythionates  $R_2S_nO_6$ , where R is a monovalent alkaline metal, and the organic series  $R_2S_nO_4$ , where R is phenyl or tolyl, it is of interest to compare the physical properties of these as far as they have been investigated. The crystal structure of the dithionate ion

has been studied by Huggins and Frank (66) and others, while the trithionate ion has been elucidated by Zachariassen (67). The space group of potassium tetrathionate has been determined by Tunell, Merwin and Ksanda (68), but has proved too complex for complete analysis and no higher members have been studied. Both the dithionate and the disulphone are markedly more stable to chemical reaction than any of the other members of the corresponding series and it is probable that this stability is due to the grouping of the sulphur atoms. Only a complete analysis would reveal if there is any reduction of the S-S bond length which would suggest an increase in strength of this bond. For the organic series  $R_2S_5O_4$  is more stable than  $R_2S_4O_4$  as, in the preparation of the latter (diphenyl disulphonyl disulphide), the product broke down and the final product was sulphur and diphenyl disulphonyl trisulphide. There is a difference for the inorganic series where the reaction is reversible so that trithionic acid will break down to dithionic and the sulphur released will recombine with the trithionic acid to form tetrathionic acid. This behaviour seems to apply irreversibly to the disulphonyl disulphide and tetrasulphide, but the disulphone, disulphonyl sulphide and trisulphide are quite stable. The explanation as to the stability of these compounds is to be sought mainly in the sulphur chain

disposition and bond lengths. The values from the inorganic series are not sufficiently accurate to warrant discussion on this point.

The analysis of the diphenyldisulphonyl sulphide is the first X-ray structure determination giving sufficiently accurate bond angles to allow discussion as to the tetrahedral or octahedral disposition of the bonds. The evidence is not conclusive but tends to support the latter contention.

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