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The unit-cell dimensions and space group of bis-*o*-phenylene disulphide.

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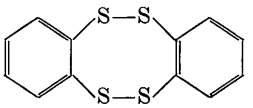
A unique compound prepared by the reaction of low concentrations of dithiocatechol and iodine in benzene by Stephens (1960) crystallizes in the space group $P\bar{1}$. On the basis of chemical evidence the product obtained was believed to be bis-*o*-phenylene disulphide (I). From molecular models three distinct conformations were found to be possible (Field, Stephens & Lippert, 1961).



(I)

In order to confirm the structure a three-dimensional X-ray investigation was begun. The density, 1·590 g.cm^{-3}, was measured by accurately determining the temperature of flotation in carbon tetrachloride. With the unit cells determined with a Buerger precession camera the calculated molecular weight was 281, in close agreement with the theoretical value 280·5.

With the crystal mounted with the *a* axis as spindle axis, *hk*0, *h*0*l*, upper level and oblique zone data were obtained. 593 independent reflections were recorded with filtered Mo $K\alpha$ radiation. For all reflections $h+k+l=2n$, indicating that a body centered cell was being photographed. A transformation to the primitive cell was made by the matrix $(-\frac{1}{2}\frac{1}{2}\frac{1}{2}/\frac{1}{2}-\frac{1}{2}\frac{1}{2}/\frac{1}{2}\frac{1}{2}-\frac{1}{2})$. Table 1 gives the crystallographic data for both cells.

A pyroelectric test to determine whether the space group was $P\bar{1}$ or $P\bar{1}$ was inconclusive, *i.e.* no detectable charge was observed to develop when a capillary of powdered compound was brought from room to near liquid nitrogen temperatures. Statistical approaches were then tried.

According to Howells, Phillips & Rogers (1950) the percentage of reflections with an intensity less than or equal to a given fraction of the average intensity is different for centric and acentric symmetries. The theoretical distributions are given in Fig. 1 as solid lines and the experimentally obtained points as crosses.

A second statistical method involved the use of normalized structure factors $E(s)$ defined by Karle (1961) as

$$E^2(s) = |F(s)|^2/\varepsilon \sum_{i=1}^{N} f_i(s).$$

$|F|^2$ is the observed intensity corrected for instrumental factors, $f_i(s)$ is the atomic scattering factor for the *i*th atom and $\varepsilon=1$ in the triclinic system. The E's were normalized by the condition that $\langle E^2\rangle = 1{\cdot}0$. The average

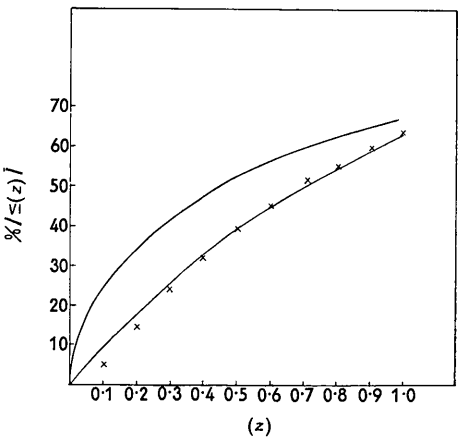


Fig. 1. The percentage of the observed, corrected intensities which are equal to or less than some fraction *z* of the average intensity. The experimentally obtained values are shown as crosses.

values $\langle E\rangle$ and $\langle|E^2-1|\rangle$ should be different in $P\bar{1}$ and $P\bar{1}$ (Karle & Hauptman, 1953). Table 2 compares the theoretical values with those found for this compound. The results of both statistical tests indicate that the space group is indeed $P\bar{1}$.

Table 2. *Theoretical and experimental values of* $\langle E\rangle$ *and* $\langle|E^2-1|\rangle$ *for bis-o-phenylene disulphide.*

	$\langle E\rangle$	$\langle\|E^2-1\|\rangle$
$P\bar{1}$	0·80	0·97
$P\bar{1}$	0·89	0·74
Found	0·887	0·757

Two- and three-dimensional Patterson maps were prepared and extensively investigated by superposition techniques without leading to the solution of the structure At the present time statistical procedures for the determination of the phases are being used. Preliminary results are encouraging in that atoms have appeared in the locations assigned to sulphur atoms on the basis of Patterson peaks in the three-dimensional map. Neither method has yielded recognizable benzene rings. For the phase determining procedure an additional 110 independent reflections have been obtained by the Weissenberg technique.

Table 1. *Crystallographic data for the body centered and primitive cells.*

	a	*b*	*c*	α	β	γ	*V*	*Z*
I	7·95 Å	9·74 Å	7·67 Å	90·0°	87·0°	88·5°	588·4 Å^3	2
P	7·17	7·39	7·30	114·6	95·7	116·6	294·2	1

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Refinement of azulene assuming rigid-body thermal motion.

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Introduction

Azulene presents a special computation problem, owing to the disordered nature of the molecules in the crystals (Robertson, Shearer, Sim & Watson, 1962). There are two non-centrosymmetric molecules in the unit cell, space group $P2_1/a$, which must each occupy a symmetry centre. This can only occur by a statistical arrangement of molecules in two orientations related by centrosymmetry. The main difficulties encountered in the refinement of the crystal structure follow from the high interactions between the positional and thermal parameters of pairs of atoms which approach each other (statistically) closer than the resolution of the measurements. Interpretation of the results of refinement is then difficult because there is no formal way of assigning the atoms to the correct molecule.

For azulene Robertson *et al.* chose the molecule with the most sensible bond lengths. They then analysed the anisotropic temperature factors for rigid body vibrations and obtained results similar to those with naphthalene.

The purpose of the present study was to re-examine the assumptions made by Robertson *et al.* and then to attempt methods which avoid some of these assumptions. The study was not encouraging in that it casts doubt on the results of any investigation with disorder, but it is thought that the methods reported will give physically meaningful results for ordered structures.

Re-examination of previous results

Independently both Hirshfeld, Sandler & Schmidt (1963) and Pawley (1962, 1963) have proposed a method of examining the anisotropic temperature factors of non-centrosymmetrical molecules for rigid body vibrations without assuming knowledge of the origin of the mean square rotational tensor $\boldsymbol{\omega}$. The latter author gives preliminary results for azulene. As mentioned above, there is difficulty in assigning atomic coordinates for a single molecule; there are in fact eight possibilities described in detail by Robertson *et al.* All eight were analysed by this least-squares rigid-body method. Two gave equally good results, and the other six were much poorer. This suggested that the choice was reduced to two, the molecule of Robertson *et al.*, and the molecule with all ambiguous pairs interchanged. The latter molecule had insignificantly poorer bond lengths, whereas the other six were again much poorer. The two 'possible' molecules had identical planarity, or aplanarity, while the remaining six were all more planar. It was therefore thought that the choice of the correct molecule was not certain.

Rigid body refinement

The crystal structure refinement procedure described by Pawley (1964) has been applied to azulene. The parameters varied were the scale factor, the six components of both $\mathbf{T}$ and $\boldsymbol{\omega}$, the origin of $\boldsymbol{\omega}$ and the thirty position parameters for the carbon atoms. Hydrogen atoms were repositioned at the end of each cycle 1·09 Å from their bonded carbon atoms away from the centre of the appropriate ring. During the course of refinement the customary R index varied quite rapidly:

Before cycle	R (%)	
1	999·0	(scale factor blunder)
2	31·0	
3	9·3	
4	7·7	
5	7·1	
6, 7, 8	6·9	

with the final R value of 6·9% corresponding to 6·5% without unobservables. This is identical with the final R value obtained by Robertson *et al.* The largest shift of any parameter in the last cycle was 0·1 e.s.d., and refinement was thought to be complete. It was previously thought that R would be somewhat larger than 6·5% owing to the parameter constraints, but this only applies if the constraints represent approximations which are not entirely valid for the measurements under investigation.

The advantages of the rigid body refinement are:

(*a*) Reduction of computer time (each cycle took less than ½ min on the IBM 7090).
(*b*) Fewer cycles necessary.
(*c*) More accurate tensors $\mathbf{T}$ and $\boldsymbol{\omega}$.
(*d*) Removal of positional and thermal parameter interactions.
(*e*) Removal of close pair ambiguity.

The last arises from the fact that as the origin of $\boldsymbol{\omega}$ is allowed to vary, the temperature factors for any atom depend on its relationship to this origin, and therefore

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