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AN EXAMINATION OF SPACE GROUP OF 2,4,6-TRIMETHYL BIPHENYL SULPHONE BY INTENSITY STATISTICS

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The process of determining the space group of a substance from the knowledge of symmetrically and systematically absent reflexions only has been proved to be incomplete. It often fails to distinguish between space groups unambiguously and accurately. The method of intensity statistics has been proved to be the best one for distinguishing between space groups not resolved by systematic absences and it can be applied to any group of reflexions.

In the present investigation $N(z)$ test and moment tests have been tried out successfully on the complete three dimensional data of 2,4,6-trimethyl biphenyl sulphone in order to distinguish unambiguously and unequivocally between the two possible space groups $Pnma$ and $Pn2_1a$ of the compound which could not be done directly from the diffraction photographs. The space group came to be $Pnma$.

1. Introduction

In crystal structure analysis the symmetry elements involving a translation may readily be recognised by the systematic absences they produce in the X-ray reflexions; the others, such as mirror planes have no immediate obvious effect on the X-ray reflexions. Consequently an unambiguous determination of the space group from a study of the diffraction symmetry and systematic absences only is not possible and the final choice often rests between two or more alternatives. Usually the choice has to be made between a centrosymmetric and a noncentrosymmetric space groups or plane groups.

Wilson[1] showed that the probability distribution of the intensities of X-ray reflexions from crystals are different for centrosymmetric and noncentrosymmetric crystals. The two distributions, known respectively as the centric and acentric distributions are uniquely determined if the unit of the crystal pattern contains a reasonably large number of approximately equal atoms situated at random.

Several practical tests have been described for making a distinction between the distributions.[2] But the one which is commonly used as an aid to space group determination is the $N(z)$ test. This statistical test was first suggested by Wilson[1] and subsequently by Howells, Phillips and Rogers,[3] and Rogers.[4] This was further modified for better discrimination by Hargreaves and Gogoi.[5] The theoretical cumulative distribution curves can be drawn and the symmetry of the crystal determined by finding out whether the actual distribution is nearer to one or the other of the two curves.

Statistical tests for crystal symmetry, which are valid when both light and heavy atoms are present, have been devised for certain rather special cases.[6,7] Foster and Hargreaves[8] suggested a test known as moment test which can be applied to a wide variety of distribution. They gave a procedure for deriving theoretical expressions for moments of intensity for any number and relative weights of atoms in crystal with different space groups and applying these results in the determination of space group symmetry.

Three-dimensional Patterson synthesis may give us a detailed information about these symmetry peaks. This involves a huge computational work and moreover the interpretation of these maps is not an easy task. In this paper, therefore, two statistical tests, viz. modified $N(z)$ test and moment test, have been applied successfully to the complete three dimensional data of 2,4,6-trimethyl biphenyl sulphone ($C_6H_2(CH_3)_3—SO_2—C_6H_5$) in order to determine precisely the space group of the compound.

2. Experimental

(a) *Crystal Data*

The crystals of 2,4, 6-trimethyl biphenyl sulphone were supplied by Dr. G. Holt of the Chemistry Department, University of Manchester Institute of Science and Technology, England. These were crystallised both from water–absolute alcohol and from benzene–petroleum ether mixtures. From the former solvent the crystals obtained were long, needle-like and most of them were very thin, but in the latter case, the crystals were rather large and platy. The crystals obtained from both solvents were examined under the polarising microscope and they gave straight extinctions suggestive of biaxial crystals. This evidence suggested that the crystal system might be othorhombic.

X-ray rotation, oscillation and Weissenberg photographs about a, b and c-crystallographic axes

using Cuk$_\alpha$ radiation were used to determine the space group. Weissenberg photographs of higher layers about the c-axis were also taken. The unit cell dimensions were measured from the rotation and Weissenberg photographs and they are : $a=16.21\pm.04$A°; $b=21.40\pm.06$A°; $c=8.05\pm.02$A° and $\alpha=\beta=\gamma=\pi/2$. With eight molecules in the unit cell the calculated density for the crystal is 1.24 g cm^{-3}, which agrees with the experimental value (1.22 g cm^{-3}) obtained by flotation method using a mixture of bromoform and ethyl alcohol. The X-ray photographs show that there are no systematic absences in the general reflexions *hkl*. Systematic absences in the X-ray reflexions (*hk*o with *h* odd and o*kl* with $(k+l)$ odd) show that the space group is either *Pnma* or $Pn2_1a$.

The intensities of *hk*o reflexions and o*kl* reflexions have been measured using (001) and (100) projection Weissenberg photographs respectively. The intensities of the higher layer photographs, viz. *hk*1, *hk*2, *hk*3 and *hk*4 reflexions, have also been measured. The intensities have been estimated using multiple film technique and visual comparison with crystal reflected calibrated spots of known relative exposures. They have been corrected for Lorentz and polarisation factors but no attempt has been made to correct for absorption. The crystal specimen that had been used for taking the *hk*o projection and higher layer photographs was cut such that it formed more or less a regular polygon; the maximum diagonal length being 0.022 mm; the length perpendicular to this diagonal being 0.014 mm.

(b) *The Examination of Space Group by Statistical Methods*

It has been mentioned in section 2(a) that systematic absences in the X-ray reflexions do not allow a choice to be made between *Pnma* and $Pn2_1a$. But with three dimensional X-ray data available it is possible to make a statistical survey of the X-ray intensities which should distinguish between the two space groups.

Two statistical tests have been carried out.

(i) *Modified $N(z)$ Test.*—The presence or absence of a mirror plane parallel to (010) has been tested by plotting $N(z)$ of the observed intensities against z. Theoretical values of $N(z)$—referred to $_1N(z)$ and $_IN(z)$ for the centric and acentric distributions respectively as deduced by Howells, Phillips and Rogers,[3] Rogers,[4] and Hargreaves and Gogoi[5] have been compared with the experimental results. The ranges of z chosen are 0 to 0.1, 0.1 to 0.3, 0.3 to 0.8 and 0.8 to 2.0 and the modified $N(z)$ test has been tried out on groups of reflexions from five different layers and the results have been summarised in Table 1. In each case the results were calculated for two of the sin θ ranges, viz. 0.2 to 0.6, 0.6 to 0.8, but average values are only shown in the table. The results suggest that the space group is *Pnma* but the result is not wholly convincing because of considerable variations observed in the experimental results in the ranges of $z=0.1$ to 0.3 and $z=0.3$ to 0.8.

TABLE 1.—VALUES OF $N(z_2)N-(z_1)$.

Reflexions		Z_1 0 Z_2 0.1	Z_1 0.1 Z_2 0.3	Z_1 0.3 Z_2 0.8	Z_1 0.8 Z_2 2.0
Number	Type				
129	*hk*0	0.229	0.203	0.212	0.178
152	*hk*1	.239	.170	.221	.219
93	*hk*2	.237	.145	.269	.184
99	*hk*3	.227	.159	.249	.213
65	*hk*4	.239	.170	.221	.170
Theoretical values	$(\bar{I})$	.248	.171	.210	.214
	(I)	.095	.164	.292	.314

(ii) *Moment Test.*—The more satisfactory and promising test[8] permitting full use of the three dimensional experimental data is provided by a comparison of theoretical and calculated moments. The rth moment of z, which is defined as $\langle z^r\rangle = \dfrac{\langle I^r\rangle}{\langle I\rangle^r}$ where $\langle I\rangle$ is the local average intensity, has been considered here. The experimental second and third moments only have been calculated from observed intensities of the five different layers separately. Reflexions with one index zero have been omitted from the calculations of the experimental three-dimensional moment since their moments are different from those of general reflexions *hkl*. Similarly reflexions with two indices zero have been omitted while calculating the moments for the *hk*o reflexions. The theoretical values of the moments of intensity when all the atoms are in general positions have been calculated for the two possible space groups *Pnma* and $Pn2_1a$ as well as for the plane groups *pgm* and *pg*1 since the plane group symmetry of the *hk*o projection is either *pgm* or *pg*1. The experimental and theoretical results have been compared in Table 2. For calculating the structure factors the atomic scattering factors of Forsyth and Wells[9] have been used.

3. Discussion

Intensity tests have been successfully carried out with different sets of reflexions by determining $N(z)$ values for different values of z and comparing them with the corresponding theoretical $N(z)$ values for the centric and acentric distributions.

TABLE 2.

	Types of reflexions	No. of reflexions	$\langle z^2 \rangle$	$\langle z^3 \rangle$
Experimental moment	*hk*0	233	3.1	13.44
	*hk*1	307	3.8	32.8
	*hk*2	296	3.5	26.6
	*hk*3	266	3.3	18.4
	*hk*4	235	3.4	21.2
Theoretical moment	*pgm*		2.9	14.8
	pg^1		2.0	5.6
	Pnma		3.06	15.96
	$Pn2_1a$		2.02	6.21

It is found that the practically calculated $N(z)$ values are nearer to those of centrosymmetrical structure suggesting that the substance under consideration possesses centrosymmetric space group. It may be noted that the presence of the heavy sulphur atom may, however, considerably reduce the effectiveness of the test. Further, the moment tests clearly indicate that the space group of 2,4,6-trimethyl biphenyl sulphone is *Pnma*.

It is, however, seen that the experimental moments, calculated from observed intensities tend to be higher than the theoretical moments. This may be due to error in evaluating the $\langle I \rangle$ function[10]—the data used here are not corrected for absorption errors which may be quite large—or to hypersymmetry;[11] both of these effects increase the value of the experimental moments. Nevertheless moment tests which can be applied to materials of any composition have been proved to be very successful in symmetry determination and it provides a test for a clear distinction between two or more space groups of a crystal which cannot be obtained from the study of systematically absent reflexions.

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