to data so far accumulated (Abrahams, 1956), a sulphur–carbon distance is about 1·61 Å in the double-bond case, and about 1·82 Å in the single-bond case. The distances found in four S–C bonds in the present compound imply that they have mostly double-bond character. As for the S–O bond length, there has been much discussion about the character of this bond. It is now considered that the double-bond length is 1·43–1·44 Å, and that a standard single-bond length may be 1·60 Å (Abrahams, 1956). Therefore the bond in the present compound may be nearly double-bonded, though the percentage double-bond character cannot be estimated.

The C–S–C bond angles have been found to be 96–97°, which is a typical value found in various compounds as discussed previously (Hosoya, 1958*c*, 1963).

The best planes were calculated for two benzene rings in relation to the molecule having the bond-length and bond-angle values shown in Table 3. They are expressed by the following equations:

$$0{\cdot}34200X+0{\cdot}92207Y+0{\cdot}18118Z=3{\cdot}8536$$

[for C(1), C(2), C(3), C(4), C(11) and C(12)],

$$-0{\cdot}44412X+0{\cdot}87779Y+0{\cdot}17945Z=6{\cdot}8615$$

[for C(5), C(6), C(7), C(8), C(9) and C(10)].

The distances of atoms from the best planes are listed in Table 4. Coplanarity of carbon atoms making each benzene ring is fairly good, while both sulphur atoms lie slightly outside the dihedral angle made by the two benzene rings. The dihedral angle was found to be 133°38′.

Table 4. *Distances of atoms from the best planes*

First benzene ring		Second benzene ring	
C(1)	−0·0122 Å	C(5)	−0·0050 Å
C(2)	0·0040	C(6)	0·0049
C(3)	0·0022	C(7)	−0·0010
C(4)	−0·0026	C(8)	−0·0040
C(11)	−0·0054	C(9)	0·0039
C(12)	0·0117	C(10)	−0·0004
S(1)	0·0713	S(1)	0·1146
S(2)	0·1164	S(2)	0·1176
O(1)	1·3542	O(1)	1·3972
O(2)	−0·3620	O(2)	−0·3908

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A Modified $N(z)$ Test for Crystal Symmetry

By A. Hargreaves and B. N. Gogoi
Physics Department, University of Manchester Institute of Science and Technology, Manchester 1, *England*

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A modified $N(z)$ test for distinguishing between the centric and acentric distributions is described. It can be performed as quickly and as easily as the standard $N(z)$ test and offers better discrimination.

Introduction

Wilson (1949) showed that the probability distributions of the intensities of X-ray reflexions from crystals are different for centrosymmetric and non-centrosymmetric crystals. The two distributions – known respectively as the centric and acentric distributions – are uniquely determined if the unit of crystal pattern contains a reasonably large number of approximately equal atoms distributed at random. Several practical tests have been devised for distinguishing between the distributions (*International Tables for X-ray Crystallography*, 1959). The one which has been most widely used in practice, as an aid to space-group determination, is the $N(z)$ test. In this each intensity is expressed as a fraction, z, of the local average intensity, and the fraction $N(z)$ of the reflexions whose intensities are less than z is plotted against z. Theoretical values of $N(z)$ – referred to as ${}_{\bar{1}}N(z)$ and ${}_{1}N(z)$ for the centric and acentric distributions respectively – have been deduced by Howells, Phillips & Rogers (1950).

Cumulative distributions are always less different than the corresponding probability distributions, but $N(z)$ distributions are used in preference to the probability distributions $P(z)$ because the number of observed reflexions is often insufficient for the construction of a satisfactorily smooth plot of experimental $P(z)$. A much smaller amount of data will give a reasonably satisfactory plot of $N(z)$.

In this paper we describe a test which is, in effect, a compromise between the $N(z)$ and $P(z)$ tests: it brings out the differences between the centric and acentric distributions more clearly than the $N(z)$ test, but does not require the large amount of experimental data needed for a $P(z)$ test.

The modified $N(z)$ test

The values of ${}_{1}N(z)$ and ${}_{\bar{1}}N(z)$ given by Howells *et al.* (1950) and in *International Tables* (1959) cover the range $0<z<1\cdot0$. For $z>1\cdot0$, ${}_{1}N(z)$ and ${}_{\bar{1}}N(z)$ are so nearly equal that it is difficult to distinguish between them experimentally. As a result it has become the usual practice to perform experimental tests only over the range $0<z<1\cdot0$. It will be shown that this procedure omits a substantial amount of data which are useful in distinguishing between the two distributions.

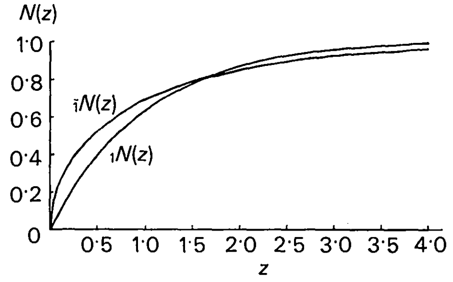

Fig. 1. Graphical comparison of functions ${}_{1}N(z)$ and ${}_{\bar{1}}N(z)$.

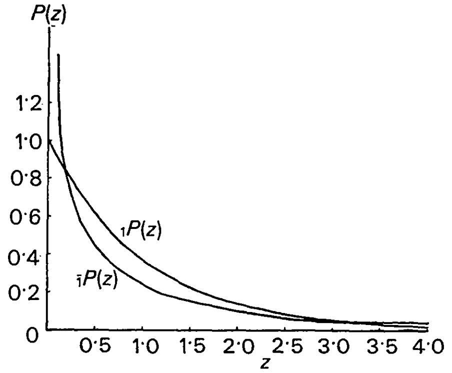

Fig. 2. Graphical comparison of functions ${}_{1}P(z)$ and ${}_{\bar{1}}P(z)$.

Recently Rogers (1965) has presented plots of $N(z)$ and of $P(z)$ over the range $0<z<5\cdot0$ and these are reproduced, with permission, in Figs. 1 and 2. The $P(z)$ curves indicate, much more clearly than the $N(z)$ curves, the important differences between the centric and acentric distributions. The greatest differences occur in ranges covered approximately by $0<z<0\cdot1$ and $0\cdot3<z<2\cdot0$, and this suggests that it is desirable to concentrate attention on these two ranges, which together cover more than two-thirds of the observed reflexions.

In the first range ${}_{\bar{1}}P(z)$ is greater than ${}_{1}P(z)$, but in the second range ${}_{1}P(z)$ is the greater. One of the weaknesses of the $N(z)$ distribution is that in the second range the differences of these two groups are opposed, so weakening the discriminatory power of the test. Another is that the clearest discrimination occurs when only about half the reflexions are used.

Fig. 2 shows that over the range $1\cdot0<z<2\cdot0$, which covers a substantial proportion of reflexions, ${}_{1}P(z)$ is about half as large again as ${}_{\bar{1}}P(z)$, suggesting that this range is particularly effective for differentiating between the two distributions. In principle this observation could also be deduced from the slopes of the cumulative distributions $N(z)$ but, as we have already commented, it appears to have been overlooked because the absolute values of ${}_{\bar{1}}N(z)$ and ${}_{1}N(z)$ are approximately equal.

Since the number of observed intensities is usually insufficient for the construction of a satisfactory experimental $P(z)$curve, it is proposed that the best features of both $P(z)$ and $N(z)$ distributions can be retained by determining the fractions of reflexions lying in limited ranges of z, the ranges being chosen so as to secure the most effective discrimination between the centric and acentric distributions. The proposed ranges of z are 0 to 0·1, 0·1 to 0·3, 0·3, to 0·8 and 0·8 to 2·0: theoretical values of the fractions for these ranges, deduced from the $N(z)$ values in Table 1, are given in Table 2. It will be seen that there are large differences between the centric and acentric values in the first, third and fourth ranges. The number of reflexions in each range is usually sufficient to give reasonable statistical averaging and the results for the three separate ranges serve as a useful crosscheck.

Table 2. *Theoretical values of* $N(z_2)-N(z_1)$

z_1, z_2	0, 0·1	0·1, 0·3	0·3, 0·8	0·8, 2·0
${}_{\bar{1}}N(z_2)-{}_{\bar{1}}N(z_1)$	0·248	0·168	0·213	0·214
${}_{1}N(z_2)-{}_{1}N(z_1)$	0·095	0·164	0·292	0·314

Table 1. *Theoretical values of* ${}_{\bar{1}}N(z)$ *and* ${}_{1}N(z)$

z	0	0·1	0·2	0·3	0·4	0·6	0·8	1·0	1·5	2·0	3·0	4·0	5·0
${}_{\bar{1}}N(z)$	0	0·248	0·345	0·416	0·473	0·561	0·629	0·683	0·779	0·843	0·917	0·955	0·975
${}_{1}N(z)$	0	0·095	0·181	0·259	0·330	0·451	0·551	0·632	0·777	0·865	0·950	0·982	0·993

Table 3. *Values of* $N(z_2)-N(z_1)$: *practical examples*

Material	Space group	Reflexions Number	Reflexions Type	Symmetry	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
2,2′-Dimethylbenzidine dihydrochloride	$I2$	84	0*kl*	1	0·112	0·158	0·253	0·318
3,3′-Dimethylbenzidine	$P2_12_12_1$	223	*hk*0	$\bar{1}$	0·267	0·166	0·206	0·246
Phenyl mesityl sulphone	*Pnma*	149	*hk*1	$\bar{1}$	0·248	0·202	0·242	0·192
3,3′-Dichloro-4,4′-dihydroxydiphenylmethane	$C2/c$	99	*h*0*l*	$\bar{1}$	0·259	0·134	0·251	0·231
2,4-Dinitrobenzenesulphonyl chloride	$Pca2_1$	40	0*kl*	1	0·160	0·113	0·293	0·291
		74	*h*0*l*	1	0·079	0·237	0·243	0·330
		101	*h*1*l*	1	0·106	0·256	0·199	0·289
Hexaphenylbenzene	*Pnma* or $Pn2_1a$	87	*hk*0	?	0·255	0·144	0·217	0·213
Theoretical Values								
Centric				$\bar{1}$	0·248	0·171	0·210	0·214
Acentric				1	0·095	0·164	0·292	0·314

Reflexions in the range $z=0·1$ to 0·3, which at first sight appear to be of little use for statistical tests, may be combined usefully with those in the 0 to 0·1 range when only coarse measurements of intensity are available. For example, if the average intensity is 10 and the weakest measured intensity is 1 – typical values for reflexions in the higher ranges of sin θ – then attempts to assign reflexions of intensities 0, 1, 2 and 3 to the ranges $z=0$ to 0·1 and 0·1 to 0·3 will be subject to large errors. In these circumstances it is better to consider the range $z=0$ to 0·3 which should contain 0·419 of the reflexions for the centric distribution or 0·259 of the reflexions for the acentric distribution. There is no significant loss of discrimination by extending the range in this way.

Practical examples

The modified $N(z)$ test has been tried out on groups of reflexions from six different materials with results summarized in Table 3: in each case the results were calculated for two or three of the sin θ ranges 0·2 to 0·6, 0·6 to 0·8 and 0·8 to 1·0 but average values only are presented here.

The structures of the first four materials in Table 3 are known and for all four the balance of evidence is clearly in favour of the correct space group. One of these materials, 3,3′-dichloro-4,4′-dihydroxydiphenylmethane, was chosen for study because the standard $N(z)$ test was reported to give ambiguous results (Whittaker, 1953). The modified $N(z)$ test was performed on Whittaker's X-ray data; it strongly supports the correct space group.

The structures of the last two materials listed in Table 3 have not yet been determined. Nevertheless moment tests (Foster & Hargreaves, 1963) and structural considerations indicate beyond reasonable doubt that the true space group of 2,4-dinitrobenzenesulphonyl chloride is $Pca2_1$ rather than the alternative *Pcam*. And the results for hexaphenylbenzene justify the choice of *Pnma* because they agree so closely with those for a centric distribution.

We see, therefore, that for every material examined so far, the test appears to have been successful.

On the whole, the best results are in the range $z=0·8$ to 2·0, which is usually mostly omitted from the $N(z)$ test; this range gives much clearer indications than the range 0·3 to 0·8 for the eight sets of reflexions given in Table 3. A possible explanation is that the intensities of stronger reflexions are more accurately measured than those of weaker reflexions.

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