Acta Cryst. (1974). A30, 310

Probability Distribution of X-ray Intensities in a Non-centrosymmetric Crystal with a Degree of Centrosymmetry*

BY S. PARTHASARATHY AND V. PARTHASARATHI
Centre of Advanced Study in Physics, University of Madras, Madras-600025, India

(*Received* 26 *November* 1973; *accepted* 28 *November* 1973)

The expression for the probability distribution of X-ray intensities is obtained for a non-centrosymmetric crystal possessing an approximate centre of symmetry and from this the acentric and centric distributions of Wilson are deduced as limiting cases. Theoretical expressions for the variance, test ratio ϱ and moments of the normalized intensity z are also obtained in terms of the parameter $\langle|\Delta\mathbf{r}|\rangle$ which is a measure of the degree of centrosymmetry. From the theoretical results it appears that the non-centrosymmetric nature of such a crystal could be detected by statistical tests, provided accurate z values are available and reflexions with high (sin θ/λ) values are used for the test.

Introduction

Statistical tests for centrosymmetry conducted with the basic centric and acentric distributions of Wilson (1949) for choosing the correct space group from the two possible alternatives *Cc* and *C*2/*c* for dibenzyl disulphide have not led to any conclusive results (van Dijk & Visser, 1971; Einspahr & Donohue, 1971; Lee, 1971), though later Srinivasan & Vijayalakshmi (1972; this paper will be briefly referred to as SV, 1972) have assigned the space group *C*2/*c* by the X-ray anomalous scattering method. The failure of the statistical tests in this case has been attributed to the possibility that the mean deviation $\langle|\Delta\mathbf{r}|\rangle$ of atomic positions from an approximate centre of symmetry (if the crystal were really non-centrosymmetric) might be very small, say $\langle|\Delta\mathbf{r}|\rangle \simeq 0{\cdot}05$ Å (SV, 1972). The question that naturally arises now is whether it is possible or not to ascertain by statistical tests the *absence* of an *exact* centre of symmetry in a non-centrosymmetric crystal possessing an approximate centre of symmetry. This problem has been qualitatively studied by Srinivasan, Swaminathan & Chacko (1972) by plotting the probability density function (abbreviated as pdf in this paper) of the normalized structure amplitude y from the values of y calculated for a number of hypothetical two-dimensional non-centrosymmetric structures which have been obtained from a centrosymmetric structure by destroying the centre of symmetry by the introduction of random coordinate shifts. Making use of these empirical distributions, these workers have concluded that statistical tests are unlikely to be useful in confirming the absence of an exact centre of symmetry in a non-centrosymmetric crystal with a high degree of centrosymmetry. It may be noted here that this conclusion has been arrived at from 'experimental' $P(y)$ curves with an inherent scatter of points. Further it is not clear in *quantitative terms* how the degree of centrosymmetry affects the $P(y)$ curve and other statistical criteria such as the moments of the normalized intensity z, the variance of z, the test ratio ϱ *etc.* In this paper we shall therefore derive the probability distribution of y for such a non-centrosymmetric crystal by a rigorous theory based on the central-limit theorem. This procedure is quite analogous to the one adopted by Wilson (1949) for deriving the basic centric and acentric distributions for ideally centrosymmetric and ideally non-centrosymmetric crystals respectively. The theoretical distribution function $P(y)$ and the quantities $v(z)$, $\langle z^n\rangle$ and ϱ derived in this paper are found to depend on the parameter $\langle|\Delta\mathbf{r}|\rangle$ which, being the mean deviation of the atomic positions from the approximate centre of symmetry, is a good measure of the degree of centrosymmetry. It may be noted here that the distribution $P(y)$ obtained in this paper is general in the sense that it obtains the centric and acentric distributions† of Wilson as limiting cases (see Discussion).

Derivation of the probability distribution of y

Consider a non-centrosymmetric crystal (space group *P*1) containing a sufficiently large number (N) of atoms of similar scattering power in the unit cell. Suppose that the structure has an approximate centre of symmetry. That is, we can imagine the N atoms in the unit cell to be put in two groups containing an equal number ($N/2$) of atoms such that if one group of atoms is at locations $\mathbf{r}_j$ ($j=1$ to $N/2$), the positions of the atoms in the other groups related by the approximate centre of symmetry‡ could be written as $-\mathbf{r}_j+\Delta\mathbf{r}_j$ ($j=1$ to $N/2$). Evidently the $\Delta\mathbf{r}_j$'s are independent random vec-

* Contribution No. 369 from the Centre of Advanced Study in Physics, University of Madras, Guindy Campus, Madras-600025.

† The pdf of the normalized structure amplitude y for the centric and acentric distributions of Wilson (1949) will be denoted by $P_c(y)$ and $P_A(y)$ in this paper. It is known that (Ramachandran & Srinivasan, 1959) $P_c(y)=\sqrt{2/\pi}\exp(-y^2/2)$ and $P_A(y)=2y\exp(-y^2)$. The pdf of y obtained in the present paper will be denoted by $P(y)$.

‡ We have chosen the origin to be at the position of the approximate centre of symmetry. The centre of gravity of the unit cell is such a point [see equation (10) of Wilson (1949)].

tors and following Luzzati (1952) we shall assume that they obey a Gaussian distribution.

The contribution to the real part of the structure factor of a reflexion $\mathbf{H}(=hkl)$ from all the N atoms in the unit cell can be written as

$$A=\sum_{j=1}^{N/2} f_j[\cos\varphi_j+\cos(-\varphi_j+\psi_j)]=\sum_{j=1}^{N/2} A_j\,, \quad \text{say,} \qquad (1)$$

where we have used the simplifying notation

$$\varphi_j=2\pi\mathbf{H}\,.\,\mathbf{r}_j \quad \text{and} \quad \psi_j=2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_j\,. \qquad (2)$$

We shall derive the probability distribution of A for a given reflexion $\mathbf{H}$ by treating the $\mathbf{r}_j$'s and $\Delta\mathbf{r}_j$'s as random variables and this theoretical distribution is evidently identical with the one that could be obtained by varying $\mathbf{H}$ in the reciprocal space (Karle & Hauptman, 1953) for a given crystal structure.

Since the real part A [see equation (1)] is the sum of a large number of similarly distributed independent random variables A_j, it follows from the central limit theorem that A is normally distributed with mean $\langle A\rangle$ and variance σ_A^2 given by

$$\langle A\rangle=\sum\langle A_j\rangle \quad \text{and} \quad \sigma_A^2=\sum\sigma_j^2 \qquad (3)$$

where σ_j^2 is the variance of A_j. It is shown in the Appendix that

$$\langle A\rangle=0 \quad \text{and} \quad \sigma_A^2=\left(\frac{1+D}{2}\right)\sigma_N^2 \qquad (4)$$

where D and σ_N^2 are given by

$$D=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}\rangle \quad \text{and} \quad \sigma_N^2=\sum_{j=1}^{N} f_j^2\,. \qquad (5)$$

Thus the pdf of A can be written as

$$P(A)=\frac{1}{\sqrt{\pi(1+D)\sigma_N^2}}\exp\left[-A^2/(1+D)\sigma_N^2\right]. \qquad (6)$$

Since the pdf of B, the imaginary part of the structure factor, can be obtained by a similar procedure, we shall give only the essential steps. We thus have

$$\begin{aligned} B&=\sum_{j=1}^{N/2} f_j[\sin\varphi_j+\sin(-\varphi_j+\psi_j)]\\ &=\sum_{j=1}^{N/2} f_j[\sin\varphi_j(1-\cos\psi_j)+\cos\varphi_j\sin\psi_j]\\ &=\sum_{j=1}^{N/2} B_j\,, \quad \text{say}\,, \end{aligned} \qquad (7)$$

$$\langle B\rangle=\sum_{j=1}^{N/2}\langle B_j\rangle=0 \qquad (8)$$

$$\sigma_B^2=\sum_{j=1}^{N/2}\langle B_j^2\rangle=\left(\frac{1-D}{2}\right)\sigma_N^2 \qquad (9)$$

$$P(B)=\frac{1}{\sqrt{\pi(1-D)\sigma_N^2}}\exp\left[-B^2/(1-D)\sigma_N^2\right]. \qquad (10)$$

The joint pdf of A and B will therefore be given by

$$P(A,B)=\frac{1}{\pi\sigma_N^2\sqrt{1-D^2}}\times\exp\left[-\frac{1}{\sigma_N^2}\left(\frac{A^2}{1+D}+\frac{B^2}{1-D}\right)\right], \qquad (11)$$

changing to plane polar coordinates $(|F|,\alpha)$ where $A=|F|\cos\alpha$ and $B=|F|\sin\alpha$ we obtain the joint pdf of $|F|$ and α to be

$$P(|F|,\alpha)=\frac{|F|}{\pi\sigma_N^2\sqrt{1-D^2}}\times\exp\left[-\frac{|F|^2}{\sigma_N^2}\left(\frac{\cos^2\alpha}{1+D}+\frac{\sin^2\alpha}{1-D}\right)\right] \qquad (12)$$

where $|F|$ is the Jacobian of the transformation. The joint pdf of $y(=|F|/\sigma_N)$ and α can be obtained from (12) to be

$$P(y,\alpha)=\frac{y}{\pi\sqrt{1-D^2}}\exp\left[-y^2\left(\frac{1-D\cos 2\alpha}{1-D^2}\right)\right]. \qquad (13)$$

The pdf of y will therefore be given by

$$\begin{aligned} P(y)&=\int_{-\pi}^{\pi} P(y,\alpha)\mathrm{d}\alpha\\ &=\frac{2y}{\sqrt{1-D^2}}\exp\left[-y^2/(1-D^2)\right]I_0[Dy^2/(1-D^2)] \end{aligned} \qquad (14)$$

which yields the pdf of $z(=y^2)$ to be

$$P(z)=\frac{1}{\sqrt{1-D^2}}\exp\left[-z/(1-D^2)\right]I_0[Dz/(1-D^2)]\,. \qquad (15)$$

Making use of (14) we obtain the nth moment of y to be

$$\begin{aligned} \langle y^n\rangle&=\frac{2}{\sqrt{1-D^2}}\int_0^{\infty} y^{n+1}\\ &\quad\times\exp\left[-y^2/(1-D^2)\right]I_0[Dy^2/(1-D^2)]\mathrm{d}y\\ &=\Gamma\left(\frac{n}{2}+1\right)\,{}_2F_1\left(-\frac{n}{4},\frac{2-n}{4}\,;\,1;\,D^2\right) \end{aligned} \qquad (16)$$

which yields for $n=1$

$$\langle y\rangle=\frac{\sqrt{\pi}}{2}\,{}_2F_1(-\tfrac{1}{4},\tfrac{1}{4};\,1;\,D^2)\,. \qquad (17)$$

Since $z=y^2$ it follows that $\langle z^n\rangle=\langle y^{2n}\rangle$. Thus putting $n=2$, 4, 6 and 8 in (16) and expanding the hypergeometric function we readily obtain

$$\begin{aligned} &\langle z\rangle=1\,, \quad \langle z^2\rangle=2+D^2\\ &\langle z^3\rangle=6+9D^2 \quad \text{and} \quad \langle z^4\rangle=24+72D^2+9D^4. \end{aligned} \qquad (18)$$

The variance of z will be given by

$$v(z)=\langle z^2\rangle-\langle z\rangle^2=1+D^2. \qquad (19)$$

Since the test ratio ϱ of Wilson is given by $\varrho=\langle y\rangle^2$ it can be readily obtained by making use of (17).

Discussion of the theoretical results

It is seen from the results of the previous section that the pdf of y and the quantities $v(z)$, $\langle z^n \rangle$ and ϱ all depend on the parameter D which has been defined in (5). It has been shown by Luzzati (1952) that the quantity D is related to the mean value $\langle|\Delta\mathbf{r}|\rangle$ of the magnitudes of the random vectors $\Delta\mathbf{r}_j$'s through the relation

$$D=\exp\left[-\frac{\pi^3}{4}\langle|\Delta\mathbf{r}|\rangle^2 H^2\right] \tag{20}$$

where $H[=(2\sin\theta)/\lambda]$ is the magnitude of the position vector of the reciprocal-lattice point hkl. The quantity $\langle|\Delta\mathbf{r}|\rangle$, namely,

$$\langle|\Delta\mathbf{r}|\rangle=\frac{1}{(N/2)}\sum_{j=1}^{N/2}|\Delta\mathbf{r}_j| \tag{21}$$

can be taken to be a quantitative measure of the degree of centrosymmetry, since $\langle|\Delta\mathbf{r}|\rangle=0$ for an ideally centrosymmetric crystal and $\langle|\Delta\mathbf{r}|\rangle$ is large for an ideally non-centrosymmetric crystal. It is seen from (20) that

$$D=\begin{cases}1 & \text{when } \langle|\Delta\mathbf{r}|\rangle=0\\ 0 & \text{when } \langle|\Delta\mathbf{r}|\rangle \text{ is large}\end{cases} \tag{22}$$

which shows that the centric and acentric distributions of Wilson should follow from the general distribution (14) as limiting cases. It is seen from (14) that

$$\lim_{D\to 0} P(y)=2y\exp(-y^2)=P_A(y) \tag{23}$$

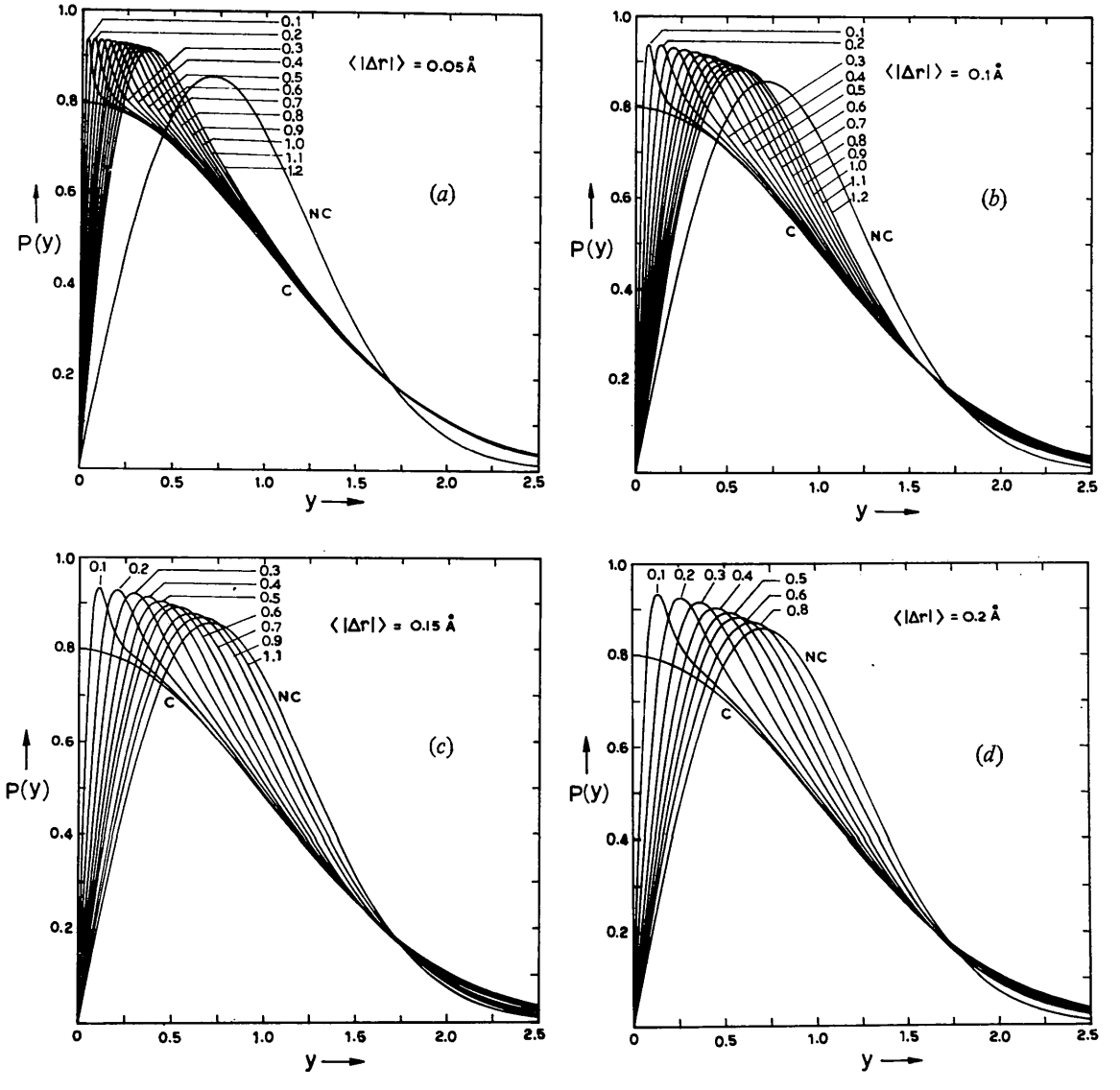

Fig. 1. The probability density function of the normalized structure amplitude y for a non-centrosymmetric crystal with a degree of centrosymmetry for different values of $(\sin\theta)/\lambda$ when (*a*) $\langle|\Delta\mathbf{r}|\rangle=0{\cdot}05$ Å, (*b*) $\langle|\Delta\mathbf{r}|\rangle=0{\cdot}1$ Å, (*c*) $\langle|\Delta\mathbf{r}|\rangle=0{\cdot}15$ Å and (*d*) $\langle|\Delta\mathbf{r}|\rangle=0{\cdot}2$ Å.

which is the pdf of y for Wilson's acentric distribution. Making use of the asymptotic expansion for $I_0(x)$ for large x (see Abramowitz & Stegun, 1965) in (14) it is seen

$$\lim_{D\to 1} P(y) = \sqrt{\frac{2}{\pi}} \exp(-y^2/2) = P_C(y) \qquad (24)$$

which is the pdf of y for Wilson's centric distribution. It is readily seen from (18) and (19) that the values of the other statistical parameters for the acentric and centric distributions of Wilson also follow from (18) and (19) under the limiting conditions $D \to 0$ and $D \to 1$ respectively.

Since the pdf of y has been found to be superior to the pdf of z in the statistical tests for centrosymmetry (Ramachandran & Srinivasan, 1959) our discussions will be mainly based on the former. Since the $P(y)$ function has an implicit dependence on $H(=2\sin\theta/\lambda)$ and $\langle|\Delta\mathbf{r}|\rangle$ [see (14) and (20)], $P(y)$ curves have been drawn for $(\sin\theta)/\lambda = 0{\cdot}1$, $0{\cdot}2$, $0{\cdot}3$, *etc.*, for $\langle|\Delta\mathbf{r}|\rangle =$ $0{\cdot}05$, $0{\cdot}10$, $0{\cdot}15$ and $0{\cdot}2$ Å [see Fig. 1(*a*)–1(*d*)].

A common feature of the $P(y)$ curve (see Fig. 1) for any given values of $\langle|\Delta\mathbf{r}|\rangle$ ($\neq 0$) and $(\sin\theta)/\lambda$ is that it starts from the origin and, as y increases, rises steeply, crossing the $P_C(y)$ curve during its ascent at a point whose abscissa is y_1, say. After this sharp rise and cross-over, it attains a maximum whose height exceeds that of even the $P_A(y)$ curve. Thereafter the $P(y)$ curve falls towards the $P_C(y)$ curve though it systematically lies above the latter in the region $y_1 \le y \le 1{\cdot}5$. For values of y greater than about $1{\cdot}5$ the $P(y)$, $P_C(y)$ and $P_A(y)$ curves are all close to each other. It may be noted that the location of the cross-over point (*i.e.* the value of y_1) actually depends on the values of $\langle|\Delta\mathbf{r}|\rangle$ and $(\sin\theta)/\lambda$. For a given value of $\langle|\Delta\mathbf{r}|\rangle$, the $P(y)$ curve tends more and more towards the $P_A(y)$ curve as $(\sin\theta)/\lambda$ increases. This tendency is markedly visible when $\langle|\Delta\mathbf{r}|\rangle$ is greater than about $0{\cdot}05$ Å. Thus it appears that the $P(y)$ test conducted with reflexions of large $(\sin\theta)/\lambda$ values could enable us to detect the absence of an exact centre of symmetry in a non-centrosymmetric crystal possessing an approximate centre of symmetry. It is obvious that the power of the test could be improved by collecting data with Mo $K\alpha$ radiation.

We have stated above that the $P(y)$ curve for any given values of $\langle|\Delta\mathbf{r}|\rangle$ and $(\sin\theta)/\lambda$ intersects the $P_C(y)$ curve at the point y_1 and that it becomes close to the $P_C(y)$ curve for $y > 1{\cdot}5$. Thus the area under the $P(y)$ curve in the interval $y_1 \le y \le 1{\cdot}5$ would be different for the $P_C(y)$ and $P(y)$ curves and hence could be conveniently used as a test parameter.* It is obvious that this area is nothing but the probability that y takes a value in the interval $y_1 \le y \le 1{\cdot}5$. The intervals and the corresponding probabilities depend on the values of $(\sin\theta)/\lambda$ and $\langle|\Delta\mathbf{r}|\rangle$ and are summarized in Table 1. It may be noted here that the experimental values of the interval probabilities for any given crystal are given by the fractional number of reflexions with y values in the relevant intervals. Further it may be mentioned here that while the $P(y)$ test does not require *a priori* the probable value of $\langle|\Delta\mathbf{r}|\rangle$ (if any), it is required *a priori* for the interval probability test (see later).

Table 1. *The mean values of the higher moments of z as a function of* $\langle|\Delta\mathbf{r}|\rangle$ *over the ranges* $0{\cdot}35 \le (\sin\theta)/\lambda \le 0{\cdot}55$ *and* $0{\cdot}50 \le (\sin\theta)/\lambda \le 1{\cdot}0$

The subscripts 1 and 2 to the symbol $\langle - \rangle$ refer to the ranges $0{\cdot}35 \le (\sin\theta)/\lambda \le 0{\cdot}55$ and $0{\cdot}5 \le (\sin\theta)/\lambda \le 1{\cdot}0$ in which the mean values of the moments of z are calculated.

$\langle\lvert\Delta\mathbf{r}\rvert\rangle$	$\langle z^2\rangle_1$	$\langle z^3\rangle_1$	$\langle z^4\rangle_1$	$\langle z^2\rangle_2$	$\langle z^3\rangle_2$	$\langle z^4\rangle_2$
0·00*	3·0	15·0	105·0	3·0	15·0	105·0
0·01	2·9	14·9	104·8	2·9	14·9	104·5
0·02	2·9	14·9	104·3	2·9	14·8	103·5
0·03	2·9	14·8	103·8	2·9	14·6	101·7
0·04	2·9	14·8	103·0	2·9	14·4	99·3
0·05	2·9	14·7	102·0	2·9	14·1	96·3
0·06	2·9	14·5	100·7	2·8	13·7	92·8
0·07	2·9	14·4	99·2	2·8	13·3	89·0
0·08	2·9	14·2	97·5	2·7	12·9	84·8
0·09	2·8	14·0	95·7	2·7	12·4	80·5
0·10	2·8	13·8	93·7	2·6	12·0	76·1
0·15	2·7	12·6	82·1	2·4	9·7	55·4
0·20	2·5	11·2	69·3	2·2	7·9	40·4
0·25	2·4	9·9	57·2	2·1	6·9	31·8
0·30	2·3	8·7	47·0	2·0	6·4	27·4
0·35	2·2	7·8	39·1	2·0	6·1	25·4
0·40	2·1	7·1	33·5	2·0	6·0	24·6
0·50	2·0	6·4	27·3	2·0	6·0	24·0
0·60	2·0	6·1	25·0	2·0	6·0	24·0
0·70	2·0	6·0	24·2			
0·80*	2·0	6·0	24·0			

* The values of the moments corresponding to $\langle|\Delta\mathbf{r}|\rangle = 0$ are the same as those for Wilson's centric distribution for large $\langle|\Delta\mathbf{r}|\rangle$ (say, 0·8 Å); they tend to the values for Wilson's acentric distribution.

From equations (18) and (20) it is seen that the moments of z are also functions of $(\sin\theta)/\lambda$ and $\langle|\Delta\mathbf{r}|\rangle$. The average values of these moments over the region $0{\cdot}35 \le (\sin\theta)/\lambda \le 0{\cdot}55$ and over the region $0{\cdot}5 \le (\sin\theta)/\lambda \le 1{\cdot}0$ are given in Table 2 for various given values of $\langle|\Delta\mathbf{r}|\rangle$. While the former average is convenient for data collected with Cu $K\alpha$ radiation, the latter is suitable for the data collected with Mo $K\alpha$ radiation.

It may be noted that when the absence of an exact centre of symmetry in the case of any crystal suspected to have an approximate centre of symmetry could not be detected at the beginning of structure analysis, it is convenient to assume the higher symmetry and proceed with the structure determination (Parthasarathy, Sime & Speakman, 1969; Donohue, 1971). When the final refinement stage is reached one could

* Such a test has been referred to as modified $N(z)$ test by Hargreaves & Gogoi (1966) and semi-cumulative function test by Srikrishnan (1971). We prefer the term interval probability test [see Davenport (1970) for the origin of this term] since what is calculated here is the interval probability $P_r(y_1 \le y \le 1{\cdot}5)$. Hargreaves & Gogoi (1966) have shown that this test is superior to the conventional $N(z)$ and $P(y)$ tests since it has the advantages of both.

carry out the above $P(y)$ and higher-moment tests with the accurate F_o data which would then be available. From a study of the tendency of the experimental $P(y)$ functions obtained in the different ranges of $(\sin\theta)/\lambda$ the absence of the exact centre of symmetry could be inferred and, further, one could obtain a rough estimate of the expected value of $|\Delta\mathbf{r}|$. If such an estimate could be made then the more effective interval probability test could be performed. The methodology of this test can be briefly summarized in the following steps: (i) Obtain the approximate value of $\langle|\Delta\mathbf{r}|\rangle$ (if any) by first conducting the $P(y)$ and higher-moment tests. For the purpose of illustration we shall take $\langle|\Delta\mathbf{r}|\rangle > \simeq 0{\cdot}1$ Å. (ii) Corresponding to this value* of $\langle|\Delta\mathbf{r}|\rangle$, obtain the values of y_1 (which fix the intervals of y as $y_1 \le y \le 1{\cdot}5$) and the theoretical values of the interval probabilities for $(\sin\theta)/\lambda = 0{\cdot}3$, $0{\cdot}4$, *etc.*, from Table 1 for the crystals with an exact centre of symmetry and with an approximate centre of symmetry. (These are given against the rows named *C* and *NC* respectively in Table 1.) Thus if $\langle|\Delta\mathbf{r}|\rangle = 0{\cdot}1$ Å, then $y_1 = 0{\cdot}12$, $0{\cdot}15$, $0{\cdot}19$, *etc.*, when $(\sin\theta)/\lambda = 0{\cdot}3$, $0{\cdot}4$ and $0{\cdot}5$, *etc.* (iii) Divide the reflexions into regions of $(\sin\theta)/\lambda$ and obtain in each range the fractional number of reflexions with y values in the corresponding intervals $y_1 \le y \le 1{\cdot}5$. For example, if the total number of independent reflexions in the region $0{\cdot}45 \le (\sin\theta)/\lambda \le 0{\cdot}55$ is n and if of these n_i have their y values in the interval $0{\cdot}19 \le y \le 1{\cdot}5$, then n_i/n represents the experimental value of the interval probability corresponding to $(\sin\theta)/\lambda = 0{\cdot}5$ and $\langle|\Delta\mathbf{r}|\rangle = 0{\cdot}1$ Å. A comparison of the experimental values of the interval probabilities with the corresponding theoretical values in the various $(\sin\theta)/\lambda$ ranges could enable us to identify the nature of the crystal. It is to be noted here that accurate intensity data and accurate y values would be needed to conduct the tests since the distinction sought for here is subtle.

We have not applied the present test to the case of dibenzyl disulphide for the following two reasons: (i) The intensity data for Mo $K\alpha$ radiation, which are necessary for this compound, are not available; and (ii) The effect of the presence of heavy atoms is not taken into account in the present theory. When atoms of different scattering powers are present in the unit cell, the other symmetry elements of the space group also affect the intensity distribution significantly (Fos-

* For a given $\langle|\Delta\mathbf{r}|\rangle$, the quantity y_1 and the interval probability $P_r(y_1 \le y \le 1{\cdot}5)$ depend on the value of $(\sin\theta)/\lambda$.

Table 2. *Theoretical values of the fractional number of reflexions whose y values lie in the interval y_1 to* 1·50 *for the ideally centrosymmetric crystal and a non-centrosymmetric crystal with a degree of centrosymmetry*

The entries in the row against y_1 are the values of the lower limit y_1 of the interval for y and those in the row against *C* are the theoretical values of the fractional number of reflections with y values in the interval (y_1 to 1·50) for the ideally centrosymmetric crystal. Those in the row against *NC* are the corresponding values for the non-centrosymmetric crystal with a degree of centrosymmetry which is denoted by the parameter $\langle|\Delta\mathbf{r}|\rangle$ in column 1.

$\langle\lvert\Delta\mathbf{r}\rvert\rangle$		$\sin\theta/\lambda$	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1	1·2
0·04	y_1		0·05	0·06	0·08	0·09	0·11	0·12	0·14	0·15	0·17	0·18
	C		82·7	81·9	80·3	79·5	77·9	77·1	75·5	74·7	73·1	72·4
	NC		84·3	84·1	83·1	82·9	81·8	81·6	80·6	80·4	79·3	79·1
0·05	y_1		0·06	0·08	0·10	0·12	0·14	0·15	0·17	0·19	0·20	0·22
	C		81·9	80·3	78·7	77·1	75·5	74·7	73·1	71·6	70·8	69·2
	NC		84·0	83·1	82·2	81·3	80·4	80·4	79·5	78·6	78·5	77·6
0·06	y_1		0·07	0·09	0·12	0·14	0·16	0·18	0·20	0·22	0·24	0·25
	C		81·1	79·5	77·1	75·5	73·9	72·4	70·8	69·2	67·7	66·9
	NC		83·6	82·9	81·3	80·6	79·8	79·1	78·3	77·6	76·8	76·7
0·07	y_1		0·08	0·11	0·14	0·16	0·18	0·21	0·23	0·25	0·27	0·28
	C		80·3	77·9	75·5	73·9	72·4	70·0	68·4	66·9	65·4	64·6
	NC		83·2	81·8	80·4	79·8	79·2	77·8	77·2	76·5	75·8	75·8
0·08	y_1		0·09	0·12	0·15	0·18	0·20	0·23	0·25	0·27	0·29	0·31
	C		79·5	77·1	74·7	72·4	70·8	68·4	66·9	65·4	63·8	62·3
	NC		82·9	81·6	80·4	79·1	78·6	77·3	76·7	76·1	75·5	74·8
0·09	y_1		0·10	0·14	0·17	0·20	0·23	0·25	0·28	0·30	0·32	0·33
	C		78·7	75·5	73·1	70·8	68·4	66·9	64·6	63·1	61·5	60·8
	NC		82·5	80·6	79·5	78·3	77·2	76·7	75·5	75·0	74·4	74·5
0·10	y_1		0·12	0·15	0·19	0·22	0·25	0·27	0·30	0·32	0·34	0·35
	C		77·1	74·7	71·6	69·2	66·9	65·4	63·1	61·5	60·0	59·3
	NC		81·3	80·4	78·6	77·6	76·5	76·1	75·0	74·5	73·9	74·0
0·12	y_1		0·14	0·18	0·22	0·25	0·28	0·31	0·33	0·35	0·37	0·38
	C		75·5	72·4	69·2	66·9	64·6	62·3	60·8	59·3	57·8	57·0
	NC		80·6	79·1	77·6	76·7	75·8	74·8	74·5	74·0	73·4	73·4
0·15	y_1		0·17	0·22	0·26	0·30	0·33	0·35	0·38	0·39	0·40	0·41
	C		73·1	69·2	66·1	63·1	60·8	59·3	57·0	56·3	55·6	54·8
	NC		79·5	77·6	76·3	75·0	74·2	74·0	72·9	73·0	73·0	72·8
0·20	y_1		0·22	0·27	0·32	0·35	0·38	0·40	0·41	0·42	0·43	0·43
	C		69·2	65·4	61·5	59·3	57·0	55·6	54·8	54·1	53·4	53·4
	NC		77·6	76·1	74·5	74·0	73·2	72·8	72·8	72·5	72·1	72·3

ter & Hargreaves, 1963). Thus to study dibenzyl disulphide a more exact theory taking into account the other symmetry elements of the relevant space groups would be needed. Such a theory is under consideration.

One of the authors (V.P.) would like to thank the University Grants Commission, India, for financial assistance.

APPENDIX

Evaluation of the mean and variance of A

We shall evaluate the mean and variance of the real part $A(=\sum_{j=1}^{N/2} A_j)$ of (1) in terms of those of the A_j's as they are required for obtaining the pdf of A. Since the expectation of the sum is the sum of the expectations

$$\langle A\rangle=\sum_{j=1}^{N/2}\langle A_j\rangle \qquad \text{(I1)}$$

where A_j can be shown to be [see equation (1)]

$$A_j=f_j[\cos\varphi_j(1+\cos\psi_j)+\sin\varphi_j\sin\psi_j]\,. \qquad \text{(I2)}$$

Since the A_j's arise from contributions from different atoms, they can be treated as independent random variables and hence we have

$$\sigma_A^2=\sum_{j=1}^{N/2}\sigma_j^2 \qquad \text{(I3)}$$

where σ_j^2 is the variance of A_j. Since the vector $\Delta\mathbf{r}_j$ can be taken to be independent of the position of atom j, it follows that φ_j and ψ_j of equation (I2) are independent random variables and hence for any functions of φ_j and ψ_j we have

$$\langle f_1(\varphi_i)f_2(\psi_i)\rangle=\langle f_1(\varphi_i)\rangle\,\langle f_2(\psi_i)\rangle. \qquad \text{(I4)}$$

Assuming that coordinates x_j,y_j,z_j of atom j are independent random variables uniformly distributed in the interval 0 to 1, we can take φ_j to be a random variable distributed uniformly in the interval 0 to 2π (Hauptman & Karle, 1953; Foster & Hargreaves, 1963). Thus we have

$$\langle\cos^p\varphi_j\rangle=\langle\sin^p\varphi_j\rangle=\begin{cases}0 & \text{if } p=1\\ \frac{1}{2} & \text{if } p=2\,.\end{cases} \qquad \text{(I5)}$$

Since $\Delta\mathbf{r}_j$ is assumed to obey the Gaussian distribution which is symmetric it follows that (Luzzati, 1952)

$$\langle\sin\psi_j\rangle=0\,. \qquad \text{(I6)}$$

We shall, following Luzzati (1952), define a parameter D to be

$$D=\langle\cos\psi_j\rangle=\langle\cos 2\pi\mathbf{H}\,.\,\Delta\mathbf{r}_j\rangle\,. \qquad \text{(I7)}$$

From equation (I2) and the results in (I4) to (I7) we obtain $\langle A_j\rangle=0$ which when substituted in (I1) yields

$$\langle A\rangle=0\,. \qquad \text{(I8)}$$

Since $\langle A_j\rangle=0$, it also follows that $\sigma_j^2=\langle A_j^2\rangle$. From equation (I2) and the results in (I4) to (I7) we thus obtain

$$\sigma_j^2=\langle A_j^2\rangle=f_j^2(1+D)\,. \qquad \text{(I9)}$$

Substituting (I9) in (I3) we thus obtain

$$\sigma_A^2=(1+D)\sum_{j=1}^{N/2}f_j^2=\frac{(1+D)}{2}\,\sigma_N^2 \qquad \text{(I10)}$$

where

$$\sigma_N^2=\sum_{j=1}^{N}f_j^2\,. \qquad \text{(I11)}$$

It may be noted here that D will be independent of the index j since all the $\Delta\mathbf{r}_j$'s obey the same Gaussian law.

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