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Test of the New Statistical Formula for Distinguishing Between Centrosymmetric and Non-Centrosymmetric Structures

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New statistical formulae, which make use of the probability distribution function for the normalised structure amplitude, have been developed and are shown to be very efficient in distinguishing between centrosymmetric and non-centrosymmetric structures. The effect of the presence of one and two heavy atoms in the unit cell on these distribution functions is discussed theoretically and the results are also verified experimentally. Tables and curves of these theoretical distribution functions are also given.

1. Introduction

In a recent short paper, the authors (Ramachandran & Srinivasan, 1959) have suggested a new method for distinguishing between centrosymmetric and non-centrosymmetric structures. The method consists in using the probability distribution function for amplitudes instead of intensities and in using the actual distribution function $P(y)dy$, i.e., the probability that the quantity $y=|F|/\sqrt{\langle I\rangle}$ lies between y and $y+dy$, rather than the cumulative distribution function as has been adopted by earlier workers (Howells, Phillips & Rogers, 1950). The distribution function ${}_cP(y)$ and ${}_NP(y)$ for centrosymmetric and non-centrosymmetric structures are very different in shape (see equation (3) and (4) below). They were tested in a few cases and were found to be decidedly superior to the earlier $N(z)$ function. However, when the structure contained a small number of heavy atoms in addition to a large number of light atoms, the observed distribution deviated significantly from the theoretical function. The present paper is concerned with a detailed test of the new formulae. The theory is extended to the case when a small number of heavy atoms (one or two) is present in the structure. The essential formulae for the one-atom case have been developed by Sim (1958*a*) although he worked out only the form of the function $N(z)$. In this paper the effect on the function $P(y)$ is discussed. The two-atom case has also been considered by Sim (1958*b*) but the final formula is given in the form of an integral. Here the distribution function $P(y)$ is itself evaluated numerically, but the procedure is rather different from that used by Sim.

It may be interesting to summarize briefly the previous work in this field. The problem of intensity distribution in the resultant of n vibrations of equal amplitude was considered by Lord Rayleigh (1880). Its close relation to the problem of 'random walk' in one and two dimensions was also pointed out by him (Rayleigh, 1920; see also Chandrasekhar, 1943). If the steps are restricted to one dimension, namely either forward or backward along the same line, we have the analogue of a centrosymmetric crystal where the phase can only be 0 or π. If the steps can be in any direction in a plane, then we have the analogue of a non-centrosymmetric crystal. That the problem of distribution of X-ray intensities is basically related to the random-walk problem has been pointed out by Karle & Hauptman (1950). The functions ${}_cP(y)$ and ${}_NP(y)$ are implicit in Rayleigh's formulae. In fact, using an optical analogy Ramachandran (1943) found that the distribution of intensity in the scattering of light by a cloud of particles agreed closely with the predicted distribution.

Wilson (1949) derived the distribution functions using the central-limit theorem but most of his formulae deal essentially with intensitics. More recently Karle & Hauptman (1953) and Hauptman & Karle (1953) have developed a more complete theory in which the functions assume the form of a series containing higher-order terms. Wilson (1949) suggested that the ratio of the square of the mean amplitude to the mean-square amplitude may be used to test for the presence of a centre of symmetry, as this ratio has values 0·785 and 0·637 for non-centrosymmetric and centrosymmetric structures. Later, Wilson (1951) also suggested the use of the variance of intensity *viz.*, $\langle(z-1)^2\rangle$ where $z=I/\langle I\rangle$, for the purpose, this having values 1 and 2 respectively for the two cases. However, it must be mentioned that a detailed comparison of the observed $P(y)$ with theory includes, in effect, all these tests.

The effect of some of the atoms occupying special positions, and of groups of atoms having a symmetry not utilized by the space group, have been considered by various workers (Wilson, 1950*a*, *b*; Rogers, 1950; Lipson & Woolfson, 1952; Rogers & Wilson, 1953; Hauptman & Karle, 1953; Karle & Hauptman, 1953; Herbstein & Schoening, 1957). These will not be considered further in this paper. The distribution function, when the number of atoms in the unit cell is small, does not appear to have been worked out system-

atically, although it appears that they could be obtained from the work of Hauptman & Karle (1953). A similar difficulty occurs when the structure contains a small number of heavy atoms whose contribution to the intensity is predominant, although the total number of atoms is large. It is proposed to work out in this paper only the cases when there are one or two heavy atoms in addition to a large number of light atoms. The situation when the number of atoms is more than two, but still small, will be considered later.

2. The new statistical test

If the intensity I of each reflexion is expressed as a fraction of the local average $\langle I \rangle$, the probability distribution functions assume the form

$$ {}_NP(z)dz = \exp(-z)dz \tag{1}$$

$$ {}_CP(z)dz = \frac{1}{(2\pi z)^{\frac{1}{2}}} \exp(-\tfrac{1}{2}z)dz\,, \tag{2}$$

where $z = I/\langle I \rangle$ and $P(z)dz$ represents the probability that z lies between z and $z+dz$. The subscripts N and C refer to non-centrosymmetric and centrosymmetric structures respectively.

If we modify these probability functions such that the argument is $y = z^{\frac{1}{2}}$ we obtain,

$$ {}_NP(y)dy = 2y \exp(-y^2)dy \tag{3}$$

$$ {}_CP(y)dy = (2/\pi)^{\frac{1}{2}} \exp(-y^2/2)dy \tag{4}$$

where

$$ y = z^{\frac{1}{2}} = |F|/\sqrt{\langle I \rangle} = F/\sigma \text{ (say)}\,. \tag{5}$$

As was pointed out in the preliminary report, the function $P(y)$ is superior to $N(z) = \int_0^z P(z)dz$ for distinguishing between centrosymmetric and non-centrosymmetric structures, since the functions ${}_CP(y)$ and ${}_NP(y)$ for the two cases are very different in shape: the former starts from a finite value at $y=0$ and gradually decreases with increasing value of y, while the latter starts from zero for $y=0$ and increases initially reaching a maximum at $y=0{\cdot}707$ and decreases for further increase in the value of y. However, the above expressions (3) and (4) for the function are valid only if all atoms are alike. Actually it can be shown (from the central limit theorem) that they would still be valid even if the atoms differ widely in scattering power provided the number of atoms of each type is large (say more than 5 or 6).

On the other hand if there are just one or two heavy atoms in the structure whose contribution to the total scattering is appreciable, then the shape of the two functions is appreciably altered. However, the way in which the shape is changed cannot be readily predicted by qualitative arguments. For instance, we know that a group consisting of just one or two atoms must necessarily be centrosymmetric whether the crystal is so or not. So it would appear that the occurrence of such a group should alter ${}_NP(y)$ more than ${}_CP(y)$. Actually it is found to be the other way round, as will be seen from the following sections. The reason for this is that for both the one and two-atom cases the maximum of $P(y)$ occurs at a finite value of y as in ${}_NP(y)$ and not at $y=0$ as in ${}_CP(y)$ and hence the former is modified less than the latter.

We shall consider the two cases in detail in the next two sections.

3. One heavy atom in the unit cell

The notation used is as follows: The structure factor for the composite structure is denoted by F and can be expressed as the vector sum

$$ F = F_1 + F_2\,, \tag{6}$$

where F_1 and F_2 are the contributions due to the light and heavy atoms respectively. The average intensity, which is identifiable with $\sum_j f_j^2$ (Wilson, 1949), is denoted by σ^2 and for convenience this quantity is normalised to unity. Thus,

$$ \sigma^2 = \sigma_1^2 + \sigma_2^2 = 1\,, \tag{7}$$

σ_1^2 and σ_2^2 being the normalised mean-square values of the light and heavy atom contributions.

When the structure contains one heavy atom only, the origin may always be chosen on the heavy atom itself. The remaining atoms (say m in number) may be centrosymmetrically arranged in groups $m/2$, with respect to the heavy atom, leading to a centrosymmetric structure, or may be completely non-centrosymmetric, giving rise to a non-centrosymmetric structure. The distribution functions for these cases have been obtained by Sim (1958*a*, *b*). The function $P(y)$ may be obtained from his results and it takes the following forms:

$$ {}_{1N}P(y)dy = 2y/\sigma_1^2 \exp -[(y^2+\sigma_2^2)/\sigma_1^2] I_0(2y\sigma_2/\sigma_1^2)dy \tag{8}$$

$$ {}_{1C}P(y)dy = (2/(\pi\sigma_1^2))^{\frac{1}{2}} \exp -[(y^2+\sigma_2^2)/\sigma_1^2] \cosh(y\sigma_2/\sigma_1^2)dy\,, \tag{9}$$

where $I_0(x)$ is the zero order Bessel function with imaginary argument (Watson, 1944, p. 77). The subscripts $1N$ and $1C$ indicate that they refer to a non-centrosymmetric and centrosymmetric crystal with one heavy atom in the structure.

4. Two heavy atoms in the unit cell

4·1. *The two-atom distribution*

In order to arrive at the probability distribution functions for a structure which contains two heavy atoms in addition to a large number of light atoms, we shall first work out the function for a structure which contains only two heavy atoms and consider

later how the standard distributions (3) and (4) are altered by the introduction of the two heavy atoms.

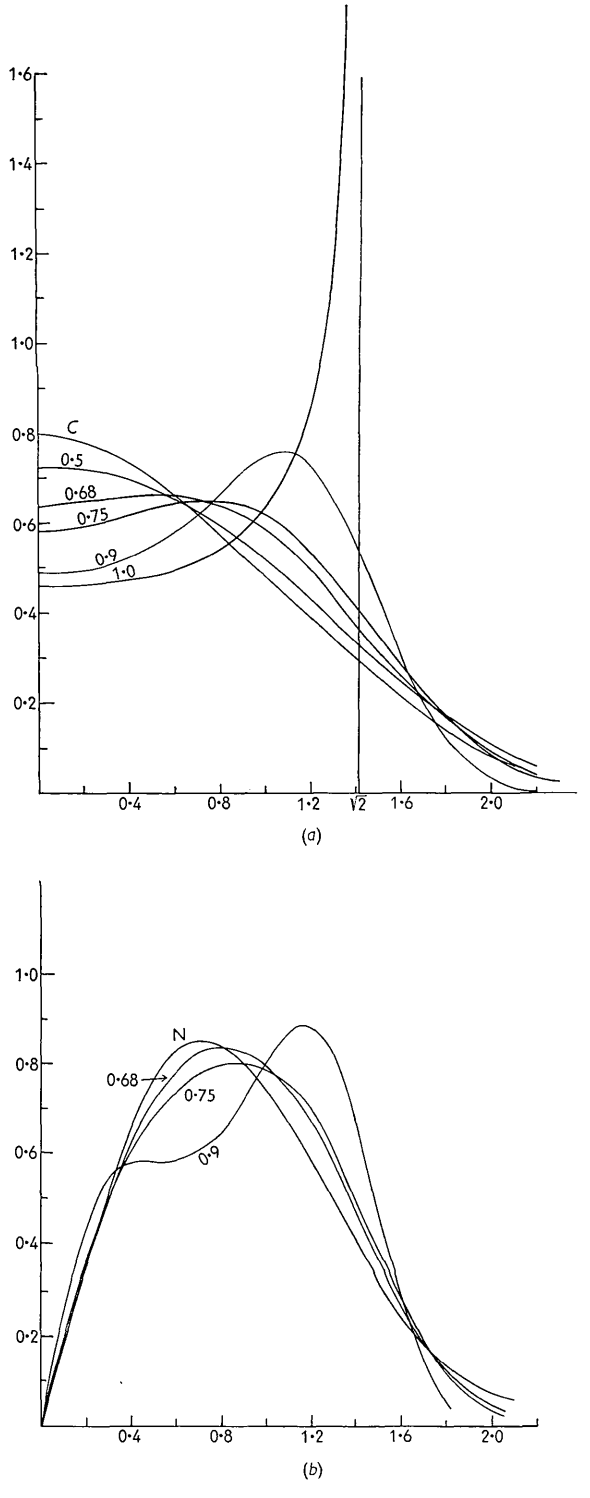

Fig. 1. Probability distribution function for (*a*) centrosymmetric and (*b*) non-centrosymmetric structures containing two heavy atoms. The number close to each curve denotes the value of σ_2^2.

Let the unit cell contain two atoms of equal scattering power f. In such a case we may always take the origin midway between the two atoms, so that the structure factor can be written as

$$F=2f\cos\theta\,, \tag{10}$$

where $\theta=2\pi\mathbf{S}.\mathbf{r}$, where $\mathbf{S}$ is the reciprocal vector of the reflection and $\mathbf{r}$ is the position vector of one of the atoms respectively. If the atoms are in general positions, θ can be considered to be a random variable, resulting in

$$P(\theta)d\theta=Cd\theta\,, \tag{11}$$

where C is a constant. The probability function for F can therefore be written as

$$P(F)dF=C|d\theta/dF|dF\,. \tag{12}$$

Since $|dF/d\theta|=|2f\sin\theta|$ we have, by eliminating θ from (12)

$$P(F)dF=C(4f^2-F^2)^{-\frac{1}{2}}dF\,. \tag{13}$$

Since the probability that $|F|$ lies between $|F|$ and $|F|+d|F|$ is twice the probability that F lies between F and $F+dF$ we get

$$P(|F|)d|F|=\frac{2C}{\sqrt{(4f^2-F^2)}}d|F|\,. \tag{14}$$

In terms of the normalised structure amplitude $y=|F|/\sigma$ we get, since $\sigma^2=2f^2$,

$$P(y)dy=\frac{2C}{\sqrt{(2-y^2)}}dy \tag{15}$$

and normalisation gives the value of C to be $1/\pi$. Thus,

$${}_2P(y)dy=\frac{2}{\pi}\frac{1}{\sqrt{(2-y^2)}}dy\,, \tag{16}$$

where the subscript 2 has been used to denote that it refers to a set of two heavy atoms. A graph of ${}_2P(y)$ versus y is shown in Fig. 1(*a*) (curve marked 1·0). The curve starts at $\sqrt{2}/\pi$ at $y=0$ and continuously increases reaching infinity at $y=\sqrt{2}$. Its real part is zero beyond $y=\sqrt{2}$, so that the probability function can be taken to be zero.

4·2. *Combination of distributions*

(*a*) *Centrosymmetric case.*—When the structure contains a sufficiently large number of similar light atoms and also two heavy atoms in the unit cell, it is obvious that the resultant distribution will deviate more and more from the standard distributions (3) and (4) with increasing proportion of the heavy-atom contribution. In the limiting case when the two heavy atoms alone are present, the distribution will obviously be as given by (16). We shall first work out the distribution when the composite structure is centrosymmetric.

Writing

$$F=F_1+F_2 \tag{17}$$

it will be seen that F_1 and F_2 can be considered to be random variables. Again, since the contribution to F by the light atoms is independent of the presence of the heavy atoms, we can write

$$ {}_{2C}P(F) = \int_{-\infty}^{\infty} {}_{2}P(F_2)\,{}_{C}P(F-F_2)\,dF_2 \,. \qquad (18) $$

The probability function for F can therefore be obtained by evaluating the convolution integral (18) and to do this, the expressions (3), (4) and (16) have to be recast in terms of the structure factors. Using the appropriate subscripts we get from (4)

$$ {}_{C}P(|F_1|)\,d|F_1| = \frac{1}{\sigma_1}(2/\pi)^{\frac{1}{2}} \exp\left(-|F_1|^2/(2\sigma_1^2)\right) d|F_1| \,. \qquad (19) $$

Since the probability that F_1 lies between F_1 and F_1+dF_1 is half the probability that $|F_1|$ lies between $|F_1|$ and $|F_1|+d|F_1|$ we get

$$ {}_{C}P(F_1)\,dF_1 = 1/(2\pi\sigma_1^2)^{\frac{1}{2}} \exp\,-(F_1^2/(2\sigma_1^2))\,dF_1 \,. \qquad (20) $$

Similarly (16) gives

$$ {}_{2}P(F_2)\,dF_2 = 1/(\pi\sigma_2/2).1/(1-F_2^2/2\sigma_2^2)^{\frac{1}{2}}\,dF_2 \,. \qquad (21) $$

These have to be substituted in (18) to get the function ${}_{2C}P(F)$, twice the value of which gives the required ${}_{2C}P(y)$, since $\sigma=1$.

(*b*) *Non-centrosymmetric case.*—Since the contribution to F from the two-atom group is always real, though the structure is non-centrosymmetric, we can write in the present case

$$ F = F' + iF'' = (F_1' + F_2') + iF_1'' \,. \qquad (22) $$

From (3) we get

$$ {}_{N}P(|F_1|)\,d|F_1| = 2|F_1|/\sigma_1^2 \exp\,-(|F_1|^2/\sigma_1^2)\,d|F_1| \,. \qquad (23) $$

Since the probability that $|F_1|$ lies between $|F_1|$ and $|F_1|+d|F_1|$ is equal to the probability that the terminus of the vector F_1 lies within an annulus of inside and outside radii $|F_1|$ and $|F_1|+d|F_1|$, we get

$$ {}_{N}P(|F_1|)\,d|F_1| = {}_{N}P(F_1)\,dA_1 \,, $$

where dA_1 is the element of area in the plane in which F_1 lies and whose magnitude is $2\pi|F_1|\,d|F_1|$. Hence we get,

$$ {}_{N}P(F_1) = {}_{N}P(|F_1|)/(2\pi|F_1|) = 1/(\pi\sigma_1^2) \exp\left(-|F_1|^2/\sigma_1^2\right) \,. \qquad (24) $$

This can again be written as a joint probability distribution in the two-dimensional space defined by F_1' and F_1'' in which $dA_1 = dF_1'\,dF_1''$. Thus

$$ \begin{aligned} {}_{N}P(F_1)\,dA_1 &= 1/(\pi\sigma_1^2) \exp\,-[F_1'^2 + F_1''^2/\sigma_1^2]\,dA_1 \\ &= [1/(\pi\sigma_1^2)^{\frac{1}{2}} \exp\,(-F_1'^2/\sigma_1^2)] \\ &\quad \times [1/(\pi\sigma_1^2)^{\frac{1}{2}} \exp\,(-F_1''^2/\sigma_1^2)]\,dF_1'\,dF_1'' \,. \end{aligned} \qquad (25) $$

As regards the component F_2, which does not have an imaginary component, we can circumvent the difficulty by writing

$$ {}_{2}P(F_2)\,dA_2 = {}_{2}P(F_2')\,\delta(F_2'')\,dF_2'\,dF_2'' \,, \qquad (26) $$

where $\delta(F_2'')$ is the delta function, i.e.,

$$ \begin{aligned} \delta(F_2'') &= 0, \quad F_2'' \neq 0 \\ &= 1, \quad F_2'' = 0 \end{aligned} $$

and

$$ \int_{-\infty}^{\infty} \delta(F_2'')\,dF_2'' = 1 \,. $$

The convolution integral (18) takes the form

$$ \begin{aligned} {}_{2N}P(F) &= \int_{-\infty}^{\infty} {}_{2}P(F_2)\,{}_{N}P(F-F_2)\,dA_2 \\ &= \left[\int_{-\infty}^{\infty} {}_{2}P(F_2')\,{}_{N}P(F'-F_2')\,dF_2'\right] \\ &\quad \times \left[\int_{-\infty}^{\infty} {}_{N}P(F_1'')\,\delta(F_2'')\,dF_2''\right] \\ &= \left[\int_{-\infty}^{\infty} {}_{2}P(F_2')\,{}_{N}P(F_1')\,dF_2'\right] {}_{N}P(F_1'') \,, \end{aligned} \qquad (27) $$

where ${}_{N}P(F_1')$ and ${}_{N}P(F_1'')$ denote the two factors in expression (25).

The separation of the real and imaginary components, F' and F'' of F makes the computation easy.

Finally,

$$ {}_{2N}P(y) = 2\pi|F|\;{}_{2N}P(F) \,. \qquad (28) $$

4·3. *Nature of the probability distribution curves with heavy atoms*

Figs. 2(*a*) and (*b*) exhibit the shape of the curves (8) and (9) for different values of the heavy-atom contribution ($\sigma_2^2=0{\cdot}5$, 0·75 etc.). When $\sigma_2^2=0$ (i.e., $\sigma_1^2=1$), it will be noticed that the formulae (8) and (9) reduce to the standard equations (3) and (4) as obviously they should. It is interesting to note that while the standard distributions (3) and (4) for centrosymmetric and non-centrosymmetric structures are quite dissimilar in shape the distributions for a structure containing one heavy atom for both centrosymmetric and non-centrosymmetric arrangements tend to be more and more similar with increasing heaviness of the atom.

The functions ${}_{2C}P(y)$ and ${}_{2N}P(y)$ were evaluated numerically and are shown in Figs. 1(*a*) and (*b*). The theoretical curves for the centrosymmetric case were computed for different percentage contributions of the heavy atoms namely, for $\sigma_2^2=0{\cdot}9$, 0·75 and 0·5. It will be seen from Fig. 1(*a*) that computation for still smaller values of σ_2^2 is unnecessary since even for $\sigma_2^2=0{\cdot}50$ the curve practically coincides with ${}_{C}P(y)$. In the non-centrosymmetric case calculations showed that, even for a large contribution from the heavy atoms, the shape of the ${}_{2N}P(y)$ is not very much different from the standard ${}_{N}P(y)$ curve, the general

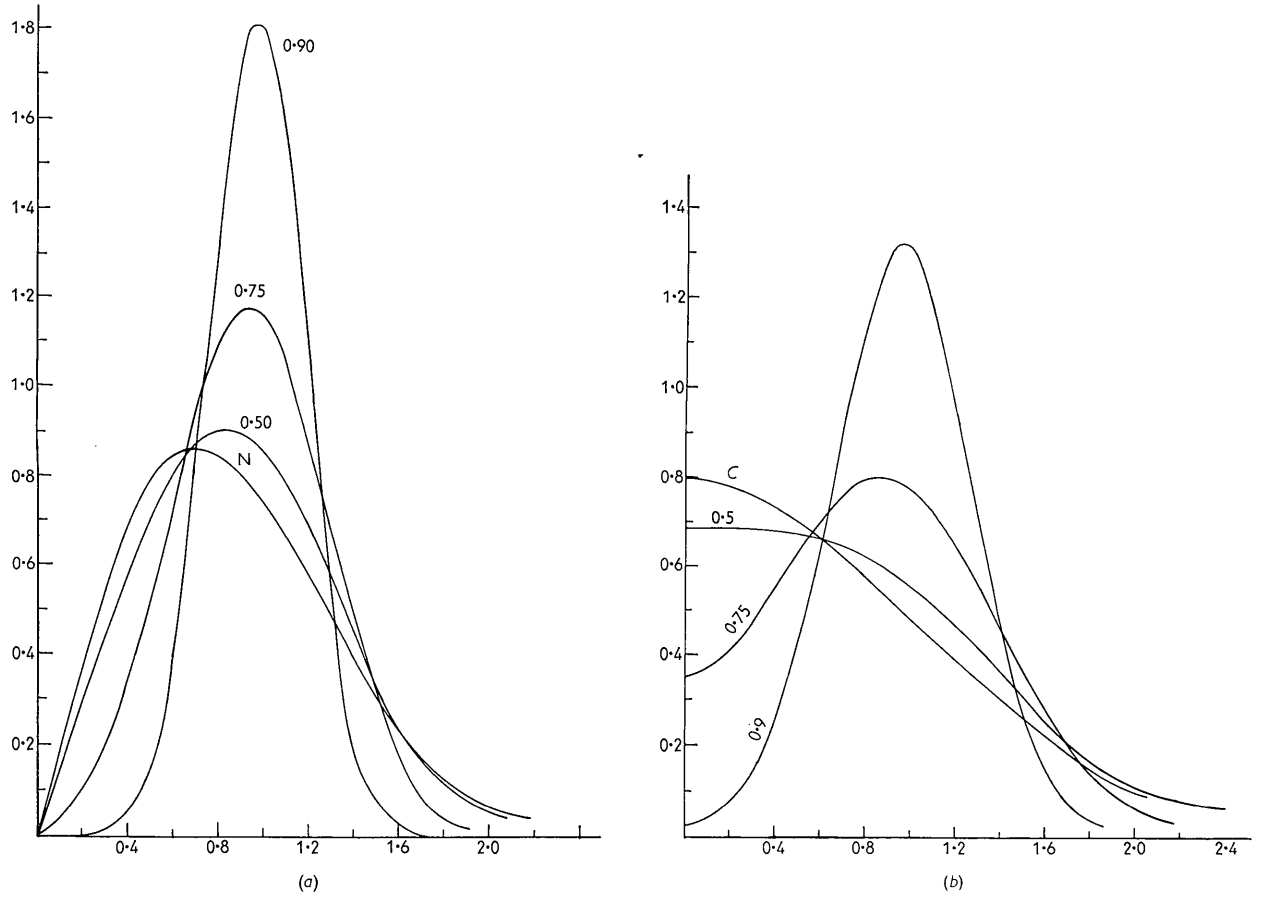

Fig. 2. Probability distribution function for (*a*) centrosymmetric and (*b*) non-centrosymmetric structures containing one heavy atom. The number close to each curve denotes the value of σ_2^2.

Table 1. *Numerical data for distribution functions*

FUNCTION	$_CP(y)$	$_{1C}P(y)$			$_{2C}P(y)$					$_NP(y)$	$_{1N}P(y)$			$_{2N}P(y)$		
σ_2^2 / y	0·0	0·50	0·75	0·90	0·50	0·68	0·75	0·90	1·00	0·0	0·50	0·75	0·90	0·68	0·75	0·90
0·0	0·798	0·685	0·356	0·028	0·726	0·646	0·587	0·490	0·450	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·1	0·794	0·685	0·370	0·040	0·724	0·647	0·589	0·492	0·451	0·198	0·147	0·043	0·000	0·184	0·192	0·256
0·2	0·782	0·684	0·411	0·079	0·718	0·651	0·596	0·498	0·460	0·384	0·294	0·105	0·003	0·354	0·364	0·445
0·3	0·762	0·683	0·473	0·155	0·710	0·655	0·607	0·509	0·461	0·548	0·438	0·201	0·015	0·504	0·508	0·548
0·4	0·736	0·680	0·549	0·282	0·696	0·660	0·621	0·525	0·469	0·682	0·575	0·341	0·056	0·625	0·612	0·584
0·5	0·704	0·672	0·629	0·465	0·679	0·662	0·634	0·549	0·481	0·779	0·700	0·523	0·176	0·717	0·681	0·586
0·6	0·666	0·661	0·703	0·687	0·657	0·660	0·646	0·581	0·497	0·838	0·802	0·735	0·426	0·784	0·736	0·589
0·7	0·625	0·643	0·761	0·927	0·630	0·653	0·653	0·621	0·518	0·858	0·868	0·937	0·834	0·833	0·783	0·617
0·8	0·579	0·618	0·794	1·133	0·598	0·638	0·652	0·667	0·546	0·843	0·899	1·097	1·327	0·841	0·800	0·650
0·9	0·532	0·587	0·800	1·250	0·561	0·614	0·641	0·712	0·584	0·801	0·896	1·170	1·715	0·834	0·809	0·724
1·0	0·484	0·549	0·767	1·245	0·521	0·581	0·619	0·745	0·637	0·736	0·846	1·153	1·801	0·803	0·798	0·803
1·1	0·436	0·505	0·715	1·104	0·478	0·539	0·583	0·752	0·716	0·656	0·769	1·039	1·541	0·752	0·769	0·871
1·2	0·389	0·457	0·640	0·941	0·433	0·491	0·537	0·723	0·851	0·569	0·665	0·861	1·075	0·674	0·708	0·880
1·3	0·343	0·408	0·545	0·643	0·386	0·431	0·480	0·654	1·144	0·481	0·559	0·663	0·612	0·575	0·615	0·817
1·4	0·299	0·356	0·450	0·461	0·339	0·379	0·418	0·552	3·184	0·395	0·449	0·504	0·174	0·467	0·503	0·647
1·5	0·259	0·304	0·358	0·259	0·293	0·321	0·352	0·432		0·315	0·338	0·307	0·108	0·362	0·389	0·454
1·6	0·222	0·256	0·272	0·157	0·250	0·265	0·287	0·311		0·246	0·252	0·175	0·034	0·272	0·283	0·264
1·7	0·188	0·214	0·199	0·070	0·209	0·213	0·227	0·205		0·190	0·178	0·104	0·009	0·183	0·189	0·133
1·8	0·158	0·171	0·137	0·036	0·172	0·167	0·173	0·124		0·140	0·119	0·049	0·002	0·122	0·115	0·050
1·9	0·131	0·136	0·090	–	0·139	0·128	0·127	0·068		0·103	0·075	0·023	–	0·075	0·068	0·016
2·0	0·108	0·105	0·054	–	0·111	0·094	0·091	0·034		0·072	0·044	0·010	–	0·045	0·036	0·005
2·1	0·088	0·094	0·038	–	0·087	0·068	0·062	0·016		0·050	0·025	–	–	–	–	–
2·2	0·071	0·080	0·026	–	0·067	0·048	0·041	0·006		0·035	0·015	–	–	–	–	–

FUNCTION VANISHES BEYOND $y = \sqrt{2}$

tendency being to shift the whole curve in the positive direction of the x-axis. The calculations were made for $\sigma_2^2=0{\cdot}68$, 0·75 and 0·90 and the results are shown in Fig. 1(*b*).

Here again it will be noticed that the two curves ${}_{2N}P(y)$ and ${}_{2C}P(y)$ become more and more similar with increasing heaviness of the atom. However, the original curves, namely ${}_{N}P(y)$ and ${}_{C}P(y)$, are not so strongly modified in this case as in the one-atom case for the same proportion of the heavy atom contribution. This shows in a general way that if the number of heavy atoms is more than two, the actual distribution functions would approach ${}_{N}P(y)$ and ${}_{C}P(y)$ closer and closer, with increase in the number of heavy atoms.

The numerical data for the various functions are given in Table 1.

5. Comparison of theory with experimental data

5·1. *Computation of the experimental curves*

A number of structures, for which the experimental data were available, was used in testing the above theoretical curves. The method of calculating the function $P(y)$ from the observed data was as follows. The reflexions were grouped into regions of $\sin\theta$ namely 0 to 0·2, 0·2 to 0·4, etc. and in each range the local average intensity $\langle I\rangle$ was determined. This was assumed to be the same for all the reflexions in the particular group and the values of $|F|/\sqrt{\langle I\rangle}=y$ were computed. The number of reflexions having values of y between y and $y+dy$ were determined and from these the value of the function $P(y)$ at the midpoints of the ranges was calculated.

Moreover for statistical reasons the reflexions with $\sin\theta$ less than about 0·2 were neglected. It was, in fact, observed in a number of cases that in this region the observed values of $\langle I\rangle$ did not fit well with the theoretical mean, namely $\sum_j f_j^2$.

The above method of computation was found to suffice practically for all cases. However, the assumption that $\langle I\rangle$ was the same for all reflexions in a particular range seemed to be rather too drastic an approximation, particularly in cases where the variation of $\langle I\rangle$ with $\sin\theta$ was too rapid and also when the total number of reflexions was small. In those cases it was found better to use the value of $\langle I\rangle$ for each reflexion from a graph of $\sum_j f_j^2$ versus $\sin\theta$.

While calculating the values of σ_2 for the heavy-atom compounds the effect of the variation of f with θ should be taken into account. If the temperature factor is assumed to be the same for all atoms the values of σ_2^2 and σ_1^2 are given by

$$\sigma_2^2=(\sum_H f_H^2/\sum_j f_j^2);\quad \sigma_1^2=(\sum_L f_L^2/\sum_j f_j^2),$$

where

$$\sum_j f_j^2=\sum_H f_H^2+\sum_L f_L^2.$$

Consequently, the value of σ_2^2 will invariably increase with increase in the value of θ. Thus for example, in the case of L-tyrosine-hydrobromide the values are 0·68, 0·78, 0·83, 0·87, 0·88 and 0·87 respectively for $\sin\theta=0$, 0·2, 0·3, 0·5, 0·7 and 0·9. Since the distribution curve has been averaged over all the ranges, the value of σ_2^2 was also averaged over these ranges and only this value is quoted in the discussion that follows.

5·2. *Centrosymmetric case*

The data available for the following compounds were examined. α-rhamnose monohydrate, 3:3′ dichloro 4:4′ dihydroxy-diphenyl-methane, L-tyrosine hydrochloride, L-ephedrine hydrochloride, L-tyrosine hydrobromide and p-chlorobenzene seleninic acid. The experimental data are compared with the theoretical distributions in Figs. 3 and 4.

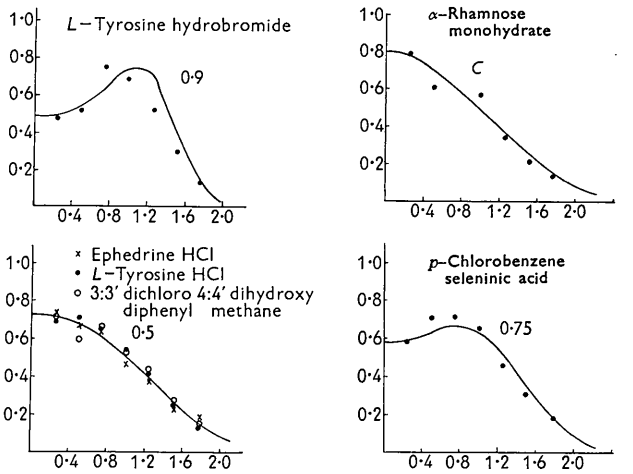

Fig. 3. Comparison of the experimental data with theoretical distributions for centrosymmetric structures.

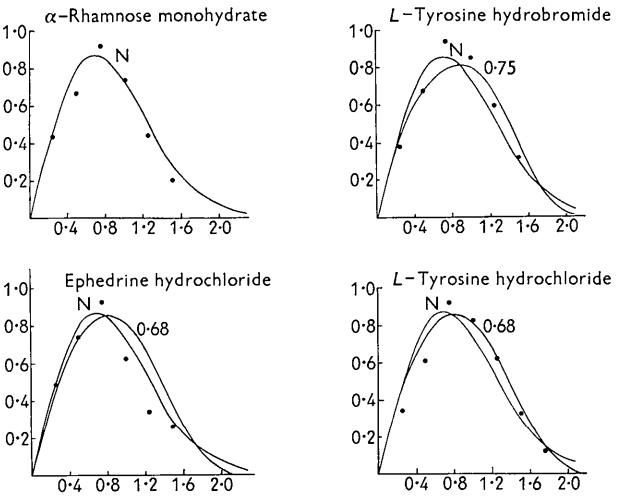

Fig. 4. Comparison of the experimental data with the theoretical distributions for non-centrosymmetric structures.

A short account of each of these is given below and details can be obtained by referring to original papers. Explanations are provided only where they are necessary. In all cases where a heavy atom is present, it will be seen that the experimental data fit the appropriate curve for ${}_{2C}P(y)$ better than for ${}_{C}P(y)$.

α-Rhamnose monohydrate.—This is a simple light-atom compound (McGeachin & Beevers, 1957) the space group being $P2_1$. The data agree well with the theoretical curve ${}_{C}P(y)$.

3:3′. *Dichloro* 4-4′ *dihydroxy-diphenyl-methane.*—This case is of particular interest since the $N(z)$ test of Howells *et al.* (1950) for the [010] projection is reported to have led to a negative result (Whittaker, 1953). Ultimately the structure was found to have the space group $C2/c$. The new $P(y)$ test was applied to the [010] projection (Fig. 3) and there can be no doubt that this projection is centrosymmetric. σ_2^2 for this compound is 0·65 and the agreement is clearly better with the curve for $\sigma_2^2=0{\cdot}5$ than with ${}_{C}P(y)$.

L-*Tyrosine hydrochloride.*—The space group of this compound is $P2_1$ (Srinivasan, 1956) and $\sigma_2^2=0{\cdot}55$. The data closely fit the curve for $\sigma_2^2=0{\cdot}5$ (See Ramachandran & Srinivasan, 1959).

L-*Ephedrine hydrochloride.*—The space group is $P2_1$ (Phillips, 1954) and $\sigma_2^2=0{\cdot}55$. Just as in the last case the date agree with the curve for $\sigma_2^2=0{\cdot}50$.

L-*Tyrosine hydrobromide.*—The space group is $P2_1$ (Srinivasan, 1956) and $\sigma_2^2=0{\cdot}86$. The effect of the presence of the heavy atoms is striking in this case and the agreement of the data with the curve for $\sigma_2^2=0{\cdot}90$ is quite good.

p-Cholorobenzene seleninic acid.–The space group is $P2_1/c$ (Bryden & McCullough, 1956) and $\sigma_2^2=0{\cdot}68$.

5·3. *Non-centrosymmetric case*

The data analysed were those of the compounds α-rhamnose monohydrate, L-ephedrine hydrochloride, L-tyrosine hydrochloride and L-tyrosine hydrobromide. For all these compounds the data for a non-centrosymmetric projection were available.

It can be noticed from Fig. 4 that in each case the data definitely show that the projection is non-centrosymmetric though, however, it is not possible to say distinctly that they follow more closely the appropriate curve ${}_{2N}P(y)$ than the curve ${}_{N}P(y)$. The reason for this is that the experimental data seem to have appreciable spread and the different curves, ${}_{2N}P(y)$, are not very different from each other.

On the other hand for the centrosymmetric case, the curves ${}_{2C}P(y)$ are appreciably different and in fact, for large values of σ_2^2 the curve even tends to be similar to ${}_{N}P(y)$. It is therefore highly important, when carrying out a test, to use the appropriate theoretical curve ${}_{2C}P(y)$, whereas it may not be so essential to choose the appropriate ${}_{2N}P(y)$.

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