The remainder terms in the basic formulas are especially simple for the special case, $p = q = r = 2$. For this case, the formulas reduce to those obtainable by the algebraic methods proposed by us (1957).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

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A new statistical test for distinguishing between centrosymmetric and non-centrosymmetric structures.

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The problem of the distribution of intensity in the resultant obtained by compounding n vibrations of equal amplitude, but of random phase, was considered by Lord Rayleigh (1880) (see also Ramachandran, 1943). He considered two cases—one in which the phases are assumed to have only the values 0 or π, and the other, the more general case, in which the phases are arbitrary. It will be readily recognized that these two correspond to the problem of calculating the distribution of X-ray intensities for a centrosymmetric and a non-centrosymmetric crystal structure, in which all the atoms are alike. The formulae obtained by Lord Rayleigh may be stated in the following form:

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

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

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

These formulae have also been derived by Wilson (1949) and on their basis Howells, Phillips & Rogers (1950) have suggested a test for distinguishing between centrosymmetric and non-centrosymmetric structures. However, they have used the fraction

$$N(z) = \int_0^z P(z)dz \tag{3}$$

for this purpose. The $N(z)$ curves, as is characteristic of all cumulative distribution functions, start at the origin and are more or less similar in their general shape for both types of structures. Consequently a critical distinction between the two is not always possible and, although success has been reported in various cases using this test, it has led to negative results (Whittaker, 1953; Eriks & McGillavry, 1954; Paton & MacDonald, 1957) and even false results in a few cases (e.g., see Robertson & Shearer, 1956; Robertson, Shearer, Sim & Watson, 1958).

However, if we modify the original probability distribution functions such that the argument is $y = \sqrt{z}$ and not z, then the following formulae are obtained:

$$_NP(y)dy = 2y\exp(-y^2)dy \tag{4}$$

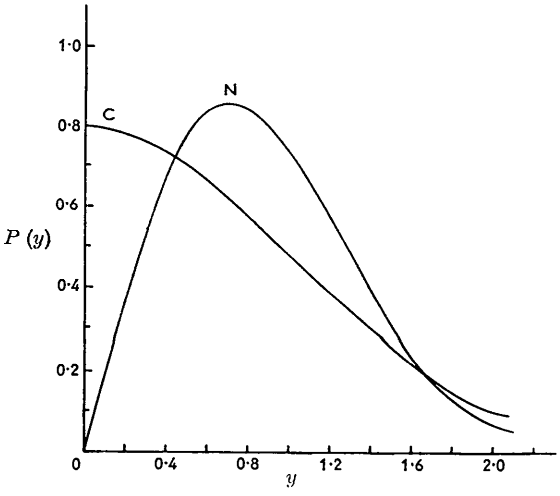

Fig. 1. Theoretical curves of $P(y)$ against y for centrosymmetric (C) and non-centrosymmetric (N) distributions.

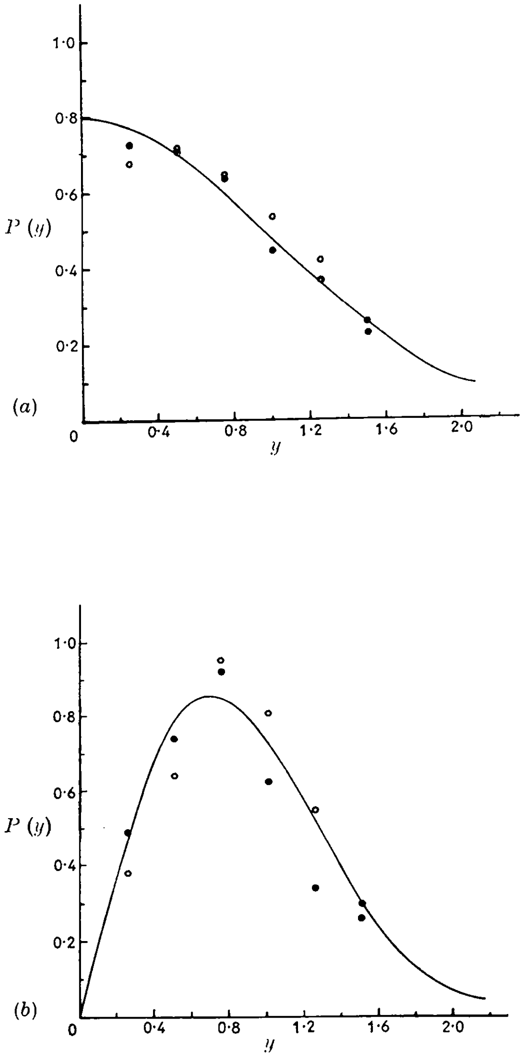

Fig. 2. The distribution of $P(y)$ observed in L-ephedrine hydrochloride (closed circles) and L-tyrosine hydrochloride (open circles) for (*a*) centrosymmetric and (*b*) non-centrosymmetric projections. Theoretical curves are shown by full lines.

$$_CP(y)dy = (2/\pi)^{\frac{1}{2}} \exp\left(-y^2/2\right)dy \qquad (5)$$

where

$$y = z^{\frac{1}{2}} = |F|/\sqrt{\langle I\rangle}\ . \qquad (6)$$

If the function $P(y)$ is plotted against y as shown in Fig. 1, it will be seen that the curves for the two cases are quite different. While the curve C starts with a maximum value of $(2/\pi)^{\frac{1}{2}} = 0{\cdot}798$ at $y = 0$ and decreases with increasing value of y, the curve N starts from zero at $y = 0$, and rapidly increases until it reaches the maximum value of 0·857 at $y = 0{\cdot}707$ and then decreases with further increase in the value of y. The two curves, however, agree closely beyond $y \simeq 1{\cdot}6$. In view of the very dissimilar shapes of the two curves, particularly in the region of y less than about 0·7, it should be possible to distinguish between the two cases with a large margin of safety, if the test is carried out using the function $P(y)$.

We have applied the above test to the known structures of L-ephedrine hydrochloride (A) (Phillips, 1954) and L-tyrosine hydrochloride (B) (Srinivasan, 1958) both of which have a centrosymmetric and a non-centrosymmetric projection. The results are shown in Figs. 2(*a*) and 2(*b*). It will be noticed that the experimental values closely follow the theoretical curves. The test has also been applied to the [010] projection of 3:3′ dichloro-4:4′ dihydroxy diphenyl methane. The space group of this compound is $C2/c$ and the $N(z)$ test to detect the centre of symmetry in the [010] projection is reported to have led to a negative result (Whittaker, 1953). However, the $P(y)$ test showed clearly that this projection is centrosymmetric.

The following ratio test is suggested as a quick method for detecting the presence or absence of a centre of symmetry. If N_1 and N_2 are the number of reflexions having values of y between 0 and 0·5 and between 0·5 and 1·0 respectively, then the ratio (N_2/N_1) can be shown to take the values 1·96 and 0·776 for the non-centrosymmetric and centrosymmetric cases. Table 1 gives the calculated value of this ratio for the compounds A, B and also for two other compounds, L-tyrosine hydrobromide (C) (Srinivasan, 1958) and 3:3′:dichloro-4:4′ dihydroxy diphenyl methane (D) (Whittaker, 1953). The values agree fairly well with the theoretical ones. The larger observed values in the case of L-tyrosine hydrobromide (C) is probably due to the presence of the heavy atom bromine in the structure. This is under investigation.

Table 1. *Calculated values of* N_2/N_1

Compound	$(N_2/N_1)_N$	$(N_2/N_1)_C$
A	1·89	0·89
B	2·52	0·96
C	2·97	1·58
D	—	0·92
Theoretical	1·96	0·776

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