LETTERS TO THE EDITOR

ON THE DEGREE OF CENTROSYMMETRY OF A NON-CENTROSYMMETRIC STRUCTURE*

It is well known that the two basic statistical distribution laws governing X-ray intensities of a centrosymmetric and a non-centrosymmetric crystal derived by Wilson[1] tend to be violated under a variety of conditions, such as for instance when a few of the atoms have predominantly larger scattering power than the rest or when some of the atoms occupy special positions in the unit cell and so on. The distributions also tend to be affected by the presence of any pseudosymmetry in the structure. We use the term pseudosymmetry in a rather general sense to signify the presence of any symmetry property associated with the structural unit† such as to invalidate the assumption of random distribution of atoms in the unit cell. A variety of pseudosymmetries would then be possible. For instance, symmetry elements of an exact type, such as one or more of centre of inversion, may be present in the unit which leads to different types of hyper-centrosymmetric distributions.[2,3] We may also have cases when symmetry associated with the unit is not of an exact type as for instance in the case of feldspars[4] where a part of the unit is obtained by the translation from another *plus* small deviations in the atomic co-ordinates. This may be categorized under translational pseudosymmetry.

Another type of pseudosymmetry possible and which does not appear to have been considered earlier in literature is when a part of the unit possesses symmetry of an exact type the remaining part having no symmetry at all. A special case of this, which is of considerable practical interest, is when a molecule, a major portion of which is centric, the remaining portion being acentric‡ makes up the unit and takes the non-centrosymmetric space group $P1$. It is clear that in such a case, it should be possible to talk of the "degree of centrosymmetry" of the structure, since the distribution of intensities could be expected to depend on the relative proportion of the two parts. This particular problem has been considered by the author.[5] In fact, the result for this case comes out as a special case of the problem which has been considered more generally, namely the problem of the distribution of intensities for a structure containing n_1 centric and n_2 acentric groups in random orientations in the unit cell. The special case mentioned above actually corresponds to $n_1 = n_2 = 1$. The purpose of this note is to briefly outline the main results thus obtained, details of which are given in the paper cited above.[5]

In the discussion to follow, we use the following notations. σ_N^2 and σ_C^2 stand for the mean square value of the contribution to the intensity from the entire acentric and centric parts respectively, n_1 and n_2 denote the numbers of centric and acentric groups respectively. The following cases arise.

When $n_1 = 0$, and n_2 is finite, the resultant distribution tends to the acentric one. This is obviously a trivial case, since any number of acentric groups would obviously lead only to a final acentric distribution. When $n_2 = 0$ and n_1 is large, the distribution again tends to the acentric one. This, again, is obvious from central limit theorem. The case of interest will be when $n_2 = 0$ and n_1 is small. Here again when $n_1 = 1$ the result is trivial since when only one centric group is present the resultant distribution becomes centric. The case when $n_2 = 0$, $n_1 = 2$ is shown in Fig. 1, where the probability distribution of the normalised structure

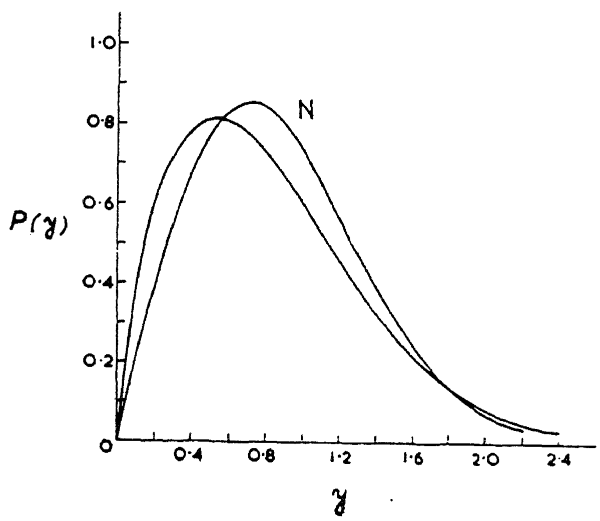

FIG. 1. The distribution of normalised structure amplitude for a non-centrosymmetric structure containing two centric groups. The ideal non-centrosymmetric curve is marked *N*.

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amplitude[6] $y = |F|/<|F|^2>^{\frac{1}{2}}$ is shown. The distribution, for this case, is surprisingly very close to the non-centrosymmetric distribution ${}_NP(y)$ (marked N in Fig. 1). This would mean that, in practice, even if one has a symmetric molecule, so long as there are at least two of them in the unit cell randomly oriented, the distribution is close to the ideal acentric one. This result makes it unnecessary to consider cases when $n_2 > 2$. So also, when both n_1 and n_2 are finite, it is enough to consider the case when $n_1 = n_2 = 1$. The distribution $P(y)$ for this case is shown in Fig. 2, for different values of σ_1^2

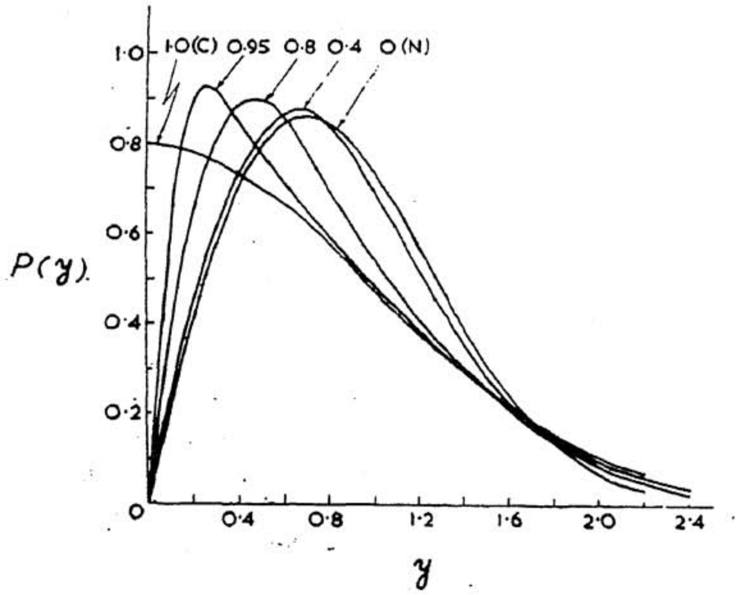

FIG. 2. Curves showing the degrees of centrosymmetry of a structure containing one centric and one acentric groups. The value of σ_1^2 is marked near each curve. $\sigma_1^2 = 1\cdot0$ and 0 correspond to ideal centrosymmetric (C) and non-centrosymmetric (N) cases respectively.

where σ_1^2 stands for the ratio $\sigma_C^2/(\sigma_C^2 + \sigma_N^2)$, When $\sigma_1^2 = 1\cdot0$ it tends to the ideal centric curve (C) while when $\sigma_1^2 = 0$ it tends to the ideal acentric curve (N). For intermediate values of σ_1^2 the curves fall in between the two limiting ones and may be taken to represent different 'degrees of centrosymmetry' of the structure.

The last two cases discussed above lead us to the conclusion that the intensity distribution for the case of a structure containing an "almost centrosymmetric" molecule would be practically unaltered from the acentric one so long as there are at least two of them in the unit cell. This is likely to be a case of frequent occurrence in practice, since molecules containing benzene ring and a few additional atoms appended to them very often crystallize in the space group $P2_1$ with two molecules in the unit cell.

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Centre of Advanced Study in Physics, University of Madras, Madras-25, India, *July* 22, 1965.

R. SRINIVASAN.

† The term structural unit or simply the unit, for brevity, is used in preference to the conventional term asymmetric unit since the latter is ambiguous in the present context.

‡ We use the terms centric and acentric as shortened versions of centrosymmetric and non-centrosymmetric respectively.

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5. Srinivasan, R., *Ind. J. Pure and Appl. Phys.*, 1965, **3** (7), 187.
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