LETTERS TO THE EDITOR

DEGREE OF CENTROSYMMETRY OF A CRYSTAL STRUCTURE AND THE STATISTICAL DISTRIBUTION OF X-RAY INTENSITIES*

THE notion of degree of centrosymmetry of a non-centrosymmetric crystal structure was considered earlier from the point of view of intensity statistics (Srinivasan[1]). The degree of centrosymmetry considered therein arose out of a non-centrosymmetric structure in which a part or major portion has a centrosymmetric arrangement. Another possible situation is the case of a structure which takes up essentially non-centrosymmetric space group but which could be imagined to be obtained from an original centrosymmetric arrangement by destroying the centrosymmetry through introduction of small deviations in atomic coordinates. We consider in this paper semi-empirically the intensity distribution for such a situation. This arose out of some interesting recent reports in the literature on the structure of dibenzyl disulphide. The structure has been reported in the two alternative space groups of Cc (Lee and Bryant[2], Lee[3], hereafter LB and L respectively) and C2/c (Dijk and Visser[4], Einspahr and Donohue[5], hereafter DV and ED respectively). If the structure in the space group Cc were correct there would be an *approximate* twofold axis in the structure relating one-half of the dibenzyl disulphide molecule to the other. In fact the mean deviation of the atoms related by this approximate symmetry works out to about 0·05 Å. It is obvious that these deviations are rather small to be readily detected. One might expect that the intensity statistics should show closeness to centrosymmetry as is indeed the case (ED, L).

We have carried out on a hypothetical two-dimensional model a series of calculations varying the mean deviations $\langle|\triangle r_j|\rangle$ from ideal centrosymmetry to study its effect on the resultant intensity distribution. The rtsults are presented graphically in Fig. 1. The P(y) curves of Ramachandran and Srinivasan[6] have been drawn using the F_c's generated for the different sets. As is to be expected until $\langle|\triangle r_j|\rangle$ tends to be fairly large ($\sim 0{\cdot}25$ Å) the curves are fairly close to the centric case. Statistical tests are therefore unlikely to be effective in revealing small deviations from centrosymmetry.

A convenient parameter which we would like to suggest for use as a measure of the degree of centrosymmetry is the function $\langle \cos 2\pi \mathrm{H}.\triangle r_j\rangle$. This is suggested here based on our earlier results in a different context (*e.g.*, see Srinivasan and Chandrasekharan[7]; Srinivasan and Ramachandran[8]). This parameter will have a value zero when $\triangle r_j$ are large which corresponds to non-centrosymmetric arrangement and a value unity when all $\triangle r_j = 0$ which corresponds to ideal centrosymmetry. For dibenzyl disulphide, using the curves of Chandrasekharan and Srinivasan[9], the degree of centrosymmetry works out to about 98%.

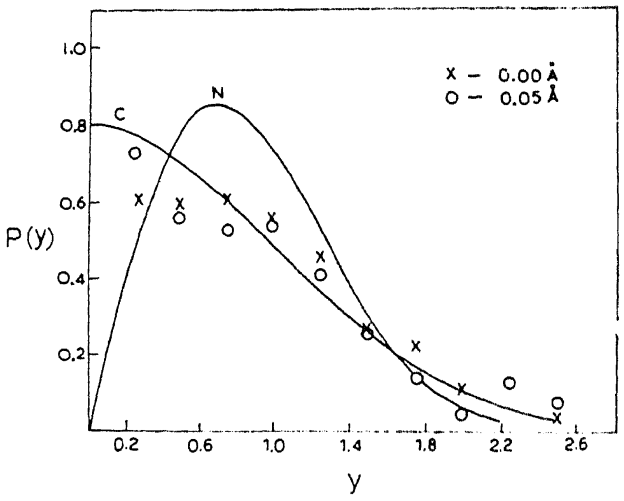

FIG. 1 *a*

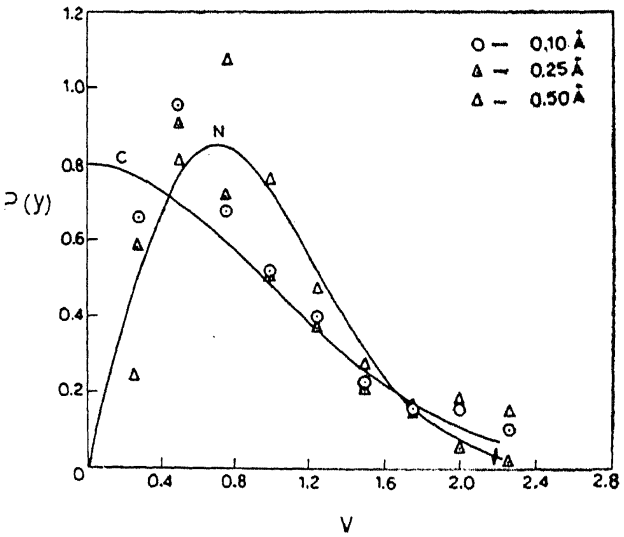

FIG. 1 *b*

FIG. 1. The P(*y*) curves for structures with small deviations from centrosymmetry. (*a*) with small errors; (*b*) with medium and large errors.

In this context the following remarks on the statistical tests on dibenzyl disulphide may be pertinent. The $N(z)$ test on *hk*o data is reported

to follow the acentric curves (L). In the light of our earlier discussion the behaviour of the *hko* data should be considered to be anomalous. An explanation is readily found if we look at the projection of the structure down the *c*-axis. Four of the sulphur atoms superpose almost exactly one over the other simulating a pseudoheavy atom in projection with $Z \simeq 64$. A plot of $\langle I_0 \rangle$ for *hko* data did show that the curve was close to the above approximation upto $\sin\theta \simeq 0{\cdot}6$. Using this curve the value of σ_1^2, which stands for the ratio of the mean contribution to the intensity from the pseudoheavy atom to that from the entire structure, was calculated to be 75%.

The P(*y*) curve appropriate to the situation is then the one corresponding to a centrosymmetric structure with one heavy atom in the unit cell, for which theoretical curves are available (Srinivasan[10]). Interestingly the distribution for such a case specially for value of $\sigma_1^2 \simeq 75\%$ tends to be rather similar to the acentric curve. The observed P(*y*) curve of the *hko* data is seen to fit with theoretical curve fairly well (Fig. 2).

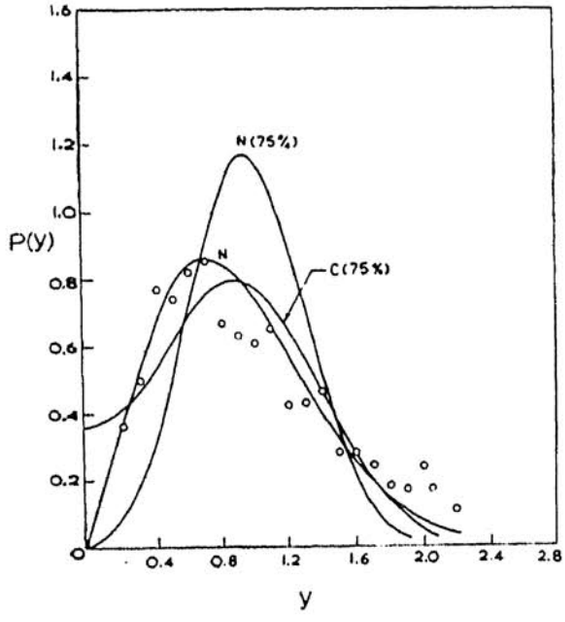

FIG. 2. The P(*y*) curve for *hko* data of dibenzyl disulphide. The curves (solid line) correspond to theoretical P(*y*) curves for centrosymmetric (C) and non-centrosymmetric (N) cases corresponding to heavy atom (one per cell) contribution of $\sigma_1^2 = 75\%$. The ideal non-centric curve ($\sigma_1^2 = 0$) is marked N.

Tests on three-dimensional data tend to show closeness to centrosymmetry. In fact the tendency for the 3D data is to show dispersion slightly beyond the centric case (*e.g.*, circles in Fig. 1 of L fall slightly above the $\bar{1}$ curve which are in broad agreement with Table I of ED). This may be attributed to the fact that the asymmetric part (in this case half of the molecule of dibenzyl disulphide) contains a benzene ring and tends to have pseudosymmetry†.

Thus to conclude, statistical tests are unlikely to be useful in detecting a non-centrosymmetric structure with a high degree of centrosymmetry. In such situation structure refinement in the possible altenative space groups coupled with other criteria of significance may prove useful in resolving the ambiguity. It may however be pointed out that the use of X-ray anomalous scattering as a sensitive tool to handle such a situation has been suggested recently and successfully applied in the case of dibenzyl disulphide (Srinivasan and Vijayalakshmi)[11].

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† Following Srinivasan[1] we use here the term pseudosymmetry in a general sense to denote the presence of any symmetry associated with the "asymmetric unit" and not used by the space group symmetry.

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