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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Practical resolution of the centrosymmetric/noncentrosymmetric ambiguity with the use of E statistics.*

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Abstract

An analysis of $\langle |E^2 - 1| \rangle$ values (calculated using all reflections) is reported for 167 data sets representing organic and organometallic compounds. It is shown that such an analysis may be a useful aid in assigning a centre of symmetry when a centrosymmetric/noncentrosymmetric (C/NC) ambiguity exists (for nontriclinic space groups). Distributions with average $\langle |E^2 - 1| \rangle$ values >0·82 are assigned as C space groups and those with values <0·82 are assigned to NC space groups. However, we note that often the only way of ensuring the correct choice of space group is a careful refinement of all options with particular emphasis on the possible role of disorder in the structure under investigation.

A commonly encountered problem in X-ray diffraction studies is the correct assignment of space group when a centrosymmetric/noncentrosymmetric (C/NC) ambiguity exists, *e.g.* $P1$–$P\bar{1}$, Cc–$C2/c$, and $Pna2_1$–$Pnam$ (Marsh,

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1981, 1986). While much attention has been directed to the use of statistics to resolve the C/NC ambiguity we are not aware of a detailed analysis applied to a large number of structures. In this communication the average E statistics, $\langle |E^2 - 1| \rangle$, have been plotted for 167 data sets representing both organic and organometallic compounds obtained in these laboratories; see Fig. 1. The $\langle |E^2 - 1| \rangle$ values were calculated from the *SHELX*76 (Sheldrick, 1976) program which calculates the E statistics as a function of $\sin(\theta)/\lambda$; reflections with $F \le 0$ were ignored in the calculation. Only values from those regions which had a significant number of reflections ($\ge$ 100 reflections) were used in the averaging process. Data were obtained routinely at room temperature on an Enraf–Nonius CAD-4 diffractometer utilizing mainly Mo $K\alpha$ radiation; $\theta_{max} = 22\cdot5$–$30\cdot0°$. The data sets were corrected for Lorentz and polarization effects, and, in most cases, an analytical absorption correction was applied (Sheldrick, 1976). Generally the data sets were refined to final weighted residuals of <6% after weak reflections [usually the $I \ge 2\cdot5\sigma(I)$ criterion of observability was applied] were omitted from the final refinement cycles.

Fig. 1(*a*) shows the distribution of $\langle |E^2 - 1| \rangle$ values for 167 data sets where the circles represent centrosymmetric

(C) structures (132 cases; 80%) and the triangles represent the noncentrosymmetric (NC) structures (35 cases; 20%). Note that the weak reflections have *not* been excluded from the calculation of the $\langle |E^2 - 1| \rangle$ values. The two populations overlap with values of $\langle |E^2 - 1| \rangle$ as low as 0·638 for C structures and as high as 0·891 for NC structures; we note however that these extremes represent either disordered structures or have very weak intensity data sets (see below). An average value for $\langle |E^2 - 1| \rangle$ of 0·903 has been calculated for C structures and 0·778 for NC structures. These compare with the theoretical expectations of 0·968 and 0·736 for C and NC structures respectively (Stout & Jensen, 1968). As many space groups are uniquely determined by their systematic absences (*e.g.* $P2_1/c$, $P2_12_12_1$), and hence the CNC ambiguity does not arise, only the ambiguous space groups, including $P1-P\bar{1}$, are shown in Fig. 1(b) where the triclinic cases are shaded. The triclinic space groups shown in Fig. 1(b) have all been assigned space group $P\bar{1}$ during their respective refinements despite the occurrence of some low values for $\langle |E^2 - 1| \rangle$. These observations may be related to the presence of one or more heavy atoms in the structures; *i.e.* these represent examples of small-molecule compounds
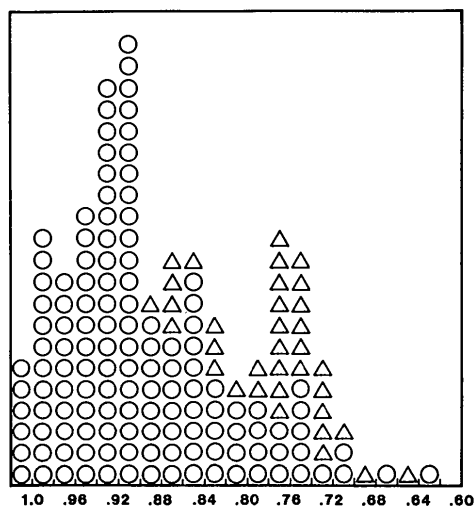
containing the elements Ru, Bi, Au or W. The consequence of such a dominance of few atoms to the overall scattering is a low value, *i.e.* an acentric distribution, of $\langle |E^2 - 1| \rangle$ (Hargreaves, 1955). Ignoring the triclinic (shaded) examples in Fig. 1(b) it can be seen that, except for two examples at $\langle |E^2 - 1| \rangle$ values of 0·891 and 0·878 (discussed further below), there are two populations. Those with $\langle |E^2 - 1| \rangle$ values greater than 0·82 are C structures whilst those with values less than 0·82 belong to NC space groups. The two exceptions are special cases which are now discussed in detail. The first, at $\langle |E^2 - 1| \rangle$ of 0·891, is represented by the orthorhombic polymorph of $HgCl_2[P(C_6H_5)_3]_2$ (Lobana, Sandhu, Snow & Tiekink, 1988). This compound crystallizes in the NC space group $Pna2_1$ though the molecule possesses a pseudomirror plane. If the mirror plane was crystallographically imposed the space group would be $Pnam$ (nonstandard setting of $Pnma$); however, from the structure analysis it is clear that though the heavy atoms, $HgCl_2P_2$, conform closely to ideal mirror symmetry the relative disposition of the phosphine-bound phenyl groups precludes this choice of space group. For crystals of [Co(azacapten)]-$[ClO_4]_2$ (Hambley & Snow, 1986) the systematic absences are again consistent with the NC space groups $Pna2_1$ or the C space group $Pnam$. Refinement in $Pna2_1$ proved successful with modelled disorder corresponding to the occupation of each enantiomer in the complex, *i.e.* while the CH_3C-$(-CH_2-)_3$ cap is common to both enantiomers, there are separate contributions to the cystamine groups. The contribution of one enantiomer over the other was found to be 0·58 : 0·42. If $Pnam$ was the correct space group there would be equal proportions of the enantiomers in the structure. Thus while both the structures of $HgCl_2$-$[P(C_6H_5)_3]_2$ and [Co(azacapten)][ClO_4]_2$ are, by virtue of the presence of disorder or heavy atoms, almost C (hence the relatively high $\langle |E^2 - 1| \rangle$ values) the final refinements show in fact that the lower symmetry space groups were correct.

The importance of including weak reflections when values of $\langle |E^2 - 1| \rangle$ are calculated has also been investigated. If reflections for which $I < 2·5\sigma(I)$ are excluded from the $\langle |E^2 - 1| \rangle$ calculation the magnitudes of $\langle |E^2 - 1| \rangle$ are decreased markedly. Further, there is an increased overlap of the C/NC populations and thus there is no clear distinction between the two populations. The general importance of weak reflections in resolving the C/NC ambiguity has been discussed in some detail (Marsh, 1981).
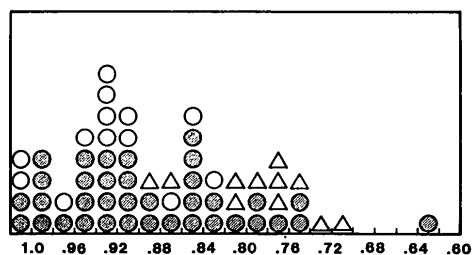
Fig. 1. (a) Distribution of average $\langle |E^2 - 1| \rangle$ values for all compounds: ○ = centrosymmetric space group and △ = noncentrosymmetric space group. (b) Distribution of average $\langle |E^2 - 1| \rangle$ values for ambiguous space groups. Triclinic examples are shaded.

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