17.5-6 IDENTIFICATION OF MEROHEDRICAL TWINS OF STRUCTURES SHOWING SUPERSTRUCTURE EFFECTS
G. Lampert, Institut für Mineralogie, Ruhr-Universität Bochum, 4630 Bochum, West Germany

In the case of twinning by merohedry, the twinning operation exactly superimposes non-equivalent reflections from the twin domains. But unlike most experimental errors which tend to increase the dispersion twinning will always reduce the dispersion and this provides a mean for identifying twins from the distribution of the x-ray intensities (Stanley, J.Appl.Cryst. (1972), 5, 191). Rees (Acta Cryst.(1980), A36, 578) developed a simple test based on intensity statistics.

Structures showing superstructure effects are those having systematically strong and systematically weak reflections in the reciprocal space. Therefore these effects disturb the estimation. Nevertheless the cumulative distribution function N(E) which gives the fraction of reflections having normalized structure factors less than E can be used to identify twinning by merohedry provided that the main and superstructure reflections were normalized separately according to the pseudotranslation.

This will be demonstrated on $KAlGeO_4$, a structure showing a pseudotranslation t=(1/3 2/3 0) (Lampert & Böhme (1986), Z. Kristallogr. 176, 29) and related structures.

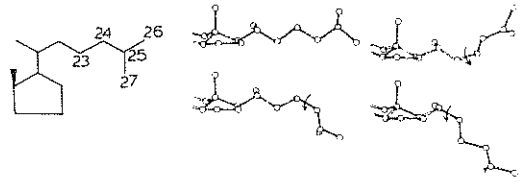
17.5-7 EFFECTS OF SYMMETRY AND ATOMIC HETEROGENEITY ON CUMULATIVE DISTRIBUTION FUNCTION -SOME HYPERSYMMETRIC SITUATIONS
By Sikha Ghosh, Department of Physics, Indian Institute of Technology,Kharagpur721302 INDIA.

A series expansion distribution function of the structure amplitude |F| which takes into account the effect of symmetry and atomic heterogeneity, has been used to calculate the generalised cumulative distribution function $N_n(Z)$ for a hypersymmetric crystal having n-fold repetition ofa motif at regular intervals 'D' along a straight line.The resultant change from the corresponding Wilson-type distribution (Rogers,D., Wilson,A.J.C.(1953), Acta Cryst. 6, 439-449) is illustrated with the help of a hypothetical example and the effects of expansion terms have been discussed for both centrosymmetric and non-centrosymmetric cases. Cases of (i) hyperparallelism and (ii) many parallel repetitions at random have also been dealt with similarly. It is observed that the inclusion of expansion terms is important, particularly when heterogeneity is present in the sample, to distinguish between centrosymmetry and hypersymmetry.

17.6-1 FACTOR ANALYSIS OF THE CHOLESTEROL SIDE CHAIN CONFORMATION.
W.L. Duax, Z. Wawrzak and J. Griffin, Medical Foundation of Buffalo, Buffalo, NY 14203 and C. Cheer, University of Rhode Island, Kingston, RI 02881.

The conformation of the cholesterol side chain was analyzed using the factor analysis routines in Version II of the software for the Cambridge Structural Database (CSD). Most effective analysis required incorporation of conformational prochirality into the search fragment. A specific range for the torsion angle of the fragment analogous to C(23)-C(24)-C(25)-C(26) was defined. Search of the CSD using a fragment composed of the steroid D ring and the seven atom cholesterol side chain produced 123 hits. Two primary factors account for 46% of the variation in the set. A two-dimensional plot of those factors separated the 123 structures into four classes. The classes included 87 structures having fully extended side chains (Class A), 11 structures in which the major variation was due to the fact that the C(22)-C(23)-C(24)-C(25) torsion angle was ± gauche (Class B), 10 structures in which the major variation was due to the fact that the C(20)-C(22)-C(23)-C(24) torsion angle is + gauche (Class C), and 15 structures in which the major variation was due to the fact that the C(17)-C(20)-C(22)-C(23) torsion angle is ± gauche (Class D). Classes A and C were well defined. Classes B and D were more diffuse and mutually overlapping because of the existence of conformers with both ± gauche conformations and additional flexibility associated with rotation about more than one of the side chain bonds.

Not surprisingly, in the majority of structures, one of the terminal carbons [C(26) or C(27)] is observed to be trans to C(23). The third and fourth factors further separate the molecules of Class A into those subgroups in which either C(26) or C(27) is trans to C(23). The average values of the C(22)-C(23)-C(24)-C(25) torsion angles in these two subsets differ by 10°. These two distinct conformations of the extended chain occur with a relative frequency of 2:1, respectively. This population difference indicates that the conformer in which the C(21) and C(27) atoms are on the same side of the plane of the rest of the carbon atoms of the side chain is more stable than the conformer in which these methyls are on opposite sides of the plane. Conformers of Class B and D occur with greater frequency in crystal structures incorporating pseudo bilayers. The molecules in each of the major conformations observed crystallographically were subjected to energy minimization calculations (Allinger and Yuh). The calculations confirm that in most cases the observed structures are local minimum energy conformations and reproduce conformational features in some detail. Twelve distinct conformers have energies with a total range in magnitude of 1 kcal/mol. There is no correlation between the frequency of observations and the relative energies of the conformers. The energy calculations appear to be insensitive to intramolecular factors that account for the prevalence of the extended form and the unequal distribution of subsets of that form.




Research supported in part by NIAMDD Grant No. RR-05716.