

LETTERS TO THE EDITOR

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On the space-group frequency in organic structures

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Donohue (1985) revises the space-group frequency distribution table arrived at by Mighell, Himes & Rodgers (1983), based on about 30 000 organic compounds, on the grounds that space-group determination, in certain cases where symmetry of the second kind is not present, automatically determines an additional structure (the enantiomeric structure). He cites the example of space group $P2_1$ for an L amino acid determining the enantiomeric crystal for the D form. In cases where enantiomeric space groups are part of the list of 230 space groups, he adds the observed data under each category and gives equal weight based on the total for each space group. This results in promoting space group $P2_12_12_1$ to second place instead of $P\bar{1}$.

This method of treating the data seems, to the author, questionable. Firstly, from the standpoint of statistical analysis, enlarging the observed data to include additional data which are unobserved, however strong the arguments may be for them, is itself questionable. Secondly, the arguments advanced for such enlargements, although possibly valid theoretically, cannot always make such enantiomorphs readily realizable in practice. The procedure of doubling the observed value for an enantiomorphic space group (complementing them in the case of both space groups being part of the 230) implies equal probability of occurrence in practice and should not be based on theoretical feasibility alone. The common and trivial cases when enantiomeric distinguishability of crystal structures with corresponding identity of enantiomeric molecular species such as L and D amino acids need not always be true such as in cases where the enantiomers result from readily interconvertible conformers (rotational isomers), not uncommon in 'disymmetric' organic structures. Simple examples are the cases of hydrogen peroxide (Srinivasan, 1970) and ammonium oxalate (Robertson, 1965) where the distinguishability is non-existent in solution but structurally they take enantiomorphic space groups, presumably with equal probability of occurrence. In other organic structures with asymmetric centres, different conformational species are possible as in the case of D-alloisoleucine hydrochloride which has two forms both having the same space group, a result one would not have anticipated (Srinivasan, Varughese & Swami-

nathan, 1974). Although in simple disymmetric cases such as hydrogen peroxide or other symmetrically substituted peroxides, disulfides (Foss, 1954) *etc.* the enantiomeric forms may be expected, from energy considerations, to be equally probable, this, again, will lead to complications in terms of observability in complex systems of organic structures. As an extreme example, a small protein crystallizing in an enantiomorphic space group cannot be expected to have its enantiomeric structure in practice.

It would thus seem that structural and conformational variations vitiate the assumptions of equal probability of occurrence of enantiomeric structures, which assumption is implicit in the procedure adopted for enlargement of observed data.

The proper procedure would appear to be to confine oneself to the 'observed data' only under each space group, irrespective of whether enantiomeric space groups are or are not part of the 230 space-group listings. However, if enantiomeric structures are experimentally determined [which, in some cases might hold surprising and unexpected results as for NaClO_3 and NaBrO_3 (Beurskens Kerssen, Kroon, Endeman, Vanlaar & Bijvoet, 1963)] they should be included since they are established as structures with different physical properties. Thus, the sole criterion should be that experimentally observed and established structures enter the statistics.

It would thus seem appropriate that the revision as proposed by Donohue is not warranted and the earlier result of Mighell *et al.* (1983) should be accepted and space group $P\bar{1}$ restored to second place and $P2_12_12_1$ to third place.

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