match no. 9 pp. 13-14 1980

SPACE GROUP-LIKE SYMMETRIES IN THE CONFORMATIONAL ANALYSIS OF FLEXIBLE MOLECULES

H.B. Bürgi
Lab. für anorg. Chemie, ETH
CH-8092 Zürich, Switzerland[1]

Non-rigid molecules that can be regarded as consisting of a set of internal rotors attached to an essentially rigid frame (e.g. propane with two C_{3v}-symmetrical methylgroups rotating freely on a rigid C_{2v}-symmetrical frame) can always be described in terms of an appropriate finite group $\underset{\sim}{H}$ [2]. Such groups $\underset{\sim}{H}$ may be represented in general as a semidirect or a wreath product of a group $\underset{\sim}{F}$ accounting for the symmetry of the frame and a group $\underset{\sim}{R}$ accounting for the non-rigid internal rotation. The groups $\underset{\sim}{F}$ and $\underset{\sim}{R}$ are related to unit cell groups $\underset{\sim}{S}$ and translation groups $\underset{\sim}{T}$ respectively of crystallographic space groups $\underset{\sim}{U}$ [3,4].

For the cases mentioned (internal rotors on a rigid frame) $\underset{\sim}{F}$ is isomorphous to a unit cell group $\underset{\sim}{S}$ and $\underset{\sim}{R} = \underset{\sim}{T} / \underset{\sim}{N}$ where $\underset{\sim}{N}$, a normal divisor of $\underset{\sim}{T}$, is an infinite group of translations. For a molecule with p m-fold rotors, for example , the p unit translations of $\underset{\sim}{N}$ are m times as large as the p unit translations of $\underset{\sim}{T}$. Thus the group $\underset{\sim}{R}$ accounts for the m^p lattice points on the p-dimensional torus containing all structures accessible to the nonrigid molecule. The general positions of the group $\underset{\sim}{H}$ depend essentially on the appropriate point group symmetry $\underset{\sim}{F}$ of the frame. The number of general positions on the torus is $m^p.f$ where f is the order of $\underset{\sim}{F}$. The special positions of the finite group $\underset{\sim}{H}$ correspond to molecular conformations that are distinguished by having some non-trivial point group symmetry (kernel or cokernel symmetry).

The number p of free rotors in a particular molecule may well exceed three. This creates an interest in space groups of dimensionality higher than 3; however only a part of all space groups possible in a given dimension seems to be needed in problems of the kind described here.

1] Present address : Labor. für chem. u. mineral. Kristallographie, Univ., Freiestr. 3, CH-3012 Bern, Schweiz.

2] H. Frei, A. Bauder and H.H. Günthard, Topics in Current Chemistry 81, 1 (1979) and references therein.

3] P. Murray-Rust, H.B. Bürgi and J.D. Dunitz, Acta Cryst. A35, 703 (1979).

4] J.D. Dunitz, X-Ray Analyses and the Structure of Organic Molecules, Cornell (1979), Chap. 10.