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RESTRICTIONAL ISOMERISM: A NEW CONCEPT IMPORTANT FOR MOLECULES IN RESTRICTED ENVIRONMENTS

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Although hinted at by a few writers the ideas described in this communication seem never to have been stated explicitly. In view of the importance of chemical phenomena occurring in what we shall term restricted environments it would appear that a complete statement is needed.

Here we present the bare bones; the meat will appear elsewhere[1]

The number of substitutional isomers of a more-or-less rigid molecule can be obtained using Polyá's enumeration theorem and the point symmetry group $\underline{G}$ of the molecule[2] Stereoisomers are determined from the subgroup $\underline{R}$ of $\underline{G}$ which contains all the rotations but none of the roto-reflections; while those permutational isomers among which enantiomers are not distinct are obtained from the full group $\underline{G}$[3] The purpose of this note is to point out that the remaining subgroups of $\underline{G}$ lead to other types of physically meaningful isomers. Each subgroup represents a state of restriction imposed by the environment of the molecule. The isomers can be termed restrictional isomers, and the concept of restrictional isomerism is one that depends on the relation of a molecule to its environment. The concept is a logical extension of ideas of Prelog and Helmchen[4] The group $\underline{G}$ has a definite number of subgroups and, therefore, each molecule has a definite number of classes of restrictional isomers: thus the classification is complete.

A simple example is provided by benzene. The substituted molecule 1-bromo-3-chloro-benzene when confined to lie flat on a surface, at an interface or within a thin membrane has two distinct restrictional isomers. They can be distinguished as 1-bromo-3-chloro-benzene and 1-bromo-5-chloro-benzene. They are related by reflection in a mirror perpendicular to the surface and are therefore enantiomers. Of course released from the restriction they are no longer distinct species. Confined to a surface in a similar fashion 1-bromo-4-chloro-benzene has only one restrictional isomer, but in a pore of suitably small diameter whose axis is directed along the line connecting Br and Cl it has two: 1-bromo-4-chloro-benzene and 1-chloro-4-bromo-benzene. Again they are enantiomers.

In general each subgroup of pure rotations represents a type of restriction, the restrictional isomers being stereoisomers. Adding roto-reflections to the subgroup leads to another subgroup and a smaller class of restrictional isomers. The difference gives the number of pairs of enantiomers among the stereoisomers. All groups, of course, have the group of order unity, that is the group containing the identity only, as a subgroup. It represents one extreme, the state of full orientational restriction. All other subgroups of pure rotations represent states of orientational restriction intermediate between that extreme and the other extreme of no orientational restriction associated with the subgroup $\underline{R}$.

Restrictional isomerism is a concept that is likely to prove important in studies of processes that occur at solid-fluid and fluid-fluid interfaces, within anisotropic fluids such as liquid crystals and in the many processes that occur in physical and biological membranes.

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