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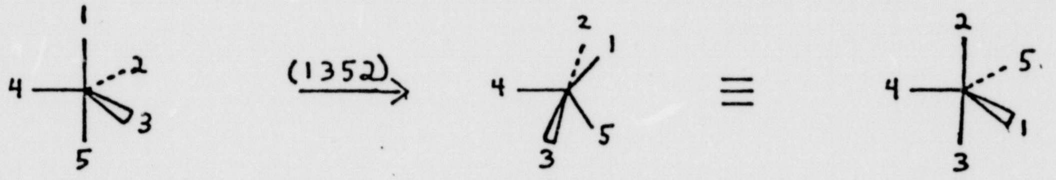
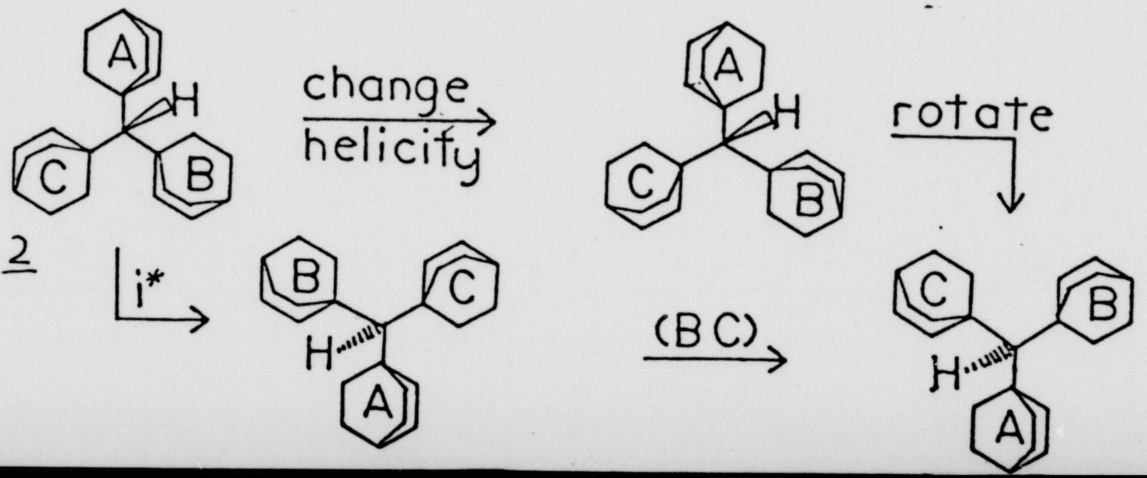
A typical problem in dynamic stereochemistry is to determine the mechanism of the rearrangement of a chemical structure such as 1.



1a 1b 1c

The ligands may be the same or different and the rearrangement may be skeletally degenerate or nondegenerate. Many of the problems already studied have involved degenerate rearrangements (those which interconvert chemical structures of the same geometry apart from any difference in the ligands) and only these will be considered here. Two groups and the mapping (homomorphism) between them are crucial to the proper description of problems of this kind. The first of these is the symmetry group of the chemical structure's skeleton (i.e, without ligands) and is designated P. This may be a point group, the rotation subgroup of a point group, or a nonrigid symmetry group [1]. Generally, this group can be represented as a permutation group on the ligands or on the skeletal sites however, in the most general case, this group is best represented as a permutation-inversion group [1]. In particular, when treating problems involving the degenerate rearrangement of chemical structures with chiral skeletons, the proper description of overall changes requires the permutation-inversion designation. For example, to describe the rearrangement of the chiral (C_3 symmetry) propeller molecule shown:



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in which the configuration of the central carbon does not change but in which the helicity of the propeller (as defined by the dihedral angle between the phenyl rings and the central carbon-hydrogen bond) does change, the proper description is the permutation shown coupled with overall coordinate inversion. Coordinate inversion changes both the configuration of the central carbon (as determined by the labelling of the rings) and the helicity. Ring permutation changes only the configuration. Separately these operations are not feasible by the Longuet-Higgins criteria [1], however, the combined operation changes only the helicity and is feasible for these systems.

The second group is the group which includes all possible permutations of either the identical atoms in the molecule or the possible ligand sites on the molecule. The distinction between the two is important in many cases [2]. This group is designated, G, and is usually one of the symmetric groups or a direct product of symmetric groups. However, in many cases only a subgroup is needed because of a feasibility condition [1]. That is, only certain overall changes are considered to be feasible under the experimental conditions at hand. This group is also best represented as a permutation inversion group although a permutation representation is often adequate.

The homomorphism between these two groups is just the injective mapping of P into G:

$$P \dashrightarrow G$$

This necessarily preserves the permutation (inversion) representation. For example, consider the two structures 1 and 2. The relevant groups are:

Example	P	G
1	D_{3h}	S_5
2	C_3	$S_3[S_2] \times C_i$

For the trigonal-bipyramidal structure 1, the point group is D_{3h} and the rotation subgroup is D_3. The permutation group G is the symmetric group S_5 which exchanges all 5 sites in all possible ways. Because the skeleton is not chiral, the permutation-inversion designations are not necessary. For the triphenylmethane structure 2, the point group is C_3 as the skeleton is chiral. The permutation inversion group is the direct product of the wreath product $S_3[S_2]$ and the overall coordinate inversion C_i. However, if inversion of configuration of the central carbon is not considered feasible, then the group G is a subgroup which includes only those operations which do not invert the configuration of the central carbon as discussed above. Wreath products are very common in problems of this kind since they represent the feasible changes which correspond to exchanges within exchanges. Given this formulation of the problem a number of associations of group theoretical structures and chemical concepts can be made. Isomers of the chemical structure with all the sites substituted differently correspond to the cosets gR of the rotation subgroup $R < P$ where g is in G. If some of the ligands are identical, the the isomers correspond to the double cosets [3]:

$$L / P \backslash R$$

where L is the symmetry group of the identical ligands and is usually a direct product of symmetric groups [4].

The possible modes of isomerization for a structure with all ligands identical correspond to the double cosets:

$$R / P \backslash R$$

or to unions of these double cosets [5].More generally these modes correspond to bilateral classes [6]. Each mode is a collection of permutations which are made equivalent by the symmetry of the skeleton. Each permutation represents the overall change caused by a degenerate isomerization which can occur by a variety of physical mechanisms. In the well studied trigonal bipyramid example, there are six double cosets : $D_3 / S_5 \backslash D_3$ which correspond to the six modes or permutationally distinct isomerizations [5]. One of these modes includes the permutation corresponding to the familiar Berry [7] pseudorotation indicated by the sequence of structures 1a-c.

If the ligands are not all identical then modes are defined by considering the ligand symmetry as well as the site symmetry and are called generalized stereoisomerization modes [2].

Another key group theoretical construction is the lattice of subgroups between P and G [8]. Here P will be the rotation subgroup of the point group. Properties of this lattice and the subgroups involved can be used in at least three ways.

First, chains of subgroups between P and G can be used to provide descriptors for the possible isomers which correspond to the cosets gP in G. In most problems of interest there is a very large number of these isomers and a means of keeping track of them is important. This also provides a general method of classification of permutation isomers [9]. Consider such a chain of subgroups between P and G:

$$P \dashrightarrow H_1 \dashrightarrow H_2 \dashrightarrow H_3 \dashrightarrow \ldots\ldots \dashrightarrow H_n \dashrightarrow G$$

Starting from the largest group G, the cosets of H_n in G collect the isomers into i_{nG} classes where i_{nG} is the index of H_n in G. Each class contains i_{Pn} isomers where i_{Pn} is the index of P in H_n. All the isomers in each coset gH_n receive the same descriptor while each coset gH_n receives a different descriptor. This process is repeated for the cosets of H_{n-1} in H_n etc. until P is reached. At each stage the isomers receive a new descriptor. Finally, there will be as many descriptors as there are subgroups in the chain. These are not absolute designations and depend on the choice of a reference isomer of some kind. Once this reference isomer is chosen and has its descriptors assigned, all the other isomers will have unique descriptors. This idea has been applied to the problem of giving descriptors to the 192 possible isomers of tetraphenylmethane [8]. It is possible to choose any of the possible chains of subgroups and an optimal choice is not apparent [8]. One choice with a kind of uniqueness property is a composition series which is a chain of maximal normal subgroups [10], each maximal in the group directly above it. By the Jordan-Holder theorem, all composition series in a group are equivalent although the actual chain of groups can vary.

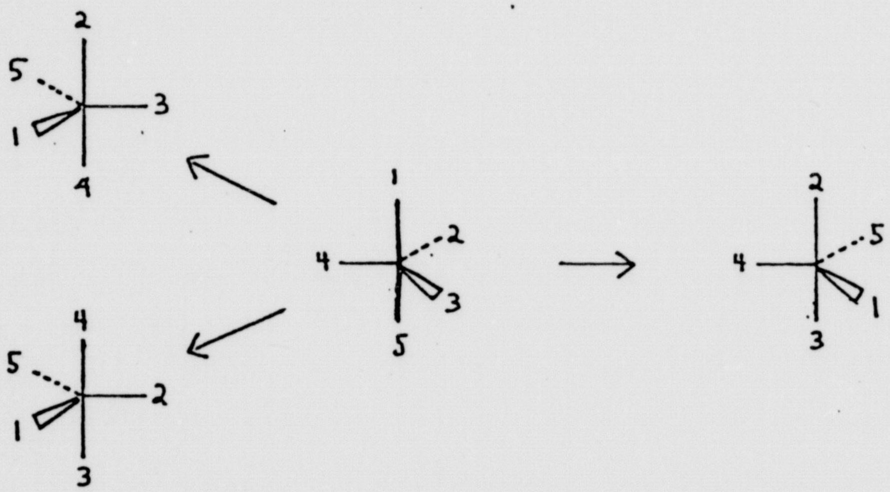
A second use of the subgroup lattice concerns the concept of "residual stereoisomerism". It has been observed that for propeller-like molecules such as 2 with each ortho position distinguished , the preferred mode of rearrangement does not interconvert all the possible isomers and two distinct isomers are observed [11]. In group theoretic terms, the double coset which corresponds to the energetically preferred mode of rearrangement when multiplied exhaustively times itself generates only a subgroup of the maximal permutation inversion group G. For a given problem with point group P and maximal group G, the possibilities for residual stereoisomerism correspond to the subgroups on the lattice between G and P. Each of these subgroups is composed of intact double cosets of G in P and each of these double cosets can correspond to a possible rearrangement mode. The actual preferred mode and hence the number of residual stereoisomers depends on the energetics of the problem and is outside the realm of the permutation group description.

The third use of the subgroup lattice involves the determination of the effect of combining two or more experiments to determine a preferred rearrangement mode. Here, use is made of the lattice operation of intersection. On the subgroup lattice the intersection of two groups is the largest subgroup common to both of them. Consider the subgroups:

$$H_1 \longleftarrow P \longrightarrow H_2$$

i.e., the intersection of subgroups H_1 and H_2 is P. It is possible that an experiment can be designed which has as its effective symmetry group the subgroup H_1. Thus the results of the experiment are invariant to operations in the group H_1 rather than just the smaller group P. Certain NMR experiments and experiments involving structures with identical substituents can have effective symmetry groups larger than P [8]. Performing such an experiment would determine a rearrangement mode corresponding to a double coset of H_1 in G. This double coset is a collection of the double cosets of P in G since P is a subgroup of H_1. Doing another experiment with effective symmetry group H_2 would likewise determine a mode corresponding to a double coset of H_2 in G which would be a different collection of the double cosets of P in G. Now assuming the actual favored mode to be the same in both experiments, this mode must be common to the collections of modes determined for the two experiments. That is, the actual mode must be in the intersection of the two collections. The overall effect is that combining the two experiments with effective symmetry groups H_1 and H_2 has the effect of doing the one experiment with effective symmetry group P. More precisely, the upper limit of the information available by doing the two experiments with effective symmetry groups H_1 and H_2 is the information available by doing the experiment with effective symmetry group P which is the intersection of H_1 and H_2. The qualifier is necessary since the intersection of a double coset of H_1 with a double coset of H_2 need not give just one double coset of P. An example of the use of this idea has been given [7]. The idea is useful only if the two experiments together are simpler to perform than the one which corresponds to their intersection.

In the usual sense the group G is generally not considered to be a symmetry group of the chemical structure in question except occasionally as a nonrigid symmetry group [1]. However, G is a symmetry group for the potential energy surface which corresponds to the set of atoms which make up the structure since G includes permutations of identical atoms. The potential energy surface in question starts out with 3n+1 coordinates (3 for each of the n atoms and 1 energy coordinate). This is reduced by the identification of all the points on the surface which are related by translation or rotation in space. Each point on this surface represents a chemical structure in all possible orientations. For structures with nontrivial rotation symmetry, this process identifies structures related by the permutations of the rotation group, R. Hence the cosets gR are represented by single points. Starting from any of these points it is possible to find paths to another isomer (coset) which correspond to one of the possible modes of rearrangement. For example consider the Berry pseudorotation of a trigonal bipyramid structure:



There are three possible symmetrically related Berry processes which have the indicated overall permutational change. Each of these permutations is in the same double coset or mode. Now the group G (S_5 in this case) acts on the surface (and the cosets) as a symmetry group relating all the isomers (20 cosets in this case). Similarly, this group relates all the symmetrically equivalent paths which correspond to the Berry process. This set of isomers and paths can be symbolized by a graph in which the nodes are the isomers and the edges are the paths. These interconversion graphs have seen wide application in problems in dynamic stereochemistry [12]. The incidence matrices for these graphs are the double coset matrices discovered by Frame [13]. These matrices commute with the permutation representation of G and therefore have G as a symmetry group. Another interesting symmetry property of the paths connecting the isomers on the potential energy surface follows from an intrinsic property of double cosets. If there is a path from isomer a to isomer b with overall change the permutation p, then there will be a symmetrically equivalent path from b to a if p^{-1} is in the same double coset as p. Stated differently, the double coset which includes p must be selfinverse [3]. There is an overall symmetry of the potential energy surface which exchanges isomers a and b [14].

Further use can be made of the idea of group homomorphism to describe the observed similarity between seemingly diverse chemical systems termed stereochemical correspondence [15]. For two chemical systems characterized by groups P_1, G_1, P_2, G_2 and the homomorphisms between P_1 and G_1 and between P_2 and G_2, there is a correspondence from chemical system 1 to chemical system 2 if there is a diagram of homomorphisms of the groups:

$$\begin{tikzcd}
P_1 \arrow[r] \arrow[d] & P_2 \arrow[d] \\
G_1 \arrow[r] & G_2
\end{tikzcd}$$

that commutes. That is, composing the homomorphisms around the diagram in either direction yields the same overall homomorphism. This condition assures a correspondence between cosets (isomers) and double cosets (modes). Stronger conditions insure a correspondence between the subgroup lattices [15c]. Such a correspondence can be thought of as a description of the similarity between regions of the potential energy surfaces describing the two chemical systems. This similarity is in the connectivity of the surface and not necessarily in the energetics. However, more closely related systems for which there is stereochemical correspondence have been observed to be similar energetically [11]. The observation of such a correspondence aids in the design of experiments, particularly if one of the chemical systems has already been studied. This is also an interesting relationship between chemical systems in that it can be described algebraically in a very compact way [15c]. This yields a new means of classifying chemical systems based on an intrinsic algebraic property of these systems and resembles the methods used to classify various mathematical structures by their intrinsic algebraic properties [16]. A number of other examples of stereochemical correspondence have been given [15]. A summary of the correspondence of some concepts in dynamic stereochemistry with their permutation group theoretical structures is given below.

Chemical Concept	Permutation Group Structure
maximally substituted isomers	cosets, gR
isomers with some identical substituents	double cosets, LgR
isomerization modes	(unions of) double cosets, RgR bilateral classes
residual stereoisomers (closed system of interconverting isomers)	subgroup between R and G
interconversion graphs (topological representations)	(unions of) double coset matrices
isomer descriptors	subgroup chains
combined experiments with different effective symmetry groups	subgroup lattice intersection

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References

[1] H. C. Longuet-Higgins, Mol. Phys., 6, 445 (1963).

[2] J. G. Nourse, J. Amer. Chem. Soc., 99, 2063 (1977).

[3] J. S. Frame, Bull. Amer. Math. Soc., 47, 458 (1941).

[4] E. Ruch, W. Hasselbarth, and B. Richter, Theor. Chim. Acta., 19, 288 (1970).

[5] (a) M. Gielen and N. Vanlautem, Bull. Soc. Chim. Belg., 79, 679 (1970)
  (b) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, J. Amer. Chem. Soc., 93, 4701 (1971).
  (c) W. G. Klemperer, J. Chem. Phys., 56, 5478 (1972).
  (d) W. Hasselbarth and E. Ruch, Theor. Chim. Acta, 29, 259 (1973).
  (e) D. J. Klein and A. H. Cowley, J. Amer. Chem. Soc., 97, 1633 (1975).

[6] W. Hasselbarth, E. Ruch, D. J. Klein, and T. H. Seligman, in "Group Theoretical Methods in Physics, R. T. Sharp and B. Kolman, eds.,Academic, New York, 1977, p. 617.

[7] R. S. Berry, J. Chem. Phys., 32, 923 (1960)

[8] J. G. Nourse and K. Mislow, J. Amer. Chem. Soc., 97, 4571 (1975).

[9] Related ideas of descriptors and "stereochemical quantum numbers" have been discussed. See E. Ruch and I. Ugi, Top. Stereochem., 4, 99 (1969)

[10] J. J. Rotman, "The Theory of Groups, An Introduction", Allyn and Bacon, Boston, 1965, chap. 6.

[11] K. Mislow, Acc. Chem. Res., 9, 26 (1976).

[12] (a) M. Gielen, R. Willem, and J. Brocas, Bull. Chim. Soc. Belg., 82, 617,(1973)
  (b) K. Mislow, Acc. Chem. Res., 3, 321, (1970).

[13] J. S. Frame, Bull. Amer. Math. Soc., 49, 81 (1943); 54, 740 (1948).

[14] J. G. Nourse, to appear.

[15] (a) D. Gust, P. Finocchiaro, and K. Mislow, Proc. Natl. Acad. Sci. U.S., 70, 3445 (1973).
  (b) K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, Fortschr. Chem. Forsch. 47, 1-28.
  (c) J. G. Nourse, Proc. Natl. Acad. Sci. U.S., 72, 2385 (1975).

[16] S. MacLane, "Categories for the Working Mathematician", Springer-Verlag, New York, 1971.