An Algebraic Description of Stereochemical Correspondence

(dynamic stereochemistry/group theory)

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ABSTRACT   It is shown that a stereochemical correspondence between two molecular systems can be represented by a commuting diagram of the point groups and permutation groups involved. The effect of the diagrammatic condition on the mappings of the cosets, double cosets, subgroup lattice, and double coset algebra determined for the two molecular systems by point group to permutation group homomorphisms is detailed. Chemical similarities implied by a stereochemical correspondence are indicated, and six examples are provided and discussed.

The concept of stereochemical correspondence (SCC) has been put forth to describe an intrinsic similarity between molecular systems which is independent of widely different structural properties (1). In this article we will provide an algebraic description of this relationship and some further examples. The concept will be generalized somewhat from the previous definition, and the chemical and mathematical properties related by a SCC will be discussed.

Briefly, the problem here is to assign an algebraic structure of some kind to a molecular system and to see if the similarity or correspondence between two molecular systems can be expressed as some mapping of the algebraic structures. The fundamental importance of this sort of procedure of assigning mathematical structures *and* mappings between them has been recognized by mathematicians. The study of category theory is the study of such procedures (2). Well-known examples can be found in the field of algebraic topology, in which mappings between topological spaces can be represented by homomorphisms of groups. As an example, the homeomorphism between a donut and a coffee cup can be expressed as a homomorphism between homology groups or fundamental groups (3). The rationale is that the group homomorphisms are often easier to establish and the groups themselves describe intrinsic properties (topological invariants) of the topological spaces (such as the "hole" in the donut or coffee cup). The motivation behind the work described in this article is to apply similar considerations to molecular systems in a search for intrinsic properties and relationships.

Algebraic description of molecular systems

A typical problem in dynamic stereochemistry is the study of the degenerate rearrangements of a molecule with skeletal symmetry group P. The set of all rearrangements also form a group G, which will often be one of the symmetric groups or a direct product of symmetric groups and may or may not include an operation of overall coordinate inversion (4, 5).

Abbreviations: SCC, stereochemical correspondence; TBP, trigonal bipyramid; DCA, double coset algebra.

Of particular importance to the present discussion is the homomorphism of P into G.

$$P \rightarrow G$$

In this context the arrow between two groups designates a homomorphism. In this case the mapping is into or monomorphic. As an example, the well-studied pentavalent trigonal bipyramid (TBP) system has $P \cong D_3$ (rotation subgroup only) and $G \cong S_5$ (6).

This seemingly trivial homomorphism determines a number of algebraic structures important to the chemical problem. The right cosets of P (gP for g in G-P) correspond to the isomers of a maximally labeled skeleton. The double cosets of P (PgP for g in G-P) are used to determine the possible modes of rearrangement (7, 8). The lattice of subgroups between P and G is used to determine isomer descriptors, residual stereoisomerism possibilities, and the combined effect of independent experiments with different effective symmetry groups (9). Cosets, double cosets, and subgroup lattices are standard group-theoretical constructions which are described in most texts (10). The final algebraic structure of interest here that is determined by the above homomorphism is the double coset algebra (DCA). This seems to be a less familiar construction and deserves a more detailed description. If P were a normal subgroup of G, there would be an additional homomorphism of G onto the factor group G/P.

$$P \rightarrow G \rightarrow G/P$$

However, in nearly all chemical examples P will not be a normal subgroup of G and no factor group will exist. The corresponding structure in these cases is the double coset algebra $A(G/P)$. Two double cosets of P in G can be multiplied together to give a linear combination of intact double cosets (11):

$$B \cdot C = mB + nC + pD + \ldots$$

where B, C, and D are double cosets of P in G and m, n, and p are integral coefficients. This is an associative but not necessarily commutative algebra. The canonical mapping of G onto the DCA preserves a weaker form of the group axioms

$$G \xrightarrow{c} A(G/P) \text{ where } c(ab) \subseteq c(a) \cdot c(b) \text{ for } a, b \in G$$

where $c(a)$ is the double coset containing a. Thus, $c(ab)$ is not necessarily equal to $c(a) \cdot c(b)$, as would be required for a group homomorphism. The DCA is useful in the kinetic analysis of complicated isomer interconversions (12) and in determining the effect of multiple step processes (9, 12).

Stereochemical correspondence (SCC)

An algebraic definition of the SCC between two molecular systems with point groups P_1 and P_2 and permutation-inversion groups G_1 and G_2 can be concisely presented diagrammatically.

$$\begin{array}{ccc}
P_1 & \xrightarrow{\ j\ } & P_2 \\
\downarrow{\scriptstyle h_1} & & \downarrow{\scriptstyle h_2} \qquad h_1 k = j h_2 \\
G_1 & \xrightarrow{\ k\ } & G_2
\end{array} \qquad [1]$$

The requirement is that the diagram *commutes*, so that travelling from P_1 to G_2 by either route (through P_2 or G_1) yields the same overall homomorphism. This example would properly be called a correspondence from molecular system 1 to molecular system 2. This perhaps trivial-appearing condition is actually quite strong; for an arbitrary collection of four groups and homomorphisms, the commutativity condition would not generally hold.

Conditions on j and k can be established by considering a somewhat larger commuting diagram.

$$\begin{array}{ccccc}
K(j) & \xrightarrow{\ i_j\ } & P_1 & \xrightarrow{\ j\ } & P_2 \\
\downarrow{\scriptstyle m} & & \downarrow{\scriptstyle h_1} & & \downarrow{\scriptstyle h_2} \\
K(k) & \xrightarrow{\ i_k\ } & G_1 & \xrightarrow{\ k\ } & G_2
\end{array} \qquad [2]$$

$K(j)$ is the kernel of the homomorphism j, and i_j is the mapping (injection) of $K(j)$ into P_1. Similarly, $K(k)$ is the kernel of k and i_k the injection. In all the chemical examples considered, h_1 and h_2 are also into mappings. The commutativity condition then requires that m also be into, meaning that $K(j)$ is contained in $K(k)$.

It can now be demonstrated how the diagrammatic condition 1 determines the mappings of the relevant algebraic structures. Since P_1 is mapped to P_2, any coset of P_1 must be mapped to a coset of P_2. For g in G, p in P:

$$pg \rightarrow h_1 k(p) k(g)$$

and $h_1 k(p) = j h_2(p)$ by the commutativity condition. This is simply the statement of the condition of a group homomorphism (preservation of multiplication). Similarly, for double cosets:

$$p_1 g p_2 \rightarrow h_1 k(p_1) k(g) h_1 k(p_2)$$

Thus, the coset and double coset structures determined by the homomorphism h_1 are preserved. In a chemical example this determines a correspondence between isomers and rearrangement modes of the two molecular systems. Specifically, a mode that can be expressed as one double coset of the point group [i.e., a racemic mode (8)] in system 1 is mapped to one double coset or mode in system 2 (diagram 1). Modes that are expressed as unions of double cosets of the rotation group (8) are preserved by the SCC 1 if diagram 3 commutes.

$$\begin{array}{ccc}
P_1 & \xrightarrow{\ j\ } & P_2 \\
{\scriptstyle q}\searrow & & \swarrow{\scriptstyle s} \\
& C_i &
\end{array} \qquad [3]$$

This condition requires that the proper rotations and improper rotations of P_1 be mapped to the proper rotations and improper rotations of P_2, respectively. The homomorphisms q and s to the inversion group C_i map proper rotations to the identity and improper rotations to the inversion operation.

The effect of a general SCC 1 on the subgroup lattice determined by h_1 is less easily ascertained. For a subgroup H_1 of G_1, which contains P_1, the mapping determined by j and k is:

$$H_1 \rightarrow [H_1/H_1 \cap K(k)] \cup P_2 \qquad [4]$$

in which $H_1/H_1 \cap K(k)$ is the image of k restricted to H_1. The union ($\cup$) and intersection ($\cap$) symbols refer to the usual operations for a subgroup lattice (10). It must now be determined whether the mapping 4 preserves the lattice structure; that is, is there a mapping of the lattice determined by h_1 to the lattice determined by h_2 which preserves the operations of union and intersection? For a general SCC there will not be such a lattice homomorphism. A simple element-wise argument shows that k preserves unions and the commutativity and associativity of the union operations ensures that j preserves unions. However, intersections in the lattice determined by h_1 are not necessarily taken to intersections in the lattice determined by h_2.

$$j,k(H_{1a} \cap H_{1b}) \subseteq j,k(H_{1a}) \cap j,k(H_{1b}) \qquad [5]$$

The intersection of the images of H_{1a} [symbolized $j,k(H_{1a})$] and H_{1b} [$j,k(H_{1b})$] is greater than or equal to the image of the intersection of H_{1a} and H_{1b} [$j,k(H_{1a} \cap H_{1b})$]. This is shown by the semi-distributive property of (subgroup) lattices (13).

$$P_2 \cup [k(H_{1a}) \cap k(H_{1b})] \subseteq [P_2 \cup k(H_{1a})] \cap [P_2 \cup k(H_{1b})]$$

Also, the homomorphism k need not preserve intersections. In previous work (9) it was shown that if experiment A has effective symmetry group H_{1a} and experiment B has effective symmetry group H_{1b}, then doing both experiments is "equivalent" to doing one experiment with effective symmetry group $H_{1a} \cap H_{1b}$. [More precisely, the upper limit to the information (mode) determined by doing both experiments is that which would be obtained by doing the single experiment.] Thus, an optimal pair of experiments will have $H_{1a} \cap H_{1b}$ as small as possible. Condition [5] means that an optimal experiment for molecular system 1 need not be optimal for molecular system 2. A general SCC from system 1 to system 2 determined by j and k may not preserve this sort of experimental design rationale. Stronger conditions to be discussed with the examples will preserve this property.

The effect of the general SCC 1 on the double coset algebra (DCA) can be established by referring to diagram 6.

$$\begin{array}{ccccc}
P_1 & \xrightarrow{\ h_1\ } & G_1 & \xrightarrow{\ c_1\ } & A(G_1/P_1) \\
\downarrow{\scriptstyle j} & & \downarrow{\scriptstyle k} & & \downarrow{\scriptstyle d} \\
P_2 & \xrightarrow{\ h_2\ } & G_2 & \xrightarrow{\ c_2\ } & A(G_2/P_2)
\end{array} \qquad [6]$$

Mappings c_1 and c_2 are the canonical mappings of the groups G_1 and G_2 into the DCAs mentioned earlier. To establish whether the mapping d induced by j and k preserves the structure of $A(G_1/P_1)$, it must be established that j and k preserve this structure.

$$d(B) \rightarrow k(B) + k(C) + \ldots + k(N)$$

B is a double coset of G_1/P_1, and $k(B) + \ldots + k(N)$ is a double coset of G_2/P_2. Since the DCA is a subalgebra of the group-algebra, and group homomorphisms induce group-algebra homomorphisms (14), the homomorphism k will preserve the structure of the DCA. (The ring structure implicit in the DCA is a subring of the group ring.) In general, however, j will not preserve this structure since the kernel of the mapping of the DCA induced by j will not always be a two-sided ideal of the DCA (14). The problem is with the coefficients of the double cosets. A counterexample will be provided in the discussion of examples.

A further insight into the chemical similarity implied by SCC can be gained by consideration of the potential energy surfaces for the various molecular systems. The permutation-inversion group G is a subgroup of the symmetry group for the $3n$-dimensional potential energy surface for the molecular systems where n is the number of atoms (15). This applies to the Born–Oppenheimer surface for any electronic state so that the entire set of surfaces will have this symmetry. This is simply a consequence of nuclear identity. The Euclidean group $E(3)$ (translations, rotations, and reflections of the 3-dimensional coordinate space) is also a symmetry group of this surface. By identifying points on the $3n$-dimensional surface that are related by operations in $E(3)$ or $E^+(3)$ (rotations and translations only), one obtains a more complicated surface of lower dimension. A SCC as detailed above describes a similarity between regions of this identified surface for two molecular systems.

Examples

Six examples of SCC, as shown in Fig. 1, will now be discussed.

It has been pointed out (16) that the graph which describes the possible interconversion of the 20 maximally substituted TBP isomers by the Berry pseudorotation is isomorphic to that given by Balaban *et al.* (17) for the rearrangements of the maximally labeled ethyl cation by 1,2 shifts.

$$R_1R_2R_3C_a - \overset{+}{C}_bR_4R_5 \rightleftharpoons R_1R_2\overset{+}{C}_a - C_bR_3R_4R_5$$
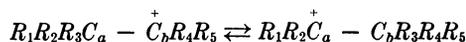
There are 20 isomers of such a carbonium ion without consideration of the absolute configuration at C_a (17). The SCC between the two systems is given in diagram **7** of Fig. 1. For the TBP case, the point group is D_3 (rotations only) and the full permutation group is S_5. For the carbonium ion, the "effective point group" for the problem defined by Balaban *et al.* (17) is $S_3 \times S_2$ [all permutations of R_1, R_2, R_3, and the permutation (R_4R_5)], while the full permutation group is $S_5 \times S_2$ (all permutations of the R groups and the permutation of the carbons). Representative element mappings for the SCC **7** are:

(345)$^\bullet \rightarrow$ (345) even permutations

(12) $\rightarrow$ (12)(C_aC_b) odd permutations
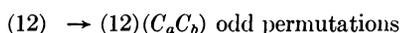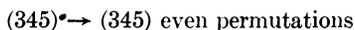
The mode (double coset), which includes the permutations of the Berry pseudorotation, corresponds to the mode for the 1,2-shift; hence, the identical graphs [double coset matrices (9, 11, 18)]. The reverse mapping from the carbonium ion to the trigonal bipyramid does *not* give a commuting diagram; hence, the "correspondence" is directional.

A SCC has been described (1) which relates three-bladed propeller systems with tris-chelated octahedral systems. The
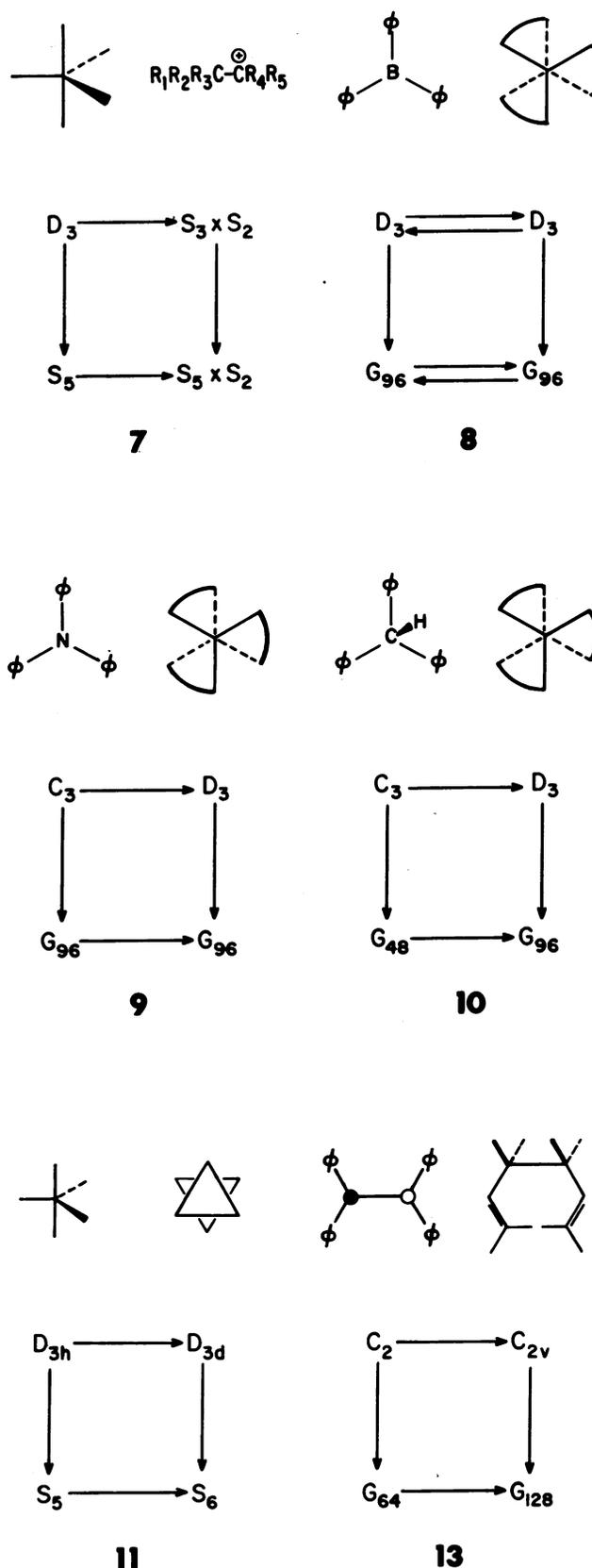

FIG. 1. Six examples of stereochemical correspondence (SCC).

next three examples (diagrams **8–10**) pertain to this SCC. A tris-chelated metal has D_3 point group symmetry if all the ligands are identical. The full permutation-inversion group

describing the possible isomerizations can be expressed as $S_3[S_2] \times C_i$, which is the direct product of the group of all the bidentate ligand permutations (the wreath product $S_3[S_2]$) and overall coordinate inversion (C_i), which accommodates enantiomerization of the chiral skeleton (4, 19). This is a group of order 96, and is designated G_{96} in Fig. 1. Triphenyl borane likewise has a D_3 skeleton and permutation inversion group G_{96} (based on permutation of the six ortho ring sites). The SCC is shown in diagram **8**. In this case, the groups are isomorphic and the correspondence can be expressed as a commuting diagram in either direction. Thus, all sequences of mappings between any two groups are equivalent. This is a stronger SCC and ensures the preservation of the subgroup lattice structure described earlier. This is a sufficient but not a necessary condition for preservation of the subgroup lattice structure.

Triphenylamine exists in a C_3 conformation, but inversion at nitrogen would be an observable process given the appropriate time scale of observation. The permutation-inversion group is again G_{96}. The SCC to the tris-chelate system is given in diagram **9**. Finally, triphenylmethane has a C_3 skeleton, but inversion of the configuration at carbon is not expected to occur during a normal time scale of observations, so that the permutation-inversion group is a subgroup of G_{96} designated G_{48}. This group includes all operations that retain the configuration at carbon and is isomorphic to $S_3[S_2]$. Permutations that require the exchange of two rings are coupled with the operation of overall coordinate inversion. The SCC to the tris-chelate is shown in diagram **10**. In each of these three examples the favored two-ring flip mechanism for the triaryl system corresponds to the Ray–Dutt twist for the tris-chelate (1).

The fifth example (diagram **11**) shows that the conditions for a SCC depend only on the abstract group structure and not on the permutational representation. The five-coordinate TBP is compared to an idealized six-coordinate system with D_{3d} symmetry. The point groups D_{3h} and D_{3d} are isomorphic, as can be verified from character tables. The subgroup S_5 of S_6 is *not* one of the obvious subgroups that permute only five ligands but is *transitive* on all six ligands (20). This SCC states that the rearrangement modes for the TBP skeleton would correspond to modes for the hexacoordinate system which interconvert only one-sixth of the isomers [residual stereo-isomerism (1)] and would yield identical graphs, etc. A counterexample to the conjecture that a general SCC preserves the structure of the DCA is given by diagram **12** in

$$
\begin{array}{ccc}
D_{3h} & \longrightarrow & S_5 & \longrightarrow & A(S_5/D_{3h}) \\
\downarrow & & \downarrow & & \not\downarrow \\
O_h & \longrightarrow & S_6 & \longrightarrow & A(S_6/O_h)
\end{array}
\qquad [12]
$$

which O_h replaces D_{3d} in **11**. The DCAs can be derived from those described by Brocas (12, 21) for these two systems.

In the final example (diagram **13**) the comparison between 1,1,2,2-tetraphenylethane and 1,5-hexadiene is made. The tetraphenylethane skeleton is assumed to have C_2 symmetry in a *trans*-rotamer. The possible conformational changes without inversion at carbon comprise a group of order 64, which has a convenient permutational representation based on the eight ortho ring sites. The hexadiene is assumed to have (idealized) C_{2v} symmetry. The group, which includes

all possible [1,3] and [3,3] shifts along with the point group, is of order 128 and can be represented by permutation of the CH_2 hydrogens (22). In a recent study (23) Dewar *et al.* have discussed the interconversion of 1,5-hexadienes in terms of "orbital isomerism" by noting that only certain appropriately substituted isomers will be interconverted by allowed processes. In the present context, the allowed changes would generate a subgroup of G_{128} and the orbital isomers would be analogous to possible residual stereoisomers in the tetraphenylethane even though the reason for the existence of the energy barriers is different. A kinetic study of labeled 1,5-hexadienes has been done (24).

Two possible means of generalization of these concepts may be briefly noted. First, only degenerate reactions have been discussed since these admit a group theoretic description. Nondegenerate reactions (25) can be described by *groupoids*, which differ from groups only by the lack of the requirement of composability (26). That is, for two arbitrary elements of a groupoid, a product element need not exist. Second, different diagrammatic constructions of the various group(oid)s might suggest other interesting relationships between molecular systems.

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