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A FIRST APPROACH TO THE STEREOCHEMICAL ANALYSIS OF TETRAARYLMETHANES

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Abstract—A mathematical model is defined to represent tetraarylmethanes. The skeletal permutations of this model are described and analyzed in terms of mode equivalent rearrangements. This analysis is applied to an interpretation of the previously published results of a DNMR study of tetra-*o*-tolylsilane and analogs. A mechanism for the rearrangement is then postulated. The group of permutational flips is described and combined with the skeletal group to give the full permutation group of tetraarylmethanes.

INTRODUCTION

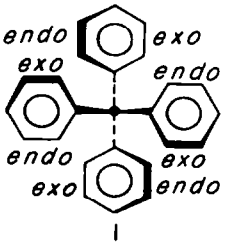
The foundations of the stereochemistry of carbon were laid in 1874 by Le Bel[1] and independently by van't Hoff who postulated the tetrahedral carbon atom thus: "The theory is brought into accord with the facts if we consider the affinities of the carbon atom directed toward the corners of a tetrahedron of which the carbon atom itself occupies the center."[2] In those early days, the phenomenon of conformational stereoisomerism naturally went unrecognized, even though van't Hoff was remarkably close to the truth in the second edition of "The Arrangement of Atoms in Space", published in 1898[3]—just a year after the first report of tetraphenylmethane, by Gomberg[4]—when he wrote, albeit in a totally different context, that "... the phenomena of isomerism are in a certain sense opposed to motion; they are certainly not a consequence thereof; for when the temperature rises they ultimately disappear, and become constantly more marked as it falls."

It would seem a fitting tribute, on the occasion of this centennial, to offer an analysis of the stereochemistry of tetraarylmethanes. The stereochemical consequences of substituting four phenyl groups for the H atoms of methane would seem, at first glance, to be quite trivial. On the contrary: the complexities of the analysis are such that it is only now, a full century after the original suggestion of tetrahedral carbon valencies, that the state of the art permits a sensible attack on this problem. The present paper represents a first step in this direction.

Static stereochemistry

Before entering on a discussion of the dynamic properties of tetraarylmethanes, which is to be the main focus of our paper, we summarize the static stereochemistry vested in the system. Reduced to its bare essentials, the stereochemistry of tetraarylmethanes concerns the behavior of four 2-fold rotors positioned on a tetrahedral skeleton. The symmetry of each rotor destroys all 3-fold symmetry inherent in the skeleton (*i.e.* the tetrahedron), with the result that the system can only belong to one of the seven subgroups† of D_{2d}: D_{2d}, D_2, S_4, C_{2v}, C_2, C_s, and C_1. In consequence, there exist no conformations of tetraphenylmethane in which all six internal C–C–C angles are precisely tetrahedral (arccos $-1/3$, *i.e.*, *ca* 109·5°).

In Fig 1 we have depicted the relationships connecting structures belonging to the most important subgroups, as follows. Rotation (by which we mean torsion) of the two pairs of aryl rings related by the unique C_2 operation (S_4^2) in opposite directions by $\pi/2$ effects interconversion of the two D_{2d} conformations *via* a continuum of conformations of S_4 symmetry. In contrast, an increment of only $\pi/6$ suffices to induce the same transition by way of D_2 conformations, provided that the four groups are rotated in the same sense. Introduction of substituents on tetraphenylmethane in a particular conformation, for instance S_4, is capable of destroying the symmetry, but if roughly the same aryl group orientations are maintained, we shall call the new symmetry which is adopted ψ-S_4. As an additional descriptive device we use the *endo–exo* nomenclature to distinguish the different edges of the aryl groups of a molecule. If, as in **1**, a molecule in an S_4



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†The following conventions are followed in this paper. (a) Schoenflies point group symbols are italicized; thus the improper rotation group of order four is S_4. Elements of a point group are also italicized, but the distinction will be clear from context. (b) Symmetric groups are represented by the boldface symbol $\mathbf{S}_n$. (c) Group multiplication of the elements of a group are to be read from right to left.

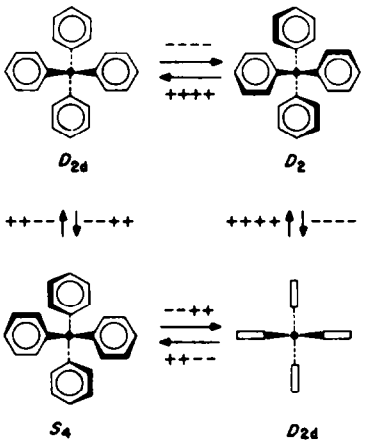


Fig 1. Torsional motions connecting four different conformations of tetraphenylmethane. A plus sign denotes clockwise rotation of a phenyl group as viewed toward the central carbon; counter-clockwise rotation is indicated by a negative sign.

conformation is represented by a Fischer projection where the central atom lies in the reference plane—the plane of the paper—then the effect of the orientation of the aryl groups is to bring four edges (*endo*) relatively near the reference plane (toward the center of the molecule), with the four others (*exo*) relatively remote (away from the center of the molecule).

The evidence at hand shows that S_4 (or ψ-S_4) symmetry is preferred by almost all tetraarylmethanes,[5] and for this reason we shall assume this conformation throughout this paper. As will be shown below, in the absence of any degeneracies (*i.e.*, in the most general case where all four aryl groups are different and none possess local C_{2v} symmetry), 192 structures may exist with ψ-S_4 symmetry.

DYNAMIC STEREOCHEMISTRY IN TERMS OF PERMUTATIONS

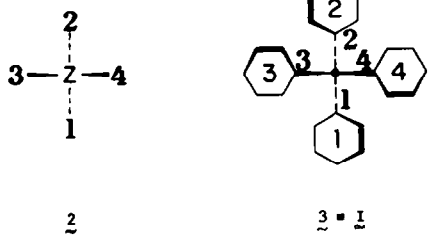
To analyze the dynamic behavior of a particular species, it is convenient to propose a mathematical model which reproduces the essential stereochemical features of the chemical system. Chemical isomerizations may then be represented by mathematical permutations. A particular permutation only gives information relating to models of a given starting structure and the final structure which results from the isomerization in question. It emphatically says nothing about the mechanism of the isomerization it describes: no information pertaining to energetics or geometries of intermediate states traversed during an isomerization is implied in, or may be inferred from, a permutation.*

Two distinct types of isomerizations, and hence permutations, can be envisaged for tetraarylmethanes. The two edges of a given aryl group may permute among themselves so that any *endo* substituent can exchange with the corresponding *exo* substituent. This overall process has the characteristics of a ring *flip*, where a flip is equivalent to a rotation of π radians about the bond to the central atom. We shall consider isomerizations represented by this type of permutation later on in this paper.

Alternatively, the four aryl groups may permute among themselves, without flipping, and it is isomerizations of this kind which we shall discuss first.

The group of skeletal permutations

Given a 4-coordinate skeleton with numbered sites s_1, s_2, s_3, and s_4 (indicated by the hollow numerals in **2**), and a set of four aryl groups as ligands l_1, l_2, l_3, and l_4, there are 4! = 24 different arrangements of ligands on the skeleton, each corresponding to a



2 $\quad$ **3** • **1**

distinct permutational structure or conformation.† We may stipulate the following.[7]‡ The tetraarylmethane model has S_4 symmetry, with the S_4 axis bisecting the angles in **2** defined by s_1, s_2, and Z, the central atom, and by s_3, s_4, and Z. The structures are represented by a set of 2×4 mapping

*Since the properties of the model and the molecule with which we are concerned are in a one–one correspondence, we sometimes find it useful to refer to the real molecular processes—isomerizations—in terms of the corresponding permutations or rearrangements of the model.

†As defined,[4] isomers are chemical species with the same molecular formula which are separated by a potential energy barrier. In contrast, the species which we discuss in this paper which are based on the mathematical model need not be differentiated by this criterion. We emphasize this distinction by deliberately referring to the latter species by the general terms "structure" or "conformation", and reserve "isomer" for those structures which are known to correspond to energy minima. Hence, permutational isomers[7] and stereoisomers become permutational structures and stereostructures, respectively. We have found it convenient, however, to retain the terms enantiomeric and diastereomeric in the context of structures.

‡The mapping matrices refer only to structures and not permutations. To simplify the representations, we have abbreviated the matrix further by the boldface lower case alphabetic label of the permutation which, when acting on the reference structure, leads to that permutational structure. The permutations themselves are abbreviated by italicized lower case alphabetic labels.

matrices $\begin{pmatrix} l \\ s \end{pmatrix}^{S_4}$ from among which a reference structure 3, $\begin{pmatrix} l \\ s \end{pmatrix}^{S_4}_{I}$, is defined in which l_1 resides in s_1, l_2 in s_2, etc., such that $\begin{pmatrix} l \\ s \end{pmatrix}^{S_4}_{1} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 2 & 3 & 4 \end{pmatrix}$. Further, the helicity of the array is defined as depicted in **3**. According to our convention,‡ **3** ≡ **I**.

Permutational isomerizations effect interconversions of permutational structures, achieved mathematically by operation of a permutation on the skeletal sites, *s*. Each of the permutational structures may be derived from the reference structure, **I**, by way of one of 23 distinct permutations which, along with the identity, comprise a realization of the symmetric permutation group of degree four, S_4. We call this the group of skeletal permutations (hereafter the skeletal group), the elements and corresponding alphabetic labels of which are given as follows.

I = (1)(2)(3)(4)	m = (12)(3)(4)
a = (12)(34)	n = (1)(2)(34)
b = (13)(24)	o = (1324)
c = (14)(23)	p = (1423)
d = (142)(3)	q = (1)(24)(3)
e = (134)(2)	r = (13)(2)(4)
f = (123)(4)	s = (1234)
g = (243)(1)	t = (1432)
h = (132)(4)	u = (14)(2)(3)
j = (124)(3)	v = (1342)
k = (143)(2)	w = (1)(23)(4)
l = (1)(234)	x = (1243)

The 24 structures are depicted in the central and left hand columns of Fig 2.

Of the group of 24 skeletal permutations, four are isomorphic to the elements of the point group S_4: (1)(2)(3)(4), (1324), (12)(34), and (1423). These four permutations merely describe the symmetry operations of the molecule, the first and third representing proper rotations, the second and fourth improper rotations.

Because of the symmetry of the S_4 structure, various permutations from the skeletal group acting on a given structure lead to other structures which differ only in their orientation in space; they are brought into equivalence by a proper rotation belonging to the point group (E or C_2). Such permutations are thus described as being *rotationally equivalent*, so that, for example, permutations leading from any given structure to **b** and **c** are rotationally equivalent and can be said to correspond to the same *rearrangement*.

The skeletal group, $\mathbf{S_4}$, is isomorphic to a union of right cosets of the point group C_2 (rotational subgroup of point group S_4).

$$\mathbf{S_4} \cong C_2x_1 \cup C_2x_2 \cup C_2x_3 \ldots, x_1, x_2, x_3 \ldots \in \mathbf{S_4}$$

The twelve disjoint cosets which are thus derived each gives rise to a rearrangement which, when allowed to act on the reference structure, **I**, gives one of twelve distinct stereostructures. These are depicted in the left panel of Fig 2.

As an example, Fig 3 portrays a series of skeletal permutations. The permutation (123)(4) for instance, means

move l_2 from s_1 to s_2, and
move l_1 from s_2 to s_3, and
move l_4 from s_3 to s_1, and
leave l_3 in s_4.

Rearrangement modes of the group of skeletal permutations

It is desirable to partition the group of permutations into double cosets with a consequent simplification in the analysis. The group theoretical methodology for performing this partition has recently been delineated by Ruch and Hässelbarth,[8] and, independently, by Klemperer.[9] Although the two approaches are essentially the same, we have opted to use the terminology of Ruch and Hässelbarth.

Owing to the S_4 symmetry of the molecule, two permutations may be *symmetry equivalent*,[8] such as, for example, (14)(2)(3) and (1)(24)(3), as is demonstrated pictorially in Fig 4. If the aryl groups are distinguishable by labels only, these two permutations will occur under the same influence of the skeleton. Fig 4 shows a permutation corresponding to a point group symmetry operation of the skeleton, in this case an improper rotation, transforming the permutation (1)(24)(3) into the symmetry equivalent permutation (14)(2)(3). The sequence shown is a pictorial representation of the mathematical operation of conjugation. Note that these two permutations are not, however, rotationally equivalent.

Under the physical conditions of experimental observations of the fluid state, the molecule will be free to rotate (tumble) in space (*e.g.*, in an NMR experiment). This freedom renders some of the permutations rotationally equivalent. Such motions, however, are obviously incapable of interconverting enantiomeric structures, and enantiomeric rearrangements may therefore be differentiated, *i.e.*, rearrangements which lead from a given stereostructure to others which are themselves pairwise enantiomeric. Clearly, this analysis is physically realistic only when the experiment of interest can distinguish between enantiomers, *i.e.*, when it occurs in a chiral environment. In the majority of experimental situations this proviso does not obtain, and it is necessary in these cases to expand the definition of rotational equivalence to include permutations which lead to stereostructures which become equivalent through operation of *either* a proper *or* an improper rotation belonging to the same point group of the molecule.

The two concepts of permutational equivalence (rotational and symmetry) may be combined to give a single definition of mode equivalence. If two per-

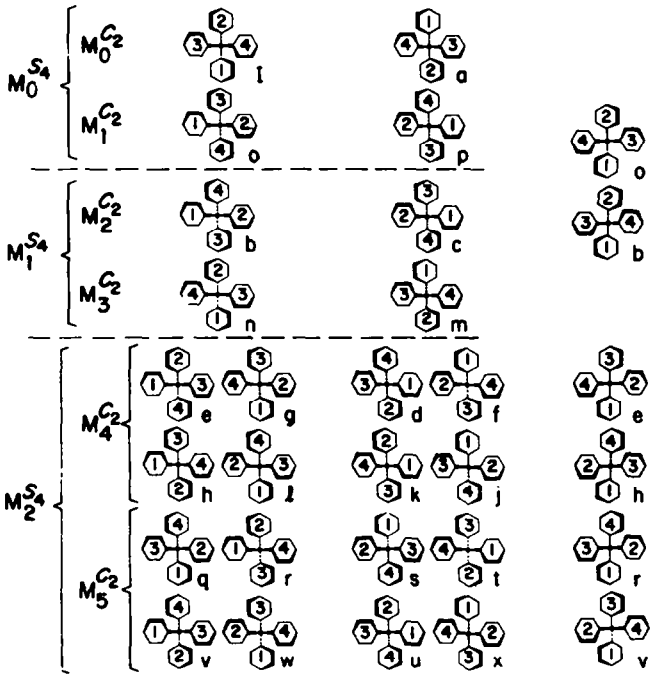


Fig 2. Left and central columns: the 24 permutational structures arranged according to modes. The six structures on the right are different orientations of correspondingly labeled structures on the left.

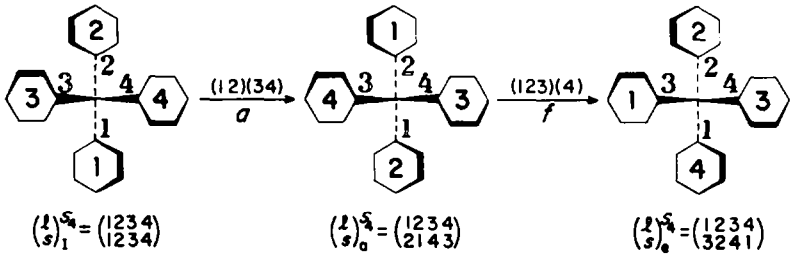


Fig 3. Examples of the operation of permutations from the skeletal group on the site indices, interconverting permutational structures. The first permutation corresponds to a symmetry operation of the skeleton (a C_2 rotation).

mutations, x and y are rotationally equivalent, or if x is symmetry equivalent to y or to a third permutation which is rotationally equivalent to y, then x and y are said to be *mode equivalent.* A complete class of mode equivalent permutations is known as a rearrangement mode, or, in brief, *mode* (M).[8]

These definitions are summarized mathematically for the specific case of tetraarylmethanes in an S_4 conformation:

for symmetry equivalence $y = gxg^{-1}$, $x, y \in \mathbf{S}_4$, $g \in G \equiv S_4$

for rotational equivalence $y = rx$, $r \in R \equiv C_2$

or $y = g'x$, $g' \in G \equiv S_4$

in a chiral and achiral environment, respectively. Combining these statements, the modes M, are given by

$$\mathbf{M}^{C_2} = \{rgxg^{-1}\} = RxR \cup R\sigma x\sigma^{-1}R,\ \sigma \in G - R$$
$$\text{or } \mathbf{M}^{S_4} = \{g'gxg^{-1}\} = GxG$$

Determination of the permutations which are mode equivalent to a given permutation, x, reduces to calculation of the double cosets of x with respect to particular subgroups. These are the terms on the right of the expressions for M, above.

Having given the background for the decomposition by means of double cosets of the group of skeletal permutations, we may now turn our attention to the results for the specific case of tetraarylmethanes of S_4 symmetry. In the following discussion we shall refer to the structures in Fig 2 as representatives of the group of skeletal permutations, with the understanding that the reference

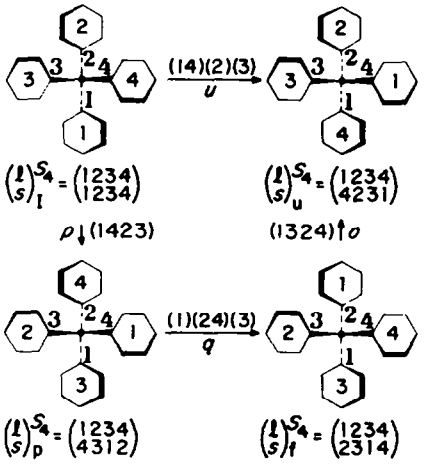


Fig 4. Demonstration of symmetry equivalence of the skeletal permutations (14) (2) (3) and (1) (24) (3) through the operation of an improper rotation belonging to the point group of the skeleton. The scheme is a pictorial demonstration of the mathematical operation of conjugation.

structure I corresponds to the identity permutation *I*.

As already noted, the twelve permutations on the left are rotationally equivalent to those in the central panel. If we restrict the discussion to isomerizations occurring in a chiral environment, the pairs of permutations *I*, *a* and *o*, *p* and *b*, *c* and *n*, *m* each comprise separate modes. For the remaining permutations, however, further mode equivalences arise. In a chiral environment, the permutation labeled *e* is rotationally equivalent only to that labeled *d*, but is symmetry equivalent to *g*, *h*, and *j*. Since *d* is symmetry equivalent to *f*, *k*, and *l*, it follows that *e* must itself be mode equivalent to *f*, *k*, and *l* as well. Hence there are eight permutations in $M_4^{C_2}$. The remaining eight permutations comprise $M_5^{C_2}$, and six modes result. If the restriction of a chiral environment is relaxed, additional mode equivalences lead to a decrease in the total number of modes to three. Specifically, the permutations contained in the enantiomeric modes $M_0^{C_2}$ and $M_1^{C_2}$ are now no longer differentiable since they become rotationally equivalent by virtue of an improper rotation of the point group S_4 and they thus belong to the single mode $M_0^{S_4}$. Similarly, $M_1^{S_4}$ and $M_2^{S_4}$ are comprised of the permutations previously included in the pairs of enantiomeric modes $M_2^{C_2}$ and $M_3^{C_2}$, and $M_4^{C_2}$ and $M_5^{C_2}$, respectively (Fig 2).

Graphical representations of the rearrangements

When dealing with a large number of interconverting structures, as in the present case, it is frequently convenient to construct graphs for the various rearrangements. In the case of the skeletal group of permutations, the graph must include twelve vertices to represent the twelve structures depicted on the left of Fig 2. An alternative view of six of these, shown on the right of Fig 2, is obtained by viewing the corresponding structure on the left down the S_4 axis but from the opposite direction, and rotating the whole molecule 90° to give a Fischer projection. The effect of this reorientation is to give a different impression of the helicity, and allows all twelve structures to be shown with one of the aryl groups (indexed 1) always in the same relative position in space. A particular advantage resulting from this reorientation is that it renders more obvious which pairs of structures are enantiomeric.*

The frame on which we have chosen to construct the graphs is a nested pair of trigonal prisms, each vertex of which corresponds to a stereostructure, as shown in Fig 5a. The broken lines in this and all subsequent graphs are only given to assist visualization, and do not correspond to rearrangements; they are a ghost of the image upon which the graphs proper are delineated. Thus, in Fig 5a no rearrangements are indicated.

As can be seen by inspection of Fig 5a, the structures represented by the vertices of the external prism are enantiomeric to those of the corresponding internal vertices. Moreover, if an order of priorities is assigned to the indices of the ligands, the structures of the outer prism are of the same ab-

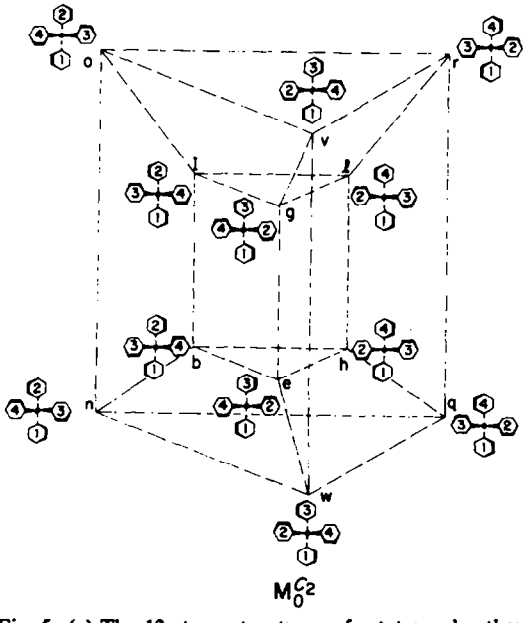


Fig. 5. (a) The 12 stereostructures of a tetraarylmethane arranged on a frame; the array is a faithful representation of the graph of the rearrangement mode $M_0^{C_2}$ for skeletal rearrangement in a chiral environment.

*A consequence of this reorientation is that the site indices as formerly defined no longer apply to the reoriented structures.

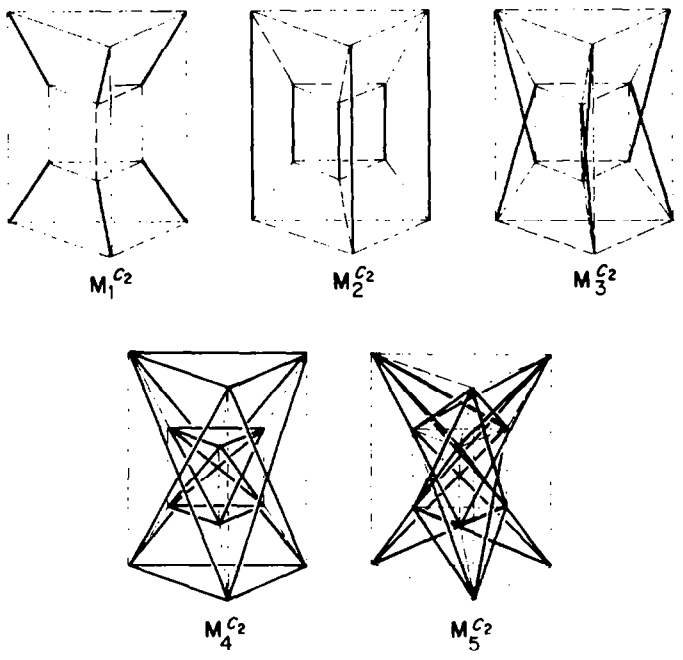


Fig 5. (b) Graphs of modes $M_1^{C_2} - M_5^{C_2}$. The vertices of each graph correspond to stereostructures as labeled in (a), and any other intersection of lines in these graphs is merely an artifact of the representation chosen and does not represent a vertex.

solute configuration and of opposite configuration to those of the inner prism. Furthermore, the structures related by vertical edges are of opposite helicity. The structures at the vertices of a trapezoid defined by the vertical edges and interconnections between the two prisms have common ring pairings in that for all four structures, the same two rings are pairwise related by a C_2 rotation of the skeleton (*e.g.*, 1/2 and 3/4 in the trapezoid on the left in Fig 5a). Lastly, the vertices of each of the four triangular faces represent structures comprising all possible ring pairings.

The graph in Fig 5a is a faithful representation of the consequences of $M_0^{C_2}$, since this mode contains only the identity operation (no rearrangement). The graphs of each of the remaining rearrangements are depicted in Fig 5b. Modes $M_1^{C_2}$, $M_2^{C_2}$, and $M_3^{C_2}$ each contain only a single rearrangement, so that each conformation is converted to one other only. The two modes $M_4^{C_2}$ and $M_5^{C_2}$ each contain four distinct rearrangements. Hence, **e** is converted into structures **I**, **b**, **l**, and **h** by the rearrangements of $M_4^{C_2}$, while in $M_5^{C_2}$ it is transformed to **n**, **o**, **q**, and **r**.

For isomerizations occurring in an achiral environment, enantiomers are no longer distinguished, so it is only necessary to represent six diastereomeric structures on the graph which in this case is merely the inner prism from Fig 5a. The rearrangement of $M_1^{S_4}$ interconverts diastereomeric structures which have the same ring pairings but differ in axial chirality, whereas all other possible rearrangements are included in $M_2^{S_4}$ (Fig 6).

Application of the group of skeletal permutations to a chemical problem

Having dissected some of the stereochemical features of the tetraarylmethane system in terms of mathematical permutations, we now ask: How can this analysis be used to assist our understanding of real systems? In fact, we might ask whether this analysis is applicable at all, since we have thus far restricted ourselves exclusively to *skeletal* permutations and thereby imposed the ostensibly serious constraint that permutational flips are not to be allowed. In this section we address ourselves to these questions.

Calculations indicate[5] that a tetraarylmethane with a bulky substituent in the *ortho* position along the *exo* edge is less strained than a conformer with the same substituent in the *endo* position. Such effects appear to be cumulative. When all four aryl groups are substituted in the *ortho* position, so that the local C_{2v} symmetry of each ring is destroyed, the strain energy of the conformer with all substituents *exo* is sufficiently less than that of any conformer with an *endo* substituent so that it is the only species significantly populated at working temperatures. Hence isomerizations only occur between stereoisomers with all substituents *exo*, and

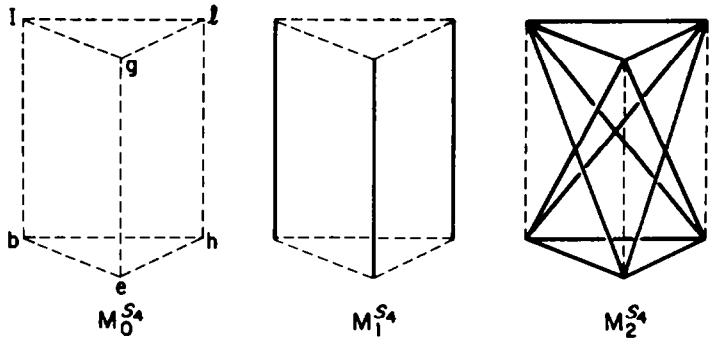


Fig 6. Graphs of the modes $M_0^{S_4} - M_2^{S_4}$ for skeletal rearrangements in an achiral environment.

there is no flipping of aryl rings (condition A).

Flipping of an aryl group which has local C_{2v} symmetry involves a degenerate isomerization (topomerization). If the flipping is not observable under the conditions of the experiment, it would be valid to ignore permutations of this kind and to consider only the skeletal rearrangements (condition B).

Under either of the two conditions described above, permutational flips need not be considered and an analysis based on skeletal permutations alone suffices to describe the system. We now turn to a concrete application.

We recently communicated results of DNMR experiments on tetra-*o*-tolylsilane and related molecules.[10] Our observations can be interpreted in terms of the group of skeletal permutations just described. Empirical force field calculations[5] indicate that the ground state geometry of tetra-*o*-tolylsilane is of S_4 symmetry, with all methyl substituents *exo* (Fig 7a). The next lowest energy minimum on the potential hypersurface,

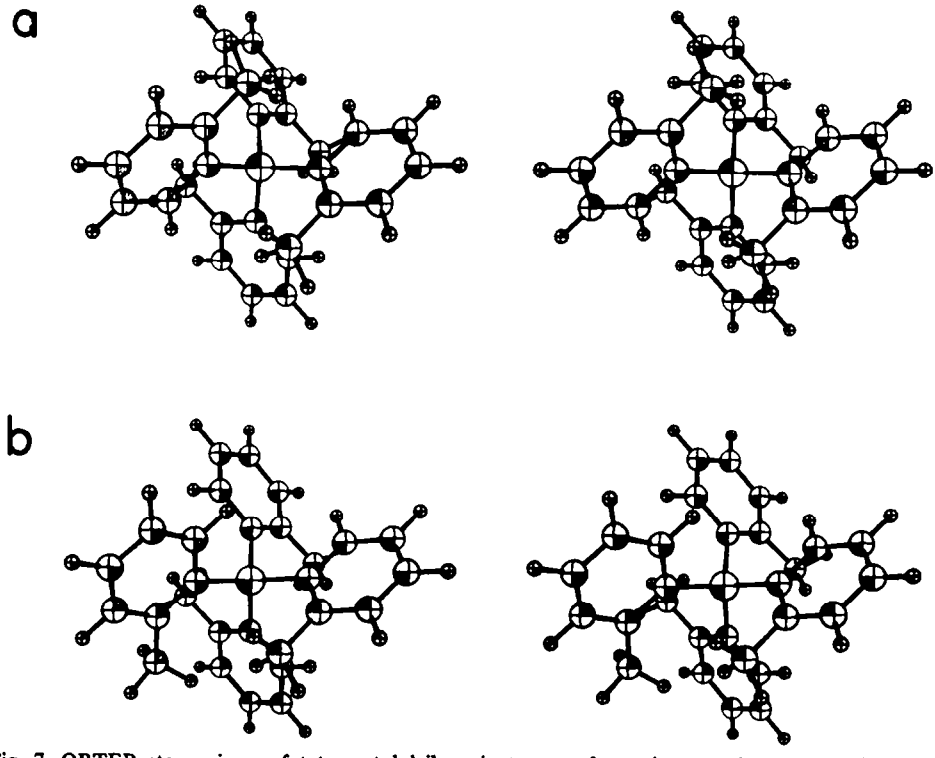


Fig. 7. ORTEP stereoviews of tetra-*o*-tolylsilane in two conformations, each corresponding to a minimum on the potential hypersurface as evidenced by empirical force field calculations: (a) the ground state of S_4 symmetry, and (b) the next lowest energy mimimum of $C_1(\psi - S_4)$ symmetry. Atoms are shown as spheres of arbitrary sizes.

3·49 kcal/mol above the ground state,[5] has ψ-S_4 symmetry, with three methyls *exo* and one *endo* (Fig 7b). Tetra-*o*-tolylsilane therefore satisfies condition A and it follows that the initial and final structures in any isomerization processes will have the all-*exo* S_4 conformation. As a result, only one methyl resonance will be observed in the ^{1}H-NMR spectrum at all temperatures, *i.e.*, at slow as well as fast exchange limits. Replacement of an *o*-tolyl group by a 1-naphthyl group leaves the steric bulk approximately the same but desymmetrizes the ground state of the molecule to ψ-S_4 (true C_1). Consequently, three methyl resonances may be observed in the ^{1}H-NMR spectrum at the slow exchange limit (Fig 8).

Any analysis of the permutations which result in temperature dependent changes of the NMR spectrum must take into account that the DNMR experiment does not allow detection of chirality changes. The two enantiomers of the naphthylsilane are represented as six permutational isomers, the aryl groups being differentiated by numeric indices, as in $M_0^{S_4}$ (Fig 9). Note that the top triangular face of the graph differs from the lower in axial chirality only, and that the three permutational isomers defining such a face are differentiated only by the relative indexing of *o*-tolyl groups, but are *physically* indistinguishable. Besides the identity rearrangement (*I*), two rearrangement modes only are possible (see Fig 6). For a rearrangement in $M_1^{S_4}$, only two of the methyl groups are exchanged, leading to a coalescence of two of the three methyl signals in the NMR spectrum, and resulting in two resonances in a 2:1 ratio. In contrast, an $M_2^{S_4}$ rearrangement would lead to total exchange of all three methyl signals. In actual fact, it is observed that all three methyl resonances coalesce to a single resonance at the same rate (Fig 8),[10] consistent with an $M_2^{S_4}$ rearrangement. Although the $M_1^{S_4}$ rearrangement is not rapid at − 14°, it cannot be excluded at higher temperatures.

Does the above analysis yield any information on the physical mechanism involved in such an isomerization? The answer was already given when we emphasized that such an analysis is solely permutational in nature, and that intermediate states are left completely undefined. Although it sometimes happens that a permutation will suggest to the chemist a particular physical mechanism, as in the permutational isomerizations of phosphoranes,[11-13] octahedral complexes,[14] and molecular propellers (di- and triarylmethanes, triarylboranes, etc.),[15] such is not the case in the current example, and we must resort to speculative arguments.

Before suggesting a mechanism for the rearrangement, we must emphasize certain *conceptual* difficulties which are inherent in this problem as exemplified by the mode $M_2^{S_4}$ rearrangements. Consider, for example, interconversion between permutational isomers I and 1 in Fig 9. *Physically*, the

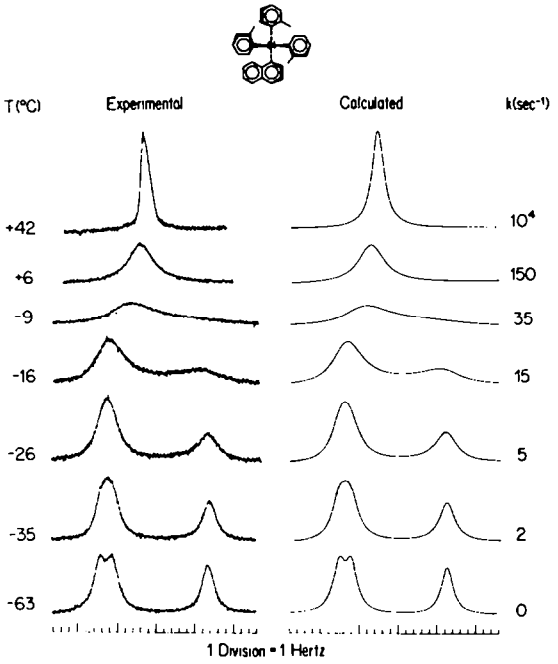


Fig 8. The methyl region of the variable temperature 60-MHz ^{1}H-NMR spectra of tri-*o*-tolyl-1-naphthylsilane (CS_2 solvent, TMS internal reference). The theoretical spectra were calculated using a random exchange matrix to describe the exchanges of methyl group environments.

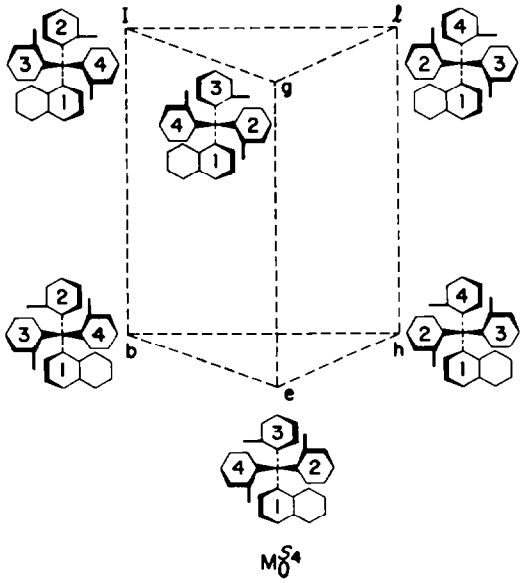


Fig 9. Permutational isomers of tri-*o*-tolyl-1-naphthylsilane for rearrangements in an achiral environment.

rearrangement involves an exchange of partners between the pairs of aryl groups related by ψ-C_2 rotations; hence 12/34⇄14/23, where the numbers refer to ligand indices. In effect, the ψ-S_4 axis is

changing its position from one in which the angle defined at the silicon center by aryl groups 1 and 2 (or by 3 and 4) is bisected, to one in which the angle defined by 1 and 4 (or by 2 and 3) is bisected. Thus, if the skeleton is held rigidly and only the necessary *physical* ring rotations are effected (plus any bond angle reorganization at silicon), we see that the ψ-S_4 axes of **I** and **l** are no longer coincident. It is this fluxional character of the pseudo-symmetry axis which makes isomerizations in these systems so difficult to envisage, and differentiates them from the isomerizations in triarylmethanes,[15] where the C_3 or ψ-C_3 axis remains fixed in space. This is also the reason, incidentally, that rotation by only $\pi/6$ of all aryl groups in a D_{2d} conformation suffices to induce conversion to the other D_{2d} conformation (Fig 1), as noted previously: the S_4 axis is reoriented in the process.

We now proceed to propose a mechanism for the rearrangement of tetra-*o*-tolylsilane by an $M_2^{S_4}$ rearrangement, *i.e.*, by the rearrangement mode which was shown to be operative in the case of the closely analogous naphthylsilane. In Fig 10, each column includes three views of the same structure so that each row shows the same steps in the postulated mechanism. The views which depict aryl rings as perpendicular or horizontal to the plane of the paper are only approximate, and in most of these cases the rings are in reality tilted somewhat from these idealized positions. The axis down which the molecule is viewed in a direction perpendicular to the plane of the paper is defined by the ligand labels. Relative physical motions (rotations) are depicted by arrows and are shown on those views where they are most likely to guide the observer. The directions of rotation have been chosen to minimize nonbonded interactions so that if this mechanism is followed, only *ortho*-hydrogen-*ortho*-methyl interactions need be overcome and not methyl–methyl. An intermediate structure with ψ-S_4 symmetry (second row, second column) is a consequence and this corresponds to a conformer with three substituents in the *endo* and one in the *exo* position. Empirical force field calculations[5] show that there is a minimum on the potential hypersurface corresponding to exactly this structure, 8·5 kcal/mol above the ground state, and since the actual activation energy for this particular isomerization is of the order of 13·5 kcal/mol,[10] corresponding to the energy of the transition state, the postulated intermediate is at least consistent with experimental result.

Fig 10 depicts isomerization between **I** and **l**; the same mechanism when applied to permutational isomer **l** would lead to **g** and thence back to **I**. The reverse sequence could equally well apply. Similarly, if permutational isomer **a**—which differs from **I** only by a rigid rotation (C_2) of the whole molecule—were chosen, the same sequence would yield **h** and thence **b** and **e**, all rearrangements occurring with the same activation energy (see Fig 6).

The situation is not quite so simple with the 1-naphthylsilane, because here the rearrangements divide into diastereomeric subsets within $M_2^{S_4}$ due to the asymmetry of the molecule. Imagine in Fig 10 that the *o*-tolyl group labeled 1 is replaced by a 1-naphthyl group. Then the same mechanism as before would lead from **I** to **l** and to **g**, or the reverse.

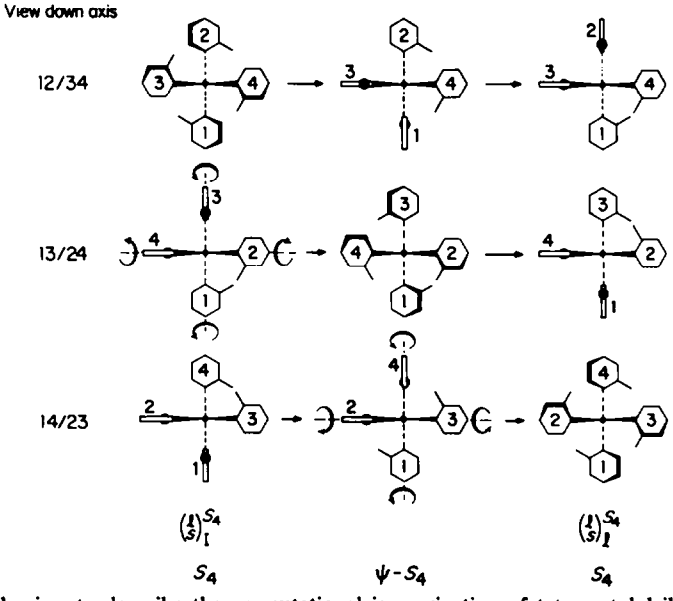


Fig 10. A mechanism to describe the permutational isomerization of tetra-*o*-tolylsilane by an $M_2^{S_4}$ rearrangement.

Similarly, **b**, **e** and **h** would be interconverted by this pathway. Although these rearrangements alone would account for the DNMR observations, the description is incomplete since it does not allow for enantiomerization. However, there are three additional pathways using this general mechanism, since the naphthyl ligand can assume one of the three other nonequivalent positions in the postulated intermediate and transition state. One of these three diastereomeric pathways has exactly the same permutational consequences as that just discussed, and hence can be represented by the same graph (Fig 11a). The other two pathways differ in that they interconvert enantiomers as shown in graphs (b) and (c) (Fig 11). All graphs are disconnected, so that total equilibration of the permutational isomers could not occur by following just one pathway by this mechanism. In principle, then, it would be possible to differentiate pathways in this system if chirality changes during the isomerization could be monitored (for instance, by using a chiral solvent or shift reagent in the NMR experiment, or by including a prochiral substituent in the molecule).

The postulated mechanism has the merit of being consistent with the data.[10] Other mechanisms are conceivable, but only more experimental input can guide our choice.

The flip group of permutations

There are circumstances where the analysis already described is insufficient to deal with all types of isomerization. For instance, if the aryl rings do not have local C_{2v} symmetry and the *ortho* positions do not differ greatly in effective bulk (as in 2-methyl-1-naphthyl or *m*-tolyl), or if *endo* substituents are not markedly disfavored energetically (as in some conformers of di-*o*-tolyldiphenylmethane[5]), the above analysis is not equal to the task. Additionally, even if the aryl groups do have local C_{2v} symmetry, it may be desirable to take account of topomerizations, as, in appropriate cases, in the interpretation of DNMR results. It therefore becomes necessary to introduce the concept of permutational flipping of the aryl rings.

The permutation group describing a single aryl ring flip is S_2. Since each of the four aryl groups has the potential to undergo a flip, the full flip group of permutations (**H**) is a direct product group.

$$\mathbf{H} = S_2 \times S_2 \times S_2 \times S_2 = (S_2)^4$$

The order of the group is 16, one element corresponding to the identity (E), and the other 15 to single flips or to a combination of flips of several aryl rings. The convention we are introducing to denote the elements of the flip group is as follows. Referring to Fig 12, the rings to be flipped are defined by the index of the skeletal site on which an aryl group resides, rather than by the index of the ligand itself. If a particular ring is to be flipped during an isomerization, the site index is primed. The reference structure **E** is defined as that conformation in which the substituents of highest priority* are oriented *exo* and may be associated with the identity of the group. The 16 permutational flips are the ones associated with the structures depicted in Fig 12, and each corresponds to an element of the flip group. The flags on the aryl rings are given to differentiate edges of the rings for permutational purposes, and do *not* represent particular chemical substituents, such as methyl. A flagged edge is assumed to have higher priority than an unflagged edge.

In contrast to the skeletal group, the flip group finds no independent application to the tetraarylmethane problem since skeletal permutations are bound to occur under all circumstances. The flip group can therefore only be used in conjunction with the skeletal group.

The full permutation group of tetraarylmethanes

The full permutation group **G** is a mathematical group describing permutations of both the types we have described above. To obtain **G**, we must combine the skeletal group S_4 with the flip group $(S_2)^4$;

*Arbitrarily, we may choose to use the Cahn–Ingold–Prelog rules for assigning priority to substituents.

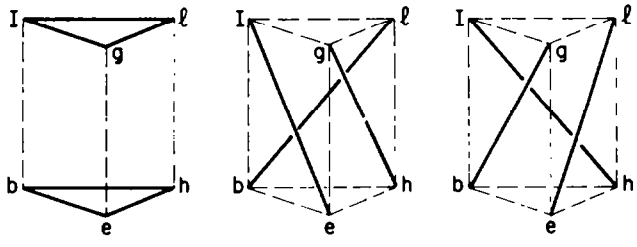


Fig 11. Graphs of the four diastereomeric pathways for isomerization of tri-*o*-tolyl-1-naphthylsilane by the mechanism depicted in Fig 10. The labels correspond to permutational isomers as shown in Fig 9.

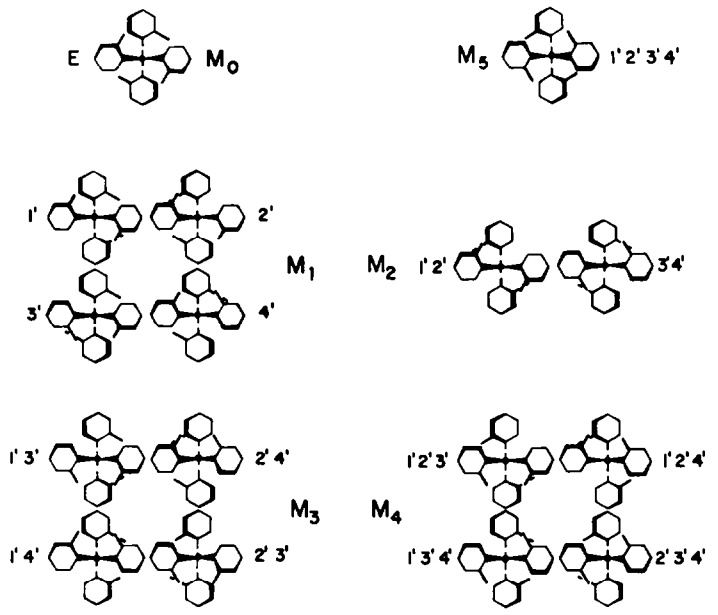


Fig 12. The 16 permutational structures corresponding to the flip group of permutations of a tetraarylmethane arranged according to modes (see text and footnote on p. 1546). The flags are shown to differentiate edges of aryl rings, and do not represent substituents.

the particular combination required is the semidirect product.[16]

$$\mathbf{G} = (\mathbf{S}_2)^4 \wedge \mathbf{S}_4$$

We show in an appendix that the mathematical requirements for a semidirect product are satisfied.

The elements of the group are ordered pairs of elements, one from each of the flip and skeletal groups,

$$g = (h, k) \qquad \begin{matrix} g \in \mathbf{G} \\ h \in (\mathbf{S}_2)^4 \\ k \in \mathbf{S}_4 \end{matrix}$$

and the order of the group is therefore given by

$$|\mathbf{G}| = |(\mathbf{S}_2)^4| \cdot |\mathbf{S}_4| = 16 \cdot 24 = 384$$

The element is to be read from right to left, and should be taken to mean: according to k, the aryl groups are first permuted among themselves coherently (*i.e.*, without regard to the question of whether or not a ring has previously been flipped: if it has flipped, it stays flipped) and then the aryl groups are flipped according to h. The identity element of the group is the ordered pair (E, I), *i.e.*, no skeletal permutations (I) and no ring flipped (E). Examples of the operation of elements of this permutation group are given in Fig 13, where the flags are again shown only to differentiate the edges of the aryl rings, and do not refer to substituents, such as methyl.

The multiplication rule for elements of this group is not Cartesian, but is given by

$$\begin{aligned}(h_2, k_2)(h_1, k_1) &= (h_2 k_2[h_1], k_2 k_1) \\ &= (h_2 k_2 h_1 k_2^{-1}, k_2 k_1)\end{aligned}$$

The permutational isomerization depicted at the bottom of Fig 13 may therefore be calculated as follows:

$$\begin{aligned}(1'3'4', (13)) \cdot (3', (243)) &= (1'3'4' \cdot (13)[3'], (13)(243)) \\ &= (1'3'4' \cdot (13)3'(13), (1324)) \\ &= (1'3'4' \cdot 1', (1324)) \\ &= (3'4', (1324))\end{aligned}$$

The elements of the point group S_4 of the tetraarylmethane are thus representable as (E, I), $(E, (12)(34))$, $(E, (1324))$ and $(E, (1423))$, and to determine mode equivalent permutations it is necessary to calculate double cosets precisely as was described for the skeletal group, but using instead the new representation of the point group elements and the particular multiplication law for semidirect products. We restrict ourselves in the first instance to the flip subgroup $((\mathbf{S}_2)^4, I)$ of the full permutation group, **G**. This subgroup is isomorphic to the flip group $(\mathbf{S}_2)^4$ previously discussed; similarly the skeletal subgroup $(E, \mathbf{S}_4)$ is isomorphic to the skeletal group $\mathbf{S}_4$.

$$(\mathbf{H}, I) = \{(h, I)\} \cong \{h\} = \mathbf{H} \qquad h \in \mathbf{H} \equiv (\mathbf{S}_2)^4$$

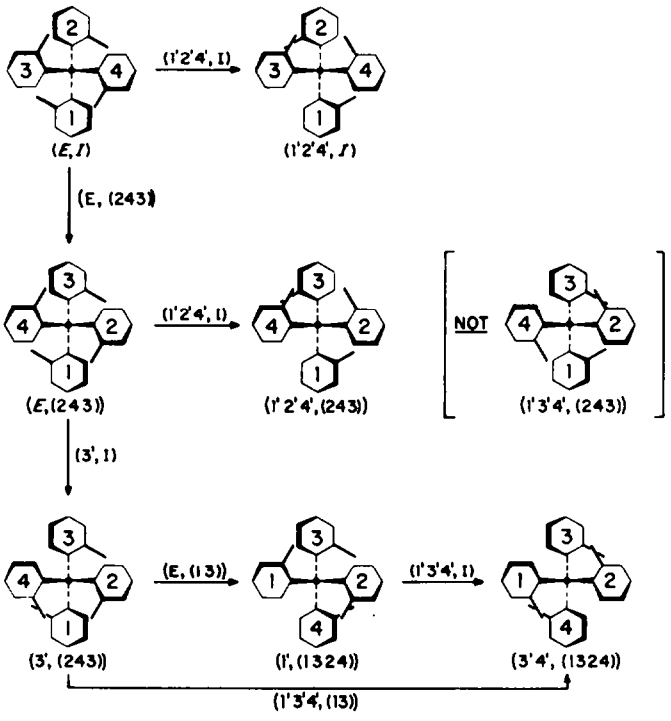


Fig 13. Examples of the operation of elements of the full permutation group $(S_2)^4 \wr S_4$ of tetraarylmethanes. The flags differentiate edges of aryl rings and do not represent substituents.

This 16-element subgroup is partitioned into six subclasses of mode equivalent flip permutations. The elements of the flip group, represented in Fig 12 by the associated structures, are subdivided into the modes as indicated in Fig 12.*

Again, we may represent the permutations or rearrangements graphically (Fig 14). The subdivision of the graphs for modes M_1, M_2, M_3, and M_4 into subgraphs is a matter of convenience; the subdivision corresponds to the nondifferentiable reactions of the subgroup in a chiral environment, as defined by Klemperer.[9]

The 384 permutations of the full group comprise 192 pairs of rotationally equivalent permutations; there are therefore 192 distinct stereostructures. Symmetry equivalence brings about further degeneracy of the permutations, so that double coset decomposition of the full permutation group yields 56 modes in a chiral environment, or 28 in an achiral environment. Additional discussion is outside the scope of this paper.

In general terms, mode equivalent rearrangements describe isomerizations which occur with the same likelihood under a given influence on the skeleton if the chemical substituents are identical and only distinguishable by labels. If the substituents become chemically nonequivalent the degeneracy is erased and rearrangements which were previously mode equivalent are no longer constrained to occur at the same rate. However, two such rearrangements can still occur by the same *mechanism*, that is, by the same general movement of ligands, with the same approximate energy trend throughout the isomerization. The use of mode equivalence is exemplified in the rearrangements of tris(2-methyl-1-naphthyl)borane.[17] The two rearrangements which are experimentally observed are mode equivalent according to the model triarylborane system, but due to the asymmetry of the rotors the two rearrangements may be differentiated (*e.g.*, by their activation energy). Nevertheless, they occur by the same mechanism—a two-ring flip.[17]

Extensions of the analysis

We have restricted our discussion of tetraarylmethanes to those of ψ-S_4 conformation, but we might ask hypothetically how the analysis would be altered if, say, D_2 or ψ-D_2 symmetry were adopted. Precisely the same general approach is followed, but the elements of the point group D_2 are substituted for those of S_4 when determining the double cosets and modes. Since the skeleton is now chiral, however, it becomes necessary to define an enan-

*More correctly in this context, the labels should be those corresponding to the flip *subgroup*, *e.g.*, 1' should be (1', *I*).

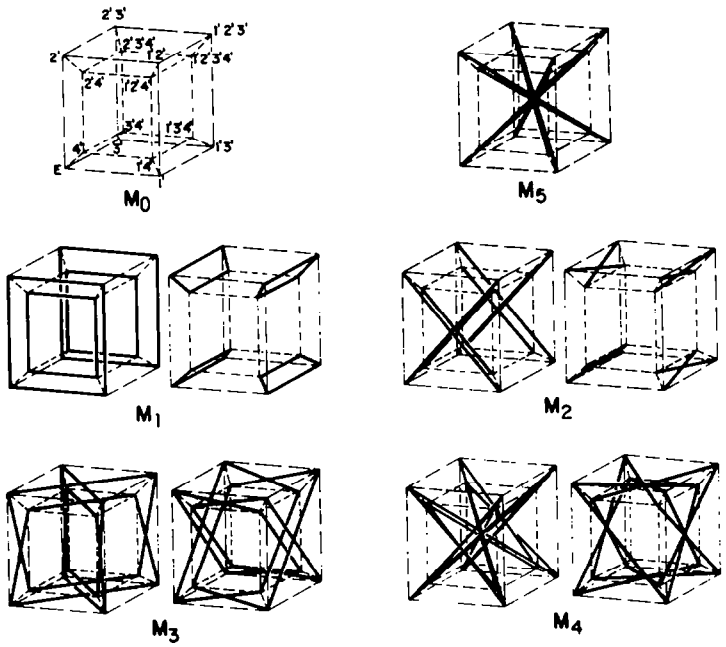


Fig 14. Graphs of the rearrangement modes of the flip subgroup ($(S_2)^4$, I) of the full permutation group. The graphs for modes M_1–M_4 are further subdivided into complementary subgraphs in order to promote visual clarity.

tiomeric set of permutational structures and then to consider permutations within this set, and between the two enantiomeric sets.[18] It is readily apparent that different rearrangment modes will be derived.

Isomerization between tetraarylmethanes belonging to different point groups brings us to the highest level of complication. The mathematical framework for such an analysis exists,[18, 19] but discussion is beyond the purview of this paper.

Tetraarylmethanes and stereochemical correspondence

In connection with a mechanistic analysis of the conformational dynamics of triarylboranes and cognate systems, a remarkable identity was noted between the stereochemical behavior of these systems and that of nonrigid transition metal trischelates.[15, 17, 20] To describe this parallelism, the term "stereochemical correspondence" was introduced. Additional examples of stereochemical correspondence, involving two-bladed propellers such as diarylmethanes and spirocyclic phosphoranes, have been discussed in detail.[21]

If it is possible to perform an isomorphic mapping of the essential stereochemical features—both static and dynamic—of each of two real systems onto the same mathematical model, an equivalence relation will exist between the real systems; it is thus that they acquire the attribute of being stereochemically correspondent. Mathematically, the concept reduces to the conditions that the two systems have the same permutation group and the same point group.

An interesting line of inquiry is whether tetraarylmethanes may be considered stereochemically correspondent to tetrakis-chelates. Since both species are described by the permutation group $(S_2)^4 \wr S_4$, the analysis presented is equally applicable to tetrakis-chelates, but only if they also adopt S_4 symmetry, and do not undergo polytopal isomerization to structures of different point group symmetry. However, it appears that S_4 is a comparatively uncommon point group for such chelates, and also that all such species thus far investigated undergo rapid interconversion (on the NMR time scale) so that no data relating to static structures in the solution state are currently available.[22] Theoretically, however, a *full* analysis for the polytopal isomerizations between tetrakis-chelates of different point group symmetries would be derivable, just as it is for tetraarylmethanes.

Diverse transition metal species can be envisaged which might satisfy the criteria for stereochemical correspondence with tetraarylmethanes. Several metals give, for instance, "tetrahedral" tetrakis(dialkylamido) compounds of general formula $M(NR_2)_4$ which might well adopt S_4 symmetry.[23]

Finally, in this context, we indicate that other systems exist which are described by the same permutation group, but, by virtue of the conformation adopted, are not stereochemically correspondent to

tetraarylmethanes. Tetraarylethylenes having D_2 symmetry fall into this category.*

To conclude, we may briefly contemplate the consequences of introducing further two-fold rotors around the central atom. The hexaaryl system, exemplified by the hexapyridine complex of iron (II)[25] and hexakis(dimethylamido)tungsten (VI)[26] (both of which have T_h symmetry) is particularly attractive, and its dynamic properties could be analyzed readily by the methods we have used in this paper. In contrast, the lower symmetry of pentaaryl derivatives of group V elements implies that an interpretation of the stereochemistry of these species by an analysis such as that presented above would be a more formidable task.

Appendix

A group **G** is the semidirect product of two groups **H** and **K**

$$\mathbf{G} = \mathbf{H} \wedge \mathbf{K}$$

if the following conditions are satisfied:[16, 27]

(1) $\mathbf{G} = \mathbf{HK} = \mathbf{KH}$

(2) $\mathbf{H} \lhd \mathbf{G}, \mathbf{K} < \mathbf{G}$

(3) $\mathbf{H} \cap \mathbf{K}$ = identity

In our case, $\mathbf{H} = (\mathbf{S}_2)^4$ and $\mathbf{K} = \mathbf{S}_4$.

Consider the element $k_x h_y$ which first flips some ring(s) and then permutes the rings among themselves coherently. Then, if the rings are permuted first by k_x, it would be possible to find one (and only one) flip operation h_z which leads to the same final result:

$$k_x h_y = h_z k_x \qquad k_x \in \mathbf{K} \qquad \text{Eq (i)}$$
$$h_y, h_z \in \mathbf{H}$$

There is therefore a one-one relationship between these two sets of operations, so that

$$\mathbf{KH} = \mathbf{HK} \quad \text{(condition 1)}$$

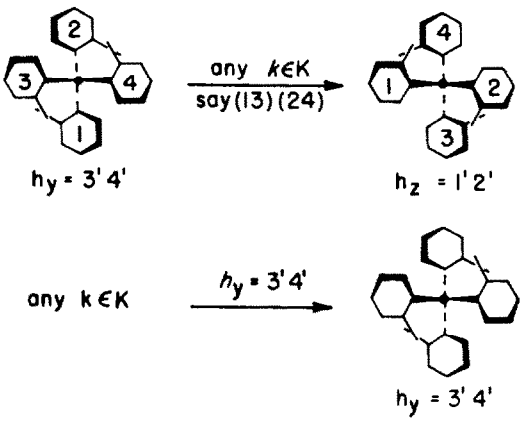
Summing Eq (i) over all $h \in \mathbf{H}$:

$$k_x \mathbf{H} = \mathbf{H} k_x$$
$$\mathbf{H} = k_x^{-1} \mathbf{H} k_x \text{ for all } k_x \in \mathbf{K}$$

and therefore **H** is a normal subgroup of **G** (condition 2). **K** is a subgroup of **G** (and isomorphic to the factor group **G/H**) but is not necessarily itself normal since in general

$$\mathbf{K} h_y \neq h_y \mathbf{K}$$

which can be demonstrated by counter example:



The two products are not the same, and hence **K** is not a normal subgroup of **G**.

Since **H** involves flips, and **K** skeletal permutations, it is obvious that $\mathbf{H} \cap \mathbf{K}$ = identity (condition 3).

The full permutation group **G** can be written equally correctly as a composition or wreath product:[18]

$$\mathbf{G} = \mathbf{S}_4[\mathbf{S}_2] \cong (\mathbf{S}_2)^4 \wedge \mathbf{S}_4$$

this group describing those permutations of the eight edges of the four aryl rings which are chemically feasible, *i.e.*, those involving pairwise transpositions of edges of the same ring.

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*For example, tetramesitylethylene has D_2 symmetry in the crystal.[24]

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