

# Dynamic Stereochemistry of Tetraarylmethanes and Cognate Systems. The Role of the Permutation Subgroup Lattice<sup>1</sup>

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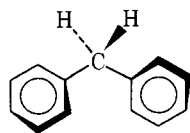
**Abstract:** The dynamic stereochemistry of tetraarylmethanes is treated using a rigorous group-theoretical approach. Perceptual difficulties inherent in the tetraaryl case, that are absent in the previously studied di- and triaryl cases, are elucidated in group-theoretical terms. The possible noninverting (of configuration) modes are given and mechanisms which require the least ring twisting to effect an overall permutational change corresponding to these modes are provided. Implications of the (non)existence of nonself-inverse double cosets on the symmetry of the potential surface are discussed. Extensive use is made of the permutation subgroup lattice to obtain isomer descriptors, to delineate the possibilities for residual stereoisomerism, and to gauge the effect of combining (intersecting) experiments. The construction of topological representations is discussed. Particular emphasis is placed on novel uses of the group and lattice structures which occur in problems of this kind.

In our first treatment of the dynamic stereochemistry of tetraarylmethanes,<sup>2</sup> a group theoretical approach was taken which permitted discussion of conformational rearrangements in this system in terms of mode equivalent rearrangements. The present paper has as its aim the introduction of concepts, based on group theory, which permit a fuller appreciation of the stereochemical subtleties of this system while capable at the same time of extension in principle to flexible molecular systems other than those explicitly treated herein.

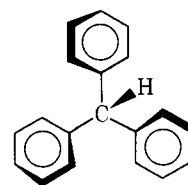
By way of background, we note that the results of empirical force field calculations<sup>3</sup> clearly indicate that all substituted tetraphenylmethanes and -silanes prefer to adopt a  $S_4$  or  $\psi$ - $S_4$  conformation.<sup>4-6</sup> Thus, our analysis is predicated on the assumption of  $S_4$  symmetry throughout.

**A Perceptual Difficulty Explained.** As was previously noted,<sup>2</sup> the physical act of ring rotation in tetraaryl systems results in a shifting of the  $S_4$  or  $\psi$ - $S_4$  axis; it is this fluxional character of the symmetry axis which makes isomerizations in these systems so difficult to envisage, and differentiates them from isomerizations in the corresponding di- and triaryl systems<sup>7</sup> where the  $C_2$  (or  $\psi$ - $C_2$ ) and  $C_3$  (or  $\psi$ - $C_3$ ) axes remain fixed in space. We shall now show that this baffling behavior of tetraaryl systems can be traced to, and understood in terms of, the special relationship between the molecular point group and the group of skeletal permutations.<sup>5</sup> For this purpose the definition of a normal subgroup is required. A subgroup is normal if it is left intact by conjugation of all the elements of the full group.<sup>8a</sup>

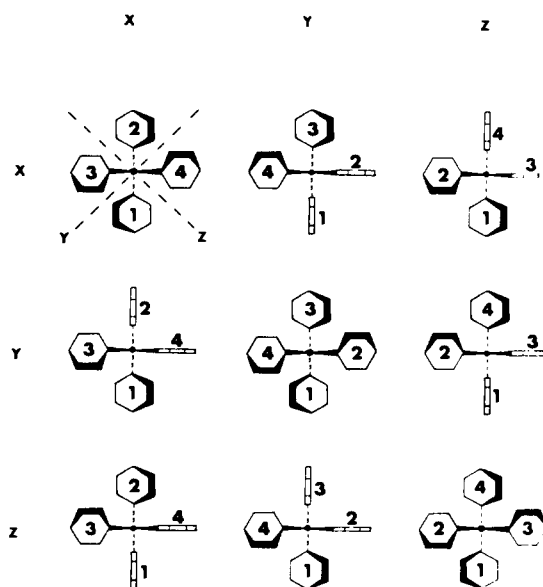
Consider diphenylmethane in the helical conformation.<sup>7</sup>



The skeletal permutation group is  $S_2 \cong C_2$ , the ring flip group<sup>5</sup> is  $(S_2)^2$ , and the full permutation group<sup>8b</sup> is  $S_2[S_2] \cong (S_2)^2 \wedge S_2$ . The molecular point group is  $C_2$ . Obviously, and trivially, the molecular point group is a normal subgroup of the skeletal permutation group,  $C_2$ . Similarly, for triphenylmethane in the propeller conformation, the skeletal permutation group is  $S_3 \cong D_3$ , the ring flip group is  $(S_2)^3$ , and the full permutation group<sup>8</sup> is  $S_3[S_2] \cong (S_2)^3 \wedge S_3$ . The molecular point group,  $C_3$ , is also a normal subgroup of  $D_3$ .



In the case of tetraphenylmethane, the skeletal permutation group is  $S_4 \cong T_d$  the ring flip group is  $(S_2)^4$ , and the full permutation group<sup>2</sup> is  $S_4[S_2] \cong (S_2)^4 \wedge S_4$ . If the molecular point group is  $S_4$  (or  $\psi$ - $S_4$ , as for all substituted tetraphenylmethanes<sup>4</sup>), a new situation arises:  $S_4$  is *not* a normal subgroup of  $T_d$ . Put differently: there is only one  $C_2$  subgroup in  $C_2$ , there is only one  $C_3$  subgroup in  $D_3$ , but there are three conjugate  $S_4$  subgroups in  $T_d$ .<sup>10a</sup> It is this characteristic that is at the heart of the previously discussed<sup>2</sup> perceptual difficulty. To illustrate: in Figure 1 are shown three views each of three  $S_4$  structures differing only in the orientation of the  $S_4$  axis. If a constant viewing axis is maintained (a column of structures in Figure 1) a sym-



**Figure 1.** Three  $S_4$  structures differing in the orientation of the symmetry axis seen from three different views. The symmetry axis orientation is maintained across each row. The viewing axis is maintained down each column.

Table I. Rearrangement Modes for  $S_4$  Tetraarylmethanes

1 0F3P	2 1F3P	3a 1F3P	3b 1F3P	4 1F3P	5a 2F3P
(137)(248) (153)(264) (175)(286) (375)(486) (157)(268) (357)(468) (135)(246) (173)(284)	(137248) (153264) (176285) (375486) (158267) (368457) (146235) (184273)	(137)(248)(56) (164253) (175286) (386475) (157)(268)(34) (12)(357)(468) (135)(246)(78) (174283)	(12)(375)(486) (135246) (168257) (357468) (153)(264)(78) (173)(284)(56) (175)(286)(34) (138247)	(136245) (376485) (173284) (186275) (148237) (157268) (358467) (154263)	(137248)(56) (164)(253) (176)(285) (386)(475) (158267)(34) (12)(368457) (146235)(78) (183)(274)
5b 2F3P	6 2F3P	7a 2F3P	7b 2F3P	8 3F3P	
(138)(247) (153264)(78) (176285)(34) (12)(375486) (167)(258) (368)(457) (146)(235) (184273)(56)	(138247)(56) (164253)(78) (175286)(34) (12)(386475) (168257)(34) (12)(357468) (135246)(78) (174283)(56)	(148237)(56) (163)(254) (186)(275) (385)(476) (157268)(34) (12)(358467) (136245)(78) (174)(283)	(147)(238) (154263)(78) (186275)(34) (12)(376485) (168)(257) (358)(467) (136)(245) (173284)(56)	(12)(368)(457) (176)(285)(34) (164)(253)(78) (183)(274)(56) (146)(235)(78) (138)(247)(56) (167)(258)(34) (12)(386)(475)	
9 2F3P	10 3F3P	11a 3F3P	11b 3F3P	12 4F3P	
(154)(263) (148)(237) (367)(458) (145)(236) (184)(273) (185)(276) (376)(485) (158)(267)	(147)(238)(56) (163)(254)(78) (186)(275)(34) (12)(385)(476) (168)(257)(34) (12)(358)(467) (136)(254)(78) (174)(283)(56)	(12)(367)(485) (185276) (163254) (183274) (145)(236)(78) (148)(237)(56) (158)(267)(34) (385476)	(12)(376)(485) (145236) (167258) (367458) (154)(263)(78) (184)(273)(56) (185)(276)(34) (147238)	(147238)(56) (163254)(78) (185276)(34) (12)(385476) (167258)(34) (12)(367458) (145236)(78) (183274)(56)	
13 0F0P	14 4F2,2P	15 1F0P	16 2F0P		
E (15)(37)(26)(48)	(14)(23)(58)(67) (18)(27)(36)(45)	(12) (1526)(37)(48) (1625)(37)(48) (15)(26)(3748) (78) (56) (34) (15)(26)(3847)	(12)(34) (1526)(3748) (1625)(3847) (1625)(3748) (12)(78) (56)(78) (34)(56) (1526)(3847)		
17 2F0P	18 3F0P	19 4F0P	20 2F2,2P		
(12)(56) (16)(25)(37)(48) (15)(26)(38)(47) (34)(78)	(12)(34)(56) (16)(25)(3748) (16)(25)(3847) (1625)(38)(47) (12)(34)(78) (12)(56)(78) (34)(56)(78) (1526)(38)(47)	(12)(34)(56)(78) (16)(25)(38)(47)	(1423)(5867) (1827)(3546) (1324)(5768) (1728)(3645)		
21 0F2,2P	22 3F2,2P	23 1F2,2P	24 2F2,2P		
(13)(24)(57)(68) (17)(28)(35)(46)	(14)(23)(5867) (18)(27)(3546) (1827)(36)(45) (14)(23)(5768) (18)(27)(3645) (1423)(58)(67) (1728)(36)(45) (1324)(58)(67)	(1423)(57)(68) (17)(28)(3546) (1827)(35)(46) (13)(24)(5768) (1728)(35)(46) (13)(24)(5867) (17)(28)(3645) (1324)(57)(68)	(1423)(5768) (17)(28)(36)(45) (18)(27)(35)(46) (13)(24)(58)(67) (1728)(3546) (1324)(5867) (1827)(3645) (14)(23)(57)(68)		

metrical structure is seen only where the viewing axis coincides with the symmetry axis.

It is thus impossible to obtain a mental fix on the  $S_4$  or  $\psi$ - $S_4$  axis when attempting to visualize the possible conformational changes. By contrast, analysis of a tetraarylmethane structure with  $D_2$  symmetry<sup>2</sup> would be far easier since  $D_2$  is a normal subgroup of  $T_d$ , i.e., there is only one  $D_2$  subgroup of  $T_d$ . Hence, one could view all possible  $D_2$

structures from the same perspective (constant viewing axis) and see a symmetrical conformation, although the three  $C_2$  axes which would spring into view would not be equivalent.

**Rearrangement Modes.** The full permutation group of tetraarylmethanes is the wreath product<sup>10b</sup>  $S_4[S_2]$  of order 384.<sup>10c</sup> To determine the possible rearrangement modes<sup>11</sup> (racemic modes,<sup>12</sup> differentiable isomerizations,<sup>13</sup> and basic

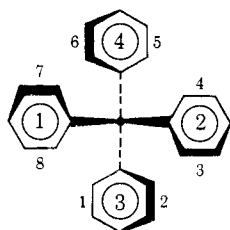
sets<sup>14</sup> are related concepts) it is necessary to find the double cosets of the  $S_4$  point group in  $S_4[S_2]$ . It is found<sup>2,15</sup> that there are 28 double cosets in the case, i.e., 28 modes (56 in a chiral environment). We must remember, however, that in considering only the conformational changes in a tetraaryl system  $Ar_4Z$ , we are restricting our inquiry exclusively to those isomerizations (permutations) in which the *absolute configuration* at the center  $Z$  is retained.<sup>16</sup> These permutations form a subgroup  $G_{192}$  of index 2 in  $S_4[S_2]$ . This subgroup of order 192 is itself a wreath product

$$G_{192} \cong A_4[S_2] \cong T[S_2]$$

where  $A_4$  is the alternating permutation group on 4 objects and  $T$  the tetrahedral rotation group.

$G_{192}$  is the *feasible permutation group* for tetraarylmethane, as defined by Longuet-Higgins.<sup>9,17</sup> Restriction of the double coset decomposition of  $S_4[S_2]$  to  $G_{192}$  yields 28 modes which are listed in Table I.<sup>18</sup> Permutational representations are based on the eight ortho ring positions shown in the structure below; the  $S_4$  point group is therefore represented by the set of permutations:

$$S_4 = \{E, (15)(37)(26)(48), (1357)(2468), (1753)(2864)\}$$



The 28 modes are reduced in number to 24 when nonself-inverse double cosets<sup>19</sup> are grouped together on the assumption of microscopic reversibility. In other words, when the inverse of a rearrangement is included in the feasible stereochemistry, only self-inverse double cosets survive, the nonself-inverse ones having been collected in pairs (four pairs in the present case).

The occurrence of nonself-inverse double cosets is a purely group-theoretical result and is independent of the particular representation.<sup>19</sup> Furthermore, the nonexistence of nonself-inverse double cosets in a double coset decomposition of a group appears to have implications on the symmetry of the potential energy surfaces involved. The surface  $E_{3n}/E_3$  is considered where  $E_{3n}$  represents the  $3n$  dimensional surface of the cartesian coordinates of  $n$  identical atoms and  $E_3$  represents the Euclidean group in three dimensions (translations and rotations-reflections).

The elements of  $E_3$  are "modded out" of  $E_{3n}$  to yield the surface  $E_{3n}/E_3$ . That is, the points on the surface  $E_{3n}$  which are related by translations or rotations-reflections are identified. Points on this surface represent isomers and their enantiomers. The nonexistence of nonself-inverse double cosets implies that for all  $g \in S_n$ , there are  $p_1, p_2 \in P$  such that  $p_1 g p_2 = g^{-1}$ . This means that for any path on  $E_{3n}/E_3$  representing a degenerate isomerization from **a** to **b** (**a** and **b** have point group symmetry  $P$ ) there is an identical path from **b** to **a**. This condition need not obtain if  $S_n/P$  yields nonself-inverse double cosets.

More restricted conditions can be established by considering the surface  $E_{3n}/E_3^+$  where  $E_3^+$  is the positive Euclidean group which includes only translations and rotations. A point on this surface represents an isomer without its enantiomer. The condition of equivalent or enantiomeric paths between **a** and **b** will obtain if there are no nonself-inverse modes of the type:<sup>12</sup>

Table II. Representative Least Motion Ar-C Dihedral Angle Changes<sup>a</sup> (degrees) for Modes in Table I

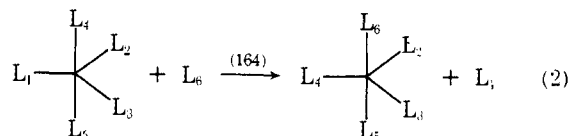
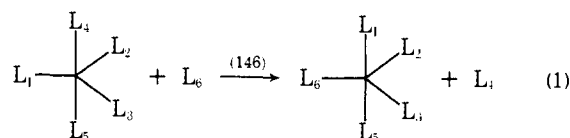
Ring	1	2	3a	3b	4	5a	5b
1	-120	-120	-120	+60	0	-120	-120
2	+120	+120	-60	0	-120	-60	+120
3	+120	+120	+120	-120	-60	+120	-60
4	0	180	0	+120	-120	180	180
	6	7a	7b	8	9	10	11a
1	-120	+60	+120	-60	+120	+60	-60
2	-60	-60	+60	-120	+60	-60	+60
3	-60	+120	0	180	180	-60	180
4	0	0	-60	-60	+120	0	+120
	11b	12	13	14	15	16	17
1	+60	+60	0	-60	180	180	180
2	180	180	0	-60	0	180	0
3	-120	+60	0	+60	0	0	180
4	-60	-60	0	+60	0	0	0
	18	19	20	21	22	23	24
1	180	180	-60	+120	-60	+120	-60
2	180	180	-60	+120	-60	+120	+120
3	180	180	-120	-120	+60	+60	-120
4	0	180	-120	-120	-120	-120	+60

<sup>a</sup> These are the dihedral angle changes for a structure with  $\phi = 60^\circ$  (ref 3, Figure 2). Mode 1 reads: the ring in site 1 is rotated  $120^\circ$  counterclockwise (as viewed toward the center of the molecule), the ring in site 2 is rotated  $120^\circ$  clockwise, etc.

$$M = RgR \cup Rg_1^{-1}gg_1R \cup Rg_2^{-1}gg_2R \cup \dots$$

for  $R$  = rotation point group and  $g_1, g_2 \in P - R$ . These are collections of double cosets of the rotation point group in the full permutation group.

A pictorial example may aid in understanding these conditions. Consider the substitution of a trigonal bipyramidal structure. Two processes which are shown are inverses of each other.



The forward reaction (reaction 1) involves equatorial attachment of the ligand while the reverse (reaction 2) involves axial attachment. These two processes do not "look alike" yet would be microscopic reverses of each other (with proper ligand labeling). No sequence of rotations and reflections will cause these single-step processes to resemble each other. Stated differently, the permutations (146) and (164) are in different double cosets of  $D_{3h}$  in  $S_6$ .<sup>20a</sup>

While it is beyond the scope of the present paper, it is possible to establish conditions for equivalence of these two processes 1 and 2 by multiple steps through other TBP or symmetrical intermediates. The necessary mathematical structure is the double coset algebra.<sup>19a,20b</sup> An example of the two-step process is given by the permutations:

$$(26)(34)(132)(26)(34) = (146)$$

$$(26)(34)(123)(26)(34) = (164)$$

Table III. Least Motion Ar-C Dihedral Angle Changes (degrees) Corresponding to Mode 11a

Ring				
1	-60	+60	180	-120
2	+60	-60	-120	180
3	180	+120	-60	+60
4	+120	180	+60	-60

Table IV. Modes for a  $D_{2d}$  Tetraarylmethane<sup>a</sup>

(1,12)	(6)	(16,21)
(3a,3b,8,10)	(9)	(17,20)
(2,4,11a,11b)	(13,14)	(18,23)
$\left[ \begin{matrix} (5a,7b) \\ (5b,7a) \end{matrix} \right]$	(15,22)	(19,21)

<sup>a</sup> Numbers correspond to modes listed in Table I.

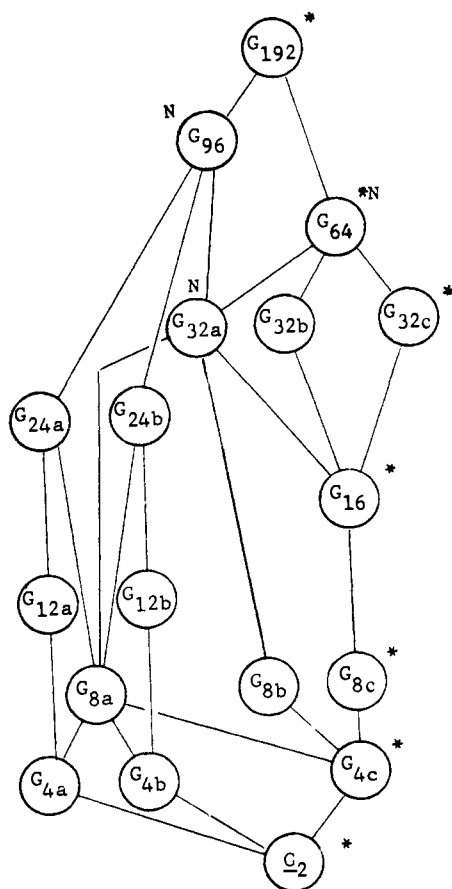


Figure 2. Lattice of subgroups between the point group  $C_2$  and the feasible permutation groups  $G_{192}$  which contain intact modes. See Tables I and V.

**Mechanistic Considerations.** Although it cannot be emphasized too strongly that a permutational description of an isomerization gives no intrinsic information about intermediate states, i.e., about the mechanism of isomerization,<sup>2</sup> it is of course possible to associate mechanisms with permutations if the physical motions bring about, and are therefore consistent with, a given permutational change. A particularly interesting mechanism is the one which requires the least motion. For a given ring, twists of . . .  $-660^\circ$ ,  $-300^\circ$ ,  $+60^\circ$ ,  $+420^\circ$  . . . cause the same permutational change but a mechanism requiring a twist of  $+60^\circ$  may be the most reasonable. Descriptions of twist angle changes corresponding to least motion for the possible modes are given in Table II. These descriptions are not unique in that the ring permutations<sup>21</sup>

(12)(34); (1423)<sup>±</sup>; (1324)<sup>±</sup>

yield a mechanism corresponding to the same mode. For example, each of the four mechanisms shown in Table III corresponds to mode 11a, and there are of course countless others.

Mode 14 can be represented by a particularly facile motion which takes an  $S_4$  structure through a  $D_{2d}$  structure and back to an  $S_4$  structure.<sup>3</sup> This "rocking" motion may have such a low barrier that it may make more sense to talk about tetraarylmethanes (in particular tetraphenylmethanes) as having "time averaged"  $D_{2d}$  symmetry (on an NMR time scale). However, this added symmetry reduces the number of possible rearrangement modes, and as a result, the 28 modes given in Table I are reduced to 13 in number (Table IV). These are the double cosets of  $D_{2d}$  in  $S_4[S_2]$  restricted to  $G_{192}$ . There is still one pair of nonself-inverse double cosets, (5a,7b) and (5b,7a), so that there are 12 modes if microscopic reversibility is assumed.<sup>22</sup>

**The Wreath Product Subgroup Lattice.** Further chemically useful information can be most efficiently obtained by considering the lattice of subgroups<sup>24</sup> between the point group  $S_4$  and the wreath product  $S_4[S_2]$ , i.e., all subgroups of  $S_4[S_2]$  which include  $S_4$ . Such subgroups will include intact double cosets of  $S_4$  in  $S_4[S_2]$ . If we limit ourselves to include just the feasible (noninverting) permutations, the pertinent lattice of subgroups is between point group  $C_2$  and wreath product  $G_{192}$ .

This lattice is shown in Figure 2. It was constructed by collecting the modes in Table I into subgroups of  $G_{192}$  which contain  $C_2$  (mode 13).<sup>25</sup> The modes contained by each group on the lattice in Figure 2 is a subgroup of any group above it to which it is connected. Subgroups with an  $N$  are normal in  $G_{192}$ . The significance of the asterisks will be discussed in the next section.

**Isomer Descriptors.** When a stereochemical problem is treated using permutation groups, the isomers of a maximally labeled structure<sup>26</sup> correspond to the right cosets,  $gR$ , of the rotation group in the full permutation group. In the tetraaryl case the rotation group is  $C_2$  (i.e., the rotational subgroup of the skeletal point group  $S_4$ ) and the full permutation group is  $S_4[S_2]$ . Consequently there are

$$\frac{|S_4[S_2]|}{|C_2|} = \frac{384}{2} = 192$$

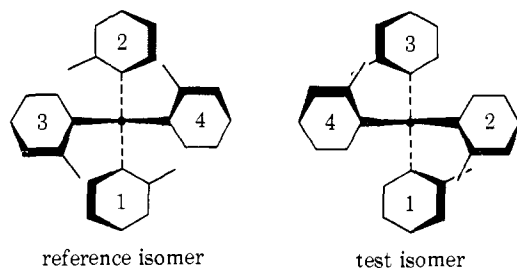
right cosets of  $C_2$  in  $S_4[S_2]$ , corresponding to 192 isomers of a maximally labeled tetraarylmethane.<sup>2</sup> In this section it will be shown how these isomers can be given descriptors<sup>27</sup> which are based on the subgroup lattice discussed in the previous section and which correspond to traditional chemical concepts.

Consider the sequence of groups in the left-hand column of Table VI, which make up part of the chain of groups designated with asterisks in Figure 2. The group  $S_4[S_2]$  contains, as we saw, all 192 right cosets of  $C_2$  (isomers). The subgroup  $G_{192}$  contains 96 of these isomers and those in  $G_{192}$  differ from those not in  $G_{192}$  by their absolute configuration at the central atom  $Z$ . Hence a two-valued descriptor such as  $C$  (configuration, which could correspond to an  $R$  or  $S$  descriptor) can be assigned to all isomers depending on whether or not they are contained in  $G_{192}$ . The 96 isomers in  $G_{192}$  can be further partitioned into three sets of 32 each, which differ by the orientation of the  $S_4$  (or  $\psi$ - $S_4$ ) symmetry axis;  $G_{64}$  is one such set. A second, three-valued descriptor such as  $O$  (orientation) designates the orientation of the  $S_4$  axis. Modes in Table I which are designated  $nF3P$  change  $S_4$  axis orientation and hence the value of this descriptor. The subgroup  $G_{32c}$  contains half the isomers in  $G_{64}$

Table V. Subgroups of  $G_{192}$  Which Contain  $C_2$ 

	$G_{192}$	$G_{96}$	$G_{64}$	$G_{32a}$	$G_{32b}$	$G_{32c}$	$G_{24a}$	$G_{24b}$	$G_{16}$	$G_{12a}$	$G_{12b}$	$G_{8a}$	$G_{8b}$	$G_{8c}$	$G_{4a}$	$G_{4b}$	$G_{4c}$	$C_2$
1	1	1	-	-	-	-	1	-	-	1	-	-	-	-	-	-	-	-
2	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3a	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3b	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5a	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5b	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	1	1	-	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-
7a	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7b	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
8	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	1	1	-	-	-	-	-	1	-	-	1	-	-	-	-	-	-	-
10	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11a	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11b	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	1	1	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-
13	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
14	1	1	1	1	-	-	1	1	-	-	1	1	-	-	-	1	-	-
15	1	-	1	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-
16	1	1	1	1	1	1	-	-	1	-	-	-	-	-	-	-	-	-
17	1	1	1	1	1	1	-	-	1	-	-	-	-	1	-	-	-	-
18	1	-	1	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-
19	1	1	1	1	1	1	1	1	1	-	-	1	1	1	-	-	1	-
20	1	1	1	1	-	-	-	-	-	-	-	-	1	-	-	-	-	-
21	1	1	1	1	-	-	1	1	-	1	-	1	-	-	1	-	-	-
22	1	-	1	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-
23	1	-	1	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-
24	1	1	1	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-

and those in  $G_{32c}$  differ from those not in  $G_{32c}$  by their helicity. A third, two-valued descriptor such as H (helicity) serves to designate each set. This is the helicity defined earlier<sup>2</sup> which can be associated with the two two-bladed propellers of the  $S_4$  structure, the two aryl rings (blades) in each propeller being interconvertible by a  $C_2$  or  $\psi$ - $C_2$  operation. Modes in Table I which are designated  $nF2,2P$  change helicity and hence the value of this descriptor. Finally,  $C_2$  represents one of the 16 isomers in  $G_{32c}$ . These 16 isomers are interconverted by flipping rings by  $\pi$  radians, and hence there are four appropriate descriptors which are two-valued and which designate the N (endo) and X (exo) edge<sup>5</sup> for each of the four rings. Any mode with  $nFmP$ ,  $n > 0$ , will change the values of some or all of these descriptors. Thus a maximally labeled tetraarylmethane isomer can be classified by giving values to seven descriptors;<sup>30</sup> for example, if the reference isomer shown below (left) were arbitrarily given the designation  $C_+O_{12}H_+X_1X_2X_3X_4$ , the test isomer (right) would be designated  $C_+O_{13}H_-N_1X_2N_3X_4$ .<sup>31</sup>



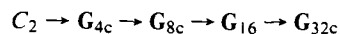
It would be possible to assign descriptors based on any group chain from  $C_2$  to  $G_{192}$  in Figure 2, although other descriptor sets would be generally less "intuitive" chemically. Nevertheless it is possible to describe a kind of uniqueness property to the set of descriptors given above. The chain of groups, marked with asterisks in Figure 2 (with which the descriptors are associated), form what is called a composition series for the group  $S_4[S_2]$ .<sup>32</sup> Briefly each group is a maximal normal subgroup of the group directly above it in

Table VI. Descriptors for  $Ar_4Z$  Isomers

Group	Isomers	Decomposition of isomer set	Descriptor
$S_4[S_2]$	192	Two enantiomeric sets	Configuration $C_+$ , $C_-$
$G_{192}$	96	Three sets differing in orientation of $S_4$ axis	Orientation $O_{12}$ , $O_{13}$ , $O_{14}$
$G_{64}$	32	Two sets differing in helicity	Helicity $H_+$ , $H_-$
$G_{32}$	16	16 isomers differing in endo-exo disposition of rings	Endo-exo $X_1$ , $X_2$ , $X_3$ , $X_4$
$C_2$	1		$N_1$ , $N_2$ , $N_3$ , $N_4$

the chain. A standard result of finite group theory is the Jordan-Hölder theorem which states that any two composition series in a group are equivalent.<sup>32b</sup> Thus a set of descriptors which can be related to a composition series are unique up to this equivalence.<sup>33</sup>

It is possible to make further use of composition series in determining the final four two-valued descriptors (rather than using endo-exo designations). The relevant group chain is



and is marked with asterisks in Figure 2. The cosets of  $G_{16}$  and  $G_{32c}$  are sets of isomers with an even or odd number of rings endo (and therefore exo). The cosets of  $G_{8c}$  in  $G_{16}$  are sets of isomers with constant pairwise relationships across the  $S_4$  axis. The cosets of  $G_{4c}$  in  $G_{8c}$  are sets of isomers with all other pairwise relationships constant. Finally the cosets of  $C_2$  in  $G_{4c}$  are isomers which differ in all endo-exo designations. These descriptors would be conceptually disadvantageous because they do not describe intuitive chemical concepts. However, in determining the action of modes on sets of isomers, these descriptors are rigorous and unique in the sense that the composition series is unique.

**Residual Stereoisomerism.** In our recent work on triarylmethanes<sup>34</sup> we found it convenient to introduce the concept of *residual stereoisomerism* to describe distinct sets of appropriately substituted interconverting isomers at a particu-

Table VII. Some Residual Stereoisomerism Possibilities in Maximally Labeled  $Ar_4Z$ 

Restriction	Group	No. of <i>dl</i> pairs <sup>a</sup>
All rings rotate freely	$G_{192}$	1
Only an even number of rings flip (0,2,4)	$G_{96}$	2
No change of $S_4$ axis orientation	$G_{64}$	3
No change of helicity	$G_{32c}$	6
No ring flips	$G_{12a}$	16
Rocking motion only	$G_{4b}$	48
All motion frozen out	$C_2$	96

<sup>a</sup> The groups listed in the center column correspond to structures with a fixed absolute configuration,<sup>16</sup>  $C_+$  or  $C_-$ . The *dl* pair in each case contains also those structures with the opposite absolute configuration, i.e., those with  $C_+$  and  $C_-$ .

lar time scale of observation. This situation will occur whenever the isomerizations (permutations) in a mode or modes which can occur at a given time scale of observation generate a subgroup of the full permutation group.<sup>35</sup> The index of this subgroup in the full permutation group is the number of residual stereoisomers for a maximally labeled structure. The possibilities for residual stereoisomerism are numerous in the tetraaryl case but can be enumerated by reference to the subgroup lattice in Figure 2. The number of residual stereoisomers resulting from a single rearrangement mode is equal to 384 divided by the order of the smallest group in Figure 2 which contains this mode. For example, mode 1 leaves  $384/12 = 32$  residual diastereomers,  $G_{12a}$  being the smallest group containing mode 1. Mode 10 leaves  $384/192 = 2$  residual enantiomers (the enantiomers based on the configuration at the central carbon),  $G_{192}$  being the smallest subgroup containing mode 10. A combination of two or more modes leaves a number of residual stereoisomers equal to 384 divided by the order of the smallest group which contains all the modes involved. The experimental observation of residual stereoisomerism depends of course on the energetics of the process involved. Thus if mode 10 were able to occur at a given time scale of observation, only the two conventional enantiomers of a maximally labeled tetraarylmethane would be observed in spite of the occurrence of any other process.<sup>3</sup>

Table VII offers a further illustration of the way in which the subgroup lattice is utilized to determine the number of residual stereoisomers. Beginning with  $G_{192}$ , corresponding to one of the two enantiomeric sets containing 96 isomers each (i.e., operationally one *dl* pair; see Table VI), the number of residual stereoisomers steadily increases (right column) as motion after motion is frozen out (left column). The example in Table VII refers of course just to a portion of the subgroup lattice in Figure 2, arbitrarily chosen for purposes of illustration; different portions could have been selected, corresponding to different restrictions on the motions and consequently different numbers of residual isomers.

**Intersecting Experiments.** Further use can be made of the subgroup lattice in the design and choice of experiments. The double cosets of any of the groups on the lattice will contain intact modes, and the lattice operations of union and intersections therefore determine analogous operations on sets of modes. It follows that a single, and possibly difficult, experiment can be replaced by a combination of simpler experiments performed on systems which share some, but not all, of the features of the more complex system.

As a specific example, consider the problem of determining whether residual stereoisomers exist in a maximally labeled tetraaryl system  $Ar_4Z$ . Such a compound would be

difficult to obtain but the problem can be solved without direct access to this system, by application of the concept developed above. Consider the following two systems, each of which is less complex (and more easily obtained) than maximally substituted  $Ar_4Z$ : one in which the four aryl rings are different but all possess local  $C_2$  symmetry (which we shall call  $(Ar_d)_4Z$ ), and one in which the four rings are all the same, but none of them have local  $C_2$  symmetry ( $(Ar_s)_4Z$ ). In  $(Ar_d)_4Z$ , ring exchange can be monitored, but ring flipping cannot, whereas the reverse is true for  $(Ar_s)_4Z$ . On the assumption of  $S_4$  or  $\psi$ - $S_4$  symmetry for all systems under discussion<sup>3</sup> it is seen by reference to Figure 2 and Table I that the effective symmetry groups<sup>36</sup> for  $Ar_4Z$ ,  $(Ar_d)_4Z$ , and  $(Ar_s)_4Z$  are  $C_2$ ,  $G_{32c}$ , and  $G_{12a}$ , respectively. Now, the number of residual diastereomers is determined by the modes which are relevant on the given time scale of measurement, and these modes will just be collections of the 28 modes already described. In the present case, the modes for the  $(Ar_d)_4Z$  experiment (double cosets of  $G_{12a}$  in  $G_{192}$ ) will contain intact modes from Table I as will the modes for the  $(Ar_s)_4Z$  experiment (double cosets of  $G_{12a}$  in  $G_{192}$ ). Performing these two experiments (assuming common mechanisms) permits a pinpointing of the actual mode (from Table I) since the mode determined by the  $(Ar_d)_4Z$  experiment will be a different collection of those in Table I from that determined by the  $(Ar_s)_4Z$  experiment. The actual mode (from Table I) must be one common to these two collections. This procedure is facilitated by noting that the *intersection* of  $G_{32c}$  and  $G_{12a}$  on the subgroup lattice (Figure 2) is  $C_2$ , which is the effective symmetry group for the  $Ar_4Z$  experiment.<sup>37</sup> The lattice structure thus determines the intersection of the collection of modes. The result is that performance of two relatively easy experiments with effective symmetry groups  $G_{32a}$  and  $G_{12a}$  is equivalent<sup>37</sup> to performing one difficult experiment with effective symmetry  $C_2$ .

This conceptually simple example (of an experiment to isolate residual diastereomers) was chosen only to illustrate the use of the lattice operations. Other experiments can have effective symmetry groups larger than the molecular point group (in a general case). For example, NMR experiments (hamiltonians) are invariant to all permutations of magnetically equivalent nuclei, not just those included in the permutation representation of the point group. The lattice theoretic considerations would apply to these or any experiments.

**Topological Representations.** In complicated stereochemical problems it is often convenient to introduce interconversion graphs or "topological representations", since such representations help to facilitate a grasp of the relationships between interconverting structures (represented by vertices). Although it seems unlikely that a full representation of  $S_4[S_2]$  (two disconnected interpenetrating 96-vertex graphs) would be of much use,<sup>38</sup> we believe that it is worthwhile to describe the appearance and construction of appropriate graphs in terms of the concepts developed in this and the preceding<sup>2</sup> paper.

We begin by pointing out that wreath products of the type  $S_n[S_2]$ , also called *hyperoctahedral groups*,<sup>39</sup> are isomorphic to symmetry groups of  $n$  dimensional cubes (Table VIII); it is this property which accounts for the appearance of so many cubical graphs in the literature<sup>40</sup> which deal with permutation processes corresponding to elements of  $S_n[S_2]$  for  $n = 2$  or 3. Since topological representations will be invariant to action of the full permutation group involved,<sup>41</sup> it is reasonable to use the hypercube as a starting point for the construction of a graph. The problem now is to determine the action of  $G_{192}$  on the 16-vertex hypercube. Since a transitive permutation representation of  $G_{192}$  is in-

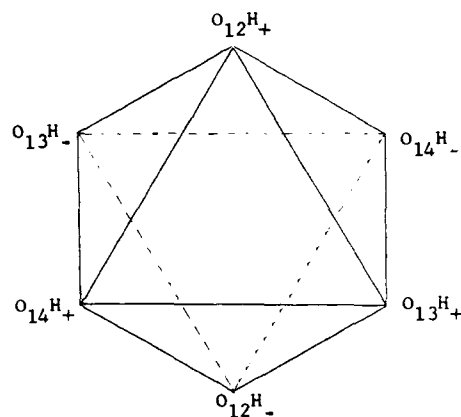


Figure 3. Octahedral graph of six isomers differing only in their orientation and helicity descriptors.

Table VIII. Realization of Wreath Products  $S_n[S_2]$  as "Hyperoctahedral Groups"

Dimension (n)	Geometric realization	No. of vertices	Isomorphism to point group	Order of group
1	Line segment	2 <sup>1</sup>	$C_2$	2
2	Square	2 <sup>2</sup>	$D_4$	8
3	Cube	2 <sup>3</sup>	$O_h$	48
4	Hypercube	2 <sup>4</sup>	$a$	384

<sup>a</sup> This is the four-dimensional point group XLVII defined by E. Goursat, *Annales Scientifique de L'Ecole Normale Supérieure*, 6, 9 (1889). We are grateful to a referee for pointing our attention to this reference.

involved there must be a group of order  $192/16 = 12$  which fixes one vertex.<sup>42</sup> Referring again to Figure 2, there are two subgroups of  $G_{192}$  of order 12 which contain  $C_2$ , and which are isomorphic to each other and to  $A_4 \cong T$ . Choosing  $G_{12a}$ , it can be seen from Tables I and V that the permutations in this group change either the helicity or the orientation of the  $S_4$  axis but none of the endo-exo designations. Thus, the vertices of the hypercube can be considered as representing the 16 possible endo-exo combinations.<sup>2</sup> Each vertex on the graph can be "expanded" into an octahedron to reflect the tetrahedral symmetry and the six possible values for the two descriptors changed by this group ( $S_4$  axis orientation and helicity). Thus the vertices of the 96-vertex graph can be situated at the vertices of 16 octahedrons which are themselves located at the vertices of a hypercube. Figure 3 shows one such octahedron, with the appropriate descriptor labels. The configuration descriptor (C) is invariant. The next two descriptors exhaust all possible combinations of orientation (O) and helicity (H), thus "filling" the six vertex positions on the octahedron. The four remaining descriptors are again invariant, since the particular vertex of the hypercube at which the octahedron is situated itself represents a given endo-exo situation. The 16 octahedra located on this particular hypercube will therefore represent all 96 isomers with a  $C_+$  configuration. The other, disjoint graph will be identical, with the one discussed above, except that all configurations are now  $C_-$ .

It should be noted that for the purpose of graphical representation, it is not essential to use an octahedron; a prism<sup>2</sup> or a hexagon would be equally satisfactory. The connectivities of these graphs would not necessarily correspond to the connectivities of the component polyhedrons. Methods for determining connectivities of topological representations (double coset matrices) have been given.<sup>19a,43</sup> For each of the modes in Table I the connectivity at one vertex is equal to the number of permutations divided by 2.<sup>44</sup> Thus mode

10, for example, connects a given isomer to four others. Totalling the connectivities for all 24 modes gives 96 as would be expected since there must be some permutation which connects any pair of isomers.

**Notation and Conventions.** Permutations are written as (1357) and read: move whatever is in site 1 to site 3; move whatever is in site 3 to site 5, etc. Multiplication of permutations is from left to right.  $G_1[G_2]$  is the wreath product of  $G_1$  and  $G_2$  or the composition of  $G_1$  around  $G_2$ .  $\times$  inserted between two groups means the direct product of the two groups.  $\Lambda$  inserted between two groups means the semidirect product of the two groups. The first group is the normal subgroup.  $S_n$  is the symbol for the symmetric group of  $n$  objects.  $S_4$ ,  $D_{2d}$ ,  $C_2$  are the usual point groups.  $|G_2|$  means the order (number of elements) of the group  $G_2$ . Positive torsion angles are clockwise as defined in ref 3.

## References and Notes

- (1) We gratefully acknowledge support of this work by the National Science Foundation (MPS74-18161).
- (2) M. G. Hutchings, J. G. Nourse, and K. Mislow, *Tetrahedron*, **30**, 1535 (1974).
- (3) M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, part I in this issue.
- (4) Note that the symbol  $S_4$  is used for the point group and  $S_4$  for the symmetric permutation group on four objects.
- (5) Notations, conventions, and definitions are those introduced in the first paper<sup>2</sup> except for those noted in the last section.
- (6) The singular exception is the parent compound, tetraphenylmethane itself, for which a  $D_{2d}$  conformation is preferred in the free state,<sup>3</sup> although  $S_4$  symmetry is maintained in the crystal.
- (7) D. Gust and K. Mislow, *J. Am. Chem. Soc.*, **95**, 1535 (1973).
- (8) (a) See F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed, Wiley-Interscience, New York, N.Y., 1971, p 11. (b) We are considering here only permutations on one of the two enantiomeric forms. This simplification reduces the number of possibilities by one-half with no loss of information. To treat helicity as well, one has to consider permutation inversions,<sup>9</sup> which effectively doubles the size of the groups by forming direct products,  $P \times C_i$ .
- (9) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).
- (10) (a) Note that it is possible for nonunique normal subgroups to be equivalent by outer automorphisms ( $C_2 \subset D_2$ ) and for normal and nonnormal subgroups to have the same designation ( $D_{2h} \subset O_h$ ). (b) G. Polya, *J. Symb. Logic*, **5**, 98 (1940). (c) A character table for this group has been published: D. E. Littlewood, "The Theory of Group Characters", Oxford-Clarendon Press, 1940, p 278.
- (11) J. I. Musher, *J. Am. Chem. Soc.*, **94**, 5662 (1972).
- (12) W. Hasselbarth and E. Ruch, *Theor. Chim. Acta*, **29**, 259 (1973).
- (13) W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).
- (14) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.*, **93**, 4701 (1971).
- (15) The number,  $n$ , of double cosets is easily found by using the formula<sup>12</sup>

$$n = \frac{|S_4[S_2]|}{|S_4|^2} \sum_{r=1}^k \frac{|C_r \cap S_4|^2}{|C_r|}$$
where  $C_r$  is a conjugacy class in  $S_4[S_2]$ , and the previously cited<sup>10</sup> character table.
- (16) Absolute configuration refers to the central atom Z and is defined by numbering the rings. An odd permutation of rings will change the configuration at Z; an even permutation will maintain it.
- (17) Note that the permutations corresponding to the  $S_4$  and  $S_4^3$  operations lie outside  $G_{192}$  since they invert the configuration<sup>16</sup> at carbon.
- (18) The symbol  $nFmP$  means that  $n$  rings are flipped and  $m$  rings are permuted by this mode. Mode 13 (OFOP) is simply the  $C_2$  rotation group. Modes with the same number designated  $a$  or  $b$  are inverses of each other.
- (19) (a) J. S. Frame, *Bull. Am. Math. Soc.*, **47**, 458 (1941); **49**, 81 (1943); **54**, 740 (1948). (b) D. J. Klein and A. H. Cowley, *J. Am. Chem. Soc.*, **97**, 1633 (1975).
- (20) (a) See W. G. Klemperer, *J. Am. Chem. Soc.*, **94**, 6940 (1972); **95**, 380 (1973), for excellent discussions on the visualization of the effect of the various group-theoretic equivalences. (b) J. Brocas and R. Willem, *Bull. Soc. Chim. Belg.*, **82**, 469 (1973).
- (21) The symbol (1423)<sup>±</sup> means that rings 1, 4, 2, 3 are permuted and all the angle descriptions change sign for a mode in Table II. These correspond to skeletal permutations.
- (22) A recent attempt<sup>23</sup> to enumerate all of the interconversion mechanisms for a generalized  $Ar_4Z$  system was patterned on the intuitive, nongroup theoretical approach which had previously been successfully employed in the analysis of analogous but far simpler di- and triaryl systems.<sup>7</sup> However, it is evident that this approach is unsatisfactory for systems as complex as the tetraarylmethanes since only nine mechanisms were found.<sup>23</sup> These correspond to the 24 modes in this paper as follows: 1  $\rightarrow$  21; 2  $\rightarrow$  14; 3  $\rightarrow$  23; 4  $\rightarrow$  20 and 24; 5  $\rightarrow$  22; 6  $\rightarrow$  12; 7  $\rightarrow$  10; 8  $\rightarrow$  3 or 4; 9  $\rightarrow$  7 and 8, where the first number of each pair refers to the mechanism discussed by Strohbusch,<sup>23</sup> and the second number to the mode in Table I.
- (23) F. Strohbusch, *Tetrahedron*, **30**, 1261 (1974).

- (24) See M. Hall, Jr., "The Theory of Groups", Macmillan, New York, N.Y., 1959, Chapter 19, for a discussion of subgroup lattices.
- (25) Note that this will not necessarily be a survey of *all* subgroups of  $G_{192}$  which contain  $C_2$  since the modes in Table I do not correspond to double cosets of  $C_2$  in  $G_{192}$ . They are, rather, collections of these double cosets.
- (26) "Maximally labeled structure" means a structure in which all four aryl rings are different and none possesses a local  $C_2$  axis.
- (27) Related ideas of descriptors and "stereochemical quantum numbers" have been discussed.<sup>28,29</sup>
- (28) E. Ruch and I. Ugi, *Top. Stereochem.*, **4**, 99 (1969).
- (29) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).
- (30) The number of possible descriptor sets corresponds to the number of isomers, as described ( $2 \cdot 3 \cdot 2 \cdot 2^4 = 192$ ).
- (31) Interesting and subtle details of this nomenclature problem depend on the full structure of this subgroup lattice (Figure 2). An unambiguous designation of helicity in isomers differing in  $S_4$  axis orientation is not possible, for the reason that there is no group which acts on the  $S_4$  axis orientation descriptor without acting also on the helicity descriptor. This can be verified by referring to Tables I and V and Figure 2. A group which acts only on the orientation descriptor would have to be of order 6. In the above example, ring 1 was arbitrarily fixed so that the necessary distinction could be made.
- (32) (a) Reference 24, Chapters 8 and 9; (b) J. J. Rotman, "The Theory of Groups, An Introduction", Allyn and Bacon, Boston, Mass., 1965, Chapter 6.
- (33) It should be pointed out that this will not be an obvious property in the general case. In the tetraaryl systems, the values of the seven descriptors are just the prime factors of the number of isomers ( $2 \cdot 3 \cdot 2 \cdot 2^4 = 192$ ); this occurs because  $S_4[S_2]$  is a solvable group.<sup>32</sup> In chemical problems involving permutation groups, in particular the symmetric groups  $S_n$  ( $n > 5$ ), this result will not obtain since these groups are not solvable. Group theoretically, the reason for these differences is that there are simple groups which are not of prime order.
- (34) P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 3198 (1974).
- (35) E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970). This article includes an interesting discussion of the group theoretical treatment of a stereochemically disjoint 12-atom polytopal process.
- (36) The "effective symmetry group" for these experiments is the group of permutations which do not interconvert any isomers based on the particular substituent pattern. For example,  $(Ar)_4Z$  structures are invariant to permutations of rings which generate the group  $G_{12a}$ .
- (37) To be more precise the *upper limit* to the information (mode) obtainable by doing both experiments is determined by the intersection of the effective symmetry groups.
- (38) Partial representatives (subgraphs) may however aid in the analysis of such systems; see ref 2.
- (39) (a) A. Kerber, "Representations of Permutation Groups. I," Springer-Verlag, New York, N.Y., 1971, p 37; (b) A. Mead, E. Ruch, and A. Schönhofer, *Theor. Chim. Acta*, **29**, 269 (1973).
- (40) For example, ref 7. See also D. Gust, P. Finocchiaro, and K. Mislow, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3445 (1973); E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 5097 (1968); **91**, 1636 (1969); M. Gielen and C. Depasse-Delit, *Theor. Chim. Acta*, **14**, 212 (1969); M. Gielen and J. Topart, *ibid.*, **18**, 7 (1969).
- (41) "Topological representations" in the chemical literature are actually representations of double coset matrices or sums of double coset matrices for permutational problems of this kind; that is, a double coset matrix is an incidence matrix for the topological representation.<sup>19</sup>
- (42) H. Wielandt, "Finite Permutation Groups", Academic Press, New York, N.Y., 1964, Chapter 1.
- (43) W. G. Klemperer, *J. Am. Chem. Soc.*, **94**, 6940, 8360 (1972).
- (44) Here the nonself-inverse modes are considered together so that the connectivity for  $[3a,3b]$  is  $16/2 = 8$ . For mode 3a alone the topological representation would be directed.

## Conformational Flexibility of Erythronolide B, the 14-Membered Aglycon Ring of the Erythromycins<sup>1</sup>

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**Abstract:** Detailed analyses of <sup>1</sup>H NMR and CD spectra of derivatives of erythronolide B have revealed that this aglycon ring is conformationally flexible. The general diamond-lattice type conformation is maintained with subtle modification in either the C-2 through C-5 or C-6 through C-9 ring segments depending on the nature and position of ring substituents. Variable temperature measurements in a series of *O*-acetyl derivatives have indicated that the conformational changes in these two regions are interdependent and enabled the determination of the limiting conformations which are populated to different extents in this series.

The erythromycin antibiotics are representative members of a group of natural products which possess unique structural and conformational characteristics. The aglycon of these glycosidic compounds, a 14-membered macrocyclic ring, possesses surprising conformational stability which is evidenced by its spectroscopic properties and the nature and selectivity of its chemical reactivity. Previously reported studies in these laboratories<sup>3</sup> using <sup>1</sup>H NMR and CD data have shown the conformation of erythronolide B (**1**) to be that depicted in Figure 1. These studies have indicated that the stability of this conformation is probably a consequence of the adoption of a diamond-lattice type framework of the ring atoms. In addition, the unique substitution pattern of this macrocycle confers additional rigidity by minimizing internal interactions and at the same time preventing free rotation of carbon-carbon bonds.

Throughout the series of derivatives studied, it was clear that a large degree of conformational homogeneity existed

as evidenced by the consistency of proton chemical shifts and coupling constants. As more and more members of the series were examined, however, it became apparent that subtle conformational effects were occurring as a result of certain substituent changes on the macrocyclic ring. It was felt that a more detailed scrutiny of the <sup>1</sup>H NMR and CD spectra of these compounds and the use of the more recent <sup>13</sup>C NMR spectroscopic technique would provide useful information about these subtle changes. This paper discusses the studies carried out using <sup>1</sup>H NMR and CD instrumentation.

### Experimental Section

The <sup>1</sup>H NMR spectra which will be discussed in the following sections were obtained on a Varian Associates HA-100 spectrometer operating in frequency sweep. Chemical shifts are reported in parts per million ( $\delta$ ) downfield from internal tetramethylsilane, and coupling constants are reported in hertz. Both chemical shifts