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Chirality Fittingness of an Orbit Governed by a Coset Representation. Integration of Point-Group and Permutation-Group Theories To Treat Local Chirality and Prochirality

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Abstract: Local chirality and prochirality are discussed by integrating point-group and permutation-group theories. Thereby, a compound of G symmetry is considered to consist of several orbits that are subject to coset representations (CRs). Such a CR is denoted by the symbol $G(/G_i)$ which comes from a coset decomposition of the group G by its subgroup G_i. The local chirality for a member of a $G(/G_i)$ orbit is determined to be G_i. The concept "chirality fittingness" is proposed to indicate symmetrical properties of the $G(/G_i)$ orbit, in which the orbit is classified into one of three categories, i.e., homospheric, enantiospheric, and hemispheric. This terminology allows us to define a prochiral compound as an achiral compound having at least one enantiospheric orbit. This membership criterion for prochirality is compared with the conventional substitution and symmetry criteria. The subduction of CRs affords a desymmetrization lattice for examining the existence and nonexistence of subgroups. Chemoselective achiral processes, chemoselective chiral processes, and stereoselective chiral processes are discussed in terms of the chirality fittingness of orbits.

La coupe du roi (the king's cut) and its relevance to stereochemistry have been discussed by Mislow et al.[1] to show that a combination of two homochiral molecules affords an achiral product. This apparently tricky fact indicates the importance of the relationship between the symmetry of a whole molecule and that of its segments. Later, Mislow et al.[2] presented the useful concept *local chirality*, which refers to the symmetry of every point and segment of a molecular model. They thereby proposed the terms *chirotopic* and *achirotopic* in order to characterize a set of atoms within an achiral or chiral environment. The paradoxical title "stereochemistry without stereoisomerism" used in Mislow's paper has indicated that the chirality/achirality dichotomy should be discussed apart from stereoisomerism. The local chirality relates to the site symmetry, the usefulness of which has been reported by Flurry.[3,4] Recent reviews have dealt with stereochemical problems from various points of view.[5,6]

We recently discussed the enumeration of isomers by unit subduced cycle indexes that are derived by the subduction of coset representations (CRs).[7,8] These papers dealt with a quantitative application of the CRs; however, there remain undeveloped their qualitative applications, which provide stereochemistry with a more systematic format. The present paper aims at discussing symmetrical properties of CRs in order to present a novel methodology concerning the "stereochemistry without stereoisomerism".

1. Orbits and Coset Representations

Although orbits and coset representations are well-known concepts in mathematics,[9-11] their chemical meanings have scarcely been discussed. In particular, the concrete forms of CRs have attracted little attention of chemists. In this section, we illustrate the construction of CRs and clarify their chemical meanings by using the T_d point group as an example.

Table I. The Coset Representation $T_d(/C_s)$

symmetry operation	element of $T_d(/C_s)$
I	(1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12)
$C_{2(1)}$	(1 2)(3 4)(5 6)(7 8)(9 10)(11 12)
$C_{2(2)}$	(1 3)(2 4)(5 7)(6 8)(9 11)(10 12)
$C_{2(3)}$	(1 4)(2 3)(5 8)(6 7)(9 12)(10 11)
$C_{3(1)}$	(1 5 9)(2 8 11)(3 6 12)(4 7 10)
$C_{3(3)}$	(1 6 11)(2 7 9)(3 5 10)(4 8 12)
$C_{3(2)}$	(1 7 12)(2 6 10)(3 8 9)(4 5 11)
$C_{3(4)}$	(1 8 10)(2 5 12)(3 7 11)(4 6 9)
$C^2_{3(1)}$	(1 9 5)(2 11 8)(3 12 6)(4 10 7)
$C^2_{3(4)}$	(1 10 8)(2 12 5)(3 11 7)(4 9 6)
$C^2_{3(3)}$	(1 11 6)(2 9 7)(3 10 5)(4 12 5)
$C^2_{3(2)}$	(1 12 7)(2 10 6)(3 9 8)(4 11 5)
$\sigma_{d(1)}$	(1)(2 3)(4)(5 9)(6 11)(7 10)(8 12)
$S_{4(3)}$	(1 2 4 3)(5 10 8 11)(6 12 7 9)
$S^3_{4(3)}$	(1 3 4 2)(5 11 8 10)(6 9 7 12)
$\sigma_{d(6)}$	(1 4)(2)(3)(5 12)(6 10)(7 11)(8 9)
$\sigma_{d(2)}$	(1 5)(2 6)(4 8)(4 7)(9)(10)(11 12)
$\sigma_{d(4)}$	(1 6)(2 5)(3 7)(4 8)(9 10)(11)(12)
$S_{4(1)}$	(1 7 2 8)(3 6 4 5)(9 11 10 12)
$S^3_{4(1)}$	(1 8 2 7)(3 5 4 6)(9 12 10 11)
$\sigma_{d(3)}$	(1 9)(2 12)(3 11)(4 10)(5)(6 8)(7)
$S^3_{4(2)}$	(1 10 3 12)(2 11 4 9)(5 6 7 8)
$\sigma_{d(6)}$	(1 11)(2 10)(3 9)(4 12)(5 7)(6)(8)
$S_{4(2)}$	(1 12 3 10)(2 9 4 11)(5 8 7 6)

Since the T_d has a C_s group as its subgroup, the corresponding coset decomposition is represented by

$$T_d = C_s + C_sC_{2(1)} + C_sC_{2(2)} + C_sC_{2(3)} + C_sC_{3(1)} + C_sC_{3(3)} + C_sC_{3(2)} + C_sC_{3(4)} + C_sC^2_{3(1)} + C_sC^2_{3(4)} + C_sC^2_{3(3)} + C_sC^2_{3(2)} \quad (1)$$

wherein $C_s = \{I, \sigma_{d(1)}\}$.[12] When we sequentially number these

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(1) Anet, F. A. L.; Miura, S. S.; Siegel, J.; Mislow, K. *J. Am. Chem. Soc.* **1983**, *105*, 1419.

(2) Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319.

(3) Flurry, R. L., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 2901.

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(5) Jonas, J. *Collect. Czech. Chem. Commun.* **1988**, *53*, 2675.

(6) O'Loane, J. K. *Chem. Rev.* **1980**, *80*, 41.

(7) Fujita, S. *Theor. Chim. Acta* **1989**, *76*, 247.

(8) (a) Fujita, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3771. (b) Fujita, S. *Ibid.* **1990**, *63*, 203. (c) Fujita, S. *Tetrahedron* **1990**, *46*, 365.

(9) Burnside, W. *Theory of Groups of Finite Order*, 2nd ed.; Cambridge University Press: Cambridge, 1911.

(10) Baumslag, B.; Chandler, B. *Theory and Problems of Group Theory*; McGraw-Hill: New York, 1968.

(11) Armstrong, M. A. *Groups and Symmetry*; Springer-Verlag: New York, 1988.

(12) For the symmetry operations of the T_d group, see: Fujita, S. *J. Chem. Educ.* **1986**, *63*, 744.

(13) (a) Fujita, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 315. (b) Fujita, S. *J. Math. Chem.*, in press.

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12 cosets, we can construct a permutation, e.g.,

$$C_{2(1)} \sim \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ 2 & 1 & 4 & 3 & 6 & 5 & 8 & 7 & 10 & 9 & 12 & 11 \end{pmatrix}$$

$$= (1\ 2)(3\ 4)(5\ 6)(7\ 8)(9\ 10)(11\ 12) \qquad (2)$$

for $C_{2(1)}$ operation, because $C_s \rightarrow C_sC_{2(1)}$, $C_sC_{2(1)} \rightarrow C_sC_{2(1)}C_{2(1)} = C_s$, and so on. This process is repeated over all of the symmetry operations of the T_d group. The resulting permutations constitute a coset representation for the T_d group, as listed in Table I. We introduce the symbol $T_d(/C_s)$ for designating this CR, since this is based on the coset decomposition of T_d by C_s (eq 1).

In a similar way, the other coset representations of the T_d group are obtained. The complete set of CRs can be proven to consist of $T_d(/C_1)$, $T_d(/C_2)$, $T_d(/C_s)$, $T_d(/C_3)$, $T_d(/S_4)$, $T_d(/D_2)$, $T_d(/C_{2v})$, $T_d(/C_{3v})$, $T_d(/D_{2d})$, $T_d(/T)$, and $T_d(/T_d)$.

In general, a group G having a complete set of subgroups G_i ($i = 1, 2, ..., s$) affords a complete set of CRs $G(/G_i)$ ($i = 1, 2, ..., s$). Each of the coset representations is a kind of permutation representation, the degree of which is equal to $|G|/|G_i|$, where $|G|$ and $|G_i|$ denote the orders of the respective point groups.[9]

A coset representation governs an orbit that consists of a set of equivalent atoms, bonds, faces, or segments. For example, the 12 methylene hydrogens of adamantane (**1a**) constitute an orbit that is subject to the CR $T_d(/C_s)$. This assignment can be verified by numbering these hydrogens sequentially as shown in the formula **1a**. It should be emphasized that, although such a CR is originally obtained by the corresponding coset decomposition, the CR characterizes the symmetry of an orbit.

The assignment of a CR to a given orbit is accomplished more conveniently with a table of marks, which goes back to Burnside.[9] However, such tables have been reported with respect to a limited number of point groups.[15-17]

Table II is the table of marks for the T_d group, which is constructed by examining the CRs mentioned above. This table collects a mark for every CR by every subgroup. For example, if the elements of $T_d(/C_s)$ are restricted to C_s, we obtain two permutations, i.e., (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)(11)(12) for I and (1)(2 3)(4)(5 9)(6 11)(7 10)(8 12) for $\sigma_{d(1)}$. This set of permutations indicates that two points, (1) and (4), are fixed on the operations of the C_s group. This value is called "a mark" by Burnside.[9] This is listed at the intersection of the $T_d(/C_s)$ row and the C_s column in Table II. The other values of Table II can be obtained in a similar way.

The method for constructing the mark table indicates how we in turn assign a CR to a given orbit. First, we select a set of equivalent atoms (or others) of a given molecule. We then count fixed points (atoms) with respect to every symmetry operation. The resulting values are listed to generate a row vector [called a fixed-point vector (FPV)]. Finally, we compare the vector with the rows of Table II. The identical row is a CR to be assigned. For example, the orbit (**1a**) having 12 atoms gives an FPV, (12 0 2 0 0 0 0 0 0 0 0), the elements of which are aligned in the order of $\{C_1, C_2, C_s, C_3, S_4, D_2, C_{2v}, C_{3v}, D_{2d}, T, T_d\}$. This vector is equal to the $T_d(/C_s)$ row of Table II and therefore indicates that this orbit is subject to the CR $T_d(/C_s)$.

Table III collects CRs for the orbits appearing in T_d molecules (Figure 1). It should be noted that atoms, bonds, faces, and segments are purely geometric objects in this paper. In most cases concerning chirality and achirality, we have no connotations of bonding type or connectivity. Thus, such CRs for the orbits of atoms are sufficient enough to describe chiral properties of molecules. Since an orbit is subject to the corresponding CR ($G(/G_i)$), we call the orbit a $G(/G_i)$ orbit. Table III also contains SCR notations for molecular symmetries. These notations specify orbits and their members.[13]

Table II. Mark Table of T_d

	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	24	0	0	0	0	0	0	0	0	0	0
$T_d(/C_2)$	12	4	0	0	0	0	0	0	0	0	0
$T_d(/C_s)$	12	0	2	0	0	0	0	0	0	0	0
$T_d(/C_3)$	8	0	0	2	0	0	0	0	0	0	0
$T_d(/S_4)$	6	2	0	0	2	0	0	0	0	0	0
$T_d(/D_2)$	6	6	0	0	0	6	0	0	0	0	0
$T_d(/C_{2v})$	6	2	2	0	0	0	2	0	0	0	0
$T_d(/C_{3v})$	4	0	2	1	0	0	0	1	0	0	0
$T_d(/D_{2d})$	3	3	1	0	1	3	1	0	1	0	0
$T_d(/T)$	2	2	0	2	0	2	0	0	0	2	0
$T_d(/T_d)$	1	1	1	1	1	1	1	1	1	1	1

Table III. Coset Representations Assigned to T_d Molecules

T_d molecule	orbit	members	coset representation	SCR notation
adamantane	**1a**	H_{12}	$T_d(/C_s)$	$T_d[/C_s(H_{12})$; $/C_{3v}(H_4,C_4)$; $/C_{2v}(C_6)]$
	1b	H_4	$T_d(/C_{3v})$	
	1c	C_6	$T_d(/C_{2v})$	
	1d	C_4	$T_d(/C_{3v})$	
methane	**2a**	H_4	$T_d(/C_{3v})$	$T_d[/C_{3v}(H_4)$; $/T_d(C_1)]$
	2b	C_1	$T_d(/T_d)$	
tetrahedrane	**3a**	H_4	$T_d(/C_{3v})$	$T_d[/C_{3v}(H_4,C_4)]$
	3b	C_4	$T_d(/C_{3v})$	

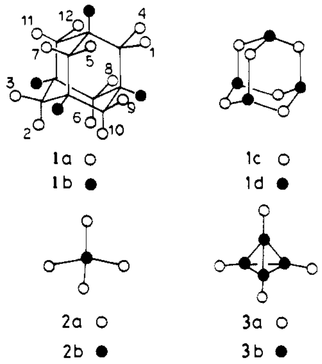

Figure 1. Orbits of T_d molecules.

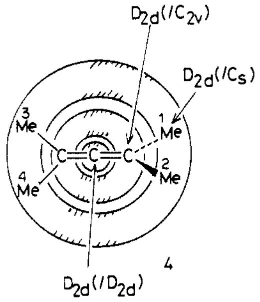

Figure 2. Orbits of D_{2d} tetramethylallene.

2. Orbit vs Local Symmetry

The concept of "orbit" is originally based on the permutation-group theory.[9-11] This is related to a coset representation that is a kind of permutation representation of a group. Thus, such CRs have been discussed only from the viewpoint of the permutation-group theory. The essence of the present methodology consists in the examination of CRs by means of the point-group theory. Figure 2 depicts the orbits and the corresponding CRs of tetramethylallene (D_{2d}).[14] Thus, the central carbon of the allene group is subject to the CR $D_{2d}(/D_{2d})$, two terminal allene carbons

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(14) Although equivalent atoms are present in a discrete fashion, we consider such a set of equivalent atoms to be an orbit.

(15) Hässelbarth, W. *Theor. Chim. Acta* **1985**, *67*, 339.

(16) Mead, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2130.

(17) Kerber, A.: Thürlings, K.-J. In *Lecture Notes in Mathematics*; Springer: New York, 1982; Vol. 969, p 191.

Table IV. Mark Table of D_{2d}

	C_1	C_2	C_2'	C_s	S_4	C_{2v}	D_2	D_{2d}
$D_{2d}(/C_1)$	8	0	0	0	0	0	0	0
$D_{2d}(/C_2)$	4	4	0	0	0	0	0	0
$D_{2d}(/C_2')$	4	0	2	0	0	0	0	0
$D_{2d}(/C_s)$	4	0	0	2	0	0	0	0
$D_{2d}(/S_4)$	2	2	0	0	2	0	0	0
$D_{2d}(/C_{2v})$	2	2	0	2	0	2	0	0
$D_{2d}(/D_2)$	2	2	2	0	0	0	2	0
$D_{2d}(/D_{2d})$	1	1	1	1	1	1	1	1

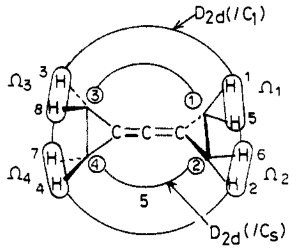

Figure 3. Orbits and local symmetry in a D_{2d} molecule.

belong to the $D_{2d}(/C_{2v})$ orbit, and four methyl carbons are governed by the CR $D_{2d}(/C_s)$. The assignment of the CRs to the respective orbits is accomplished by referring to the table of marks shown in Table IV.

The carbon atoms in this molecule have been reported to possess D_{2d}, C_{2v}, and C_s local symmetries.[2] These exactly correspond to the CRs assigned above. In general, a coset representation ($G(/G_i)$) corresponds to a local symmetry (G_i) in one–one fashion; the $G(/G_i)$ orbit consists of $|G|/|G_i|$ members of the local symmetry G_i.

Although we will report a mathematical treatment of this correspondence elsewhere,[13] we here illustrate this, using a D_{2d} molecule (**5**) as an example. Figure 3 shows an orbit (eight hydrogens) subject to the regular representation $D_{2d}(/C_1)$, the degree of which is equal to the order of D_{2d} (eight). Suppose that we select two hydrogens as a block of C_s symmetry, e.g., $\Omega_1 = \{H^1, H^5\}$. If every symmetry operation of D_{2d} is operated on Ω_1, there emerge $\Omega_2 = \{H^2, H^6\}$, $\Omega_3 = \{H^3, H^8\}$, and $\Omega_4 = \{H^4, H^7\}$. As we can see easily, each of the blocks belongs to C_s symmetry. We now consider a set of the blocks, $\Gamma = \{\Omega_1, \Omega_2, \Omega_3, \Omega_4\}$ as a D_{2d} set. Because the blocks Ω_i (i = 1, 2, 3, 4) correspond to cyclopropane carbons $C^{(i)}$ in one–one fashion and because the $C^{(i)}$'s belong to $D_{2d}(/C_s)$, the orbit Γ is concluded to be subject to $D_{2d}(/C_s)$. The comparison between **4** and **5** clarifies the relationship between the regular representation $D_{2d}(/C_1)$ and the coset representation $D_{2d}(/C_s)$. This intuitive explanation indicates that the blocks Ω_i (i = 1, 2, 3, 4) having the C_s symmetry constitute a $D_{2d}(/C_s)$ orbit. Thus, the CR $D_{2d}(/C_s)$ is found to correspond to the local symmetry C_s in one–one fashion. An alternative selection of C_s blocks is possible i.e., $\Omega_1 = \{H^1, H^6\}$, $\Omega_2 = \{H^2, H^5\}$, $\Omega_3 = \{H^3, H^7\}$, and $\Omega_4 = \{H^4, H^8\}$. This selection is essentially equivalent to the former selection in a geometric sense.

The present discussion can be extended into a general case: *when a G molecule has a $G(/G_i)$ orbit, each member of the orbit belongs to the local symmetry of G_i*. Now, the concept "local symmetry" is formulated as an attribute of an orbit through the corresponding coset representation. Moreover, the member is transformed into another member of the same orbit in terms of the permutations of the CR ($G(/G_i)$). In this connection, remember that the CR $T_d(/C_s)$ (Table I) and the $T_d(/C_s)$ orbit (**1a**).

3. Chirality Fittingness of an Orbit

A coset representation ($G(/G_i)$) is a kind of permutation representation (e.g., Table I) that represents the permutational properties of the corresponding orbit. The coset representation is constructed by a coset decomposition of a point group G by its subgroup G_i. There are three cases in such combinations of G and G_i, i.e., achiral–achiral, achiral–chiral, and chiral–chiral (Table V). Here, we use a *chiral point group* for designating a point group that has proper rotations only, and an *achiral point group* for referring to a point group that contains improper rotations as well as proper rotations. The *chirality fittingness* of a $G(/G_i)$ orbit is defined as such an attribute as determined by G vs G_i, i.e., *homospheric* for the achiral–achiral case, *enantiospheric* for the achiral–chiral case, and *hemispheric* for the chiral–chiral case. Since the CR is concerned with an orbit (or sphere) as shown in Figure 2, we propose the terms having a suffix -spheric (Greek: globe, sphere).

Table V. Chirality Fittingness of an Orbit Subject to $G(/G_i)$

G	G_i	chirality fittingness of a $G(/G_i)$ orbit	ligands allowed[a]	chirotopicity by G_i[b]
achiral	achiral	homospheric	achiral	achirotopic
achiral	chiral	enantiospheric	achiral, chiral	chirotopic
chiral	chiral	hemispheric	achiral, chiral	

[a] The original symmetry of each ligand is restricted within the local symmetry G_i of the orbit. See the text. [b] See: Reference 2.

Homospheric Orbits. The chirality fittingness of a $G(/G_i)$ orbit determines the mode of substitution concerning the orbit. The chirality fittingness of a $G(/G_i)$ orbit is defined as *homospheric* if both G and G_i are achiral point groups. If a $G(/G_i)$ orbit is homospheric, the orbit has to take r of the same achiral ligands (A) only,[18] the occupation of which is schematically expressed by

$$\underbrace{\boxed{A}\boxed{A}\boxed{\cdots}\boxed{A}}_{r}$$

where r is equal to $|G|/|G_i|$. Strictly speaking, the ligand A should belong to the local chirality G_i.[13] This means that the ligand A itself should belong to a group having G_i as a subgroup.

All of the orbits shown in Figure 2 are the examples of this case. The $D_{2d}(/C_s)$ orbit requires the local symmetry C_s. Although methyl group (CH_3) itself has C_{3v} symmetry, the symmetry environment of the D_{2d} molecule restricts the symmetry of the methyl group within the C_s symmetry.

Hemispheric Orbits. A hemispheric orbit can take achiral ligands as well as chiral ones to afford

$$\underbrace{\boxed{A}\boxed{A}\boxed{\cdots}\boxed{A}}_{r}$$

or

$$\underbrace{\boxed{Q}\boxed{Q}\boxed{\cdots}\boxed{Q}}_{r}$$

where As denote achiral ligands and Qs represent chiral ligands. The achiral ligand (A) belongs to the local symmetry G_i (a chiral point group). This indicates that the A itself belongs to an achiral point group having G_i as a subgroup. The chiral ligand (Q) also belongs to the local symmetry G_i. This means that Q has a point group having G_i as a subgroup.

For illustrating hemispheric orbits, let us examine twistane (**6**) of D_2 symmetry. The 16 hydrogens of this compound are divided into four orbits (H^a_4, H^b_4, H^c_4, and H^d_4), each of which is subject to $D_2(/C_1)$, as shown in Figure 4. This assignment is accomplished by means of the mark table of the D_2 point group (Table VI). These orbits are hemispheric in terms of the criterion shown in Table V. If the four orbits are filled in such a way that the same kind of ligands (H, F, Cl, or Br) occupy each of the orbits,

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[18] We use the term "ligand" to comprise both atoms and groups.

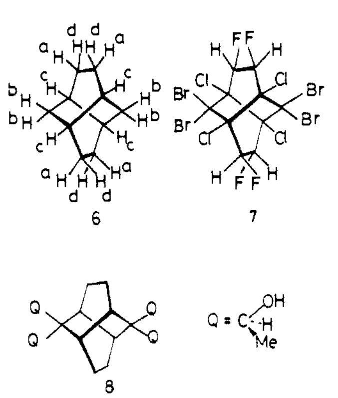

Figure 4. Hemispheric orbits of D_2 molecules. All four orbits are subject to $D_2(/C_1)$.

Table VI. Mark Table of D_2

	C_1	C_2	C_2'	C_2''	D_2
$D_2(/C_1)$	4	0	0	0	0
$D_2(/C_2)$	2	2	0	0	0
$D_2(/C_2')$	2	0	2	0	0
$D_2(/C_2'')$	2	0	0	2	0
$D_2(/D_2)$	1	1	1	1	1

the resulting $C_{10}H_4Br_4Cl_4F_4$ molecule (**7**) keeps the original D_2 symmetry invariant. The incorporated atoms of **7** are achiral in themselves, but governed by the symmetry of the whole molecule (D_2) so as to belong to the local symmetry of C_1. The D_2 molecule (**8**) is an example of chiral substitution.

Enantiospheric Orbits. An enantiospheric orbit $G(/G_i)$ of a molecule is capable of separating into two parts, each of which can take $r/2$ ligands, where r is equal to $|G|/|G_i|$. In order not to lower the symmetry (G), the packing with ligands should be schematically represented by

$$\underbrace{\begin{array}{|c|c|c|c|}\hline A & A & \cdots & A \\ \hline A & A & \cdots & A \\ \hline\end{array}}_{r/2}$$

if As are all achiral and subject to the local symmetry G_i. Each of the halves is superposable onto itself by proper rotations; the two halves are interchanged by improper rotations.

On the other hand, if the ligands are chiral, a packing represented by

$$\underbrace{\begin{array}{|c|c|c|c|}\hline Q & Q & \cdots & Q \\ \hline Q' & Q' & \cdots & Q' \\ \hline\end{array}}_{r/2}$$

appears as another possibility, where Q belongs to the local symmetry (G_i) and Q′ is its antipode.[13] This pairwise packing designates a general case that contains so-called meso-type achiral compounds and thereby reveals a potential symmetrical property of the enantiospheric orbit.

Figure 3 is an example of an enantiospheric orbit. Thus, an orbit of eight hydrogens of **5** is subject to $D_{2d}(/C_1)$, which is enantiospheric in terms of the criterion shown in Table V. Compound **9** of Figure 5 depicts another example, in which the encircled CH_2OH groups construct a half of an enantiospheric $D_{2d}(/C_1)$ orbit and the unmarked ones are categorized into the remaining half. A top view (the left) illustrates two 2-fold axes and two diagonal mirrors (σ_d).

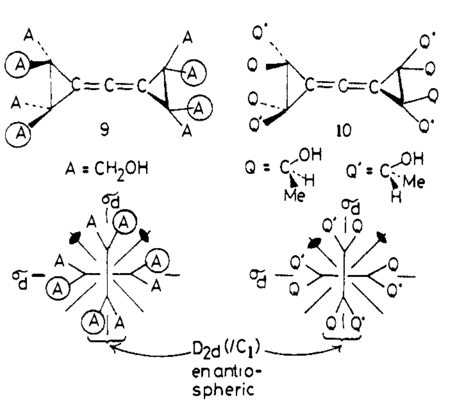

Figure 5. Enantiospheric orbits of D_{2d} molecules.

The derivative **10** also belongs to D_{2d} symmetry. A top view (the right) clarifies the symmetry of the enantiospheric $D_{2d}(/C_1)$ orbit. This example depicts a pairwise packing with chiral units for the enantiospheric orbit. It should be noted that the four ligands (Q) and the same number of their antipodes (Q′) constitute a single orbit, the length of which is equal to $|D_{2d}|/|C_1|$ (= 8).

Membership Criterion for Topicity. In this paper, the concept "topicity" is determined by a "membership" criterion. Thus, the same membership of two geometrical objects in a homospheric orbit or in each half of an enantiospheric orbit is defined as *homotopic*. The term *enantiotopic* is defined as to designate the membership of one (or more) object(s) in the half of an enantiospheric orbit and the different membership of the other object(s) in the other half. In this terminology, the relationship between the two halves of an enantiospheric orbit is referred to as enantiotopic.

The term "enantiotopic" was originally defined by a substitution criterion or by a symmetry criterion.[19,20] The latter, for example, states that two geometrical objects in a molecule of G symmetry are defined as *homotopic* if they are superposable on an appropriate proper rotation of G but not superposable on any improper rotations of G. They are defined as *enantiotopic* if they are superposable on an appropriate improper rotation of G. These methods of definition based on chemical or symmetry operations give the same results as the present membership criterion.

Since orbits represent geometric substantials, the membership criterion is operation-free in a way different from the substitution and symmetry criteria.[21] It should be noted that all of the symmetrical properties are considered to be the attributes of such orbits. Thus, the term "enantiospheric" is concerned only with a single orbit and does not depend on stereoisomerism. The membership criterion for the term "enantiotopic" thus finds a sound foundation from the viewpoint of "stereochemistry without stereoisomerism".

The concept of "chirality fittingness" is a complement concept of "local chirality" introduced in Mislow's paper.[2] However, they are conceptually distinct and there are several differences between them. The concept chirality fittingness is concerned with an orbit that contains several equivalent ligands. On the other hand, the local chirality takes no account of such an orbit and refers only to an individual site, which is an element of the orbit from the present viewpoint.

The chirality fittingness is concerned with G as well as its subgroup G_i in terms of the CR $G(/G_i)$. Hence, there emerge three cases to denote symmetry properties (Table V). Contrarily,

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(19) Mislow, K.; Raban, M. *Top. Stereochem.* **1967**, *1*, 1.

(20) Eliel, E. L. *Top. Curr. Chem.* **1982**, *105*, 1.

(21) There are two methods to treat problems concerning equivalency. The first is a method in which an equivalent relation is directly used to identity or to differentiate two matters. The second one uses equivalence classes (orbits), in which the members of such an equivalence class are regarded as equivalent. The conventional criteria are categorized into the first method. The present "membership criterion" stems from the second method.

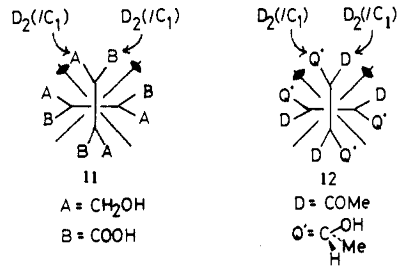

Figure 6. Chiral discrimination for enantiospheric orbits of D_{2d} molecules (**9** and **10**) to produce D_2 molecules (**11** and **12**).

the local chirality is concerned only with G_i. As a result, there appear two cases, i.e., achirotopic and chirotopic.[2]

4. Prochirality

In terms of chirality fittingness, we now reexamine the concept of "prochirality", which has been proposed by Hanson.[22] The prochirality has been restricted to systems where two ligands or faces are differentiated to generate a chiral compound. However, a general approach that treats two or more ligands is available, if we take account of the chirality fittingness of an orbit.

The two enantiotopic parts of an enantiospheric orbit do not separate energetically within achiral environments. However, if the orbit is placed under a chiral environment (e.g., an attack of a chiral reagent), they become energetically different, being diastereotopic to each other.[23] This effect is schematically represented by

$$\underbrace{\begin{array}{|c|c|c|c|}\hline A^{(Q)} & A^{(Q)} & \cdots & A^{(Q)} \\ \hline A & A & \cdots & A \\ \hline \end{array}}_{r/2}$$

where $A^{(Q)}$ represents A perturbed by a chiral reagent (Q). This perturbed molecule no longer belongs to the original G symmetry, but to the subgroup of G composed of the proper rotations.

For example, let us examine the $D_{2d}(/C_1)$ orbit of the D_{2d} molecule **9**. Since this orbit is enantiospheric, the two halves can be differentiated from each other by an attack of a chiral oxidizing agent. Hence, we recognize a potential chiral synthesis from **9** to the D_2 molecule **11**, if this process is energetically more plausible than the antipodal counterpart. It is to be noted that the antipodal oxidizing agent produces the antipode of **11**. In the same line, a conversion from the compound **10** to the D_2 molecule **12** is another type of potential chiral synthesis.

In the resulting molecule (**11**), unattacked four hydroxymethyl groups constitute a $D_2(/C_1)$ orbit and a set of four carboxyl groups is also a $D_2(/C_1)$ orbit. Similarly, the set of four $CH(CH_3)OH$ groups and that of four $COCH_3$ groups in **12** are both subject to $D_2(/C_1)$. Since the orbits are hemispheric, achiral as well as chiral substituents are allowed by means of chirality fittingness. This requirement is satisfied in the cases of **11** and **12**.

These facts can be generalized to a theorem: *an enantiospheric orbit is capable of separating into two hemispheric orbits of the same length under a chiral environment, whether the change is reversible or irreversible.*

A *prochiral* compound is defined as an achiral compound that has at least one enantiospheric orbit. The prochiral compound may possess homospheric orbits along with enantiospheric orbits. Hence, we classified prochiral compounds into two categories, i.e., type I and type II. On the other hand, an achiral compound that only consists of homospheric orbits is defined as a *para-achiral* compound. This term means that there exist no direct methods to convert this type into a chiral compound.

$$\left\{\begin{array}{ll} \textbf{achiral} & \left\{\begin{array}{ll} \textbf{prochiral-I} & \ldots\textbf{enantiospheric} \\ \textbf{prochiral-II} & \ldots\textbf{enantiospheric + homospheric} \\ \textbf{para-achiral} & \ldots\textbf{homospheric} \end{array}\right. \\ \textbf{chiral} & \qquad\qquad\quad \ldots\textbf{hemispheric} \end{array}\right.$$

In the present terminology, the term "prochiral" refers to an *enantiospheric orbit*, but not to a so-called "prochiral center". The latter conventional usage have afforded some confusion to organic stereochemistry as pointed out by Milsow.[2] On the other hand, the present usage does not contain such problems, since this is based on enantiosphericity, which is determined by the chirality fittingness of an $G(/G_i)$ orbit.

5. Desymmetrization of Homospheric Orbits

Subduction of Coset Representations. A homospheric orbit does not separate with and without a chiral environment. This means that there is no direct method for converting a para-achiral molecule into a chiral one. However, a multistep conversion is available to solve this problem. Mislow et al. discussed the desymmetrization of achiral objects that contain one or more symmetry elements of the second kind (σ, i, or S_4) and proposed the concept of (pro)^p-chirality.[2] This section deals with these issues from the present viewpoint.

For the desymmetrization of orbits, we should introduce the subduction of coset representations. Although we have reported a mathematical foundation of this concept elsewhere,[7] an intuitive illustration would be helpful to manipulate the present objective. Let us work out $T_d(/C_s)$ listed in Table I. We restrict this CR within the elements of its subgroup, e.g., D_{2d}. This restriction affords the subduction of $T_d(/C_s)$ by D_{2d}. We then obtain eight permutations expressed by

I	~	(1)(2)(3)(4)	(5)(6)(7)(8)(9)(10)(11)(12)
$C_{2(1)}$	~	(1 2)(3 4)	(5 6)(7 8)(9 10)(11 12)
$C_{2(2)}$	~	(1 3)(2 4)	(5 7)(6 8)(9 11)(10 12)
$C_{2(3)}$	~	(1 4)(2 3)	(5 8)(6 7)(9 12)(10 11)
$\sigma_{d(1)}$	~	(1)(2 3)(4)	(5 9)(6 11)(7 10)(8 12)
$S_{4(3)}$	~	(1 2 4 3)	(5 10 8 11)(6 12 7 9)
$S_{4(3)}^3$	~	(1 3 4 2)	(5 11 8 10)(6 9 7 12)
$\sigma_{d(6)}$	~	(1 4)(2)(3)	(5 12)(6 10)(7 11)(8 9)

This set of permutations constitutes a permutation representation of D_{2d}, which is called a subduced representation (SR) of D_{2d}. We use the symbol $T_d(/C_s)\downarrow D_{2d}$ to denote this SR.

Although the original $T_d(/C_s)$ is transitive, i.e., corresponding to a single orbit, the SR $T_d(/C_s)\downarrow D_{2d}$ is intransitive and can be divided into suborbits. If we examine the concrete form of the SR, we find such suborbits as being $\Delta_1 = \{1, 2, 3, 4\}$ and $\Delta_2 = \{5, 6, 7, 8, 9, 10, 11, 12\}$. Since FPV for Δ_1 is found to be (4 0 0 2 0 0 0 0), the corresponding CR is determined to be $D_{2d}(/C_s)$ by comparing the FPV with the $D_{2d}(/C_s)$ row of Table IV. The other suborbit Δ_2 proves to be subject to $D_{2d}(/C_1)$. These facts can be expressed by

$$T_d(/C_s)\downarrow D_{2d} = D_{2d}(/C_1) + D_{2d}(/C_s) \tag{3}$$

Table VII lists all subductions for the T_d group.[24]

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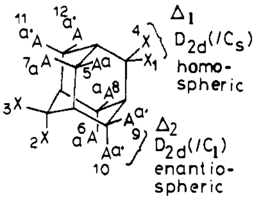
[22] Hanson, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731.

[23] We use the term "diastereotopic" in this paper to designate the relationship between the two hemispheric orbits that are generated from a separation of an enantiospheric orbit. Note that the two hemispheric orbits have been originally enantiotopic to each other in the starting enantiospheric orbit.

Table VII. Subduction of the Coset Representations of T_d

i/j	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_s$	$\downarrow C_3$	$\downarrow S_4$	$\downarrow D_2$	$\downarrow C_{2v}$	$\downarrow C_{3v}$	$\downarrow D_{2d}$	$\downarrow T$	$\downarrow T_d$
$T_d(/C_1)$	$24C_1(/C_1)$	$12C_2(/C_1)$	$12C_s(/C_1)$	$8C_3(/C_1)$	$6S_4(/C_1)$	$6D_2(/C_1)$	$6C_{2v}(/C_1)$	$4C_{3v}(/C_1)$	$3D_{2d}(/C_1)$	$2T(/C_1)$	$T_d(/C_1)$
$T_d(/C_2)$	$12C_1(/C_1)$	$4C_2(/C_1)$ $+4C_2(/C_2)$	$6C_s(/C_1)$	$4C_3(/C_1)$	$2S_4(/C_1)$ $+2S_4(/C_2)$	$2D_2(/C_2)$ $+D_2(/C_2')$ $+D_2(/C_2'')$	$2C_{2v}(/C_1)$ $+2C_{2v}(/C_2)$	$2C_{3v}(/C_1)$	$D_{2d}(/C_2)$ $+2D_{2d}(/C_2')$	$2T(/C_2)$	$T_d(/C_2)$
$T_d(/C_s)$	$12C_1(/C_1)$	$6C_2(/C_1)$	$5C_s(/C_1)$ $+2C_s(/C_s)$	$4C_3(/C_1)$	$3S_4(/C_1)$	$3D_2(/C_1)$	$2C_{2v}(/C_1)$ $+C_{2v}(/C_s)$ $+C_{2v}(/C_s')$	$C_{3v}(/C_1)$ $+2C_{3v}(/C_s)$	$D_{2d}(/C_1)$ $+D_{2d}(/C_s)$	$T(/C_1)$	$T_d(/C_s)$
$T_d(/C_3)$	$8C_1(/C_1)$	$4C_2(/C_1)$	$4C_s(/C_1)$	$2C_3(/C_1)$ $+2C_3(/C_3)$	$2S_4(/C_1)$	$2D_2(/C_1)$	$2C_{2v}(/C_1)$	$C_{3v}(/C_1)$ $+C_{3v}(/C_3)$	$D_{2d}(/C_1)$	$2T(/C_3)$	$T_d(/C_3)$
$T_d(/S_4)$	$6C_1(/C_1)$	$2C_2(/C_1)$ $+2C_2(/C_2)$	$3C_s(/C_1)$	$2C_3(/C_1)$	$S_4(/C_1)$ $+2S_4(/S_4)$	$D_2(/C_2)$ $+D_2(/C_2')$ $+D_2(/C_2'')$	$C_{2v}(/C_1)$ $+C_{2v}(/C_2)$	$C_{3v}(/C_1)$	$D_{2d}(/C_2')$ $+D_{2d}(/S_4)$	$T(/C_2)$	$T_d(/S_4)$
$T_d(/D_2)$	$6C_1(/C_1)$	$6C_2(/C_2)$	$3C_s(/C_1)$	$2C_3(/C_1)$	$3S_4(/C_2)$	$6D_2(/C_2)$	$3C_{2v}(/C_2)$	$C_{3v}(/C_1)$	$3D_{2d}(/D_2)$	$2T(/D_2)$	$T_d(/D_2)$
$T_d(/C_{2v})$	$6C_1(/C_1)$	$2C_2(/C_1)$ $+2C_2(/C_2)$	$2C_s(/C_1)$ $+2C_s(/C_s)$	$2C_3(/C_1)$	$S_4(/C_1)$ $+S_4(/C_2)$	$D_2(/C_2)$ $+D_2(/C_2')$ $+D_2(/C_2'')$	$C_{2v}(/C_1)$ $+2C_{2v}(/C_{2v})$	$2C_{3v}(/C_s)$	$S_{2d}(/C_2')$ $+D_{2d}(/C_{2v})$	$T(C_2)$	$T_d(/C_{2v})$
$T_d(/C_{3v})$	$4C_1(/C_1)$	$2C_2(/C_1)$	$C_s(/C_1)$ $+2C_s(/C_s)$	$C_3(/C_1)$ $+C_3(C_3)$	$S_4(/C_1)$	$D_2(/C_1)$	$C_{2v}(/C_s)$ $C_{2v}(/C_s')$	$C_{3v}(/C_s)$ $+C_{3v}(/C_{3v})$	$D_{2d}(/C_s)$	$T(/C_3)$	$T_d(/C_{3v})$
$T_d(/D_{2d})$	$3C_1(/C_1)$	$3C_2(/C_2)$	$C_s(/C_1)$ $+C_s(/C_s)$	$C_3(/C_1)$	$S_4(/C_2)$ $+S_4(/S_4)$	$3D_2(/D_2)$	$C_{2v}(/C_s)$ $+C_{2v}(/C_{2v})$	$C_{3v}(/C_s)$	$D_{2d}(/D_2)$ $+D_{2d}(/D_{2d})$	$T(/D_2)$	$T_d(/D_{2d})$
$T_d(/T)$	$2C_1(/C_1)$	$2C_2(/C_2)$	$C_s(/C_1)$	$2C_3(/C_3)$	$S_4(/C_2)$	$2D_2(/D_2)$	$C_{2v}(/C_2)$	$C_{3v}(/C_3)$	$D_{2d}(/D_2)$	$2T(/T)$	$T_d(/T)$
$T_d(/T_d)$	$C_1(/C_1)$	$C_2(/C_2)$	$C_s(/C_s)$	$C_3(/C_3)$	$S_4(/S_4)$	$D_2(/D_2)$	$C_{2v}(/C_{2v})$	$C_{3v}(/C_{3v})$	$D_{2d}(/D_{2d})$	$T(/T)$	$T_d(/T_d)$



13 A=Cl, X=H

14 A=COOMe, X=CH$_2$OMe

Figure 7. A D_{2d} molecule from a T_d molecule that corresponds to $T_d(/C_s)\downarrow D_{2d}$.

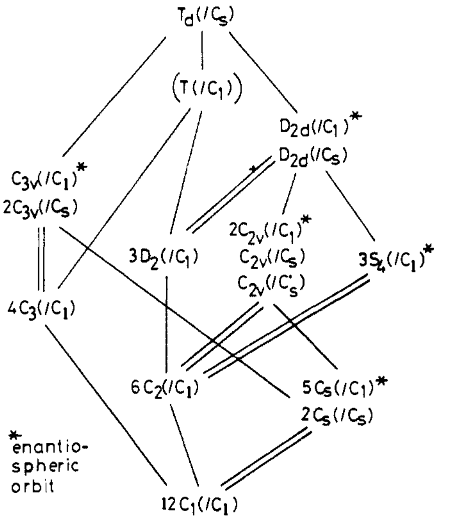


Figure 8. Desymmetrization lattice for a $T_d(/C_s)$ orbit.

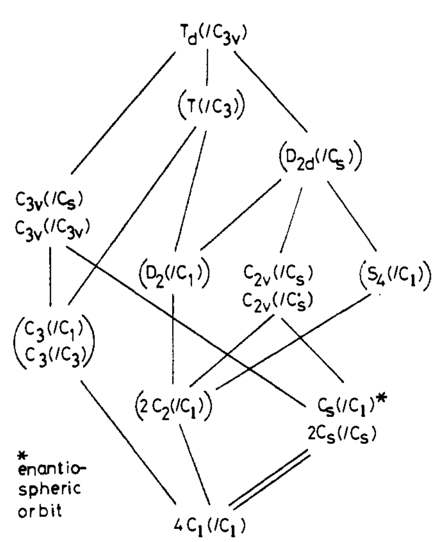


Figure 9. Desymmetrization lattice for a $T_d(/C_{3v})$ orbit.

Table VIII. Existence of Molecules Produced by Desymmetrization of T_d

	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	T	T	T*	T	T*	T	T*	T*	T*	T	T*
$T_d(/C_2)$	T	T	T*	T	T*	T	T*	T*	T*	T	T*
$T_d(/C_s)$	T	T	T*	T	T*	T	T*	T*	T*	F	T
$T_d(/C_3)$	T	T	T*	T	T*	F	T*	T*	F	T	T*
$T_d(/S_4)$	T	T	T*	T	T*	T	T*	F	T*	F	T
$T_d(/D_2)$	F	F	F	T	F	T	F	F	T*	T	T*
$T_d(/C_{2v})$	T	T	T*	F	F	T	T*	T	T*	F	T
$T_d(/C_{3v})$	T	F	T*	F	F	F	T	T	F	F	T
$T_d(/D_{2d})$	F	F	F	F	F	T	F	F	T*	F	T
$T_d(/T)$	F	F	F	F	F	F	F	F	F	T	T
$T_d(/T_d)$	F	F	F	F	F	F	F	F	F	F	T

The geometric meaning of eq 3 is illustrated in Figure 7. The numbering of the 12 positions corresponds to the integers contained in Δ_1 and Δ_2. When we consider four hydrogens for Δ_1 and eight chlorine atoms for Δ_2, we find that the resulting compound (**13**) belongs to D_{2d} symmetry. It is worthwhile to compare between the $D_{2d}(/C_1)$ orbit of **13** and that of **5** and between the $D_{2d}(/C_s)$ orbit of **13** and that of **4**. These correspondences are easy to understand, if we recognize the molecules as purely geometric objects.

Desymmetrization Lattice. A *desymmetrization lattice* for an orbit is a group–subgroup lattice that contains the data of the subduction of the orbit. This lattice illustrates what subsymmetries are realized by desymmetrizing the orbit. Here, we take no account of a case in which any new chiral units are added.[25] Figures 8 and 9 show desymmetrization lattices for a $T_d(/C_s)$ and a $T_d(/C_{3v})$ orbit, respectively.

The comparison between these lattices provides useful information on the symmetrical properties of the T_d point group. Suppose that we do not find any division of an orbit when we examine a given group and any of its supergroups in these lattices.

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(24) The procedure for subduction of CRs was programmed with FORTRAN77 and effected on a VAX-11/750 computer. This was also applied to the derivation of subduction tables for other point groups.

(25) If any chiral units are added, we should take a slightly different approach. This is accomplished conveniently by unit subduced cycle indexes with chirality fittingness. See: References 12 and 13.

Then, the group does not exist mathchemically.[26] For example, Figure 8 indicates that the conversion of $T_d(/C_s)$ into $T(/C_1)$ accompanies no division of the orbit; therefore, a T molecule having a $T(/C_1)$ orbit does not exist in this series. Molecules of the other symmetries can exist from a mathchemical point of view. On the other hand, Figure 9 indicates the nonexistence of many subgroups. Thus, there exist only four subgroups, i.e., C_{3v}, C_{2v}, C_s, and C_1 in this series.

The other coset representations for the T_d group also constitute the corresponding desymmetrization lattices. Thereby, we conclude the existence or nonexistence of molecules of the specific symmetry. Table VIII summarizes the results, in which T denotes the existence of a molecule and F denotes the nonexistence. When we examine a compound having two or more orbits, the corresponding rows of Table VIII are combined in a LOGICAL-OR fashion (i.e., TT = T, TF = FT = T, and FF = F). The result of T indicates the existence of such a molecule; F corresponds to the nonexistence.

Chemoselective and Stereoselective Processes. Although there exist no direct methods to convert para-achiral compounds into chiral compounds, some indirect methods are available to do this task. This section discusses these indirect methods.

In the preceding sections, we have generally discussed the processes of desymmetrization. We can classify such desymmetrizing conversions into chiral and achiral processes. A process producing an achiral compound is defined as an achiral process; a chiral process affords a chiral compound. This classification takes no account of achirality or chirality of the starting materials. Another classification of the desymmetrizing conversions is based on the requirement of chiral environments. If a conversion requires any additional chiral environment (e.g., an attack of a chiral reagent), this process is referred to as a stereoselective process. Otherwise, the process is called a chemoselective process.

When we combine the two classification methodologies, there can emerge four categories of desymmetrizing processes. Among them, a "stereoselective achiral process" is conceptually impossible. Thus, a desymmetrization lattice such as Figures 8 and 9 contains three types of conversions. The first is a conversion of an achiral compound of G symmetry into an achiral one of its subsymmetry (G_i). This process requires no chiral environments. Hence, we define this process as a *chemoselective achiral process*.[27] In Figures 8 and 9, the first process is shown by a straight line. The second process is a conversion of a prochiral compound into a chiral derivative, which requires a chiral environment. We define this type as a *stereoselective chiral process*. A double straight line denotes this type of process in Figures 8 and 9.[28] Table VIII contains the symbol (T*), which denotes a prochiral compound capable of undertaking a stereoselective chiral process.

The third process is a conversion of a chiral compound into a chiral derivative of the same or lower symmetry. This process is called a *chemoselective chiral process*. Note that this process requires no *additional* chiral perturbation other than the intrinsic chirality of the starting compound.

In order to convert a para-achiral compound into a chiral molecule, we first apply a chemoselective achiral process to this compound, affording a prochiral intermediate. This process involves a conversion of a homospheric orbit into an enantiospheric orbit. Then we use a chiral reagent on the intermediate in a subsequent stereoselective chiral process. The latter process contains a conversion of the enantiospheric orbit into hemispheric orbits. Figure 10 illustrates chiral molecules via D_{2d} (**14**) from a $T_d(/C_s)$ molecule. Suppose that the $T_d(/C_s)$ molecule has 12 hydroxymethyl groups. A chemoselective process can convert this compounds into **14**, which has A_8X_4, where A = COOMe and X = CH_2OMe.[29] Note that the symbol (T*) at the intersection of the $T_d(/C_s)$ row and the D_{2d} column of Table VIII indicates the presence of this conversion. This is verified by eq 3, which produces a $D_{2d}(/C_1)$ orbit. Since this orbit is enantiospheric in terms of the present criterion (Table V), the compound **14** is prochiral-II and can be converted into a D_2 molecule (**15**) by a

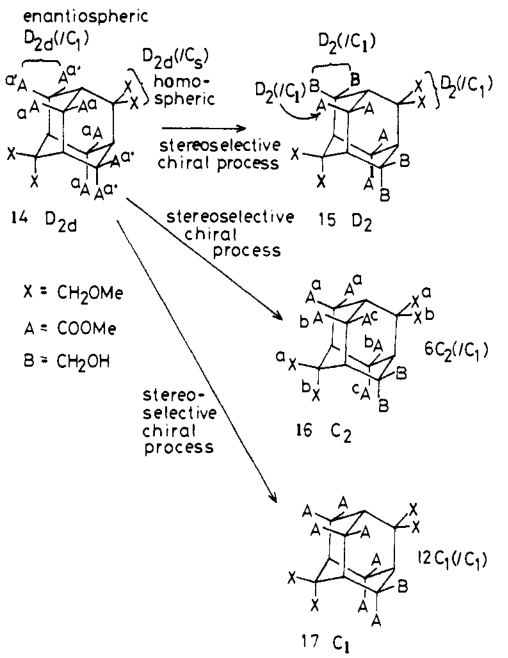

Figure 10. Potential derivation of chiral molecules from a T_d molecule via $T_d(/C_s)\downarrow D_{2d}$.

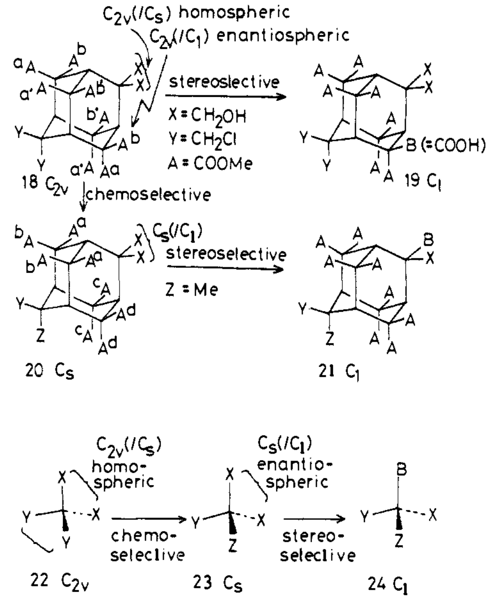

Figure 11. Potential derivation of chiral molecules via $T_d(/C_s)\downarrow C_{2v}$ and via $T_d(/C_{2v})\downarrow C_{2v}$.

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[26] A "mathchemically" possible process is defined as a process that is allowed by mathematical–chemical considerations. This process can be realized experimentally by some method, whether difficult or not.

[27] Here, experimental methods for realizing these conversions are left out of consideration. The present discussion takes account of the mathchemical possibility of such conversions. In general, a chemoselective achiral process yields a set of configurational isomers. They are regarded to be isolable by some method rather than chiral methods, even if difficult.

[28] For simplicity of discussions, we deal only with atom(group)-differentiating reactions in this paper. However, there conceptually exist bond-(edge)-differentiating and face-differentiating reactions. They can be treated in the same way as described here. For example, the compound (**22**) of C_{2v} symmetry (Figure 11) can be regarded as prochiral, since the four edges (X···Y) construct an enantiospheric $C_{2v}(/C_1)$ orbit. This is essentially identical with the C_{2v} case appearing in Figure 12. If we consider an appropriate method for differentiating the two enantiotropic edges, this compound may be directly converted into a chiral derivative. This hypothetical method suggests a new type of chiral synthesis.

[29] This hypothetical conversion can be accomplished by (1) geminal acetalization of two sets of hydroxymethyls to produce two isomers, (2) isolation of the desired isomer, (3) oxidation of eight unreacted hydroxymethyls into carboxyl groups, (4) deacetalization to regenerate four hydroxymethyl groups, (5) esterification of the carboxyl groups, and (6) O-methylation.

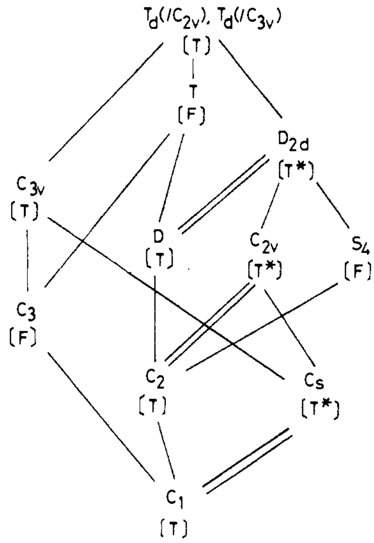

Figure 12. Abbreviated desymmetrization lattice for a molecule having $T_d(/C_{2v})$ and $T_d(/C_{3v})$ orbits.

chiral attack[30,31] via a conceptually similar process from **9** to **11**. Note that the two halves (A_4^a and $A_4^{a'}$) of the $D_{2d}(/C_1)$ orbit of **14** are enantiotopic to each other.

Among the eight methoxycarbonyl groups (A) involved in the enantiospheric $D_{2d}(/C_1)$ orbit of the molecule **14**, a set of geminal A_2 is either enantiotopic or homotopic to any other geminal set.[32] A chiral reagent can differentiate such enantiotopic sets. Thus, an attack on one set of geminal A_2 yields a product antipodal to that produced by an attack of any enantiotopic set of A_2. This effect produces an energetically preferred molecule, e.g., **16**, rather than its antipode.

Figure 10 also depicts an additional possibility, i.e., a conversion of **14** into **17**. One methoxycarbonyl group of **14** is either enantiotopic or homotopic to any other methoxycarbonyl group. Hence, a chiral reagent can differentiate A^a from $A^{a'}$ to give an energetically preferred molecule, e.g., **17**, rather than its antipode.

Figure 8 indicates that there are other potential stereoselective chiral processes at C_{3v}, C_{2v}, S_4, and C_s in this series, since they contain at least one enantiopheric orbit (*). These are also designated by T* in the $T_d(/C_s)$ row of Table VIII. The present discussions are applied to all of the CRs of the T_d group. The results are also summarized in Table VIII.

Figure 11 illustrates the dependence of desymmetrization processes upon orbits. A compound (**18**) of C_{2v} obtained by chemoselective achiral desymmetrization has two enantiospheric $C_{2v}(/C_1)$ orbits ($A_2^aA_2^{a'}$ and $A_2^bA_2^{b'}$). Hence, this can be directly converted into a chiral compound (e.g., **19**) by a stereoselective chiral process. Another possible route to a chiral molecule consists of a chemoselective achiral desymmetrization from **18** to **20** of C_s symmetry [$C_{2v}(/C_s) \rightarrow C_s(/C_1) + 2C_s(/C_s)$] and the subsequent stereoselective chiral conversion into **21** [$C_s(/C_1) \rightarrow 2C_1(/C_1)$]. On the other hand, the compound **22** has two homospheric $C_{2v}(/C_s)$ orbits but does not possess any enantiospheric orbits. Hence, there are no direct methods for converting **22** into a chiral molecule. There exits a route via **23** into a chiral molecule, since **23** contains an enantiospheric $C_s(/C_1)$ orbit.

In order to discuss a molecule having two or more orbits, we examine all of these orbits by a desymmetrization lattice, which has the data of these orbits taken from Table VII. More conveniently, we apply Table VIII to such problems. For example, Figure 12 is constructed from the data of Table VIII for manipulating a molecule having a $T_d(/C_{2v})$ and a $T_d(C_{3v})$ orbit. We combine the corresponding rows of Table VIII in a LOGICAL-OR fashion, in which the presences and the absences of a mark (*) are also combined in a LOGICAL-OR fashion., e.g., T*F = T* and T*T* = T*. Figure 12 indicates that D_{2d}, C_{2v} and C_s molecules are possible intermediates affording stereoselective chiral processes.

In connection with the preceding analysis, we should refer to the concept "(pro)^p-chirality". Mislow et al.[2] defined as (pro)^p-chiral any finite, achiral object that can be desymmetrized into a chiral object by at most p stepwise replacements of a point by a differently labeled one. Although this statement correctly indicated the dependence of the (pro)^p-chirality upon the individual object, the text implied the dependence upon point groups rather than upon individual objects. Thus, they closed their discussion by a comment, "According to our scheme, desymmetrization of an object with T_d symmetry yields an object that can belong to only one of four subsymmetries (C_{3v}, C_{2v}, C_s, or C_1)".[2] This conclusion, however, is correct only for the case of an object having a $T_d(/C_{3v})$ orbit.

Figures 8, 9, and 12 indicate that (pro)^p-chirality is determined by a given molecule, not by its point group. More strictly speaking, this is dependent upon the orbit(s) of the molecule. For example, Figure 8 shows that a T_d molecule having a $T_d(/C_s)$ orbit can be desymmetrized by the process, $T_d(/C_s) \rightarrow D_{2d} \rightarrow C_{2v} \rightarrow C_s \rightarrow C_1$. This process means that the molecule is (pro)^4-chiral. On the other hand, a T_d molecule having a $T_d(/C_{3v})$ orbit is (pro)^3-chiral, since the process, $T_d(/C_{3v}) \rightarrow C_{3v} \rightarrow C_s \rightarrow C_1$, contains a maximum three steps to desymmetrize this molecule (Figure 9).

In addition, the definition of (pro)^p-chirality implicitly presumes that an asymmetric synthesis can only be accomplished by differentiating two enantiotopic groups or faces. However, the present discussion (e.g., Figures 10 and 11) shows that stereoselective chiral reactions can occur at various enantiospheric orbits with two or more ligands. Hence, the type I and II prochiralities defined above are preferred over the (pro)^p-chirality.

6. Conclusion

Coset representations and their subductions provide us with various useful concepts concerning molecular stereochemistry. A molecule of G symmetry is considered to be a three-dimensional object that consists of several orbits, where each orbit is subject to the corresponding CR, $G(/G_i)$. The relationship between G and its subgroup G_i determines the chirality fittingness of the orbit, which is classified into homospheric, enantiospheric, or hemispheric. The presence of at least one enantiospheric orbit is the necessary and sufficient condition for prochirality. Local chirality is shown to be identical with G_i of $G(/G_i)$. The subductions of CRs and the construction of desymmetrization lattices afford a method for specifying desymmetrization processes. Three types of desymmetrizations, i.e., chemoselective achiral, chemoselective chiral, and stereoselective chiral ones, are discussed.

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(30) We can consider a hypothetical reducing agent that has four reaction sites with chiral environments.

(31) In this paper, an appropriate antipode is tentatively considered to be energetically preferred rather than the counterpart. However, we should examine by experiments or by quantum-chemical calculations whether this selection is correct or not.

(32) The proof will be reported elsewhere in a general fashion.