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Theoretical Foundation of Prochirality. Chirogenic Sites in an Enantiospheric Orbit

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Prochirality is one of the inherent properties of an enantiospheric orbit that is designated by a coset representation $\mathbf{G}(/\mathbf{G}_i)$. Desymmetrization of the $\mathbf{G}(/\mathbf{G}_i)$ orbit is discussed to present a new concept "**H**-chirogenic site". The chirogenic site in the $\mathbf{G}(/\mathbf{G}_i)$ orbit is capable of producing a chiral **H**-molecule under the influence of an appropriate chiral reagent. The condition for the existence of such a chirogenic site is discussed. A convenient method using a desymmetrization lattice is presented for determining chirogenic sites.

The concept of "prochirality" has been proposed by Hanson for specifying the steric course of asymmetric syntheses.[1,2] From the beginning, his definition has been polysemous; and its successor, the IUPAC rule, has afforded two distinct definitions of prochirality (rules E-4.12(a) and (b)).[3] Thus, the intrinsic meaning of the prochirality term ("pro"=before) has thus been changed to connote cases in which chiral compounds are converted into other chiral compounds (IUPAC rule E-4.12(b)). Prelog and Helmchen[4] have used the term "stereogenic" in order to get rid of confusion provided by the prochirality. Although they have carefully avoided the use of the term "prochirality", the essence of their proposal concerning prochirality is to differentiate between reflection-variant and -invariant stereogenic units. Seebach and Prelog[5] have proposed a method of specifying asymmetric syntheses. Hanson's definition and Prelog's proposal are implicity based upon permutation-group theory and play down point-group theory, though the latter is essential to discuss stereochemistry. Moreover, the prochirality has been restricted to molecular systems in which two ligands or faces are differentiated to create a chiral compound.

Mislow and Siegel[6] have discussed the prochirality concept. Their comment can be summarized as follows: Hanson's definition refers to (pro)stereogenicity rather than to prochirality. They have also proposed (pro)^p-chirality, which has been modified by Halevi.[7]

We have presented a new definition of prochirality, which is based on the concept of *chirality fittingness* derived by integrating the permutation- and point-group theories.[8] This definition affords a general approach that treats two or more ligands successfully. The renewed prochirality is one of the symmetrical properties inherent in an enantiospheric orbit. We have summarized our results in the form of a theorem.

Theorem 1.[8] *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.*

Then, we have defined a *prochiral* molecule as the one that has at least one enantiospheric orbit. In previous papers,[8,9] we have given a proof of this theorem in a rather intuitive fashion. We have also developed another concept *subduction of coset representations (CRs)*.[10] Combining this concept with the chirality fittingness, we have clarified the prochirality to some extent. However, the previous discussion[8] are rather qualitative. In order to understand the renewed prochirality concept comprehensively, a stricter and more detailed discussion is desirable. In a continuation of the work, the present paper deals with discussions on desymmetrization of enantiospheric orbits, where more detailed results are available for formulating prochirality. In addition, the related new concept "chirogenic" is proposed.

Results

Ligands and Local Symmetry. Atoms, functional groups, and faces are three-dimensional objects to be examined in organic stereochemistry. We use the term "ligand" to comprise these objects. The chemical term "ligand" corresponds to the mathematical term "block". A set of equivalent ligands (or blocks) in a molecule is subject to a coset representation $\mathbf{G}(/\mathbf{G}_i)$, in which $\mathbf{G}$ is the global symmetry of the molecule and $\mathbf{G}_i$ denotes the local symmetry governing each ligand.[11] In this section, we briefly discuss ligands and local symmetry to obtain a minimum set of mathematical concepts.

When $\mathbf{G}_i$ is a subgroup of $\mathbf{G}$, we have a coset decomposition,

$$\mathbf{G} = \mathbf{G}_i t_1 + \cdots + \mathbf{G}_i t_r, \qquad (1)$$

where $t_1 = I$. This decomposition provides a permutation representation of $\mathbf{G}$, which is called a coset representation (CR). We use the symbol $\mathbf{G}(/\mathbf{G}_i)$ to denote the CR. The CR $\mathbf{G}(/\mathbf{G}_i)$ acts on the set of cosets represented by

$$\mathbf{G}/\mathbf{G}_i = \{\mathbf{G}_i t_1, \cdots, \mathbf{G}_i t_r\}. \qquad (2)$$

Since we have

$$\mathbf{G}_i t_k (t_k^{-1} \mathbf{G}_i t_k) = \mathbf{G}_i \mathbf{G}_i t_k = \mathbf{G}_i t_k,$$

we obtain the following theorem.

Theorem 2. *The stabilizer of* $\mathbf{G}_i t_k$ *is* $t_k^{-1} \mathbf{G}_i t_k$.

If $\mathbf{G}_i$ and $t_k^{-1}\mathbf{G}_i t_k$ is conjugate within $\mathbf{G}$, then the corresponding CRs ($\mathbf{G}(/\mathbf{G}_i)$ and $\mathbf{G}(/t_k^{-1}\mathbf{G}_i t_k)$) are equivalent,i.e.,

$$\mathbf{G}(/\mathbf{G}_i) \cong \mathbf{G}(/t_k^{-1}\mathbf{G}_i t_k). \qquad (3)$$

When an orbit corresponds to the CR $\mathbf{G}(/\mathbf{G}_i)$, we call the orbit a $\mathbf{G}(/\mathbf{G}_i)$ orbit. If we consider a three-dimensional object Ω_1 of $\mathbf{G}_i$ symmetry, we can provide other objects according to $t_k\Omega_1=\Omega_k$ (k=1,2,$\cdots$,r). The set of the r objects, i.e.

$$\boldsymbol{\Omega} = \{\Omega_1,\Omega_2,\cdots,\Omega_r\}$$

is subject to the coset representation $\mathbf{G}(/\mathbf{G}_i)$, when Ω_k corresponds to $\mathbf{G}_i t_k$ in one-to-one fashion. We have reported the correspondence in the light of a regular body.11) This $\mathbf{G}_i$ of $\mathbf{G}(/\mathbf{G}_i)$ is called the local symmetry that governs each member (block) of $\boldsymbol{\Omega}$.8) Because the Ω_1 belongs to $\mathbf{G}_i$ symmetry, we have

$$g\Omega_1 = \Omega_1 \text{ (for } \forall g\in \mathbf{G}_i). \qquad (4)$$

This equation affords

$$t_k g t_k^{-1}\Omega_k = t_k g t_k^{-1} t_k \Omega_1 = t_k g \Omega_1 = t_k\Omega_1 = \Omega_k \qquad (5)$$

for $\forall g\in\mathbf{G}_i$ and k=1,2,$\cdots$,r. Hence, we have the following theorem.

Theorem 3. *Each* $\mathbf{G}_i$*-block* Ω_k*(*k*=1,2,*$\cdots$*,*r*) has stabilizer* $t_k\mathbf{G}_i t_k^{-1}$.

For emphasizing a chemical meaning, we also use the term $\mathbf{G}_i$-ligand in place of the $\mathbf{G}_i$-block. The stabilizer denotes the point group that corresponds to the local symmetry specifying the ligand.

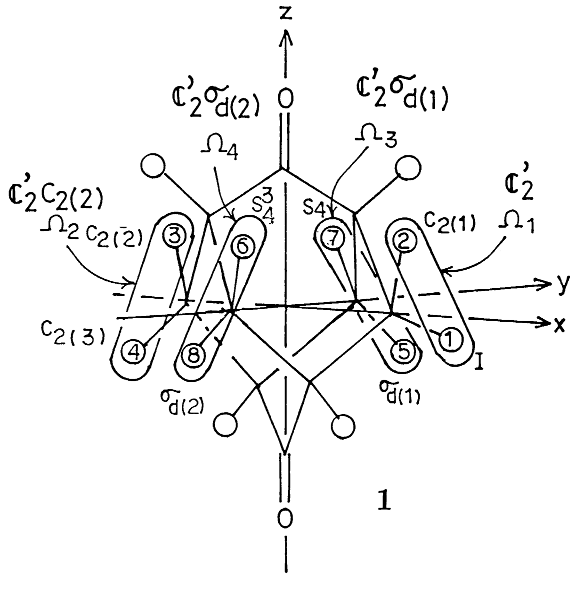

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Fig. 1. $\mathbf{C}'_2$-blocks in adamantane-2,6-dione.

Eample **1.** In order to illustrate Theorem 3, let us examine $\mathbf{C}'_2$-blocks in adamantane-2,6-dione (**1**). This molecule belongs to the $\mathbf{D}_{2d}$ group, which is composed of 8 elements (symmetry operations), i.e.,

$$\mathbf{D}_{2d} = \{I,C_{2(1)},C_{2(2)},C_{2(3)},\sigma_{d(1)},S_4^3,S_4,\sigma_{d(2)}\}.$$

Consider the 8 methylene hydrogens in **1** (Fig. 1). We first assign hydrogen no. 1 to the I element. Then, hydrogen no. 2 is assigned to the $C_{2(1)}$ operation, since the action of $C_{2(1)}$ on the hydrogen no. 1 produces the hydrogen no. 2. This treatment is repeated over all of the elements of the $\mathbf{D}_{2d}$ group. As the result, we obtain the following correspondence; $1\leftrightarrow I$, $2\leftrightarrow C_{2(1)}$, $3\leftrightarrow C_{2(2)}$, $4\leftrightarrow C_{2(3)}$, $5\leftrightarrow \sigma_{d(1)}$, $6\leftrightarrow S_4^3$, $7\leftrightarrow S_4$, and $8\leftrightarrow \sigma_{d(2)}$. Let us next consider each methylene. Starting from the above results, we obtain the following correspondence;

$$\Omega_1 = \{1,2\} \leftrightarrow \mathbf{C}'_2 = \{I,C_{2(1)}\}$$

$$\Omega_2 = C_{2(2)}\Omega_1 = \{3,4\} \leftrightarrow \mathbf{C}'_2C_{2(2)} = \{C_{2(2)},C_{2(3)}\}$$

$$\Omega_3 = \sigma_{d(1)}\Omega_1 = \{5,7\} \leftrightarrow \mathbf{C}'_2\sigma_{d(1)} = \{\sigma_{d(1)},S_4\}$$

$$\Omega_4 = \sigma_{d(2)}\Omega_1 = \{6,8\} \leftrightarrow \mathbf{C}'_2\sigma_{d(2)} = \{\sigma_{d(2)},S_4^3\}$$

This correspondence is associated with the coset decomposition,

$$\mathbf{D}_{2d} = \mathbf{C}'_2 + \mathbf{C}'_2C_{2(2)} + \mathbf{C}'_2\sigma_{d(1)} + \mathbf{C}'_2\sigma_{d(2)}. \qquad (6)$$

According to this equation, the coset representation $\mathbf{D}_{2d}(/\mathbf{C}'_2)$ governs

$$\mathbf{D}_{2d}/\mathbf{C}'_2 = \{\mathbf{C}'_2,\mathbf{C}'_2C_{2(2)},\mathbf{C}'_2\sigma_{d(1)},\mathbf{C}'_2\sigma_{d(2)}\}.$$

as well as

$$\boldsymbol{\Omega} = \{\Omega_1,\Omega_2,\Omega_3,\Omega_4\}.$$

We have four $\mathbf{C}'_2$-blocks (Ω_1 to Ω_4), the stabilizers of which are obtained by means of Theorem 3. These results are consistent with their chemical meanings.

Methylene	Stabilizer
Ω_1	$\mathbf{C}'_2=\{I,\ C_{2(1)}\}$
Ω_2	$C_{2(2)}\mathbf{C}'_2C_{2(2)}^{-1}=\mathbf{C}'_2=\{I,\ C_{2(1)}\}$
Ω_3	$\sigma_{d(1)}\mathbf{C}'_2\sigma_{d(1)}^{-1}=\mathbf{C}''_2=\{I,\ C_{2(2)}\}$
Ω_4	$\sigma_{d(2)}\mathbf{C}'_2\sigma_{d(2)}^{-1}=\mathbf{C}''_2=\{I,\ C_{2(2)}\}$

Desymmetrization of Enantiospheric Orbits. When $\mathbf{G}$ is an achiral group and $\mathbf{G}_i$ is its chiral subgroup, the $\mathbf{G}(/\mathbf{G}_i)$ orbit is defined as an *enantiospheric* orbit.8) The purpose of this section is to examine the desymmetrization corresponding to the subduction $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max}$, where $\mathbf{G}^{\max}$ is the subgroup that contains all of the proper rotations of $\mathbf{G}$. Although a general discussion on the subduction of coest representations has appeared in our previous papers,[10] the present section provides a more specified discussions concerning enantiospheric orbits.

The corresponding coset decomposition (Eq. 1) contains a transversal $\{t_1,t_2,\cdots,t_r\}$, in which $r/2$ elements are proper rotations and the remaining $r/2$ elements are improper rotations. When we designate the latter half by the symbol $u_k (k=1,2,\cdots,r/2)$, we are able to rewrite the coset decomposition as follows.

$$\mathbf{G} = (\mathbf{G}_it_1 + \mathbf{G}_it_2 + \cdots + \mathbf{G}_it_k + \cdots + \mathbf{G}_it_q)$$
$$+ (\mathbf{G}_iu_1 + \mathbf{G}_iu_2 + \cdots + \mathbf{G}_iu_k + \cdots + \mathbf{G}_iu_q), \tag{7}$$

where $q=r/2$ and $u_k=t_ku_1$. Note that u_1 can be an arbitrary improper rotation during the discussion in this section. The $\mathbf{G}/\mathbf{G}_i$ set is divided into two parts,

$$\mathbf{G}^+/\mathbf{G}_i = \{\mathbf{G}_it_1,\mathbf{G}_it_2,\cdots,\mathbf{G}_it_q\}, \tag{8}$$

and

$$\mathbf{G}^-/\mathbf{G}_i = \{\mathbf{G}_iu_1,\mathbf{G}_iu_2,\cdots,\mathbf{G}_iu_q\}. \tag{9}$$

Obviously, each coset in $\mathbf{G}^+/\mathbf{G}_i$ contains proper rotation and $\mathbf{G}^-/\mathbf{G}_i$ is concerned with improper rotations. Because we have $\mathbf{G}_it_kt_l \in \mathbf{G}^+/\mathbf{G}_i$, $\mathbf{G}_it_ku_l \in \mathbf{G}^-/\mathbf{G}_i$, $\mathbf{G}_iu_kt_l \in \mathbf{G}^-/\mathbf{G}_i$ and $\mathbf{G}_iu_ku_l \in \mathbf{G}^+/\mathbf{G}_i$, the two parts, $\mathbf{G}^+/\mathbf{G}_i$ and $\mathbf{G}^-/\mathbf{G}_i$, are mirror images to each other.

Since $\mathbf{G}^{\max}$ is the subgroup that contains all of the proper rotations of $\mathbf{G}$, we have a coset representation by using $\{t_1,t_2,\cdots,t_q\}$, i.e.,

$$\mathbf{G}^{\max} = \mathbf{G}_it_1 + \mathbf{G}_it_2 + \cdots + \mathbf{G}_it_q, \tag{10}$$

because $\mathbf{G}_i$ is also a subgroup of $\mathbf{G}^{\max}$. Obviously, the subgroup $\mathbf{G}^{\max}$ is a normal subgroup of $\mathbf{G}$, where $|\mathbf{G}^{\max}|=|\mathbf{G}|/2$.

Since any coset ($\mathbf{G}^{\max}u_k$) contains all of the improper rotations ($k=1,2,\cdots,q$), we can select u_1 as a representative without losing generality. Thereby, we have

$$\mathbf{G} = \mathbf{G}^{\max} + \mathbf{G}^{\max}u_1. \tag{11}$$

When Eq. 10 is introduced into Eq. 11, we have $u_k=t_ku_1 (k=1,2,\cdots,q)$.

We rewrite the notation of Ω_k as follows: $\Omega_k^+=\Omega_k$ ($1\leqslant k\leqslant q$) and $\Omega_k^-=\Omega_{q+k}$ ($1\leqslant k\leqslant q$). Thereby, Ω is divided into two subsets,i.e.,

$$\boldsymbol{\Omega}^+ = \{\Omega_1^+,\Omega_2^+,\cdots,\Omega_q^+\}, \tag{12}$$

$$\boldsymbol{\Omega}^- = \{\Omega_1^-,\Omega_2^-,\cdots,\Omega_q^-\}, \tag{13}$$

We have the following correspondences, $\boldsymbol{\Omega}_k^+ \leftrightarrow \Omega_it_k$ and $\boldsymbol{\Omega}_k^- \leftrightarrow \Omega_iu_k$, where $k=1,2,\cdots,q$. Obviously, $\boldsymbol{\Omega}^+$ and $\boldsymbol{\Omega}^-$ are mirror images to each other under the action of the $\mathbf{G}$ group. As for Example 1 (Fig. 1), we construct $\boldsymbol{\Omega}^+=\{\Omega_1,\Omega_2\}$ and $\boldsymbol{\Omega}^-=\{\Omega_3,\Omega_4\}$, which are the mirror images to each other. The two sets coincide with each other under the action of the improper rotations of $\mathbf{D}_{2d}$, but not under the action of the proper rotations of $\mathbf{D}_{2d}$.

Since Theorem 3 holds for any $\boldsymbol{\Omega}_k^-$, $u_k\mathbf{G}_iu_k^{-1}$ is the stabilzer of the $\boldsymbol{\Omega}_k^-$. Consider $u_l \in \mathbf{G}_iu_l$. Since u_l and u_k are improper rotations (i.e., $u_l,u_k\mathbf{G}^{\max}u_1$), Eq. 11 indicates that there exists a proper rotation (t_k) that satisfies $t_k=u_ku_l^{-1} \in \mathbf{G}^{\max}$. Hence, we have $u_k=t_ku_l$. It follows that

$$u_k\mathbf{G}_iu_k^{-1} = t_ku_l\mathbf{G}_i(t_ku_l)^{-1} = t_k(u_l\mathbf{G}_iu_l^{-1})t_k^{-1} \tag{14}$$

Here, we consider two cases:

Case (a) there exists an improper rotation (u_l) that satisfies $u_l\mathbf{G}_iu_l^{-1}=\mathbf{G}_i$ (i.e. $u_l\mathbf{G}_i=\mathbf{G}_iu_l$) and

Case (b) there exists no improper rotation (u_l) that satisfies $u_l\mathbf{G}_iu_l^{-1}\mathbf{G}_i$ (i.e., $u_l\mathbf{G}_i\neq\mathbf{G}_iu_l$ for $\forall u_l \in \mathbf{G}^{\max}u_1$).

In Case (a), Eq. 14 is further converted into

$$u_k\mathbf{G}_iu_k^{-1} = t_k(u_l\mathbf{G}_iu_l^{-1})t_k^{-1} = t_k\mathbf{G}_it_k^{-1}\cdot$$

This equation means that the stabilizer of Ω_k^- is $t_k\mathbf{G}_it_k^{-1}$, which is identical with that of Ω_k^+. Because the stabilizer $t_k\mathbf{G}_it_k^{-1}$ is a chiral subgroup of $\mathbf{G}$, it is also a subgroup of $\mathbf{G}^{\max}$. Hence, all of the $t_k\mathbf{G}_it_k^{-1}$'s are conjugate to $\mathbf{G}_i$ under the action of $\mathbf{G}^{\max}$ as well as that of $\mathbf{G}$. Then, we have

$$\mathbf{G}^{\max}(/u_k\mathbf{G}_iu_k^{-1}) \cong \mathbf{G}^{\max}(/t_k\mathbf{G}_it_k^{-1}) \cong \mathbf{G}^{\max}(/\mathbf{G}_i) \text{ for } \boldsymbol{\Omega}^+$$

and

$$\mathbf{G}^{\max}(/t_k\mathbf{G}_it_k^{-1}) \cong \mathbf{G}^{\max}(/\mathbf{G}_i) \text{ for } \boldsymbol{\Omega}^-$$

for $k=1,2,\cdots,q$. It follows that the subduction $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max}$ produces two $\mathbf{G}^{\max}(/\mathbf{G}_i)$ orbits (i.e. $\boldsymbol{\Omega}^+$ and $\boldsymbol{\Omega}^-$ as $\mathbf{G}^{\max}$-sets).

In case (b), $\mathbf{G}_i$ is not conjugate to any $u_l\mathbf{G}_iu_l^{-1}$ within $\mathbf{G}^{\max}$. Equation 14 indicates that $u_k\mathbf{G}_iu_k^{-1}$ ($k=1,2,\cdots,q$) is conjugate to $u_l\mathbf{G}_iu_l^{-1}$ within $\mathbf{G}^{\max}$. Obviously, $t_k\mathbf{G}_it_k^{-1}$ ($k=1,2,\cdots,q$) is conjugate to $\mathbf{G}_i$ within $\mathbf{G}^{\max}$. These facts mean that $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max}$ produces two orbits according to the following equation,

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max} = \mathbf{G}^{\max}(/\mathbf{G}_i)+\mathbf{G}^{\max}(/\mathbf{G}_i'),$$

where $\mathbf{G}_i'=u_l\mathbf{G}_iu_l^{-1}$. As a result, $\boldsymbol{\Omega}^+$ and $\boldsymbol{\Omega}^-$ are governed by $\mathbf{G}^{\max}(/\mathbf{G}_i)$ and $\mathbf{G}^{\max}(/\mathbf{G}_i')$, respectively. The above discussions are summarized as follows.

Theorem 4. *Let* $\mathbf{G}$ *be an achiral point group. Consider an enantiospheric orbit governed by* $\mathbf{G}(/\mathbf{G}_i)$, *where* $\mathbf{G}_i$ is a chiral subgroup of $\mathbf{G}$. *Let* $\mathbf{G}^{\max}$ *be a maximal chiral subgroup of* $\mathbf{G}$. *Then, there are two possibilities.*

$$\text{Case (a): } \mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max} = 2\mathbf{G}^{\max}(/\mathbf{G}_i) \tag{15}$$

$$\text{Case (b): } \mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max} = \mathbf{G}^{\max}(/\mathbf{G}_i)+\mathbf{G}^{\max}(/\mathbf{G}_i'), \tag{16}$$

Table 1. Subduction of Coset Representations for $\mathbf{D}_{2d}$ Point Group

	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_2'$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{S}_4$	$\downarrow\mathbf{C}_{2v}$	$\downarrow\mathbf{D}_2$	$\downarrow\mathbf{D}_{2d}$
$\mathbf{D}_{2d}(/\mathbf{C}_1)$	$8\mathbf{C}_1(/\mathbf{C}_1)$	$4\mathbf{C}_2(/\mathbf{C}_1)$	$4\mathbf{C}_2'(/\mathbf{C}_1)$	$4\mathbf{C}_s(/\mathbf{C}_1)$	$2\mathbf{S}_4(/\mathbf{C}_1)$	$2\mathbf{C}_{2v}(/\mathbf{C}_1)$	$2\mathbf{D}_2(/\mathbf{C}_1)$	$\mathbf{D}_{2d}(/\mathbf{C}_1)$
$\mathbf{D}_{2d}(/\mathbf{C}_2)^{a)}$	$4\mathbf{C}_1(/\mathbf{C}_1)$	$4\mathbf{C}_2(/\mathbf{C}_2)$	$2\mathbf{C}_2'(/\mathbf{C}_1)$	$2\mathbf{C}_s(/\mathbf{C}_1)$	$2\mathbf{S}_4(/\mathbf{C}_2)$	$2\mathbf{C}_{2v}(/\mathbf{C}_2)$	$2\mathbf{D}_2(/\mathbf{C}_2)$	$\mathbf{D}_{2d}(/\mathbf{C}_2)$
$\mathbf{D}_{2d}(/\mathbf{C}_2')$	$4\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_1)$	$\mathbf{C}_2'(/\mathbf{C}_1)+2\mathbf{C}_2'(/\mathbf{C}_2)$	$2\mathbf{C}_s(/\mathbf{C}_1)$	$\mathbf{S}_4(/\mathbf{C}_1)$	$\mathbf{C}_{2v}(/\mathbf{C}_1)$	$\mathbf{D}_2(/\mathbf{C}_2')+\mathbf{D}_2(/\mathbf{C}_2'')$	$\mathbf{D}_{2d}(/\mathbf{C}_2')$
$\mathbf{D}_{2d}(/\mathbf{C}_s)$	$4\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_1)$	$2\mathbf{C}_2'(/\mathbf{C}_1)$	$\mathbf{C}_s(/\mathbf{C}_1)+2\mathbf{C}_s(/\mathbf{C}_s)$	$\mathbf{S}_4(/\mathbf{C}_1)$	$\mathbf{C}_{2v}(/\mathbf{C}_s)+\mathbf{C}_{2v}(/\mathbf{C}_s')$	$\mathbf{D}_2(/\mathbf{C}_1)$	$\mathbf{D}_{2d}(/\mathbf{C}_s)$
$\mathbf{D}_{2d}(/\mathbf{S}_4)^{a)}$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_2)$	$\mathbf{C}_2'(/\mathbf{C}_1)$	$\mathbf{C}_s(/\mathbf{C}_1)$	$2\mathbf{S}_4(/\mathbf{S}_4)$	$\mathbf{C}_{2v}(/\mathbf{C}_2)$	$\mathbf{D}_2(/\mathbf{C}_2)$	$\mathbf{D}_{2d}(/\mathbf{S}_4)$
$\mathbf{D}_{2d}(/\mathbf{C}_{2v})$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_2)$	$\mathbf{C}_2'(/\mathbf{C}_1)$	$2\mathbf{C}_s(/\mathbf{C}_s)$	$\mathbf{S}_4(/\mathbf{C}_2)$	$2\mathbf{C}_{2v}(/\mathbf{C}_{2v})$	$\mathbf{D}_2(/\mathbf{C}_2)$	$\mathbf{D}_{2d}(/\mathbf{C}_{2v})$
$\mathbf{D}_{2d}(/\mathbf{D}_2)^{a)}$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_2)$	$2\mathbf{C}_2'(/\mathbf{C}_2)$	$\mathbf{C}_s(/\mathbf{C}_1)$	$\mathbf{S}_4(/\mathbf{C}_2)$	$\mathbf{C}_{2v}(/\mathbf{C}_2)$	$2\mathbf{D}_2(/\mathbf{D}_2)$	$\mathbf{D}_{2d}(/\mathbf{D}_2)$
$\mathbf{D}_{2d}(/\mathbf{D}_{2d})$	$\mathbf{C}_1(/\mathbf{C}_1)$	$\mathbf{C}_2(/\mathbf{C}_2)$	$\mathbf{C}_2'(/\mathbf{C}_2)$	$\mathbf{C}_s(/\mathbf{C}_s)$	$\mathbf{S}_4(/\mathbf{S}_4)$	$\mathbf{C}_{2v}(/\mathbf{C}_{2v})$	$\mathbf{D}_2(/\mathbf{D}_2)$	$\mathbf{D}_{2d}(/\mathbf{D}_{2d})$

a) Forbidden CR.

where $\mathbf{G}_i$ *and* $\mathbf{G}_i'$ *are conjugate in* $\mathbf{G}$ *but not conjugate in* $\mathbf{G}^{\max}$ This thorem is the basis of Theorem 1, since it indicates that the enantiospheric $\mathbf{G}(/\mathbf{G}_i)$ orbit behaves differently under $\mathbf{G}$ and $\mathbf{G}^{\max}$.

Table 1 is a subduction table for $\mathbf{D}_{2d}$ group, which lists all of the subductions concerning the $\mathbf{D}_{2d}$ group by its subgroups. From the data of this table, we select the following examples that illustrate the two possibilities described in Theorem 4.

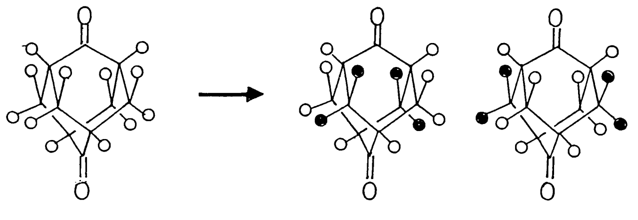
Example **2.** Let us consider $\mathbf{D}_{2d}(/\mathbf{C}_1)\downarrow\mathbf{D}_2$. Since the $\mathbf{D}_{2d}(/\mathbf{C}_1)$ is a regular representation, each coset consists of each symmetry operation of $\mathbf{D}_{2d}$. All of the eight cosets (symmetry operations) are commutable with $\mathbf{C}_1$; hence, this case is an example of Case (a). We obtain

$$\mathbf{D}_{2d}(/\mathbf{C}_1)\downarrow\mathbf{D}_2 = 2\mathbf{D}_2(/\mathbf{C}_1). \tag{17}$$

This equation exemplifies Theorem 4.

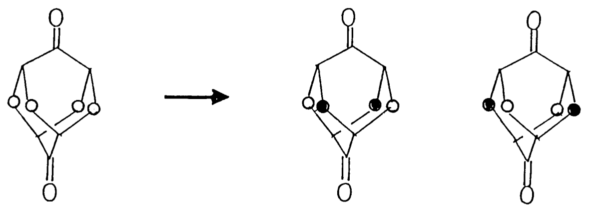
In order to illustrate the chemical meaning of this equation, let us consider derivation of adamantane-2,6-dione (**1**). The 8 methylene hydrogen atoms (○) are taken into consideration (Fig. 2). A replacement of four hydrogen atoms (○) with other atoms (●) produces a $\mathbf{D}_2$-molecule (**2a**), in which ○'s and ●'s construct $\mathbf{D}_2(/\mathbf{C}_1)$ orbits (Fig. 2). This is an example of case (a), which is algebraically represented by Eq. 17. If ○ and ● are interchanged, the resulting molecule (**2b**) is enantiomeric to **2a**.

Example **3.** Let us examine $\mathbf{D}_{2d}(/\mathbf{C}_2')\downarrow\mathbf{D}_2$(See Example 1). We have obtained the coset decomposition represented by Eq. 6. Since we have $\mathbf{C}_2'\ \sigma_{d(1)}\neq\sigma_{d(1)}\mathbf{C}_2'$ and $\mathbf{C}_2'\ \sigma_{d(2)}\neq\sigma_{d(2)}\mathbf{C}_2'$, Theorem 4 indicates that this is an



1 D_{2d} 2a 2b

D_2



3 D_{2d} 4a 4b

D_2

Fig. 2. $\mathbf{D}_2$ molecules derived from a $\mathbf{D}_{2d}$ molecule.

example of Case (b). In fact, we obtain

$$\mathbf{D}_{2d}(/\mathbf{C}'_2)\downarrow\mathbf{D}_2 = \mathbf{D}_2(/\mathbf{C}'_2) + \mathbf{D}_2(/\mathbf{C}''_2), \tag{18}$$

as shown in the intersection between the $\mathbf{D}_2(/\mathbf{C}'_2)$-row and the the $\downarrow\mathbf{D}_2$-column (Table 1).

Chemically speaking, this equation corresponds to such a conversion as the desymmetrization of **3** into **4a** (or **4b**). The four methylene carbons of **3** construct an orbit governed by $\mathbf{D}_{2d}(/\mathbf{C}'_2)$. This orbit is divided into a $\mathbf{D}_2(/\mathbf{C}'_2)$ orbit and $\mathbf{D}_2(/\mathbf{C}''_2)$ orbit in each of the desymmetrized compounds (**4a** and **4b**).

Example **4**. Let us consider $\mathbf{S}_8(/\mathbf{C}_2)\downarrow\mathbf{C}_4$. We have the following coset decomposition,

$$\mathbf{S}_8 = \mathbf{C}_2 + \mathbf{C}_2\mathbf{C}_4 + \mathbf{C}_2 S_8 + \mathbf{C}_2 S_8^3. \tag{19}$$

Among the four cosets, the $\mathbf{C}_2 S_8$ satisfies the relationship, $\mathbf{C}_2 S_8 = S_8\mathbf{C}_2$; hence, this case is an example of Case (a). We obtain

$$\mathbf{S}_8(/\mathbf{C}_2)\downarrow\mathbf{C}_4 = 2\mathbf{C}_4(/\mathbf{C}_2). \tag{20}$$

This equation exemplifies Theorem 4. Consider $\mathbf{A} = \mathbf{C}_2 + \mathbf{C}_2 S_8$. This set is not a group as shown later. Note that $S_8 S_8 \in \mathbf{C}_2 C_4 (S_8 S_8 \notin \mathbf{C}_2)$.

Further Desymmetrization of Enantiospheric Orbits. For Case (a) of Theorem 4, consider the subduced representation (SR) $\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, where $\mathbf{G}_j$ is a subgroup of $\mathbf{G}^{\max}$. Suppose that we obtain the following equation

$$\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} \gamma_k^{(ij)}\mathbf{G}_j(/\mathbf{G}_k^{(j)}), \tag{21}$$

where the multiplicities ($\gamma_k^{(ij)}$'s) are non-negative integers.$^{10)}$ Since both $\mathbf{G}_i$ and $\mathbf{G}_j$ are subgroups of $\mathbf{G}$ as well as those of $\mathbf{G}^{\max}$, Eqs. 15 and 21 afford the following theorem. Note that $(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max})\downarrow\mathbf{G}_j = \mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$.

Theorem 5, *Supose that an enantiospheric orbit follows Case (a) of Theorem 4. Then, any chiral subduction,* $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, *is represented by*

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} (2\gamma_k^{(ij)})\mathbf{G}_j(/\mathbf{G}_k^{(j)}), \tag{22}$$

wherein $\mathbf{G}$ *contains proper and improper rotations; and its subgroups,* $\mathbf{G}_i$ *and* $\mathbf{G}_j$, *consist of proper rotations only.*

As a result, any $\mathbf{G}_k^{(j)}$ is a proper rotation and any $\mathbf{G}_j(/\mathbf{G}_k^{(j)})$ represents a hemispheric orbit.

This theorem is exemplified by the following examples, which are selected from the data of Tables 1 and 2.

Example **5.** We take the equations,

$$\mathbf{D}_2(/\mathbf{C}_1)\downarrow\mathbf{C}_2 = 2\mathbf{C}_2(/\mathbf{C}_1) \text{ and}$$

$$\mathbf{D}_2(/\mathbf{C}_1)\downarrow\mathbf{C}'_2 = 2\mathbf{C}'_2(/\mathbf{C}_1),$$

from Table 2. When we introduce these equations into Eq. 17, we have

$$\mathbf{D}_{2d}(/\mathbf{C}_1)\downarrow\mathbf{C}_2 = 4\mathbf{C}_2(/\mathbf{C}_1) \text{ and}$$

$$\mathbf{D}_{2d}(/\mathbf{C}_1)\downarrow\mathbf{C}'_2 = 4\mathbf{C}'_2(/\mathbf{C}_1).$$

As for Case (b) of Theorem 4, consider the SR $\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ where $\mathbf{G}_j$ is a subgroup of $\mathbf{G}^{\max}$. Then, we obtain following equations.

$$\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} \gamma_k^{(ij)}\mathbf{G}_j(/\mathbf{G}_k^{(j)}), \tag{23}$$

$$\mathbf{G}^{\max}(/\mathbf{G}'_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} \delta_k^{(ij)}\mathbf{G}_j(/\mathbf{G}_k^{(j)}), \tag{24}$$

where the multiplicities ($\gamma_k^{(ij)}$'s and $\delta_k^{(ij)}$'s) are non-negative integers. Since $\mathbf{G}_i$, $\mathbf{G}'_i$ and $\mathbf{G}_j$ are subgroups of $\mathbf{G}$ and of $\mathbf{G}^{\max}$, Eqs. 23 and 24 are combined with Eq. 15 to afford the following theorem.

Theorem 6. *Suppose that an enantiospheric orbit follows Case (b) of Theorem 4. Then, any chiral subduction,* $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, *is represented by*

$$\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} (\gamma_k^{(ij)} + \delta_k^{(ij)})\mathbf{G}_j(/\mathbf{G}_k^{(j)}), \tag{25}$$

wherein $\mathbf{G}$ *contains proper and improper rotations; and its subgroups,* $\mathbf{G}_i$ *and* $\mathbf{G}_j$, *consist of proper rotations only.*

As a result, any $\mathbf{G}_k^{(j)}$ is a proper rotation and any $\mathbf{G}_j(/\mathbf{G}_k^{(j)})$ represents a hemispheric orbit.

Theorem 6 is verified as follows.

Example **6.** When we introduce

$$\mathbf{D}_2(/\mathbf{C}'_2)\downarrow\mathbf{C}_2 = \mathbf{C}_2(/\mathbf{C}_1) \text{ and}$$

$$\mathbf{D}_2(/\mathbf{C}''_2)\downarrow\mathbf{C}_2 = \mathbf{C}_2(/\mathbf{C}_1)$$

Table 2. Subduction Table of $\mathbf{D}_2$ Group

	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}'_2$	$\downarrow\mathbf{C}''_2$	$\downarrow\mathbf{D}_2$
$\mathbf{D}_2(/\mathbf{C}_1)$	$4\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_1)$	$2\mathbf{C}'_2(/\mathbf{C}_1)$	$2\mathbf{C}''_2(/\mathbf{C}_1)$	$\mathbf{D}_2(/\mathbf{C}_1)$
$\mathbf{D}_2(/\mathbf{C}_2)$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$2\mathbf{C}_2(/\mathbf{C}_2)$	$\mathbf{C}'_2(/\mathbf{C}_1)$	$\mathbf{C}''_2(/\mathbf{C}_1)$	$\mathbf{D}_2(/\mathbf{C}_2)$
$\mathbf{D}_2(/\mathbf{C}'_2)$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$\mathbf{C}_2(/\mathbf{C}_1)$	$2\mathbf{C}'_2(/\mathbf{C}_2)$	$\mathbf{C}''_2(/\mathbf{C}_1)$	$\mathbf{D}_2(/\mathbf{C}'_2)$
$\mathbf{D}_2(/\mathbf{C}''_2)$	$2\mathbf{C}_1(/\mathbf{C}_1)$	$\mathbf{C}_2(/\mathbf{C}_1)$	$\mathbf{C}'_2(/\mathbf{C}_1)$	$2\mathbf{C}''_2(/\mathbf{C}_2)$	$\mathbf{D}_2(/\mathbf{C}''_2)$
$\mathbf{D}_2(/\mathbf{D}_2)$	$\mathbf{C}_1(/\mathbf{C}_1)$	$\mathbf{C}_2(/\mathbf{C}_2)$	$\mathbf{C}'_2(/\mathbf{C}_2)$	$\mathbf{C}''_2(/\mathbf{C}_2)$	$\mathbf{D}_2(/\mathbf{D}_2)$

into Eq. 18, we have

$$\mathbf{D}_{2d}(/\mathbf{C}_2')\downarrow\mathbf{C}_2 = 2\mathbf{C}_2(/\mathbf{C}_1).$$

This result is identical with the equation listed in the intersection between $\mathbf{D}_{2d}(/\mathbf{C}_2')$-row and $\downarrow\mathbf{D}_2$-column of Table 1. This example produces a result similar to Theorem 5, though the process is different. A more typical example is as follows. Since we have

$$\mathbf{D}_2(/\mathbf{C}_2')\downarrow\mathbf{C}_2 = 2\mathbf{C}_2'(/\mathbf{C}_2) \text{ and}$$

$$\mathbf{D}_2(/\mathbf{C}_2'')\downarrow\mathbf{C}_2 = \mathbf{C}_2'(/\mathbf{C}_1)$$

in Table 2, we introduce these equations into Eq. 18 to obtain

$$\mathbf{D}_{2d}(/\mathbf{C}_2')\downarrow\mathbf{C}_2' = 2\mathbf{C}_2'(/\mathbf{C}_2) + \mathbf{C}_2'(/\mathbf{C}_1).$$

Example 7. For illustrating Theorem 6, let us examine an enantiospheric orbit ($\mathbf{T}_h(/\mathbf{C}_3)$) appearing in the compound (**5**) of $\mathbf{T}_h$ symmetry. The subduction of this orbit into **T** is represented by

$$\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{T} = 2\mathbf{T}(/\mathbf{C}_3). \quad (26)$$

This subduction is realized by compounds **6a** and **6b**, which belong to **T** symmetry (Fig. 3). These compounds are enantiomeric to each other. The occupation of the orbit is changed from $\mathbf{T}_h(/\mathbf{C}_3(A_8)]$ to $\mathbf{T}[/\mathbf{C}_3(A_4, B_4)]$.[12]

The subduction of the orbit into $\mathbf{C}_2$ is represented by

$$\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{C}_2 = 4\mathbf{C}_2(/\mathbf{C}_1). \quad (27)$$

This equation is obtained according to Theorem 6 by introducting

$$\mathbf{T}(/\mathbf{C}_3)\downarrow\mathbf{C}_2 = 2\mathbf{C}_2(/\mathbf{C}_1)$$

into Eq. 26.

The chemical meaning of Eq. 27 is illustrated as follows. If we replace appropriate A_2 with B_2 according to this subduction, there appear **7a** and **7b** (Fig. 4). The resulting packing of the divided orbit is expressed by $\mathbf{C}_2[/\mathbf{C}_1(3A_2, B_2)]$.[12]

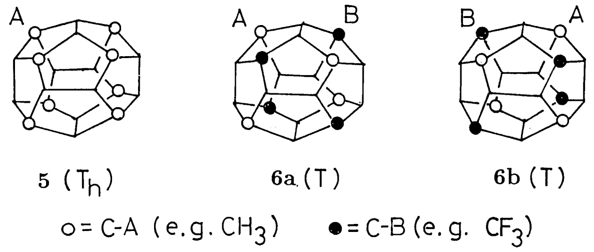
On the other hand, we introduce the equation,

$$\mathbf{T}(/\mathbf{C}_3)\downarrow\mathbf{C}_3 = \mathbf{C}_3(/\mathbf{C}_1) + \mathbf{C}_3(/\mathbf{C}_3), \quad (28)$$

into Eq. 26. Thereby, we obtain

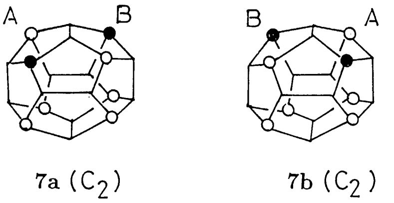
$$\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{C}_3 = 2\mathbf{C}_3(/\mathbf{C}_1) + 2\mathbf{C}_3(/\mathbf{C}_3). \quad (29)$$

Figure 5 shows examples of the subduction into $\mathbf{C}_3$. The hemispheric orbits in the products (**8a** and **8b**) are filled in a way of $\mathbf{C}_3[/\mathbf{C}_1(2A_3), /\mathbf{C}_3(A,B)]$, which is in agreement with Eq. 29.



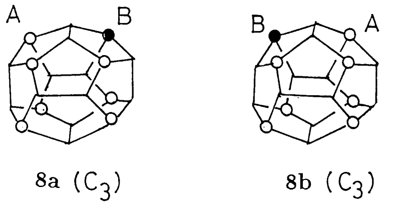
5 (T_h) 6a (T) 6b (T)

Fig. 3. **T** molecules derived from a $\mathbf{T}_h$ molecule.



7a (C_2) 7b (C_2)

Fig. 4. $\mathbf{C}_2$ molecules derived from a $\mathbf{T}_h$ molecule.



8a (C_3) 8b (C_3)

Fig. 5. $\mathbf{C}_3$ molecules derived from a $\mathbf{T}_h$ molecule.

Chirogenic Sites in Direct Chiral Synthesis. We are able to differentiate the two halves (Ω^+ and Ω^-) of an enantiospheric $\mathbf{G}(/\mathbf{G}_i)$ orbit (Ω) under chiral environment. Thereby, we obtain either one of enantiomeric $\mathbf{G}^{\max}$-molecules. If we differentiate an appropriate part of the one half from the corresponding mirror image contained in the other half, we can obtain a chiral molecule. However, it is a problem to determine which subsymmetry is realized in this operation. This section deals with this problem. If the differentiation of the parts produces a chiral **H**-molecule, we call the part an **H**-*chirogenic site*. Each chirogenic site is always accompanied with the mirror image counterpart.

To begin with, we examine two extreme cases. The discussions in the preceding section afford the following theorem.

Theorem 7. *Each of the two halves of a* $\mathbf{G}(/\mathbf{G}_i)$ *orbit is a* $\mathbf{G}^{\max}$*-chirogenic site.*

When $\mathbf{G}_1 = \mathbf{C}_1 = \{I\}$, the corresponding $\mathbf{G}(/\mathbf{G}_1)$ is a regular representation of **G**. In this case, we have a simple result as follows.

Theorem 8. *An orbit governed by the regular representation* $\mathbf{G}(/\mathbf{G}_1)$ *has a chirogenic site that corresponds every subgroup.*

Proof. When $\mathbf{G}_1=\mathbf{C}_1$, we have

$$\mathbf{G}(/\mathbf{G}_1)\downarrow\mathbf{G}_i = \frac{|\mathbf{G}|}{|\mathbf{G}_i|}\mathbf{G}_i(\mathbf{G}_1^{(i)}),$$

where $\mathbf{G}_i(/\mathbf{G}_1{}^{(i)})$ is the regular representation of the $\mathbf{G}_i$ group. This equation indicates that every subduction is accompanied with the division of respective orbits. Hence, the $\mathbf{G}_i(/\mathbf{G}_1{}^{(i)})$ part in the $\mathbf{G}(/\mathbf{G}_1)$ orbit is $\mathbf{G}_i$-chirogenic.

In order to formulate general cases other than the extreme ones, we should examine division (or conservation) of an orbit through a desymmetrization process. For this purpose, we prove the following theorem.

Theorem 9. *Let* $\mathbf{G}_i$ *and* $\mathbf{G}_j$ *be any subgroups of* $\mathbf{G}$. *If* $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ *is transitive, then we have* $\mathbf{G}_i\mathbf{G}_j=\mathbf{G}$. *Conversely, if we have* $\mathbf{G}_i\mathbf{G}_j=\mathbf{G}$, *then* $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ *is transitive.*

Proof. (a) Consider a coset $\mathbf{G}_i t_\alpha$ appearing in the coset decomposition (Eq. 1). Then, we obtain another coset, $\mathbf{G}_i t_\alpha g$, which obviously constructs a double coset, $\mathbf{G}_i t_\alpha \mathbf{G}_j$, when g runs over all $g\in\mathbf{G}_j$. Obviously, the double coset corresponds to an orbit produced by the subduction, $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$. If $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ is transitive, all of the double cosets should be identical, i.e. $\mathbf{G}_i t_\alpha\mathbf{G}_j=\mathbf{G}_i t_\beta\mathbf{G}_j$ for $\forall t_\mathrm{A}$ *and* $\forall t_\beta$. Let t_β be equal to I. Then, we have $\mathbf{G}_i t_\alpha\mathbf{G}_j=\mathbf{G}_i\mathbf{G}_j$. Hence, we have

$$\bigcup_{\alpha=1}^{r}\mathbf{G}_i t_\alpha\mathbf{G}_j = \bigcup_{\alpha=1}^{r}\mathbf{G}_i\mathbf{G}_j. = \mathbf{G}_i\mathbf{G}_j.$$

Since the left-hand side contains all of the elements of $\mathbf{G}$ (i.e., $\mathbf{G}=\bigcup_{\alpha=1}^{r}\mathbf{G}_i t_\alpha\mathbf{G}_j$), the equation is converted into

$$\mathbf{G} = \mathbf{G}_i\mathbf{G}_j. \tag{30}$$

(b) Conversely, suppose that $\mathbf{G}_i\mathbf{G}_j=\mathbf{G}$. Then, we have $\mathbf{G}_i t_1\mathbf{G}_j=\mathbf{G}$ for $t_1=I$. This equation indicates the double coset $\mathbf{G}_i t_1\mathbf{G}_j$ contains all of the elements of $\mathbf{G}$. Hence, there appears one orbit during the subduction, $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$; that is to say, $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ is transitive.

It should be noted that this thorem holds for any $\mathbf{G}_i$, $\mathbf{G}_j$, and $\mathbf{G}$, no matter whether they are proper or improper. The following examples clarify the scope of the theorem.

Example **8.** (a) For $\mathbf{T}_\mathrm{d}(/\mathbf{C}_\mathrm{s})\downarrow\mathbf{T}$, we have $\mathbf{C}_\mathrm{s}\mathbf{T}=\mathbf{T}_\mathrm{d}$. Hence, Theorem 9 indicates that there emerges no division of the orbit; i.e., $\mathbf{T}_\mathrm{d}(/\mathbf{C}_\mathrm{s})\downarrow\mathbf{T}=\mathbf{T}(/\mathbf{C}_1)$.

(b) For $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{3\mathrm{v}})\downarrow\mathbf{D}_{2\mathrm{d}}$, we have $\mathbf{C}_{3\mathrm{v}}\mathbf{D}_{2\mathrm{d}}=\mathbf{T}_\mathrm{d}$. Hence, Theorem 9 indicates that there emerges no division of the orbit; i.e., $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{3\mathrm{v}})\downarrow\mathbf{D}_{2\mathrm{d}}=\mathbf{D}_{2\mathrm{d}}(/\mathbf{C}_\mathrm{s})$.

(c) For $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{3\mathrm{v}})\downarrow\mathbf{D}_{3\mathrm{v}}$, we have $\mathbf{C}_{3\mathrm{v}}\mathbf{C}_{3\mathrm{v}}=\mathbf{C}_{3\mathrm{v}}\neq\mathbf{T}_\mathrm{d}$. Hence, Theorem 9 indicates that the orbit is divided during the process as follows; $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{3\mathrm{v}})\downarrow\mathbf{C}_{3\mathrm{v}}=\mathbf{C}_{3\mathrm{v}}(/\mathbf{C}_\mathrm{s})+\mathbf{C}_{3\mathrm{v}}(/\mathbf{C}_{3\mathrm{v}})$.

(d) For $\mathbf{T}(/\mathbf{C}_3)\downarrow\mathbf{C}_3$, we have $\mathbf{C}_3\mathbf{C}_3=\mathbf{C}_3\neq\mathbf{T}$. Hence, Theorem 9 indicates that the orbit is divided during the process as follows; $\mathbf{T}(/\mathbf{C}_3)\downarrow\mathbf{C}_3=\mathbf{C}_3(/\mathbf{C}_1)+\mathbf{C}_3(/\mathbf{C}_3)$.

Let $\mathbf{G}(/\mathbf{G}_i)$ be enantiospheric. Then, $\mathbf{G}_i$ and $\mathbf{G}^{\max}$ are chiral subgroups; hence, $\mathbf{G}_i\mathbf{G}^{\max}=\mathbf{G}^{\max}\neq\mathbf{G}$. In this case, Theorem 9 is converted into a corollary.

Corollary 1. *An enantiospheric orbit* $\mathbf{G}(/\mathbf{G}_i)$ *is divided during* $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}^{\max}$.

The concrete form of the division has been given by Theorem 4.

Let $\mathbf{H}$ be a nearest subgroup of $\mathbf{G}_j$. The term "nearest" is used when there is no subgroup of $\mathbf{G}_j$ between $\mathbf{G}_j$ and $\mathbf{H}$. Thus, $\mathbf{H}$ is one of the nearest subgroups of $\mathbf{G}_j$ and $\mathbf{G}_j$ is one of the nearest supergroups of $\mathbf{H}$. Since $\mathbf{G}_j$ is chiral, $\mathbf{H}$ is also chiral. Suppose that each CR in Eq. 21 is subduced by means of

$$\mathbf{G}_j(/\mathbf{G}_k^{(j)})\downarrow\mathbf{H} = \sum_{l=1}^{\nu_l}\zeta_l{}^{(ij)}\mathbf{H}(/\mathbf{H}_l)$$

We have derived Eq. 21 for Case (a) and Eq. 23 for Case (b). Thereby, we derive the following equation from Eq. 21.

$$\begin{aligned}\mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{H} &= \mathbf{G}^{\max}(/\mathbf{G}_i)\downarrow\mathbf{G}_j\downarrow\mathbf{H}\\ &= \sum_{k=1}^{\nu_j}\gamma_k{}^{(ij)}\mathbf{G}_j(/\mathbf{G}_k^{(j)})\downarrow\mathbf{H}\\ &= \sum_{k=1}^{\nu_j}\gamma_k{}^{(ij)}\sum_{l=1}^{\nu_\mathbf{H}}\zeta_l{}^{(ik)}\mathbf{H}(/\mathbf{H}_l)\\ &= \sum_{l=1}^{\nu_\mathbf{H}}\eta_l{}^{(ij)}\mathbf{H}(/\mathbf{H}_l),\end{aligned} \tag{32}$$

where

$$\eta_l{}^{(ij)} = \sum_{k=1}^{\nu_j}\gamma_k{}^{(ij)}\zeta_l{}^{(ik)}. \tag{33}$$

We arrive at the following theorem.

Theorem 10. *Let* $\mathbf{H}$ *be a nearest subgroup of* $\mathbf{G}_j$. *If there is an appropriate CR* ($\mathbf{G}_j(/\mathbf{G}_k{}^{(j)})$) *that satisfies* $\mathbf{G}_k{}^{(j)}\mathbf{H}\neq\mathbf{G}_j$, *then the site governed by* $\mathbf{H}(/\mathbf{H}_l)(l=1,2,\cdots,\nu_l)$ *is an* $\mathbf{H}$-*chirogenic site during the desymmetrization process* $(\mathbf{G}\rightarrow\mathbf{G}_j\rightarrow\mathbf{H})$.

Proof. If there is an appropriate CR ($\mathbf{G}_j(/\mathbf{G}_k{}^{(j)})$) that satisfies $\mathbf{G}_k{}^{(j)}\mathbf{H}\neq\mathbf{G}_j$, then the subduction represented by Eq. 31 produces two or more orbits (Theorem 9). This means that the site governed by $\mathbf{H}(/\mathbf{H}_l)(l=1,2,\cdots,\nu_\mathrm{H})$ is an $\mathbf{H}$-chirogenic site.

This theorem also holds for Case (b), since Eqs. 23 and 24 of Case (b) are essentially identical with Eq. 21 of Case (a). It is the next problem to determine whether the $\mathbf{H}(/\mathbf{H}_l)$ part is an $\mathbf{H}$-chirogenic site during all of the desymmetrization processes toward $\mathbf{H}$. For this purpose, we should examine all of the nearest chiral supergroups of $\mathbf{H}$. If there exists such a chiral synthesis, we call the synthesis a $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{H}$-ligand-differentiating reaction.

Example **9.** Let us consider $\mathbf{T}_\mathrm{h}(/\mathbf{C}_3)\downarrow\mathbf{C}_2$. We take account of $\mathbf{D}_2$ group as a nearest chiral supergroup of $\mathbf{C}_2$.

$$\mathbf{T}_\mathrm{h}(/\mathbf{C}_3)\downarrow\mathbf{D}_2 = 2\mathbf{D}_2(/\mathbf{C}_1) \text{ and}$$

$$\mathbf{D}_2(/\mathbf{C}_1)\downarrow\mathbf{C}_2 = 2\mathbf{C}_2(/\mathbf{C}_1)$$

We apply Theorem 10 to $\mathbf{G}_j=\mathbf{D}_2$, $\mathbf{G}_k{}^{(j)}=\mathbf{C}_1$ and $\mathbf{H}=\mathbf{C}_2$.

Since we have $\mathbf{C}_1\mathbf{C}_2=\mathbf{C}_2\neq\mathbf{D}_2$, there emerge two or more orbits during the conversion of $\mathbf{D}_2$ into $\mathbf{C}_2$. Theorem 10 indicates that the resulting $\mathbf{C}_2(/\mathbf{C}_1)$ parts are $\mathbf{C}_2$-chirogenic. The overall process is represented by

$$\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{C}_2 = 4\mathbf{C}_2(/\mathbf{C}_1). \tag{34}$$

This conclusion is illustrated by a potential chiral synthesis (Fig. 6). Consider the attack of a chiral reagent (containing two chiral active sites) onto the molecule (**5**). One of the $\mathbf{C}_2$-chirogenic sites of the $\mathbf{T}_h(/\mathbf{C}_3)$ orbit is represented by the symbol (⦶) in **9a**, which is generated by the attack. The attack of the mirror-image part (⦶) creates the diastereomeric intermediate (**9b**). If **9a** is energetically preferred, the corresponding $\mathbf{C}_2$-molecule is created preferably.

If all of the CRs in Eq. 21 ($\mathbf{G}_j(/\mathbf{G}_k^{(i)})$'s) satisfy $\mathbf{G}_k^{(i)}\mathbf{H}=\mathbf{G}_j$, then each subduction represented by Eq. 31 produces one orbit (Theorem 9). This means that there appears no division of each orbit during the process of converting $\mathbf{G}_j$ into $\mathbf{H}_j$. Thus, the site governed by $\mathbf{G}_j(/\mathbf{G}_k^{(i)})$ is converted, with no division, into the one governed by $\mathbf{H}(/\mathbf{H}_l)$(for $\exists l$), where $|\mathbf{G}_j|/|\mathbf{G}_k^{(i)}|=|\mathbf{H}|/|\mathbf{H}_l|$. Hence, this site is not an $\mathbf{H}$-chirogenic site but $\geqslant\mathbf{G}_j$-chirogenic site.

The following corollary is practically important, since its chemical meaning is quite concrete.

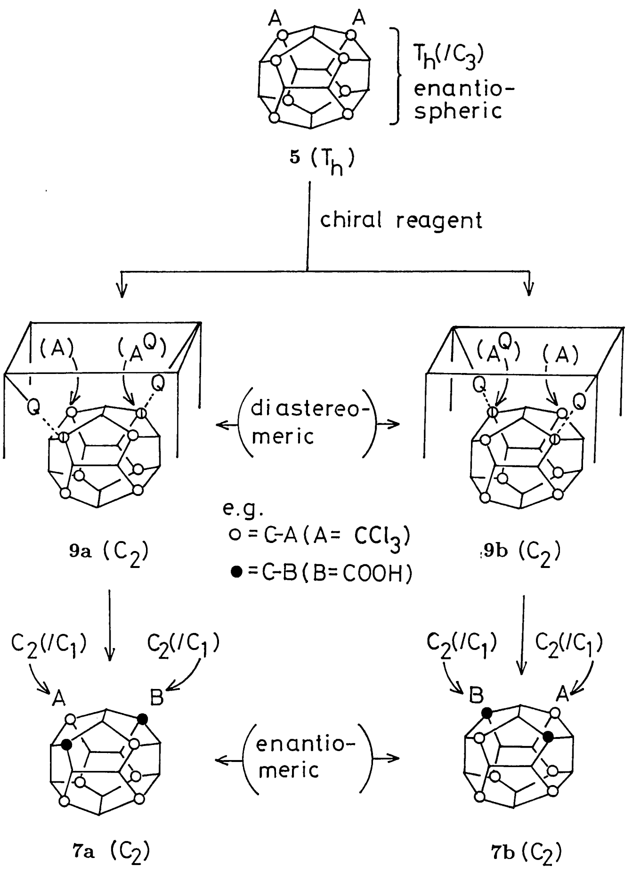


Fig. 6. A potential chiral synthesis generating $\mathbf{C}_2$ molecules from a $\mathbf{T}_h$ molecule.

Corollary 2. *Each $\mathbf{G}_i$-ligand in a $\mathbf{G}(/\mathbf{G}_i)$ orbit is a $\mathbf{G}_i$-chirogenic site.*

Proof. Let $\mathbf{G}_i$ and $\mathbf{G}_j$ be chiral subgroups of $\mathbf{G}$. Suppose that $\mathbf{G}_j$ is an arbitrary nearest supergroup of $\mathbf{G}_i$. We consider a coset representation acting on $\mathbf{G}_it_1$ or $\Omega_1(t_1=I)$. The stabilizer of $\mathbf{G}_it_1(\Omega_1)$ is $\mathbf{G}_i$, under the actions of $\mathbf{G}$, of $\mathbf{G}_j$ and of $\mathbf{G}_i$. Hence, the orbit containing $\mathbf{G}_it_1$ (or Ω_1) is subject to $|\mathbf{G}|/|\mathbf{G}_i|$-membered $\mathbf{G}(/\mathbf{G}_i)$ in the case of $\mathbf{G}$; to $|\mathbf{G}_j|/|\mathbf{G}_i|$-membered $\mathbf{G}_j(/\mathbf{G}_i)$ in the case of $\mathbf{G}_j$; and to one-membered $\mathbf{G}_i(/\mathbf{G}_i)$ in the case of $\mathbf{G}_i$. If the second step of the desymmetrization ($\mathbf{G}\rightarrow\mathbf{G}_j\rightarrow\mathbf{G}_i$ (i.e. $\mathbf{G}_j(/\mathbf{G}_i)\downarrow\mathbf{G}_i$)) produces no division of the orbit, then Theorem 9 affords $\mathbf{G}_i\mathbf{G}_i=\mathbf{G}_j$. It follows that $\mathbf{G}_i=\mathbf{G}_j$. Hence, there exists no such $\mathbf{G}_j$.

This corollary indicates that we can produce a $\mathbf{G}_i$ molecule by differentiating one of the $\mathbf{G}_i$-ligands in Ω^+ from the counterpart in Ω^+. Although there are $|\mathbf{G}|/|\mathbf{G}_i|$ ways for selecting such a chirogenic site, they produce homomers that are chemically identical.

It is rather tedeous task to determine chirogenic sites by means of Theorem 10. A desymmetrization lattice[8] is effective to determine such chirogenic sites of an orbits. Figure 7 depicts the desymmetrization lattice of $\mathbf{D}_{2d}(/\mathbf{C}_2')$. Compare $\mathbf{D}_2(/\mathbf{C}_2')+\mathbf{D}_2(/\mathbf{D}_2'')$ and $2\mathbf{C}_2(/\mathbf{C}_1)$. Thus, the orbits of the $\mathbf{D}_2$ are not divided in the process of converting into the $\mathbf{C}_2$. This fact is equivalent to the fact that Theorem 10 holds for this case. Hence, the $\mathbf{C}_2(/\mathbf{C}_1)$ part in the $\mathbf{D}_{2d}(/\mathbf{C}_2')$ orbit is not a $\mathbf{C}_2$-chirogenic site. This means that there is no direct method of generating a $\mathbf{C}_2$-molecule from the $\mathbf{D}_{2d}(/\mathbf{C}_2')$ orbit.

On the other hand, there is a direct method of generating a $\mathbf{C}_2'$-molecule from the $\mathbf{D}_{2d}(/\mathbf{C}_2')$ orbit by the inspection of the desymmetrization lattice. This result is alternatively verified by Corollary 2.

Special Cases. In the preceding discussion, the chiral subgroup $\mathbf{H}$ ($\leqslant\mathbf{G}_j$) is examined. The $\mathbf{H}$ part in Ω^+ can be differentiated from the mirror image in Ω^-, if Theorem 10 holds for all of the nearest supergroups $\mathbf{G}_j$. It should be

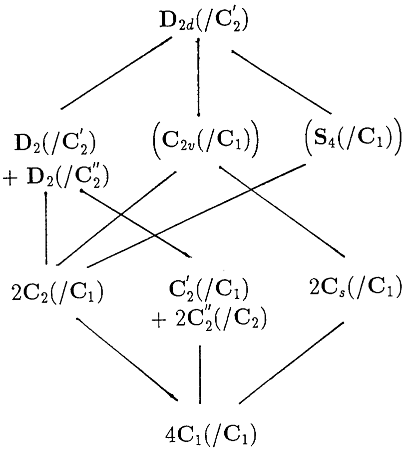


Fig. 7. Desymmetrization lattice of $\mathbf{D}_{2d}(/\mathbf{C}_2')$.

noted that the combination of the two parts does not always construct a group.

With respect to this point, we have the following theorem in general.

Theorem 11. *Let* $\mathbf{H}$ *be a chiral subgroup of an achiral group* $\mathbf{G}$ *and* u_1 *be an improper rotation contained in* $\mathbf{G}$. *If* $\widetilde{\mathbf{H}}=\mathbf{H}+\mathbf{H}u_1$ *is a subgroup of* $\mathbf{G}$, *then we have* $u_1\mathbf{H}=\mathbf{H}u_1$ *and* $u_1u_1\in\mathbf{H}$. *Conversely, if the relations* $u_1\mathbf{H}=\mathbf{H}u_1$ *and* $u_1u_1\in\mathbf{H}$ *hold, then* $\widetilde{\mathbf{H}}$ *is a subgroup of* $\mathbf{G}$.

Proof. (a) Suppose that $u_1\mathbf{H}=\mathbf{H}u_1$ and $u_1u_1\in\mathbf{H}$. (i) For $\forall a,b\in\mathbf{H}$, we have $ab^{-1}\in\mathbf{H}\subseteq\widetilde{\mathbf{H}}$, since $\mathbf{H}$ is a group. (ii) Consider $\forall a\in\mathbf{H}$ and $\forall b\in\mathbf{H}u_1$. There exists $b'\in\mathbf{H}$ that satisfies $b=b'u_1\in\mathbf{H}u_1$. By means of the above assumption, we have $u_1u_1=c\in\mathbf{H}$ for $\exists c\in\mathbf{H}$, $u_1c^{-1}=c'u_1$ for $\exists c'\in\mathbf{H}$, and $u_1(b')^{-1}=b''u_1$ for $\exists b''\in\mathbf{H}$. It follows that $ab^{-1}au_1^{-1}(b')^{-1}au_1c^{-1}(b')^{-1}=\mathrm{a}c'b''u_1\in\mathbf{H}u_i\subseteq\widetilde{\mathbf{H}}$. (iii) If $a\in\mathbf{H}u_1$ and $b\in\mathbf{H}u_1$, then there exist $a',b'\in\mathbf{H}$ that satisfy $a=a'u_1\in\mathbf{H}u_1$ and $b=b'u_1\in\mathbf{H}u_1$. It follows that $ab^{-1}=a'u_1u_1^{-1}(b')^{-1}=a'(b')^{-1}\in\mathbf{H}\subseteq\widetilde{\mathbf{H}}$, On the basis of (i), (ii), and (iii), $\mathbf{H}$ is a group.

(b) Suppose that $\widetilde{\mathbf{H}}=\mathbf{H}+\mathbf{H}u_1$ is a subgroup of $\mathbf{G}$. Since $\mathbf{H}u_1$ is the set of all improper rotations in $\widetilde{\mathbf{H}}$ and $u_1\mathbf{H}$ is also the set of all improper rotations $\widetilde{\mathbf{H}}$, they must be equal. It follows that $\mathbf{H}u_1=u_1\mathbf{H}$. Since u_1 is an improper rotation, we have $u_1^{-1}\in\mathbf{H}u_1$. Since we take $u_1u_1=c$, we have $cu_1^{-1}=u_1\in\mathbf{H}u_1$. This means that $c\in\mathbf{H}$. Hence, we have $u_1u_1=c\in\mathbf{H}$.

In continuation of the preceding section, suppose that $\mathbf{H}$ is the nearest subgroup of $\mathbf{G}_j$ and $\mathbf{H}\leqslant\mathbf{G}_j\leqslant\mathbf{G}^{\mathrm{max}}\leqslant\mathbf{G}$. Suppose that $\mathbf{G}$ contains u_1 satisfying $u_1u_1\in\mathbf{H}$ as an improper rotation and that $\mathbf{H}u_1=u_1\mathbf{H}$. Then, Theorem 11 indicates that we are able to obtain the point group $\widetilde{\mathbf{H}}$ ($\leqslant\mathbf{G}$) that contains $\mathbf{H}$ as the maximum chiral subgroup; i.e., $\widetilde{\mathbf{H}}$ $\{h,hu_1 \mid \forall h\in\mathbf{H}\}=\mathbf{H}+\mathbf{H}u_1$. Let us examine a subduction represented by $\mathbf{G}(/\mathbf{G}_i)\downarrow\widetilde{\mathbf{H}}$, where $\mathbf{G}(/\mathbf{G}_i)$ is enantiospheric. Since the relationship between $\widetilde{\mathbf{H}}(/\mathbf{H}_l)$ and $\mathbf{H}(/\mathbf{H}_l)$ is the same as that between $\mathbf{G}(/\mathbf{G}_i)$ and $\mathbf{G}^{\mathrm{max}}(/\mathbf{G}_i)$, we arrive at the following theorem by means of Eq. 31.

Theorem 12. *Suppose that an enantiospheric orbit* $\mathbf{G}(/\mathbf{G}_i)$ *is in accord with Case* [*a*] *of Theorem 4. If we can construct* $\widetilde{\mathbf{H}}$ *as above, the subduction* $\mathbf{G}(/\mathbf{G}_i)\downarrow\widetilde{\mathbf{H}}$ *is represented by*

$$\mathbf{G}(\mathbf{G}_i)\downarrow\widetilde{\mathbf{H}}=\sum_{l=1}^{{}^{\nu}\mathbf{H}}\eta_l^{(ij)}\widetilde{\mathbf{H}}(/\mathbf{H}_l), \tag{35}$$

where $\mathbf{H}_l$ *is chiral subgroups.*

The $\widetilde{\mathbf{H}}(/\mathbf{H}_l)$ orbits appearing in the right-hand side of Eq. 35 are enantiospheric. This theorem is exemplified by comparing $\mathbf{D}_{2\mathrm{d}}(/\mathbf{C}_1)\downarrow\mathbf{C}_{2\mathrm{v}}$ with $\mathbf{D}_{2\mathrm{d}}(/\mathbf{C}_1)\downarrow\mathbf{C}_2$. Note that the summation in Eq. 35 is concerned with the chiral $\mathbf{H}$, not with $\widetilde{\mathbf{H}}$. In Eq. 35, $\widetilde{\mathbf{H}}(/\mathbf{H}_l)$ may be equivalent to $\widetilde{\mathbf{H}}_j(/\mathbf{H}_l')$ if $\mathbf{H}_l$ is conjugate to $\mathbf{H}_l'$ as subgroups of $\widetilde{\mathbf{H}}$ and if they are not conjugate as subgroups of $\mathbf{H}$. For example, compare the subduction $\mathbf{T}_\mathrm{d}(/\mathbf{C}_2)\downarrow\mathbf{D}_{2\mathrm{d}}=\mathbf{D}_{2\mathrm{d}}(/\mathbf{C}_2)+2\mathbf{D}_{2\mathrm{d}}(/\mathbf{C}_2')$ with $\mathbf{T}_\mathrm{d}(/\mathbf{C}_2)\downarrow\mathbf{D}_2=\mathbf{D}_2(/\mathbf{C}_2)+\mathbf{D}_2(/\mathbf{C}_2')+\mathbf{D}_2(/\mathbf{C}_2'')$. It should be noted that, if there appears no division during the subduction $\mathbf{G}(/\mathbf{G}_i)\downarrow\widetilde{\mathbf{H}}$ as compared with the subduction to its supergroup(s), this process is not effective in chiral synthesis. For example, Fig. 7 contains such non-effective cases ($\mathbf{C}_{2\mathrm{v}}$ and $\mathbf{S}_4$).

By means of Theorem 12, we have the following corollary.

Corollary 3. *a)* Let $\mathbf{G}(/\mathbf{G}_i)$ *be enantiospheric* . *If* $\mathbf{G}$ *contains* $\mathbf{C}_s$ *(a mirror plane) and* $\mathbf{C}_i$ *(inversion), then we have*

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{C}_\mathrm{s}=\frac{|\mathbf{G}|}{2|\mathbf{G}_i|}\mathbf{C}_\mathrm{s}(/\mathbf{C}_1), \tag{36}$$

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{C}_i=\frac{|\mathbf{G}|}{2|\mathbf{G}_i|}\mathbf{C}_i(/\mathbf{C}_1). \tag{37}$$

Discussion

In preceding section, we have presented the theoretical foundation of asymmetric syntheses. In the light of the resulting logical framework, we reexamine asymmetric syntheses reported so far and propose alternative possibilities of chiral syntheses. Figure 8 illustrates a potential experiment in which an enantiospheric orbit is subject to $\mathbf{C}_s(/\mathbf{C}_1)$. The starting material (**10**) of the $\mathbf{C}_s$ symmetry has two CH_2OH ligands. We regard each ligand as A in the lump. Then the two A's are subject to $\mathbf{C}_s(/\mathbf{C}_1)$, belonging to an enantiospheric orbit. In order to obtain a chiral product, we must differentiate only two ligands belonging to the orbit. Suppose that a chiral reagent (Q) attacks either of ligands. Then, such an interaction as $CH_2OH\cdots Q$ (A^Q) appears; the attack produces a chiral environment. Either one of such possible intermediates (**11a** or **11b**) is energetically predominant and yields a final product of $\mathbf{C}_1$.

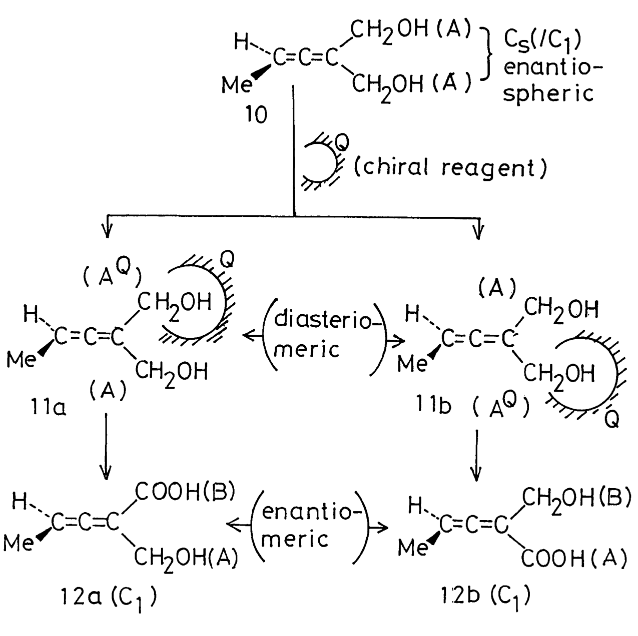


Fig. 8. A potential chiral synthesis generating $\mathbf{C}_1$ molecules from a $\mathbf{C}_s$ molecule.

All of the asymmetric syntheses reported so far[13] are classified to the above-described simple case, in which an enantiospheric orbit is governed by $\mathbf{C}_s(/\mathbf{C}_1)$. For an example of this type, Fuji[14] reported an asymmetric protonation of a dicarboxylate, in which two carboxylate groups belonging to an enantiospheric orbit are differentiated. These reactions have been classified into enantiotopic-group-differentiating reactions.[15] In the light of the present notation, they are characterized as $\mathbf{C}_s(/\mathbf{C}_1)\downarrow\mathbf{C}_1$-ligand-differentiating reactions. An enantiospheric orbit of the faces of a carbonyl group or of the related functional group, which is subject to the $\mathbf{C}_s(/\mathbf{C}_1)$ representation, undergoes a chiral synthesis. For example, hydrogen transfers from chiral reducing agents to achiral substrates, asymmetric additions to alkenes, asymmetric syntheses at hetero atoms, and so forth have been reported.[13] Additional examples have been recently reviewed.[16] These reactions have been classified into enantiotopic-face-differentiating reactions.[15] They are characterized more specifically as $\mathbf{C}_s(/\mathbf{C}_1)\downarrow\mathbf{C}_1$-face-differentiating reactions in terms of the present terminology.

The discussions in the previous section indicate that there can exist more general cases, in which an enantiospheric orbit is subject to a coset representation other than $\mathbf{C}_s(/\mathbf{C}_1)$. Figure 9 shows a potential experiment that produces a $\mathbf{C}_2$ molecule (**15a** or **15b**) from an $\mathbf{S}_4$ molecule (**13**). The two carbonyl groups belong to an enantiospheric orbit subject to $\mathbf{S}_4(/\mathbf{C}_2)$. The attack of a chiral reducing agent perturbs the carbonyls to belong to disteromeric environments (**14** and **14b**), either of which is energetically preferred. Hence, either one of an enantiomeric pair (**15a** and **15b**) is produced predominantly. This is characterized as an $\mathbf{S}_4(/\mathbf{C}_2)\downarrow\mathbf{C}_2$-group-differentiating reaction. The reaction is a novel type of chiral reaction in the sense that it involves no explicit faces to be differentiated. Thus, the two carbonyl groups in **13** are associated with each other not by a mirror plane, but by S_4 operation. To the best of our knowledge, this type of reactions has never been reported. The mode of the differentiation of **13** (Fig. 9) is different from that of **10** (Fig. 8).

Example 9 (Fig. 6) illustrates a $\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{C}_2$-group-differentiating reaction. It is to be noted that $\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{T}$-group-differentiating reactions (e.g. **5**→**6a** or **6b**) and $\mathbf{T}_h(/\mathbf{C}_3)\mathbf{C}_3$-group-differentiating reactions (e.g. **5**→**8a** or **8b**) are also possible. It is challenging problems to realize such novel chiral syntheses. In

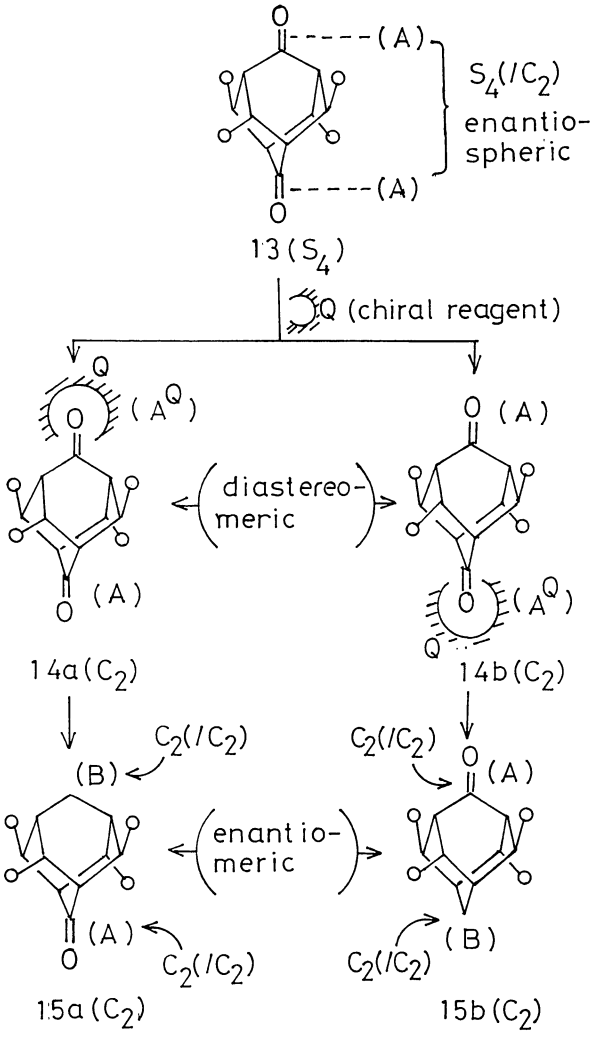


Fig. 9. A potential chiral synthesis generating $\mathbf{C}_2$ molecules from a $\mathbf{S}_4$ molecule.

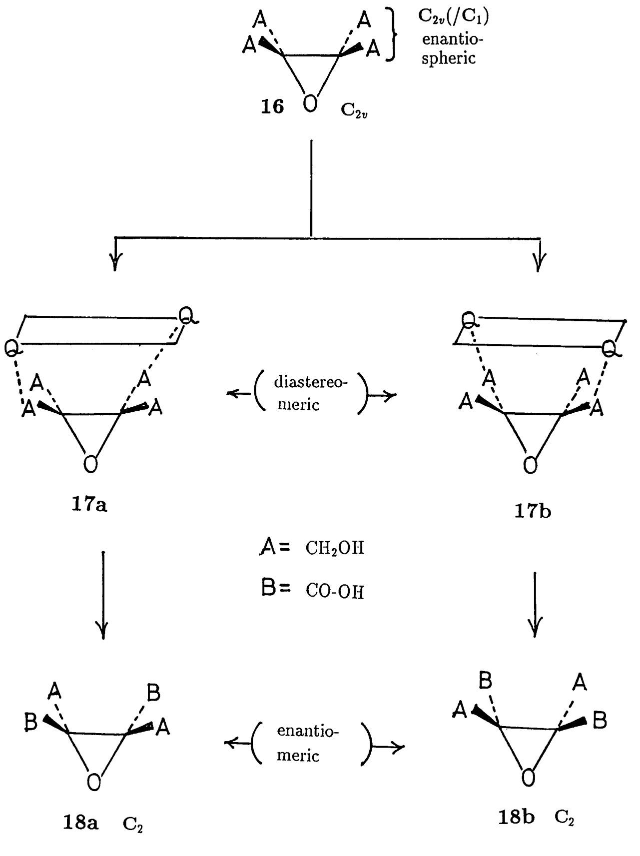


Fig. 10. A potential chiral synthesis generating $\mathbf{C}_2$ molecules from a $\mathbf{C}_{2v}$ molecule.

particular, the $\mathbf{T}_h(/\mathbf{C}_3)\downarrow\mathbf{C}_3$-group-differentiating reaction can be accomplished if the reaction is ceased at the point that only one group of the eight functional groups (Fig. 6) has been attacked. Note that this reaction is based on Corollary 2.

Let us examine the $\mathbf{C}_{2v}$-molecule (**16**), in which four CH_2OH ligands construct an orbit subject to $\mathbf{C}_{2v}(/\mathbf{C}_1)$. This orbit is enantiospheric and active to a chiral synthesis. Figure 10 indicates a model of chiral synthesis which produces a $\mathbf{C}_2$-molecule from a $\mathbf{C}_{2v}$-molecule. This process corresponds to the subduction represented by $\mathbf{C}_{2v}(/\mathbf{C}_1)\downarrow\mathbf{C}_2=2\mathbf{C}_2(/\mathbf{C}_1)$. We can consider a potential chiral reagent that has two chiral units (Q) in diagonal positions, which are concerned with a $\mathbf{C}_2$-chirogenic site of the substrate. Since the resulting intermediates (**17a** and **17b**) are diastereomeric, the energetically predominant intermediate yields either of enantiomeric products (**18a** or **18b**). We refer to this reaction as a $\mathbf{C}_{2v}(/\mathbf{C}_1)\downarrow\mathbf{C}_2$-group-differentiating reaction.

Conclusion

Prochirality is defined logically by examining the desymmetrization of an enantiospheric orbit. A chirogenic site in the enantiospheric orbit provides a basis of operating chiral syntheses.

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