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Subsymmetry-Itemized Enumeration of Flexible Cyclohexane Derivatives

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The symmetry of a pair of two chair-forms of cyclohexane is represented by the pseudo-point group $\hat{\boldsymbol{D}}_{6h}$ of order 24. Preparation of the mark table of the group $\hat{\boldsymbol{D}}_{6h}$ shows the twelve substitution positions of the pair to be governed by the coset representation $\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$. After the calculation of subduction of the $\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$, cyclohexane derivatives are combinatorially enumerated by the USCI (unit-subduced-cycle-index) approach. A generating-function method and the elementary superposition theorem are used, giving values itemized with respect to molecular formulas and subsymmetries of $\hat{\boldsymbol{D}}_{6h}$. Since pseudo-point groups can be classified into iso- and anisoenergetic groups as well as into achiral and chiral groups, four categories (isoenergetic-achiral, isoenergetic-chiral (Type II), anisoenergetic-achiral (Type III), and anisoenergetic-chiral (Type IV)) are generated. The isoenergetic-achiral case is further subdivided into two cases (Type I and I′). Several pairs are illustrated and discussed in the light of this classification. The concept of chronality is also discussed.

Enumeration of flexible cyclohexane derivative has been reported by Leonard et al.[1,2] Their method has combined the Pólya–Redfield theorem with extended point groups, in which a ring-flip-rotation operator (R_6) is used to describe flipping between the chair-forms of a cyclohexane skeleton. An alternative method reported by Flurry[3,4] is based on an isodynamic operator which was presented by Altmann.[5]

Although the pioneering studies have discussed brief aspects of enumeration, more elaborate and essential problems have remained unsolved:

1. From the viewpoint of combinatorial enumeration, both the two methods have been concerned only with the total numbers of each molecular formula. In other words, the resulting values have not been itemized with respect to symmetry. Hence, more detailed enumeration is desirable, regarding both molecular formulae and symmetries.
2. Although the flipping cyclohexane itself has been assigned to the group $\boldsymbol{D}_{3d}R_6$ by Leonard et al.[1,2] and to the group $\mathbf{F}\times\boldsymbol{D}_{3d}$ by Flurry,[3] the symmetry of each derivative enumerated has not been identified in either of the methods. It should be an appropriate subsymmetry of the symmetry of the flipping cyclohexane skeleton; however, there have been no methods suitable to represent such a subsymmetry.
3. The operations described in both the methods have been presumed to act on either of the fixed conformers. In effect, the methods are conceptually concerned only with the starting conformer, while the product conformer is subsidiarily considered through the R_6 or the isodynamic operations. Since the methods have not taken into explicit consideration the equilibrium pair of the starting and resulting conformers, the methods are not easily applied to the characterization of equivalency between two conformers. Hence, we seek to develop an alternative method which regards a pair of chair forms of a cyclohexane skeleton as an equilibrium system and which counts such equilibrium pairs.
4. Neither of the methods has involved effective discussions on cases in which two energetically-different conformers participate in an equilibrium. In particular, the isodynamic groups used by Flurry give no explicit consideration to such cases, since they were created conceptually for discussing an equilibrium between two isoenergetic conformers. Although the investigation of the cases requires the group–subgroup relationship of each group, no attention has been paid to this matter.

We have recently proposed the USCI (unit-subduced-cycle-index) approach and revealed its usefulness in enumerating derivatives of a rigid skeleton[6,7] and of a skeleton with rotatable substitution positions.[8,9] As an extention, we will here apply the USCI approach to the itemized enumeration of flexible cyclohexane derivatives. The itemized enumeration inevitably requires a more systematic method of specifying the subsymmetry of each pair of interchangeable conformers. For this purpose, we adopt the concepts of equi-axial transformations and pseudo-point groups which we have formulated in the preceding paper, where we discussed the coset representations of pseudo-point group $\hat{\boldsymbol{D}}_{3h}$ and their subduction. The present paper deals with pseudo-point group $\hat{\boldsymbol{D}}_{6h}$ for describing symmetrical properties of flexible cyclohexane.

Theoretical Formalism and Results

1 The Operation $\hat{C}'_2$ and the Pseudo-Point Group $\hat{\boldsymbol{D}}_{6h}$. Let us consider a pair of chair-form conformers (**1a** and **1b**) of cyclohexane, where the substitution positions are numbered from 1 to 12. Since the pair is regarded as an equiaxial transformation, its symmetry is characterized by a pseudo-point group.

First, we shall clarify the pseudo-point group that characterizes the symmetry of the pair (**1a**$\rightleftarrows$**1b**). The pair coincides with itself on the action of the twelve symmetry operations of the group $\boldsymbol{D}_{3d}$, i.e.,

$$\boldsymbol{D}_{3d} = \{I, C_3, C_3^2, S_6, i, S_6^5, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}, \}, \tag{1}$$

where each symmetry operation is considered to act on each conformer (A or B) of the pair. However, additional operations should be introduced to treat conformational changes of cyclohexane. For the purpose of exchanging axial and equatorial positions, we introduce a pseudo-dihedral rotation ($\hat{C}'_2$-operation), which is a combination of flipping and exchange (A⇄B), as shown in Fig. 1.

It should be noted that the operation $\hat{C}'_2$ has apparent similarity to the C'_2-operation of group $\boldsymbol{D}_{6h}$, which is created by adding a C'_2-axis to the point subgroup $\boldsymbol{D}_{3d}$. Thus, the operation $\hat{C}'_2$ is analogously considered to be generated by adding a symmetry element (a $\hat{C}'_2$-axis) that is perpendicular to the main axis (i.e., the C_3-axis of the point subgroup $\boldsymbol{D}_{3d}$).

By considering the operation $\hat{C}'_2$, we can construct the set $\hat{\boldsymbol{D}}_{6h}$,

$$\hat{\boldsymbol{D}}_{6h} = \boldsymbol{D}_{3d} + \hat{C}'_{2(1)}\boldsymbol{D}_{3d}, \tag{2}$$

$$= \{I, C_3, C_3^2, S_6, i, S_6^5, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}, \hat{C}'_{2(1)}, \hat{C}'_{2(2)}, \hat{C}'_{2(3)}, \hat{\sigma}_{v(3)}, \hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)}, \hat{C}_2, \hat{C}_6^5, \hat{C}_6, \hat{\sigma}_h, \hat{S}_3, \hat{S}_3^5, \tag{3}$$

where the $\hat{C}'_2$-operation is numbered to be $\hat{C}'_{2(1)}$ for distinguishing from other operations of the same kind. The operations of $\hat{C}'_{2(1)}\boldsymbol{D}_{3d}$ are defined by the following equations:

$$\hat{C}'_{2(1)}C_3 = \hat{C}'_{2(2)}, \quad \hat{C}'_{2(1)}C_3^2 = \hat{C}'_{2(3)},$$
$$\hat{C}'_{2(1)}S_6 = \hat{\sigma}_{v(3)}, \quad \hat{C}'_{2(1)}i = \hat{\sigma}_{v(1)}, \quad \hat{C}'_{2(1)}S_6^5 = \hat{\sigma}_{v(2)},$$
$$\hat{C}'_{2(1)}C'_{2(1)} = \hat{C}_2, \quad \hat{C}'_{2(1)}C'_{2(2)} = \hat{C}_6^5, \quad \hat{C}'_{2(1)}C'_{2(3)} = \hat{C}_6.$$
$$\hat{C}'_{2(1)}\sigma_{v(1)} = \hat{\sigma}_h, \quad \hat{C}'_{2(1)}\sigma_{v(2)} = \hat{S}_3, \quad \hat{C}'_{2(1)}\sigma_{v(3)} = \hat{S}_3^5.$$

For example, the operation $\hat{\sigma}_{v(3)}$ is represented by the consecutive operation of S_6 and $\hat{C}'_2$, as shown in Fig. 2. The other operations can be obtained in similar ways. The resulting set $\hat{\boldsymbol{D}}_{6h}$ is a pseudo-point group.

The operators contained in the $\hat{C}'_{2(1)}\boldsymbol{D}_{3d}$ are called *pseudo-rotations*, while the operators of $\boldsymbol{D}_{3d}$ are simply called *rotations* or more distinctly *usual rotations*. In the present paper, a pseudo-rotation is designated by a italicized letter with a hat symbol. Since there is another criterion concerning proper and improper rotations, the operators of the pseudo-point group $\hat{\boldsymbol{D}}_{6h}$ are classified into four classes, i.e.,

proper rotation: $I, C_3, C_3^2, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}$
improper rotation: $\sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}, S_6, i, S_6^5$
proper pseudo-rotation: $\hat{C}'_{2(1)}, \hat{C}'_{2(2)}, \hat{C}'_{2(3)}, \hat{C}_2, \hat{C}_6^5, \hat{C}_6$,
and
improper pseudo-rotation: $\hat{\sigma}_{v(3)}, \hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)}, \hat{\sigma}_h, \hat{S}_3, \hat{S}_3^5$.

The operator $\hat{C}'_2$ is a generator of a group $\hat{\boldsymbol{C}}'_2$ ($= \{I, \hat{C}'_2\}$) of order 2, because two successive applications of $\hat{C}'_2$ return the system to the original conformation ($(\hat{C}'_2)^2 = I$). Since $\hat{C}'_2$ commutes with all elements of $\boldsymbol{D}_{3d}$, the group $\hat{\boldsymbol{D}}_{6h}$ defined by Eq. 2 is alternatively represented by the direct product:

$$\hat{\boldsymbol{D}}_{6h} = \hat{\boldsymbol{C}}'_2 \times \boldsymbol{D}_{3d}. \tag{4}$$

It is worthwhile to mention the methodologies of Leonard's approach and Flurry's approach in the present context. The operation R_6 (a ring flip from one chair form to another, followed by a 60° rotation) has been selected as a generator in Leonard's approach.[1,2] It is apparently equivalent to the operation $\hat{C}_6$ generated by $\hat{C}'_{2(1)}C'_{2(3)}$ in the present approach, though

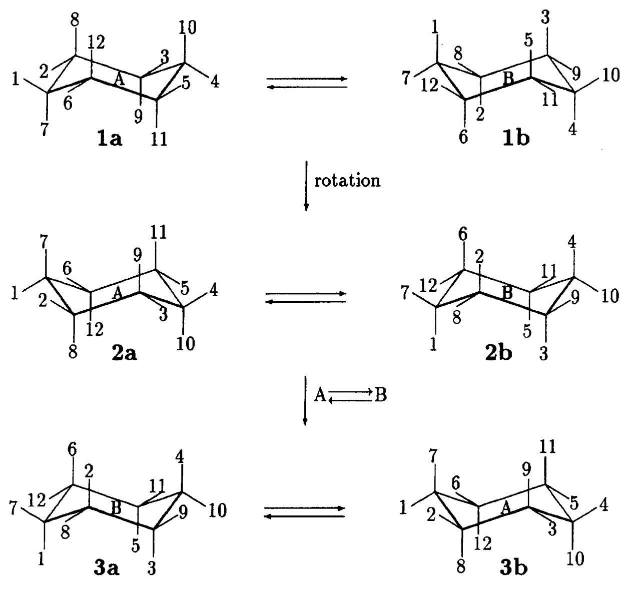


Fig. 1. The definition of the operation $\hat{C}'_2$.

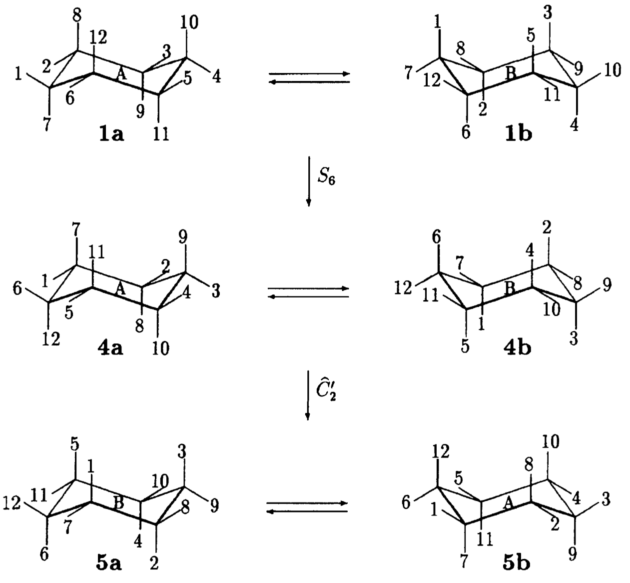


Fig. 2. The operation $\sigma_{v(3)}$ defined by $\hat{C}'_2 S_6$.

the operations R_6 and $\hat{C}_6$ are different in their objects (molecules vs. pairs). It should be noted that the present generator $\hat{C}'_{2(1)}$ forms a group $\hat{\boldsymbol{C}}'_2=\{I,\hat{C}'_{2(1)}\}$, while the set $\{I,R_6\}$ is not a group. This fact reveals that the direct-product nature of the present group $\hat{\boldsymbol{D}}_{6h}$ can be easily recognized, as shown in Eq. 4, while some efforts may be required to clarify the group-theoretical structure of the same kind in the corresponding group of Leonard's approach, i.e., $\boldsymbol{D}_{3d}R_6=\{I,2R_6,3C_2,2C_3,R_6^3, 3R_6C_2,i, 3\sigma_v,2iR_6,2S_6,iR_6^3,3\sigma_vR_6\}$. Moreover, Eq. 4 reveals that the present formalism is related to Flurry's approach,3) though the group $\hat{\boldsymbol{C}}'_2$ is different from the group **F** generated from an isodynamic operator.

2 Subgroups of the Group $\hat{\boldsymbol{D}}_{6h}$. In order to apply the USCI approach to the enumeration of cyclohexane derivatives, we shall clarify the group-subgroup relationship of $\hat{\boldsymbol{D}}_{6h}$. We have distinct, up to conjugacy, subgroups of $\hat{\boldsymbol{D}}_{6h}$ as summarized in the following list.

$$\boldsymbol{C}_1=\{I\}$$
$$\hat{\boldsymbol{C}}_2=\{I,\hat{C}_2\}$$
$$\hat{\boldsymbol{C}}'_2=\{I,\hat{C}'_{2(1)}\}$$
$$\boldsymbol{C}'_2=\{I,C'_{2(1)}\}$$
$$\boldsymbol{C}_s=\{I,\sigma'_{v(1)}\}$$
$$\hat{\boldsymbol{C}}_s=\{I,\hat{\sigma}'_{v(1)}\}$$
$$\hat{\boldsymbol{C}}'_s=\{I,\hat{\sigma}_h\}$$
$$\boldsymbol{C}_i=\{I,i\}$$
$$\boldsymbol{C}_3=\{I,C_3,C_3^2\}$$
$$\hat{\boldsymbol{D}}_2=\{I,\hat{C}_2,\hat{C}'_{2(1)},C'_{2(2)}\}$$
$$\hat{\boldsymbol{C}}_{2v}=\{I,\hat{C}_2,\sigma_{v(1)},\hat{\sigma}_{v(2)}\}$$
$$\hat{\boldsymbol{C}}'_{2v}=\{I,\hat{C}'_{2(1)},\hat{\sigma}_h,\sigma_{v(1)}\}$$
$$\hat{\boldsymbol{C}}''_{2v}=\{I,C'_{2(1)},\hat{\sigma}_h,\hat{\sigma}_{v(1)}\}$$
$$\hat{\boldsymbol{C}}_{2h}=\{I,\hat{C}_2,\hat{\sigma}_h,i\}$$
$$\hat{\boldsymbol{C}}'_{2h}=\{I,\hat{C}'_{2(1)},i,\hat{\sigma}_{v(2)}\}$$
$$\boldsymbol{C}_{2h}=\{I,C'_{2(1)},i,\sigma_{v(3)}\}$$
$$\hat{\boldsymbol{C}}_6=\{I,\hat{C}_6,C_3,\hat{C}_2,C_3^2,\hat{C}_6^5\}$$
$$\hat{\boldsymbol{D}}_3=\{I,C_3,C_3^2,\hat{C}'_{2(1)},\hat{C}'_{2(2)},\hat{C}'_{2(3)}\}$$
$$\boldsymbol{D}_3=\{I,C_3,C_3^2,C'_{2(1)},C'_{2(2)},C'_{2(3)}\}$$
$$\boldsymbol{C}_{3v}=\{I,C_3,C_3^2,\sigma_{v(1)},\sigma_{v(2)},\sigma_{v(3)}\}$$
$$\hat{\boldsymbol{C}}_{3v}=\{I,C_3,C_3^2,\hat{\sigma}_{v(1)},\hat{\sigma}_{v(2)},\hat{\sigma}_{v(3)}\}$$
$$\hat{\boldsymbol{C}}_{3h}=\{I,C_3,C_3^2,\hat{\sigma}_h,\hat{S}_3,\hat{S}_3^5\}$$
$$\boldsymbol{C}_{3i}=\{I,C_3,C_3^2,S_6,i,S_6^5\}$$
$$\hat{\boldsymbol{D}}_{2h}=\{I,\hat{C}_2,\hat{C}'_{2(1)},C'_{2(2)},\hat{\sigma}_h,i,\sigma_{v(1)},\hat{\sigma}_{v(2)}\}$$
$$\hat{\boldsymbol{D}}_6=\{I,\hat{C}_6,C_3,\hat{C}_2,C_3^2,\hat{C}_6^5,\hat{C}'_{2(1)},C'_{2(1)},\hat{C}'_{2(2)}, C'_{2(2)}, \hat{C}'_{2(3)},C'_{2(3)}\}$$
$$\hat{\boldsymbol{C}}_{6v}=\{I,\hat{C}_6,C_3,\hat{C}_2,C_3^2,\hat{C}_6^5,\sigma_{v(1)},\hat{\sigma}_{v(1)},\sigma_{v(2)}, \hat{\sigma}_{v(2)},\sigma_{v(3)},\hat{\sigma}_{v(3)}\}$$
$$\hat{\boldsymbol{C}}_{6h}=\{I,\hat{C}_6,C_3,\hat{C}_2,C_3^2,\hat{C}_6^5,\hat{\sigma}_h,S_6,\hat{S}_3,i,\hat{S}_3^5,S_6^5\}$$
$$\hat{\boldsymbol{D}}_{3h}=\{I,C_3,C_3^2,\hat{C}'_{2(1)},\hat{C}'_{2(2)},\hat{C}'_{2(3)},\hat{\sigma}_h, \hat{S}_3,\hat{S}_3^5,\sigma_{v(1)}, \sigma_{v(2)},\sigma_{v(3)}\}$$
$$\hat{\boldsymbol{D}}'_{3h}=\{I,C_3,C_3^2,C'_{2(1)},C'_{2(2)},C'_{2(3)},\hat{\sigma}_h,\hat{S}_3,\hat{S}_3^5,\hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)},\hat{\sigma}_{v(3)}\}$$
$$\hat{\boldsymbol{D}}_{3d}=\{I,C_3,C_3^2,\hat{C}'_{2(1)},\hat{C}'_{2(2)},\hat{C}'_{2(3)},S_6,i,S_6^5,\hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)},\hat{\sigma}_{v(3)}\}$$
$$\boldsymbol{D}_{3d}=\{I,C_3,C_3^2,C'_{2(1)},C'_{2(2)},C'_{2(3)},S_6,i,S_6^5,\sigma_{v(1)}, \sigma_{v(2)},\sigma_{v(3)}\}$$
$$\hat{\boldsymbol{D}}_{6h}=\{I,\hat{C}_6,C_3,\hat{C}_2,C_3^2,\hat{C}_6^5,\hat{C}'_{2(1)},C'_{2(1)},\hat{C}'_{2(2)},C'_{2(2)}, \hat{C}'_{2(3)},C'_{2(3)},\hat{\sigma}_h, S_6,\hat{S}_3,i,\hat{S}_3^5,S_6^5,\sigma_{v(1)},\hat{\sigma}_{v(1)},\sigma_{v(2)}, \hat{\sigma}_{v(2)},\sigma_{v(3)},\hat{\sigma}_{v(3)}\}.$$

These subgroups construct a non-redundant set of subgroups (SSG) for $\hat{\boldsymbol{D}}_{6h}$,

$$SSG_{\hat{\boldsymbol{D}}_{6h}} = \{\boldsymbol{C}_1, \hat{\boldsymbol{C}}_2, \hat{\boldsymbol{C}}'_2, \boldsymbol{C}'_2, \boldsymbol{C}_s, \hat{\boldsymbol{C}}_s, \hat{\boldsymbol{C}}'_s, \boldsymbol{C}_i, \boldsymbol{C}_3, \hat{\boldsymbol{D}}_2, \hat{\boldsymbol{C}}_{2v}, \hat{\boldsymbol{C}}'_{2v}, \hat{\boldsymbol{C}}''_{2v}, \hat{\boldsymbol{C}}_{2h}, \hat{\boldsymbol{C}}'_{2h}, \boldsymbol{C}_{2h}, \hat{\boldsymbol{C}}_6, \hat{\boldsymbol{D}}_3, \boldsymbol{D}_3, \boldsymbol{C}_{3v}, \hat{\boldsymbol{C}}_{3v}, \hat{\boldsymbol{C}}_{3h}, \boldsymbol{C}_{3i}, \hat{\boldsymbol{D}}_{2h}, \hat{\boldsymbol{D}}_6, \hat{\boldsymbol{C}}_{6v}, \hat{\boldsymbol{C}}_{6h}, \hat{\boldsymbol{D}}_{3h}, \hat{\boldsymbol{D}}'_{3h}, \hat{\boldsymbol{D}}_{3d}, \boldsymbol{D}_{3d}, \hat{\boldsymbol{D}}_{6h}\} \quad (5)$$

The subgroups of $\hat{\boldsymbol{D}}_{6h}$ are classified into two categories, i.e., anisoenergetic groups:

$$\{\boldsymbol{C}_1, \boldsymbol{C}'_2, \boldsymbol{C}_s, \boldsymbol{C}_i, \boldsymbol{C}_3, \boldsymbol{C}_{2h}, \boldsymbol{D}_3, \boldsymbol{C}_{3v}, \boldsymbol{C}_{3i}, \boldsymbol{D}_{3d}\} \quad (6)$$

and isoenergetic groups:

$$\{ \hat{\boldsymbol{C}}_2, \hat{\boldsymbol{C}}'_2, \hat{\boldsymbol{C}}_s, \hat{\boldsymbol{C}}'_s, \hat{\boldsymbol{D}}_2, \hat{\boldsymbol{C}}_{2v}, \hat{\boldsymbol{C}}'_{2v}, \hat{\boldsymbol{C}}''_{2v}, \hat{\boldsymbol{C}}_{2h}, \hat{\boldsymbol{C}}'_{2h}, \hat{\boldsymbol{C}}_6, \hat{\boldsymbol{D}}_3, \hat{\boldsymbol{C}}_{3v},\hat{\boldsymbol{C}}_{3h}, \hat{\boldsymbol{D}}_{2h}, \hat{\boldsymbol{D}}_6, \hat{\boldsymbol{C}}_{6v}, \hat{\boldsymbol{C}}_{6h}, \hat{\boldsymbol{D}}_{3h}, \hat{\boldsymbol{D}}'_{3h}, \hat{\boldsymbol{D}}_{3d}, \hat{\boldsymbol{D}}_{6h}\}, \quad (7)$$

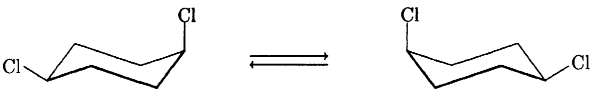
where the former category contains no pseudo-rotations and the latter involves at least one pseudo-rotation. In the light of the present notation, isoenergetic groups are represented by boldfaced letters with a hat symbol, while anisoenergetic groups are designated with boldfaced letters without a hat symbol.

The set represented by Eq. 6 contains the subgroups of $\boldsymbol{D}_{3d}$. It involves chiral and achiral subgroups. In a similar way, the set represented by Eq. 7 involves chiral and achiral subgroups. As a results, the subgroups of $\hat{\boldsymbol{D}}_{6h}$ are classified into four classes, i.e.,

anisoenergetic-chiral	$\boldsymbol{C}_1, \boldsymbol{C}'_2, \boldsymbol{C}_3, \boldsymbol{D}_3,$
anisoenergetic-achiral	$\boldsymbol{C}_s, \boldsymbol{C}_i, \boldsymbol{C}_{2h}, \boldsymbol{C}_{3v}, \boldsymbol{C}_{3i}, \boldsymbol{D}_{3d},$
isoenergetic-chiral	$\hat{\boldsymbol{C}}_2, \hat{\boldsymbol{C}}'_2, \hat{\boldsymbol{D}}_2, \hat{\boldsymbol{C}}_6, \hat{\boldsymbol{D}}_3, \hat{\boldsymbol{D}}_6$, and
isoenergetic-achiral	$\hat{\boldsymbol{C}}_s, \hat{\boldsymbol{C}}'_s, \hat{\boldsymbol{C}}_{2v}, \hat{\boldsymbol{C}}'_{2v}, \hat{\boldsymbol{C}}''_{2v}, \hat{\boldsymbol{C}}_{2h}, \hat{\boldsymbol{C}}'_{2h}, \hat{\boldsymbol{C}}_{3v}, \hat{\boldsymbol{C}}_{3h}, \hat{\boldsymbol{D}}_{2h}, \hat{\boldsymbol{C}}_{6v}, \hat{\boldsymbol{C}}_{6h}, \hat{\boldsymbol{D}}_{3h}, \hat{\boldsymbol{D}}'_{3h}, \hat{\boldsymbol{D}}_{3d}, \hat{\boldsymbol{D}}_{6h}.$

The pair of chair-form conformers of cyclohexane is considered to belong to $\hat{\boldsymbol{D}}_{6h}$ in the light of the formulation described above. As a result, the pair of chair-form conformers of a cyclohexane derivative can be represented by a subgroup of $\hat{\boldsymbol{D}}_{6h}$. We here note the equivalency of such pairs under the action of the group $\hat{\boldsymbol{D}}_{6h}$.

Let us consider *cis*-1,4-dichlorocyclohexane as an example. This derivative is generated by putting chlorine atoms on the 1- and 10-positions of **1a** and of **1b**. Thus, we take account of the following pair of conformers:



6a **6b**

(I)

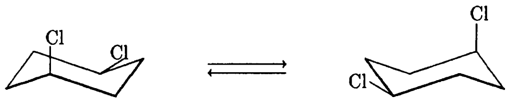
Each conformer in the fixed form belongs to $\boldsymbol{C}_s$ ($= \{I, \sigma_{v(1)}\}$) and the equilibrium pair is also fixed by the action of the pseudo-operation $\hat{C}_2$. Hence the pair belongs to $\hat{\boldsymbol{C}}_{2v}$-group:

$$\hat{\boldsymbol{C}}_{2v} = \hat{\boldsymbol{C}}_2 \times \boldsymbol{C}_s \tag{8}$$

$$= \boldsymbol{C}_s + \hat{C}_2 \boldsymbol{C}_s \tag{9}$$

$$= \{I, \sigma_{v(1)}, \hat{C}_2, \hat{\sigma}_{v(1)}\}. \tag{10}$$

Let us next consider another representation of *cis*-1,4-dichlorocyclohexane which is generated by putting chlorine atoms on the 3- and 12-positions of **1a** and of **1b**. Then we obtain the following pair of conformers:



7a **7b**

(II)

The pair belongs to $\hat{C}_{2v}^{(\mathrm{c})}$-group:

$$\hat{\boldsymbol{C}}_{2v}^{(\mathrm{c})} = \{I, \sigma_{v(2)}, \hat{C}_2, \hat{\sigma}_{v(2)}\}. \tag{11}$$

The pair (**6a**⇄**6b**) is transformed into the pair (**7a**⇄**7b**) by the operation $\hat{C}_6$. Hence, the two pairs are equivalent on the action of $\hat{\boldsymbol{D}}_{6h}$. This equivalency corresponds to the fact that $\hat{\boldsymbol{C}}_{2v}$ and $\hat{\boldsymbol{C}}_{2v}^{(\mathrm{c})}$ are conjugate to each other within the group $\hat{\boldsymbol{D}}_{6h}$.

In a similar way, other homomeric pairs can be generated by placing two chlorine atoms on other equivalent sets of positions; each pair corresponds to $\hat{\boldsymbol{C}}_{2v}$ or to its conjugate subgroup. The resulting homomeric pairs are regarded as being equivalent and are counted once as a single compound. Note that the present treatment selects an appropriate representative (e.g., $\hat{\boldsymbol{C}}_{2v}$) from the set of conjugated subgroups of $\hat{\boldsymbol{D}}_{6h}$.

It should be noted that the term *homomeric* is used to designate two pairs that are superimposable on the action of any operation of the pseudo-point group of a parent pair (e.g. $\hat{\boldsymbol{D}}_{6h}$ for a flexible cyclohexane skeleton). The term *homomeric* is also used to describe the starting and the product molecule that are superimposable on the action of any operation of the point group of the corresponding parent molecule (e.g. $\boldsymbol{D}_{3d}$ for a fixed cyclohexane skeleton). In a similar way, the term *enantiomeric* is also used with respect to both pairs and molecules.

3 Orbits and Chronality. Each orbit generated by a pseudo-point group is governed by a coset representation as discussed in the preceding paper. The complete set of such coset representations (SCR) for $\hat{\boldsymbol{D}}_{6h}$ coresponds to the SSG described above.

$$\begin{aligned} &SCR_{\hat{\boldsymbol{D}}_{6h}} = \\ &\{\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_1), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_2), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}'_2), \boldsymbol{D}_{6h}(/\boldsymbol{C}'_2), \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s), \\ &\hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_s), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}'_s), \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_i), \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_3), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_2), \\ &\hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{2v}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}'_{2v}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}''_{2v}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{2h}), \\ &\hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}'_{2h}), \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_{2h}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_6), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_3), \\ &\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{D}_3), \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_{3v}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{3v}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{3h}), \\ &\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_{3i}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_{2h}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_6), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{6v}), \\ &\hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{C}}_{6h}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_{3h}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}'_{3h}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_{3d}), \\ &\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{D}_{3d}), \hat{\boldsymbol{D}}_{6h}(/\hat{\boldsymbol{D}}_{6h})\}. \end{aligned} \tag{12}$$

Each of the coset representations is designated with the notation that contains the global symmetry and the local symmetry of the corresponding orbit. This notation has been coined by us to emphasize the close relationship between a coset representation and an orbit.[6]

A mark table for the pseudo-point group is necessary for assigning a coset representation to an orbit. Table 1 shows the mark table of the group $\hat{\boldsymbol{D}}_{6h}$, which is obtained by starting from the multiplication table of the group.

In order to assign a coset representation to an orbit, we calculate a fixed-point vector (FPV). The orbit of the twelve positions of the pair (**1a**⇄**1b**) has an FPV:

$$\begin{aligned} FPV = (&12,0,0,0,4,0,0,0,0,0,0,0,0, \\ &0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0). \end{aligned}$$

This is identical with the $\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-row of Table 1. Hence, the orbit of the twelve positions is determined to be governed by the coset representation $\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$.

Since $\hat{\boldsymbol{D}}_{6h}$ is isoenergetic and $\boldsymbol{C}_s$ is anisoenergetic, the orbit is concluded to be enantiochronal. The twelve-membered enantiochronal orbit is capable of splitting into two orbits (equatorial and axial positions) under frozen conditions.

On the other hand, the six carbon atoms of the pair construct an orbit governed by $\hat{\boldsymbol{C}}'_{2v}$, since the FPV of this orbit is calculated to be

$$\begin{aligned} FPV = (&6,0,2,0,2,0,6,0,0,0,0,2,0, \\ &0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0). \end{aligned}$$

which is identical with the $\hat{\boldsymbol{D}}_{6h}(\hat{\boldsymbol{C}}'_{2v})$-row of Table 1.

Since both $\hat{\boldsymbol{D}}_{6h}$ and $\hat{\boldsymbol{C}}'_{2v}$ are isoenergetic, the orbit is concluded to be homochronal. The homochronal orbit

Table 1. Mark Table for the Group $\hat{D}_{6h}$

	C_1	$\hat{C}_2$	$\hat{C}'_2$	C'_2	C_s	$\hat{C}_s$	$\hat{C}'_s$	C_i	C_3	$\hat{D}_2$	$\hat{C}_{2v}$	$\hat{C}'_{2v}$	$\hat{C}''_{2v}$	$\hat{C}_{2h}$	$\hat{C}'_{2h}$	C_{2h}	$\hat{C}_6$	$\hat{D}_3$	D_3	C_{3v}	$\hat{C}_{3v}$	$\hat{C}_{3h}$	C_{3i}	$\hat{D}_{2h}$	$\hat{D}_6$	$\hat{C}_{6v}$	$\hat{C}_{6h}$	$\hat{D}_{3h}$	$\hat{D}'_{3h}$	$\hat{D}_{3d}$	D_{3d}	$\hat{D}_{6h}$
$\hat{D}_{6h}(/C_1)$	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_2)$	12	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}'_2)$	12	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C'_2)$	12	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_s)$	12	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_s)$	12	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}'_s)$	12	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_i)$	12	0	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_3)$	8	0	0	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{D}_2)$	6	6	2	2	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{2v})$	6	6	0	0	2	2	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}'_{2v})$	6	0	2	0	2	0	6	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}''_{2v})$	6	0	0	2	0	2	6	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{2h})$	6	6	0	0	0	0	6	6	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}'_{2h})$	6	0	2	0	0	2	0	6	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_{2h})$	6	0	0	2	2	0	0	6	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_6)$	4	4	0	0	0	0	0	0	4	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{D}_3)$	4	0	4	0	0	0	0	0	4	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/D_3)$	4	0	0	4	0	0	0	0	4	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_{3v})$	4	0	0	0	4	0	0	0	4	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{3v})$	4	0	0	0	0	4	0	0	4	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{3h})$	4	0	0	0	0	0	4	0	4	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/C_{3i})$	4	0	0	0	0	0	0	4	4	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{D}_{2h})$	3	3	1	1	1	1	3	3	0	1	1	1	1	3	1	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{D}_6)$	2	2	2	2	0	0	0	0	2	2	0	0	0	0	0	0	2	2	2	0	0	0	0	0	2	0	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{6v})$	2	2	0	0	2	2	0	0	2	0	2	0	0	0	0	0	2	0	0	2	2	0	0	0	0	2	0	0	0	0	0	0
$\hat{D}_{6h}(/\hat{C}_{6h})$	2	2	0	0	0	0	2	2	2	0	0	0	0	2	0	0	2	0	0	0	0	2	2	0	0	0	2	0	0	0	0	0
$\hat{D}_{6h}(/\hat{D}_{3h})$	2	0	2	0	2	0	2	0	2	0	0	2	0	0	0	0	0	2	0	2	0	2	0	0	0	0	0	2	0	0	0	0
$\hat{D}_{6h}(/\hat{D}'_{3h})$	2	0	0	2	0	2	2	0	2	0	0	0	2	0	0	0	0	0	2	0	2	2	0	0	0	0	0	0	2	0	0	0
$\hat{D}_{6h}(/\hat{D}_{3d})$	2	0	2	0	0	2	0	2	2	0	0	0	0	0	2	0	0	2	0	0	2	0	2	0	0	0	0	0	0	2	0	0
$\hat{D}_{6h}(/D_{3d})$	2	0	0	2	2	0	0	2	2	0	0	0	0	0	0	2	0	0	2	2	0	0	2	0	0	0	0	0	0	0	2	0
$\hat{D}_{6h}(/\hat{D}_{6h})$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

does not split so that the six carbon atoms are equivalent even under frozen conditions.

4 Subduction and Combinatorial Enumeration.

In order to enumerate flexible cyclohexane derivatives, we here discuss subduction of coset representations for $\hat{D}_{6h}(/C_s)$. From the date of $\hat{D}_{6h}(/C_s)$ and the mark tables of the subgroups listed in $SSG_{\hat{D}_{6h}}$, we calculate the following subductions.

$$\hat{D}_{6h}(/C_s) \downarrow C_1 = 12C_1(/C_1) \qquad s_1^{12} \quad 1/24 \tag{13a}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_2 = 6\hat{C}_2(/C_1) \qquad s_2^{6} \quad 1/24 \tag{13b}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}'_2 = 6\hat{C}'_2(/C_1) \qquad s_2^{6} \quad 1/8 \tag{13c}$$

$$\hat{D}_{6h}(/C_s) \downarrow C'_2 = 6C_2(/C_1) \qquad s_2^{6} \quad 1/8 \tag{13d}$$

$$\hat{D}_{6h}(/C_s) \downarrow C_s = 4C_s(/C_s) + 4C_s(/C_1) \qquad s_1^4 s_2^4 \quad 1/8 \tag{13e}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_s = 6\hat{C}_s(/C_1) \qquad s_2^{6} \quad 1/8 \tag{13f}$$

$$\hat{D}_{6h}(/C_s) \downarrow C'_s, = 6\hat{C}'_s(/C_1) \qquad s_2^{6} \quad 1/24 \tag{13g}$$

$$\hat{D}_{6h}(/C_s) \downarrow C_i, = 6C_i(/C_1) \qquad s_2^{6} \quad 1/24 \tag{13h}$$

$$\hat{D}_{6h}(/C_s) \downarrow C_3 = 4C_3(/C_1) \qquad s_3^{4} \quad 1/12 \tag{13i}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{D}_2 = 3\hat{D}_2(/C_1) \qquad s_4^{3} \quad 0 \tag{13j}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{2v} = 2\hat{C}_{2v}(/C_1) + 2\hat{C}_{2v}(/C_s) \qquad s_4^2 s_2^2 \quad 0 \tag{13k}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}'_{2v} = 2\hat{C}'_{2v}(/C_1) + 2\hat{C}'_{2v}(/C_s) \qquad s_4^2 s_2^2 \quad 0 \tag{13l}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}''_{2v} = 3\hat{C}''_{2v}(/C_1) \qquad s_4^{3} \quad 0 \tag{13m}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{2h} = 3\hat{C}_{2h}(/C_1) \qquad s_4^{3} \quad 0 \tag{13n}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}'_{2h} = 3\hat{C}'_{2h}(/C_1) \qquad s_4^{3} \quad 0 \tag{13o}$$

$$\hat{D}_{6h}(/C_s) \downarrow C'_{2h} = 2C_{2h}(/C_1) + 2C_{2h}(/C_s) \qquad s_4^2 s_2^2 \quad 0 \tag{13p}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_6 = 2\hat{C}_6(/C_1) \qquad s_6^{2} \quad 1/12 \tag{13q}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{D}_3 = 2\hat{D}_3(/C_1) \qquad s_6^{2} \quad 0 \tag{13r}$$

$$\hat{D}_{6h}(/C_s) \downarrow D_3 = 2D_3(/C_1) \qquad s_6^{2} \quad 0 \tag{13s}$$

$$\hat{D}_{6h}(/C_s) \downarrow C_{3v} = 4C_{3v}(/C_s) \qquad s_3^{4} \quad 0 \tag{13t}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{3v} = 2\hat{C}_{3v}(/C_1) \qquad s_6^{2} \quad 0 \tag{13u}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{3h} = 2\hat{C}_{3v}(/C_1) \qquad s_6^{2} \quad 1/12 \tag{13v}$$

$$\hat{D}_{6h}(/C_s) \downarrow C_{3i} = 2C_{3i}(/C_1) \qquad s_6^{2} \quad 1/12 \tag{13w}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{D}_{2h} = \hat{D}_{2h}(/C_1) + \hat{D}_{2h}(/C_s) \qquad s_4 s_8 \quad 0 \tag{13x}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{D}_6 = \hat{D}_6(/C_1) \qquad s_{12} \quad 0 \tag{13y}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{6v} = 2\hat{C}_{6v}(/C_s) \qquad s_6^{2} \quad 0 \tag{13z}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{C}_{6h} = \hat{C}_{6h}(/C_1) \qquad s_{12} \quad 0 \tag{13A}$$

$$\hat{D}_{6h}(/C_s) \downarrow \hat{D}_{3h} = 2\hat{D}_{3h}(/C_s) \qquad s_6^{2} \quad 0 \tag{13B}$$

$$\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \downarrow \hat{\boldsymbol{D}}'_{3h} = \hat{\boldsymbol{D}}'_{3h}(/\boldsymbol{C}_1) \qquad s_{12} \qquad 0 \tag{13C}$$

$$\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \downarrow \hat{\boldsymbol{D}}_{3d} = \hat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1) \qquad s_{12} \qquad 0 \tag{13D}$$

$$\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \downarrow \boldsymbol{D}_{3d} = 2\boldsymbol{D}_{3d}(/\boldsymbol{C}_s) \qquad s_6^2 \qquad 0 \tag{13E}$$

$$\hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \downarrow \hat{\boldsymbol{D}}_{6h} = \hat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \qquad s_{12} \qquad 0 \tag{13F}$$

The monomial shown in each equation is the corresponding unit subduced cycle index (USCI).[6] The fractions shown in the ends of the equations are the corresponding coefficients appearing in a cycle index for combinatorial enumeration.[10] The coefficients are positive for cyclic groups, but zero for any other group than cyclic ones.[10]

Let us consider a set of four substituents (W, X, Y, and Z). We select twelve substituents from the set and place them on the orbit of the twelve positions of the pair (**1a**$\rightleftarrows$**1b**). We thus consider molecular formulae $\mathrm{W}_k\mathrm{X}_l\mathrm{Y}_m\mathrm{Z}_n$, where the subscripts are non-negative integers satisfying $k+l+m+n=12$ and skeletal carbon atoms are not taken into consideration. In order to use the generating-function method of the USCI approach, we adopt the following inventory for the present enumeration.

$$s_r = w^r + x^r + y^r + z^r, \tag{14}$$

where each small letter corresponds to a substituent of its capital letter. The inventory is introduced into each of Eq. 13a to Eq. 13F.

for $\boldsymbol{C}_1$:

$$s_1^{12} = (w+x+y+z)^{12} \tag{15a}$$

for $\hat{\boldsymbol{C}}_2, \hat{\boldsymbol{C}}'_2, \boldsymbol{C}'_2, \hat{\boldsymbol{C}}_s, \hat{\boldsymbol{C}}'_s, \boldsymbol{C}_i$:

$$s_2^6 = (w^2+x^2+y^2+z^2)^6 \tag{15b}$$

for $\boldsymbol{C}_s$:

$$s_1^4 s_2^4 = (w+x+y+z)^4(w^2+x^2+y^2+z^2)^4 \tag{15c}$$

for $\boldsymbol{C}_3, \boldsymbol{C}_{3v}$:

$$s_3^4 = (w^3+x^3+y^3+z^3)^4 \tag{15d}$$

for $\hat{\boldsymbol{D}}_2, \hat{\boldsymbol{C}}''_{2v}, \hat{\boldsymbol{C}}_{2h}, \hat{\boldsymbol{C}}'_{2h}$:

$$s_4^3 = (w^4+x^4+y^4+z^4)^3 \tag{15e}$$

for $\hat{\boldsymbol{C}}_{2v}, \hat{\boldsymbol{C}}'_{2v}, \boldsymbol{C}'_{2h}$:

$$s_2^2 s_4^2 = (w^2+x^2+y^2+z^2)^2(w^4+x^4+y^4+z^4)^2 \tag{15f}$$

for $\hat{\boldsymbol{C}}_6, \hat{\boldsymbol{D}}_3, \boldsymbol{D}_3, \hat{\boldsymbol{C}}_{3v}, \hat{\boldsymbol{C}}_{3h}, \boldsymbol{C}_{3i}, \hat{\boldsymbol{C}}_{6v}, \hat{\boldsymbol{D}}_{3h}, \hat{\boldsymbol{D}}_{3d}$:

$$s_6^2 = (w^6+x^6+y^6+z^6)^2 \tag{15g}$$

for $\hat{\boldsymbol{D}}_{2h}$:

$$s_4 s_8 = (w^4+x^4+y^4+z^4)(w^8+x^8+y^8+z^8) \tag{15h}$$

for $\hat{\boldsymbol{D}}_6, \hat{\boldsymbol{C}}_{6h}, \hat{\boldsymbol{D}}'_{3h}, \hat{\boldsymbol{D}}_{3d}, \hat{\boldsymbol{D}}_{6h}$:

$$s_{12} = w^{12}+x^{12}+y^{12}+z^{12} \tag{15i}$$

The generating function (Eq. 15a to Eq. 15i) are expanded and the coefficients of the terms $w^k x^l y^m z^n$ are collected to give Table 2. Each column of Table 2 is concerned with a subsymmetry and each row with the term $w^k x^l y^m z^n$. Each term is represented by a partition $[k,l,m,n]$ in which we presume $k \geq l \geq m \geq n$ without losing generality. This term corresponds to the molecular formula $\mathrm{W}_k\mathrm{X}_l\mathrm{Y}_m\mathrm{Z}_n$.

Table 2 is regarded as a matrix, which is multiplied by the inverse of Table 1. Then we obtain a matrix shown in Table 3, in which the value at each intersection indicates the number of pairs with $\mathrm{W}_k\mathrm{X}_l\mathrm{Y}_m\mathrm{Z}_n$ and the subsymmetry. In the case of any chiral group (whether it is isoenergetic or anisoenergetic), the value is concerned with every racemic pair throughout the present paper.

The generating-function method described above is useful to obtain a prospect over the whole aspect of isomer numbers, since it gives a table such as Table 3. However, the isomer numbers of a specific molecular formula are sometimes desirable. For this purpose, we can use the elementary superposition theorem presented recently by us.[11] Let us consider pairs of $\mathrm{W}^8\mathrm{X}^4$ (or [8, 4,0,0]). This partition of substituents corresponds to a permutation group represented by $\mathrm{S}^{[4]}\times\mathrm{S}^{[8]}$, where $\mathrm{S}^{[4]}$ is the symmetric group of degree 4 and $\mathrm{S}^{[8]}$ is the symmetric group of degree 8. Since the present case involves one orbit, each USCI (Eq. 13a to Eq. 13F) is used as the corresponding subduced cycle index (SCI). We first find combinations of dummy variables effective for the group $\mathrm{S}^{[4]}\times\mathrm{S}^{[8]}$; for example, the SCI s_1^{12} for the group $\boldsymbol{C}_1$ has an effective combination, $\{s_1^4 \times s_1^8\}$. Such combinations for the other subgroups are found in braces following right arrows. Then, we calculate the number of fixed points by using the elementary superposition theorem.[11]

for $\boldsymbol{C}_1 : s_1^{12} \rightarrow \{s_1^4 \times s_1^8\}$:

$$\frac{1}{1^4 4!} \times \frac{1}{1^8 8!} \times 1^{12} 12! = 495, \tag{16a}$$

for $\hat{\boldsymbol{C}}_2, \hat{\boldsymbol{C}}'_2, \boldsymbol{C}'_2, \hat{\boldsymbol{C}}_s, \hat{\boldsymbol{C}}'_s, \boldsymbol{C}_i, : s_2^6 \rightarrow \{s_2^2 \times s_2^4\}$:

$$\frac{1}{2^2 2!} \times \frac{1}{2^4 4!} \times 2^6 6! = 15, \tag{16b}$$

for $\boldsymbol{C}_s : s_1^4 s_2^4 \rightarrow \{s_1^4 \times s_2^4, s_2^2 \times s_1^4 s_2^2, s_1^2 s_2 \times s_1^2 s_2^3,\}$:

$$\left(\frac{1}{1^4 4!} \times \frac{1}{2^4 4!} + \frac{1}{2^2 2!} \times \frac{1}{1^4 4! 2^2 2!} + \frac{1}{2^2 2! 2^1 1!} \times \frac{1}{1^2 2! 2^3 3!}\right) \times 1^4 4! \times 2^4 4! = 1+6+24 = 31, \tag{16c}$$

for $\boldsymbol{C}_3, \boldsymbol{C}_{3v} : s_3^4 \rightarrow \{\text{none}\} : 0,$

$$\tag{16d}$$

for $\hat{\boldsymbol{D}}_2, \hat{\boldsymbol{C}}''_{2v} \hat{\boldsymbol{C}}_{2h} \hat{\boldsymbol{C}}'_{2h} : s_4^3 \rightarrow \{s_4 \times s_4^2\}$:

$$\frac{1}{4^1 1!} \times \frac{1}{4^2 2!} \times 4^3 3! = 3, \tag{16e}$$

Table 2. Coefficients for Eqs. 15a to 15i

	C_1	$\hat{C}_2$	$\hat{C}'_2$	C'_2	C_s	$\hat{C}_s$	$\hat{C}'_s$	C_i	C_3	$\hat{D}_2$	$\hat{C}_{2v}$	$\hat{C}'_{2v}$	$\hat{C}''_{2v}$	$\hat{C}_{2h}$	$\hat{C}'_{2h}$	C_{2h}	$\hat{C}_6$	$\hat{D}_3$	D_3	C_{3v}	$\hat{C}_{3v}$	$\hat{C}_{3h}$	C_{3i}	$\hat{D}_{2h}$	$\hat{D}_6$	$\hat{C}_{6v}$	$\hat{C}_{6h}$	$\hat{D}_{3h}$	$\hat{D}'_{3h}$	$\hat{D}_{3d}$	D_{3d}	$\hat{D}_{6h}$
[12,0,0,0]	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
[11,1,0,0]	12	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[10,2,0.0]	66	6	6	6	10	6	6	6	0	0	2	2	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[10,1,1,0]	132	0	0	0	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[9,3,0,0]	220	0	0	0	20	0	0	0	4	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0
[9,2,1,0]	660	0	0	0	28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[9,1,1,1]	1320	0	0	0	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[8,4,0,0]	495	15	15	15	31	15	15	15	0	3	3	3	3	3	3	3	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
[8,3,1,0]	1980	0	0	0	52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[8,2,2,0]	2970	30	30	30	66	30	30	30	0	0	2	2	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[8,2,1,1]	5940	0	0	0	60	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[7,5,0,0]	792	0	0	0	40	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[7,4,1,0]	3960	0	0	0	72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[7,3,2,0]	7920	0	0	0	112	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[7,3,1,1]	15840	0	0	0	96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[7,2,2,1]	23760	0	0	0	144	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[6,6,0,0]	924	20	20	20	44	20	20	20	6	0	4	4	0	0	0	4	2	2	2	6	2	2	2	0	0	2	0	2	0	0	2	0
[6,5,1,0]	5544	0	0	0	88	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[6,4,2,0]	13860	60	60	60	148	60	60	60	0	0	4	4	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[6,4,1,1]	27720	0	0	0	120	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[6,3,3,0]	18480	0	0	0	176	0	0	0	12	0	0	0	0	0	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0	0	0	0
[6,3,2,1]	55440	0	0	0	208	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[6,2,2,2]	83160	120	120	120	312	120	120	120	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,5,2.0]	16632	0	0	0	168	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,5,1,1]	33264	0	0	0	144	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,4,3,0]	27720	0	0	0	216	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,4,2,1]	83160	0	0	0	264	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,3,3,1]	110880	0	0	0	288	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[5,3,2,2]	166320	0	0	0	432	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[4,4,4,0]	34650	90	90	90	234	90	90	90	0	6	6	6	6	6	6	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[4,4,3,1]	138600	0	0	0	312	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[4,4,2,2]	207900	180	180	180	492	180	180	180	0	0	4	4	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[4,3,3,2]	277200	0	0	0	528	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
[3,3,3,3]	369600	0	0	0	576	0	0	0	24	0	0	0	0	0	0	0	0	0	0	24	0	0	0	0	0	0	0	0	0	0	0	0

Table 3. The Numbers of Flexible Cylohexane Derivatives

	C_1	$\hat{C}_2$	$\hat{C}'_2$	C'_2	C_s	$\hat{C}_s$	$\hat{C}'_s$	C_i	C_3	$\hat{D}_2$	$\hat{C}_{2v}$	$\hat{C}'_{2v}$	$\hat{C}''_{2v}$	$\hat{C}_{2h}$	$\hat{C}'_{2h}$	C_{2h}	$\hat{C}_6$	$\hat{D}_3$	D_3	C_{3v}	$\hat{C}_{3v}$	$\hat{C}_{3h}$	C_{3i}	$\hat{D}_{2h}$	$\hat{D}_6$	$\hat{C}_{6v}$	$\hat{C}_{6h}$	$\hat{D}_{3h}$	$\hat{D}'_{3h}$	$\hat{D}_{3d}$	D_{3d}	$\hat{D}_{6h}$	Total
[12,0,0,0]	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
[11,1,0,0]	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
[10,2,0,0]	0	0	1	1	1	1	0	0	0	0	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7
[10,1,1,0]	4	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7
[9,3,0,0]	7	0	0	0	4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	12
[9,2,1,0]	24	0	0	0	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	31
[9,1,1,1]	52	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	58
[8,4,0,0]	13	0	2	2	6	2	0	0	0	1	1	1	1	0	1	1	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	32
[8,3,1,0]	76	0	0	0	13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	89
[8,2,2,0]	102	2	7	7	15	7	2	2	0	0	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	147
[8,2,1,1]	240	0	0	0	15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	255
[7,5,0,0]	28	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	38
[7,4,1,0]	156	0	0	0	18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	174
[7,3,2,0]	316	0	0	0	28	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	344
[7,3,1,1]	648	0	0	0	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	672
[7,2,2,1]	972	0	0	0	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1008
[6,6,0,0]	26	1	4	4	8	4	1	1	0	0	1	1	0	0	0	1	0	0	0	0	0	0	0	0	0	1	0	1	0	0	1	0	55
[6,5,1,0]	220	0	0	0	22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	242
[6,4,2,0]	532	4	14	14	34	14	4	4	0	0	2	2	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	626
[6,4,1,1]	1140	0	0	0	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1170
[6,3,3,0]	749	0	0	0	41	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	793
[6,3,2,1]	2284	0	0	0	52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2336
[6,2,2,2]	3366	10	30	30	78	30	10	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3564
[5,5,2,0]	672	0	0	0	42	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	714
[5,5,1,1]	1368	0	0	0	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1404
[5,4,3,0]	1128	0	0	0	54	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1182
[5,4,2,1]	3432	0	0	0	66	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3498
[5,3,3,1]	4584	0	0	0	72	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4656
[5,3,2,2]	6876	0	0	0	108	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6984
[4,4,4,0]	1379	4	18	18	54	18	4	4	0	3	3	3	3	1	3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1518
[4,4,3,1]	5736	0	0	0	78	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5814
[4,4,2,2]	8514	14	44	44	120	44	14	14	0	0	2	2	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8814
[4,3,3,2]	11484	0	0	0	132	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	11616
[3,3,3,3]	15330	0	0	0	138	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	15474

$$\text{for}\quad \hat{\boldsymbol{C}}_{2v}, \hat{\boldsymbol{C}}'_{2v}, \boldsymbol{C}'_{2v} : s_2^2 s_4^2 \rightarrow \{s_2^2 \times s_4^2, s_4 \times s_2^2 s_4\} :$$
$$(\frac{1}{2^2 2!} \times \frac{1}{4^2 2!} + \frac{1}{4^1 1!} \times \frac{1}{2^2 2! 4^1 1!}) \times 2^2 2! \times 4^2 2!$$
$$= 1 + 2 = 3, \tag{16f}$$

$$\text{for}\quad \hat{\boldsymbol{C}}_6, \hat{\boldsymbol{D}}_3, \boldsymbol{D}_3, \hat{\boldsymbol{C}}_{3v}, \hat{\boldsymbol{C}}_{3h},$$
$$\boldsymbol{C}_{3i}, \hat{\boldsymbol{C}}_{6v}, \hat{\boldsymbol{D}}_{3h}, \boldsymbol{D}_{3d} : s_6^2 \rightarrow \{\text{none}\} : 0, \tag{16g}$$

$$\text{for}\quad \hat{\boldsymbol{D}}_{2h} : s_4 s_8 \rightarrow \{s_4 \times s_8\} :$$
$$\frac{1}{4^1 1!} \frac{1}{8^1 1!} \times 4^1 1! \times 8^1 1! = 1, \tag{16h}$$

$$\text{for}\quad \hat{\boldsymbol{D}}_6, \hat{\boldsymbol{C}}_{6h}, \hat{\boldsymbol{D}}'_{3h}, \hat{\boldsymbol{D}}_{3d}, \hat{\boldsymbol{D}}_{6h} : s_{12} \rightarrow \{\text{none}\} : 0. \tag{16i}$$

These values are collected to form a row vector:

$$FPV = (495, 15, 15, 15, 31, 15, 15, 15, 0, 3, 3, 3, 3, 3, 3, 3,$$
$$0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0).$$

This FPV is identical to the [8,4,0,0] row of Table 2. It follows that the multiplication of the FPV by the inverse of Table 1 gives the same row vector shown in the [8,4,0,0] row of Table 3.

The rightmost column of Table 3 involves the total number of each row, which indicates the isomer-number corresponding to the formula $W_k X_l Y_m Z_n$ or the partition [*k*,*l*,*m*,*n*]. These values can be alternatively obtained by using a cycle index.[10] The cycle index (CI) of the present case is obtained by using USCIs (Eq. 13a to Eq. 13F) and the coefficiencies placed together.

$$CI(\hat{\boldsymbol{D}}_{3h}; s_r)$$
$$= \frac{1}{24} s_1^{12} + (\frac{3}{24} + \frac{3}{8}) s_2^6 + \frac{1}{8} s_1^4 s_2^4 + \frac{1}{12} s_3^4 + \frac{3}{12} s_2^6$$
$$= \frac{1}{24} (s_1^{12} + 12 s_2^6 + 3 s_1^4 s_2^4 + 2 s_3^4 + 6 s_6^2). \tag{17}$$

After the introduction of the inventory (Eq. 14), the expansion of the resulting polynomial gives the values identical to those of the rightmost column of Table 1. Equation 17 is equivalent to counterpart obtained by using the Pólya-Redfield theorem. This fact has been generally proved by us.[10]

Discussion

1 Examples of Pairs Enumerated. Since the present enumeration (Table 3) gives itemized values with respect to formulae as well as to symmetries, each pair can be easily depicted. For example, the [6,6,0,0] row of Table 3 shows the numbers of pairs having formula H_6X_6 (the portion C_6 is abbreviated), which are itemized with respect to the subsymmetries of $\hat{\boldsymbol{D}}_{6h}$. Among the 55 pairs enumerated, Fig. 3 shows three pairs of higher symmetries.

The pair with [6,6,0,0] and $\boldsymbol{D}_{3d}$-symmetry represents a r-1,t-2,c-3,t-4,c-5,t-6-hexasubstituted cyclohexane. The pattern of substitution of the six Xs and the six hydrogens in the pair strictly complies with Eq. 13E, which predicts the appearance of two six-membered orbits. Since the pseudo-point group $\boldsymbol{D}_{3d}$ is anisoenergetic, the starting molecule (**8a**) is diastereomeric to the product molecule (**8b**). The diastereomeric nature stems from the fact that the six Xs are all equatorial in **8a** and all axial in **8b**. In the light of the present notation, such an anisoenergetic pseudo-point group is easily recognized, since it is represented by a symbol without a hat.

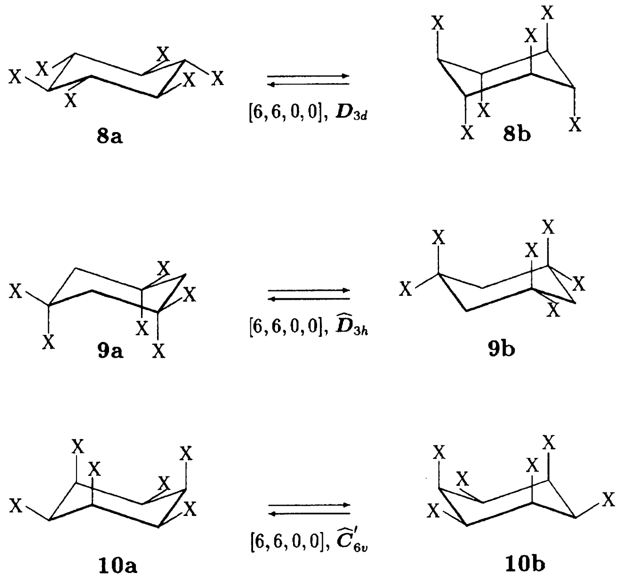


Fig. 3. [6,6,0,0]-Cyclohexane derivatives of higher symmetries.

On the other hand, an isoenergetic pseudo-point group is easily recognized by means of a symbol with a hat. Thus, the [6,6,0,0], $\hat{\boldsymbol{D}}_{3h}$-pair (**9a**$\rightleftarrows$**9b**) is a 1,1,3,3,5,5-hexasubstituted cyclohexane. The substitution pattern of the six Xs and the six hydrogens in the pair strictly complies with Eq. 13B, which also predicts the appearance of two six-membered orbits. According to the isoenergetic nature of the pseudo-point group $\hat{\boldsymbol{D}}_{3h}$, the starting molecule (**9a**) is homomeric to the product molecule (**9b**), where the three Xs are equatorial and the remaining three Xs are axial in each of the molecules.

The [6,6,0,0], $\hat{\boldsymbol{C}}_{6v}$-pair (**10a**$\rightleftarrows$**10b**) expresses an all-*cis*-1,2,3,4,5,6-hexasubstituted cyclohexane. The substitution pattern of H_6X_6 in the pair follows Eq. 13z, which also predicts the appearance of two six-membered orbits. The starting molecule (**10a**) and the product molecule (**10b**) are homomeric, in accord with the fact that $\hat{\boldsymbol{C}}_{6v}$ is isoenergetic.

When we focus our attention on the columns of Table 3, each column is regarded as being itemized with respect to molecular formulae. For the purpose of illustrating this aspect, let us examine the $\hat{\boldsymbol{D}}_2$ column (Fig. 4).

All of the substitution patterns listed in Fig. 4 follow Eq. 13j, which predicts the appearance of three four-membered orbits. Hence, the eight hydrogens of the pair (**11a**$\rightleftarrows$**11b**) are divided into two halves. This di-

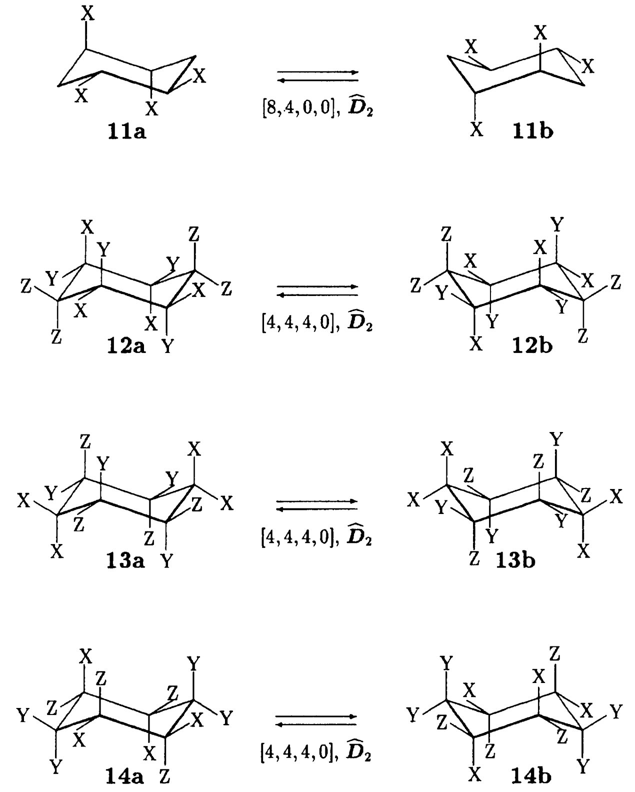


Fig. 4. Cyclohexane derivatives of the $\hat{D}_2$-symmetry.

vision are easily recognized if the pair is compared with the remaining pairs in Fig. 4.

2 Iso- vs. Anisoenergetic and Achiral vs. Chiral. In the preceding paper, we proposed the concept of iso- and anisoenergetic groups. This is useful as a criterion for classifying groups. The concept of chirality-achirality has long been used as another criterion, resulting in another type of classification of groups. Since the two criteria are independent, four categories of groups are created as described above, i.e., isoenergetic-achiral, isoenergetic-chiral, anisoenergetic-achiral, and anisoenergetic-chiral. These categories should be discussed in detail for further comprehension. It should be noted that the discussions in this section are concerned with the global symmetries and not with the local symmetries of pairs of molecules (coformers).

Let the symbols A and B represent achiral molecules. Suppose that the symbols Q and R express chiral molecules, and that $\overline{\mathrm{Q}}$ and $\overline{\mathrm{R}}$ are the corresponding antipodes. Since the isoenergetic-achiral category are divided into two subcategories (Type I and Type I′), the following cases appear.

- Isoenergetic

$\mathrm{A} \rightleftarrows \mathrm{A}$	achiral – isoenergetic	(Type I)
$\mathrm{Q} \rightleftarrows \overline{\mathrm{Q}}$	achiral – isoenergetic	(Type I′)
$\mathrm{Q} \rightleftarrows \mathrm{Q}(\overline{\mathrm{Q}} \rightleftarrows \overline{\mathrm{Q}})$	chiral – isoenergetic	(Type II)

- Anisoenergetic

$\mathrm{A} \rightleftarrows \mathrm{B}$	achiral – anisoenergetic	(Type III)
$\mathrm{Q} \rightleftarrows \mathrm{R}(\overline{\mathrm{Q}} \rightleftarrows \overline{\mathrm{R}})$	chiral – anisoenergetic	(Type IV)

In general, any isoenergetic pair consists of homomeric conformers or of enantiomeric ones, while any anisoenergetic pair is composed of diastereomeric conformers. The terms *isoenergetic* and *anisoenergetic* are coined on the basis of these facts.

Type I corresponds to an isoenergetic group that has at least an anisoenergetic-achiral subgroup. For example, $\hat{C}_{2v}$ (with a subgroup C_s) is such a group. When we deals with the subgroups of $\hat{D}_{6h}$, Type I can be assigned to any of $\hat{C}_{2v}$, $\hat{C}'_{2v}$, $\hat{C}''_{2v}$, $\hat{C}_{2h}$, $\hat{C}'_{2h}$, $\hat{D}_{2h}$, $\hat{C}_{6v}$, $\hat{C}_{6h}$, $\hat{D}_{3h}$, $\hat{D}_{3d}$, and $\hat{D}_{6h}$. Type I is concerned with a pair of achiral conformers which are homomeric to each other.

On the other hand, Type I′ corresponds to an isoenergetic group that has none of anisoenergetic-achiral subgroups. In other words, its improper operations are always pseudo-rotation. For example, $\hat{C}_s$ is such a group. Among the subgroups of $\hat{D}_{6h}$, Type I′ may be either of the following subgroups: $\hat{C}_s$, $\hat{C}'_s$, $\hat{C}_{3v}$, $\hat{C}_{3h}$, and $\hat{D}'_{3h}$. This case is concerned with a pair of a chiral molecule and its antipode. This means chemically that the pair of Type I′ represents a racemization process.

Type II is concerned with a pair of a chiral molecule (Q) and its homomer (Q), where no racemization occurs. Hence, there exists the corresponding antipodal pair ($\overline{\mathrm{Q}} \rightleftarrows \overline{\mathrm{Q}}$). The subgroups of $\hat{D}_{6h}$ ($\hat{C}_2$, $\hat{C}'_2$, $\hat{D}_2$, $\hat{C}_6$, D_3, and $\hat{D}_6$) are examples of Type II.

Type III corresponds to an anisoenergetic-achiral group, e.g. $C_s, C_i, C'_{2h}, C_{3v}, C_{3i}$, or D_{3d} for the subgroups of $\hat{D}_{6h}$. In Type III, the starting achiral molecule (A) is diastereomeric to the product achiral molecule (B).

Type IV is concerned with an anisoenergetic-chiral group, e.g., C_1, C'_2, C_3, and D_3 for the subgroups of $\hat{D}_{6h}$. In Type IV, the starting chiral molecule (Q) is diastereomeric to the product chiral molecule (R). Since no racemization occurs, the corresponding antipodal pair ($\overline{\mathrm{Q}} \rightleftarrows \overline{\mathrm{R}}$) can exist.

It should be noted that, logically speaking, we can presume a pair represented by $\mathrm{A} \rightleftarrows \mathrm{Q}$. However, this case has the parallel pair, $\mathrm{A} \rightleftarrows \overline{\mathrm{Q}}$. It follows that $\mathrm{Q} \rightleftarrows \mathrm{A} \rightleftarrows \overline{\mathrm{Q}}$; this is then attributed to Type I′.

In the light of the classification (Type I to Type IV), we shall examine the seven pairs appearing in the [10,2,0,0] row of Table 3. Figure 5 illustrates the four pairs of isoenergetic category, which belong to subgroups with a hat symbol, i.e., $\hat{C}'_2$, $\hat{C}_s$, $\hat{C}'_{2v}$, and $\hat{C}_{2v}$.

The pair **15a**⇄**15b** belongs to the $\hat{C}'_2$-symmetry; hence, it is chiral and isoenergetic (Type II). Thus, **15a** and **15b** are homomeric to each other. Since the pair (**15a**⇄**15b**) is chiral, there is an antipodal pair ($\overline{\mathbf{15a}} \rightleftarrows \overline{\mathbf{15b}}$) as shown in Fig. 6. It should be noted that we here discuss a couple of equilibrated pairs which are in enantiomeric relationship.

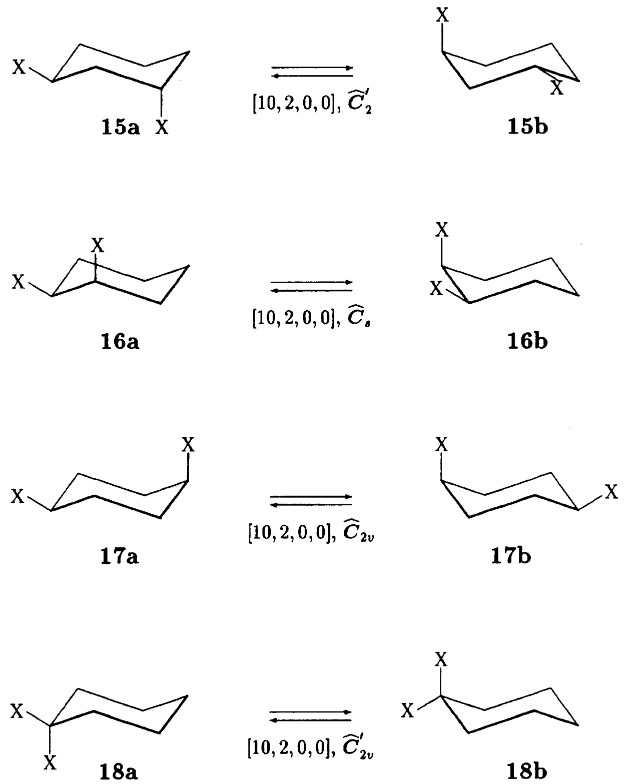


Fig. 5. Disubstitued cyclohexane derivatives of isoenergetic type.

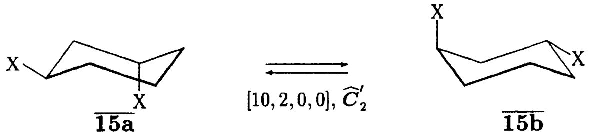


Fig. 6. The antipode of the pair (**15a**$\rightleftarrows$**15b**).

The pair **16a**$\rightleftarrows$**16b** belongs to the $\hat{C}_s$-symmetry; hence, it is achiral and isoenergetic (Type I′). The isoenergetic nature of the pair is associated with the fact that **16a** and **16b** are enantiomeric to each other. Since the achirality of the pair is related to the group, $\hat{C}_s=\{I,\hat{\sigma}_{v(1)}\}$, the equilibrated process is regarded as a racemization. More precisely speaking, the racemization is assigned to the fact that the group $\hat{C}_s$ does not contain any anisoenergetic and achiral subgroup.

The pair **17a**$\rightleftarrows$**17b** ($\hat{C}_{2v}$) and the pair **18a**$\rightleftarrows$**18b** ($\hat{C}'_{2v}$) are achiral and isoenergetic (Type I). Note that both $\hat{C}_{2v}$ and $\hat{C}'_{2v}$ contain an anisoenergetic and achiral subgroup C_s. It follows that the conformers in each of the pairs are homomeric to each other.

Figure 7 illustrates the three pairs of anisoenergetic category appearing at the [10,2,0,0] row of Table 3. They belong to subgroups without a hat symbol, i.e., C'_2, C_s, and C'_{2h}.

The pair **19a**$\rightleftarrows$**19b** belongs to the C'_2-symmetry; hence, it is chiral and anisoenergetic (Type IV). Thus, **19a** and **19b** are diastereomeric to each other. Since the pair (**19a**$\rightleftarrows$**19b**) is chiral, there is an antipodal pair

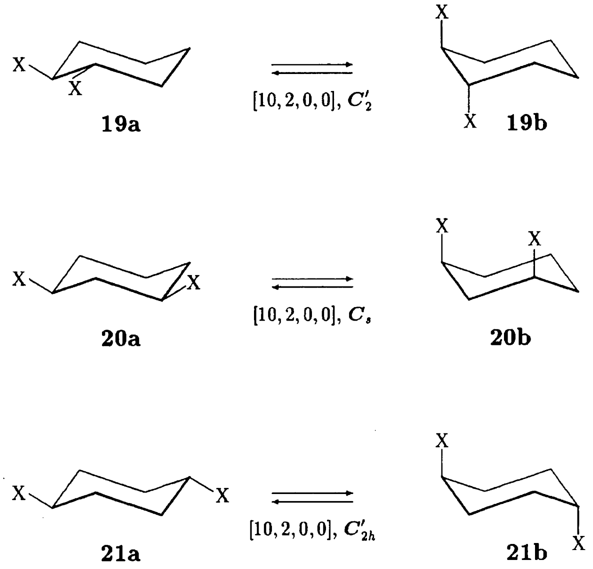


Fig. 7. Disubstitued cyclohexane derivatives of anisoenergetic type.

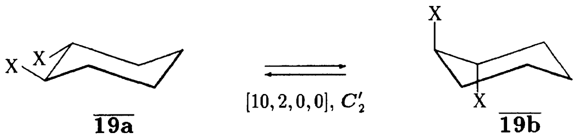


Fig. 8. The antipode of the pair (**19a**$\rightleftarrows$**19b**).

($\overline{\mathbf{19a}}\rightleftarrows\overline{\mathbf{19b}}$), as shown in Fig. 8.

The pair **20a**$\rightleftarrows$**20b** (C_s) and the pair **21a**$\rightleftarrows$**21b** (C'_{2h}) are achiral and anisoenergetic (Type III). The conformers in each of the pairs are diastereomeric to each other.

3 Comments on Stereoisomerism of Cyclohexane Derivatives. It is worth discussing the cis-trans isomerism of 1,2-, 1,3-, and 1,4-disubstituted cyclohexanes from the present point of view. In order to give rational explanations to this item, most textbooks on organic chemistry have taken one of a variety of expedient procedures based on simple polygon (planar) formulae and/or on chair-form formulae.

A typical explanation, as presented in Fessenden–Fessenden's textbook,[12] contains a statement on *cis*-1,3-dimethylcyclohexane: Though it has two chiral carbons, it has an internal plane of symmetry (in either the polygon formula or in its chair form) and is a *meso* form. Then the explanation concludes that *cis*-1,2-dimethylcyclohexane is a *meso* form, because it also has an internal plane of symmetry in the polygon formula. Obviously, the latter conclusion is silent about the fact that the *cis*-1,2-dimethylcyclohexane has no internal plane of symmetry in its chair form. A complete analysis of substituted cyclohexanes presented in Hendrikson–Cram–Hammond's textbook[13] is also based on the polygon (planar) formula. The justification of the analysis has been reported by using a ring-flip-rotation operator (R_6) as mentioned above.[1] Although Pine's discussion[14] is based on chair-form formulae, it also contains the conclusion that *cis*-1,2-dimethylcyclohexane is actually a *meso* form. Morrison–Boyd's textbook$^{15)}$ adopts chair-form formulae, where a conformation of *cis*-1,2-dimethylcyclohexane is first depicted and then its mirror conformation is given for comparison. The conclusion is that these are conformationally enantiomers, since these are not supperimposable but interconvertible; hence, "the *cis*-1,2-dimethylcyclohexane is not literally a *meso* compound, but it is a non-resolvable racemic modification, which for most practical purposes amounts to the same thing." The brief review described here indicates that a more systematic method with mathematical foundation is desirable to comprehend the stereoisomerism of cyclohexane derivatives. The present method of pseudo-point groups satisfies such requirements.

In the light of the present methodology, we are able to specify *cis*-1,2-dimethylcyclohexane simply by saying that the pair (**16a**$\rightleftarrows$**16b**, $X=CH_3$) shown in Fig. 5 belongs to the symmetry $\hat{\boldsymbol{C}}_s$. The $\hat{\boldsymbol{C}}_s$-symmetry corresponds to an achiral-isoenergetic case (Type I′) that accompanies a racemization process. In other words, the compensation of chirality occurs intermolecularly, i.e., in a pair of conformers, while a usual meso case stems from the intramolecular compensation of chirality. Since the present formulation presumes that such a pair of conformers represents a (flexible) compound, a compound of Type I′ can be called a *pseudo-meso compound*. Although the concepts *pseudo-meso* and *meso* are chemically distinct, they have a close relationship from a mathematical point of view. This will be discussed in the following section.

The stereoisomerism of *trans*-1,2-dimethylcyclohexane can be characterized by the statement that it (the pair **19a**$\rightleftarrows$**19b**, $X=CH_3$) belongs to the $\boldsymbol{C}'_2$-symmetry. This symmetry clarifies the chiral-anisoenergetic nature of the pair (Type IV) and the presence of the antipodal pair $\overline{\mathbf{19a}}\rightleftarrows\overline{\mathbf{19b}}$ shown in Fig. 8.

The $\boldsymbol{C}_s$-symmetry of the pair **20a**$\rightleftarrows$**20b** (Fig. 7, $X=CH_3$) fully characterizes the symmetrical nature of *cis*-1,3-dimethylcyclohexane, which is achiral and anisoenergetic (Type III). Both the starting conformer (**20a**) and the product one (**20b**) are respectively *meso* molecules; hence, the resulting pair (**20a**$\rightleftarrows$**20b**) is concluded to be a *meso* compound. This is distinguished from the *pseudo-meso* case by the fact that the starting *meso* molecule (**20a**) can be interchanged into the product *meso* molecule (**20b**) but they are energetically different from each other. In the light of the present formulation, a *meso* case is assigned to an anisoenergetic group (e.g. $\boldsymbol{C}_s$ for *cis*-1,3-dimethylcyclohexane), while a *pseudo-meso* case is attributed to an isoenergetic group (e.g. $\hat{\boldsymbol{C}}_s$ for *cis*-1,3-dimethylcyclohexane).

The stereoisomerism of *trans*-1,3-dimethylcyclohexane (**15a**$\rightleftarrows$**15b**) is represented by the $\hat{C}'_2$-symmetry (Fig. 5). The chiral and isoenergetic nature (Type II) reveals the presence of the antipodal pair $\overline{\mathbf{15a}}\rightleftarrows\overline{\mathbf{15b}}$ shown in Fig. 6.

The characterization of the stereoisomerism of *cis*- and *trans*-1,4-dimethylcyclohexanes can be performed respectively by using the $\hat{C}_{2v}$-symmetry for the pair **17a**$\rightleftarrows$**17b** and $\boldsymbol{C}'_{2h}$ for the pair **21a**$\rightleftarrows$**21b**. The $\hat{C}_{2v}$-symmetry reveals the achiral and isoenergetic nature of *cis*-1,4-dimethylcyclohexane (Type I), while the C'_{2h}-symmetry characterizes the achiral and anisoenergetic nature of the *trans*-isomer (Type III).

4 Chronality and Sphericity in Cyclohexane Derivatives. In the preceding paper, we have proposed the concept of chronality. Thus, a set of equivalent subsituents is recognized as an orbit, which is characterized to be homochronal, enantiochronal, or hemichronal by means of the corresponding coset representation. For exemplifying the usefulness of the chronality concept, let us examine the orbits of each pair enumerated in the preceding sections. It should be noted that the discussions in this section are concerned with the global symmetry as well as with the local symmetry of each pair of molecules (conformers), where the former and latter symmetries are characterized by means of such combined forms as coset representations.

The six Xs of the pair **8a**$\rightleftarrows$**8b** (Fig. 3) construct an orbit governed by $\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$, as indicated by Eq. 13E. Since both $\boldsymbol{D}_{3d}$ and $\boldsymbol{C}_s$ are anisoenergetic, the orbit is concluded to be hemichronal. The six Xs of the hemichronal orbit are all equatorial the starting conformer (**8a**) and all axial in the product conformer (**8b**). Under a frozen condition, **8a** and **8b** (diastereomeric) are present in a given equilibrated ratio. Hence, this ratio determines the ratio between equatorial Xs and axial Xs, which is not 1 : 1 in general.

On the other hand, the six Xs of the pair **9a**$\rightleftarrows$**9b** (Fig. 3) construct an orbit governed by $\hat{\boldsymbol{D}}_{3h}(/\boldsymbol{C}_s)$, as indicated by Eq. 13B. This orbit is enantiochronal, since the global symmetry $\hat{\boldsymbol{D}}_{3h}$ is isoenergetic and the local symmetry $\boldsymbol{C}_s$ is anisoenergetic. Under a frozen condition, the orbit is divided into two halves (axial and equatorial). Since **8a** and **8b** are homomeric to each other, the axial-equatorial ratio is frozen into 1 : 1.

The orbit of the six Xs in the pair **10a**$\rightleftarrows$**10b** (Fig. 3) is also enantiochronal because of the coset representation $\hat{C}_{6v}(/\boldsymbol{C}_s)$ shown by Eq. 13z. Hence, it is divided into two halves (axial and equatorial) under a frozen condition.

The four Xs of the pair **11a**$\rightleftarrows$**11b** (Fig. 4) belong to an enantiochronal orbit, since this orbit is governed by $\hat{\boldsymbol{D}}_2(/\boldsymbol{C}_1)$ (Eq. 13j). Hence, the orbit is into two halves under a frozen condition, producing axial Xs and equatorial Xs. The other pairs in Fig. 4 can be discussed in a similar way.

The two Xs of each pair shown in Fig. 5 construct an enantiochronal orbit as follows.

Pair with two Xs	Orbit	Chronality	Sphericity	Eq. no.
15a$\rightleftarrows$**15b**	$\hat{C}'_2(/C_1)$	Enantiochronal	Hemispheric	13c
16a$\rightleftarrows$**16b**	$\hat{C}_s(/C_1)$	Enantiochronal	Enantiospheric	13f
17a$\rightleftarrows$**17b**	$\hat{C}_{2v}(/C_s)$	Enantiochronal	Homospheric	13k
18a$\rightleftarrows$**18b**	$\hat{C}'_{2v}(/C_s)$	Enantiochronal	Homospheric	13l

Under a frozen condition, each orbit of Xs is divided into two halves (axial and equatorial). Since the starting conformer and the product one in each pair are homomeric to each other, the axial-equatorial ratio becomes 1 : 1 under a frozen condition.

Each pair depicted in Fig. 7 has a hemichronal orbit involving two Xs as follows.

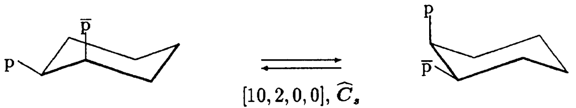
Pair with two Xs	Orbit	Chronality	Sphericity	Eq. no.
19a$\rightleftarrows$**19b**	$C'_2(/C_1)$	Hemichronal	Hemispheric	13d
20a$\rightleftarrows$**20b**	$\hat{C}_s(/C_1)$	Hemichronal	Enantiospheric	13e
21a$\rightleftarrows$**21b**	$C_{2v}(/C_s)$	Hemichronal	Homospheric	13p

The two Xs of each hemichronal orbit are all equatorial in the respective starting conformer and all axial in the respective product conformer. Under a frozen condition, the diastereomeric conformers of each pair are present in an equilibrated ratio which is determined by the energetic difference between them. Hence, this ratio determines the ratio of equatorial Xs to axial Xs, which is not 1 : 1 in general.

The concept of sphericity (chirality fittingness) proposed previously by us[16] is another tool that is also effective in discussing the symmetry of flexible cyclohexane derivatives. For example, the $\hat{C}_s(/C_1)$-orbit in the pair **16a**$\rightleftarrows$**16b** is enantiosheric, since the $\hat{C}_s$ is achiral and the C_1 is chiral.

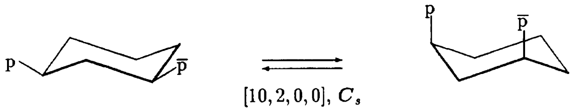
cis-1,2-Dimethylcyclohexane as a *pseudo-meso* compound is more clearly demonstrated by considering the enantiospheric $\hat{C}_s(/C_1)$-orbit, since we have previously attributed a *meso*-type achiral molecule to a pairwise packing of such an enantiospheric orbit.[16] The previous discussion has been limited within (rigid) molecules and promolecules; however, it can be extended to be applied to equilibrated pairs without any mathematical modification. In the framework of the present formulation, we first presume a combination of one X in **20a** and the corresponding one in **20b** along with another combination of the other X in **20a** and the corresponding one in **20b**. By regarding each combination as a proligand, the two proligands (combinations) are considered to belong to the enantiospheric $\hat{C}_s(/C_1)$-orbit. This fact reveals the *pseudo-meso* property of the *cis*-1,2-dimethylcyclohexane. Thus, the concepts *meso* and *pseudo-meso* have a common mathematical foundation, though they are different in chemical meanings.

The enantiosphericity is more clearly illustrated by considering a chiral proligand (p) and its antipode ($\overline{\text{p}}$) as substituents. Thus, the enantiospheric orbit can be refilled by the set of p and $\overline{\text{p}}$ without changing the governing *pseudo*-point group. Thus, we have the pair **22a**$\rightleftarrows$**22b** (Fig. 9). The term *pseudo-meso* introduced above can also be used to designate this case. It should be noted that the enantiosphericity appears under the action of *pseudo*-point groups as the extention of point groups.



22a　**22b**

Fig. 9. Enantiosphericity for a 1,2-disubstituted cyclohexane.



23a　**23b**

Fig. 10. Enantiosphericity for a 1,3-disubstituted cyclohexane.

The $C_s(/C_1)$-orbit in the pair **20a**$\rightleftarrows$**20b** is also enantiospheric. Although its chronality is different from that of the pair **16a**$\rightleftarrows$**16b**, the enantiospheric orbit can accommodate a set of a chiral proligand (p) and its antipode ($\overline{\text{p}}$) without changing the governing *pseudo*-point group. Thus, we have the pair **23a**$\rightleftarrows$**23b** (Fig. 10).

On the other hand, the $\hat{C}_{2v}(/C_s)$-orbit in the pair **17a**$\rightleftarrows$**17b** is *homospheric*, since the $\hat{C}_{2v}$ and the C_s are both achiral. This means that the orbit is capable of accomodating only achiral proligands. It should be emphasized that the chronality and the sphericity are independent concepts, both of which are effective for comprehending the stereochemisty of flexible compounds.

Conclusion

The concept of *pseudo*-point groups is effective for the combinatorial enumeration of flexible cyclohexane derivatives as well as for the characterization of their symmetries. The *pseudo*-point group $\hat{D}_{6h}$ is constructed to characterize the symmetry of a pair of two chair-forms of cyclohexane and its mark table is prepared. After the assignment of the coset representation $\hat{D}_{6h}(/C_s)$ to the twelve substitution positions of the pair, the subduction of the $\hat{D}_{6h}(/C_s)$ is calculated. The concept of chronality is also discussed to clarify the symmetrical nature of the resulting orbits.

The combinatorial enumeration of cyclohexane derivatives is performed by the USCI (unit-subduced-cycle-index) approach. Several pairs for representing cyclohexane derivatives are discussed in the light of the following categories: isoenergetic-achiral (Type I and I′), isoenergetic-chiral (Type II), anisoenergetic-achiral (Type III), and anisoenergetic-chiral (Type IV)). These categories stem from the fact that *pseudo*-point groups are classified into iso- and anisoenergetic groups as well as into achiral and chiral groups.

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