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Systematic Design of High-Symmetry Cyclohexane Derivatives and Characterization of Their Energetic and Symmetric Equivalency

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Abstract A pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ has been applied to the design of high-symmetry cyclohexane derivatives, which are assigned to the subgroups of $\widehat{\boldsymbol{D}}_{6h}$. The existence/nonexistence of these derivatives has been prediced by comparing partial cycle indices with and without chirality fittingness (PCI-CFs and PCIs). The PCI-CFs and PCIs stem from the unit-subduced-cycle-index (USCI) approach, where the subduction of coset representations (CRs) are precalculated by using mark tables. These derivatives have been classified into isoenergetic and anisoenergetic derivatives. Energetical and symmetric equivalency of ligands have been discussed by virtue of CRs, where the concepts of chronality and sphericity have been used to classify the CRs.

1 Introduction

The flexible nature of a cyclohexane skeleton has brought out difficulties in discussing its symmetry so that no reliable methodologies have been developed to design high-symmetry cyclohexane derivatives. A representative way to avoid such difficulties is to use so-called "averaged symmetry", as Eliel-Wilen's textbook on stereochemistry (Section 4-5 of Ref. [1]) has claimed, "Cyclohexane is known to exist in the chair form of symmetry $\boldsymbol{D}_{3d}$ and at -100°C the NMR spectrum of the compound is indeed appropriate for a molecule of that symmetry. At room temperature, however, due to rapid inversion of the chair, the ^{1}H NMR spectrum shows a single signal due to the equivalent averaged hydrogen atoms. This observation is what would be expected for planar cyclohexane $\boldsymbol{D}_{6h}$ and it is

therefore reasonable to assume that the average symmetry of cyclohexane is indeed $\boldsymbol{D}_{6h}$, even though the planar form is of very high energy and does not even correspond to the transition state for chair inversion. A rigorous demonstration of this intuitive conclusion has been given (Leonard, Hammond, and Simmons, 1975)." This conventional way based on $\boldsymbol{D}_{6h}$, obviously, has not discriminated between equatorial and axial positions, whereas the discriminaion is one of essential key concepts for discussing the stereochemistry of cyclohexane derivatives.

The cis-trans isomerism of flexible cyclohexane derivatives has provided an additional type of difficulties, since the chirality/achirality under fixed conditions is not always equivalent to the counterpart under flexible conditions, as found in 1,2- and 1,3-dimethylcyclohexanes. This nonequivalency has been explained with a variety of expedient procedures based on simple polygon (planar) formulas and/or on chair-form formulas. Representatives of such expedient procedures have appeared in several textbooks [2–6]. The term "stochastically achiral" proposed by Mislow [7] and the term "residual isomers" proposed by Eliel [8] have been used in discussing flexible systems of conformers. Relevant approaches have been adopted by Leonard *et al.* [9, 10] and Flurry [11, 12] in the enumeration of flexible cyclohexane isomers. For the enumeration under the fixed symmetry $\boldsymbol{D}_{3d}$, see Ref. [13].

As a more general framework of a mathematical and logical basis, we have proposed the concept of pseudo-point groups [14, 15]. Although the concept has been successfully applied to the enumeration and the stereochemical characterization of flexible cyclohexanes [16] and relevant flexible compounds [17–20], the previous results of ours have been mainly concerned with achiral ligands as substitutents of flexible compounds.

In order to comprehend the stereochemistry of such flexible compounds, more complicated cases involving chiral ligands should be investigated as the next targets. This investigation, at the same time, aims at a systematic method to design high-symmetry cyclohexane derivatives, where energetical equivalency/nonequivalency for equatorial and axial ligands will be discussed in a more sophisticated fashion. The merit of this systematic method stems from the fact that the concept of pseudo-point groups can be combined with the unit-subduced-cycle-index (USCI) approach proposed by us [21], where a new qualitative application of partial cycle indices with and without chirality fittingness (PCI-CFs and PCIs) [22] will be discussed.

2 Pseudo-Point Group $\widehat{\boldsymbol{D}}_{6h}$

Since we use the properties of the pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ and those of its subgroups throughout the present paper, essential items related to these groups shall be revisited briefly according to the previous paper [15].

2.1 Formulation of $\widehat{\boldsymbol{D}}_{6h}$

To formulate axial-equatorial exchange in a cyclohexane skeleton, we consider a *pair* of chair-form conformers (**1a** and **1b**), instead of manipulataing each conformer separately. We then introduce a pseudo-dihedral rotation ($\widehat{C}_2'$-operation), which is a combination of a rotation (around a horizontal axis through the gravity center of each conformer) and an exchange (A$\rightleftarrows$B), where a flipping of the cyclohexane skeleton is replaced by the

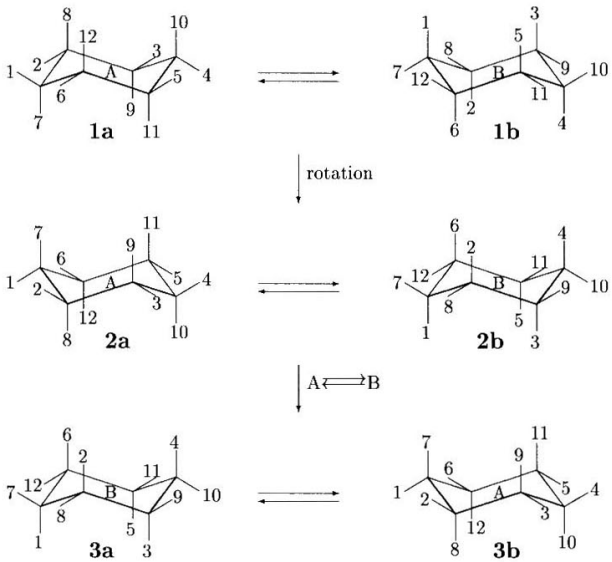

Figure 1: The Definition of the Operation $\widehat{C}_2'$ (**1a/1b** → **3a/3b**) [15]

Table 1: Classification of Operators [16]

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

combined operation shown in Fig. 1 [15]. By considering the operation $\widehat{C}'_2$ and the point group $\boldsymbol{D}_{3d}$ of the fixed cyclohexane, we can construct the set $\widehat{\boldsymbol{D}}_{6h}$,

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

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

where we place $\widehat{C}'_{2(1)} = \widehat{C}'_2$ for distinguishing from other operations of the same kind. The resulting set $\widehat{\boldsymbol{D}}_{6h}$ is called a pseudo-point group, since the gravity center of the cyclohexane skeleton is fixed on the action of each element of the $\widehat{\boldsymbol{D}}_{6h}$-group (eq. 2). Equation 1 can be regarded as a coset decomposition of the $\widehat{\boldsymbol{D}}_{6h}$-group by the $\boldsymbol{D}_{3d}$-group. This formulation has a merit that the transversal $\widehat{\boldsymbol{C}}'_2 = \{I, \widehat{C}'_{2(1)}\}$ is a subgroup of the $\widehat{\boldsymbol{D}}_{6h}$ so as to satisfy $\widehat{\boldsymbol{D}}_{6h} = \widehat{\boldsymbol{C}}'_2 \times \boldsymbol{D}_{3d}$.

The operators contained in the $\widehat{C}'_{2(1)}\boldsymbol{D}_{3d}$ are called *pseudo-rotations*, while the operators of $\boldsymbol{D}_{3d}$ are simply called *rotations* or more distinctly *usual rotations*. They are discriminated by symbols with and without a hat (circumflex). As an analogy of proper and improper rotations for usual point groups, the pseudo-rotations are classified into proper and improper ones. Thereby, the operators of the pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ are classified into four classes, as shown in Table 1.

2.2 Subgroups of $\widehat{\boldsymbol{D}}_{6h}$

In order to design cyclohexane derivatives of high-symmetry, we shall clarify the group-subgroup relationship of $\widehat{\boldsymbol{D}}_{6h}$. We have distinct, up to conjugacy, subgroups of $\widehat{\boldsymbol{D}}_{6h}$ (a non-redundnat set of subgroups), as summarized in the following list [15]:

$\boldsymbol{C}_1 = \{I\}$,

$\widehat{\boldsymbol{C}}_2 = \{I, \widehat{C}_2\}$, $\widehat{\boldsymbol{C}}'_2 = \{I, \widehat{C}'_{2(1)}\}$, $\boldsymbol{C}'_2 = \{I, C'_{2(1)}\}$,

$\boldsymbol{C}_s = \{I, \sigma_{v(1)}\}$, $\widehat{\boldsymbol{C}}_s = \{I, \hat{\sigma}_{v(1)}\}$, $\widehat{\boldsymbol{C}}'_s = \{I, \hat{\sigma}_h\}$, $\boldsymbol{C}_i = \{I, i\}$,

$\boldsymbol{C}_3 = \{I, C_3, C_3^2\}$, $\widehat{\boldsymbol{D}}_2 = \{I, \widehat{C}_2, \widehat{C}'_{2(1)}, C'_{2(2)}\}$,

$\widehat{\boldsymbol{C}}_{2v} = \{I, \widehat{C}_2, \sigma_{v(1)}, \hat{\sigma}_{v(2)}\}$, $\widehat{\boldsymbol{C}}'_{2v} = \{I, \widehat{C}'_{2(1)}, \hat{\sigma}_h, \sigma_{v(1)}\}$, $\widehat{\boldsymbol{C}}''_{2v} = \{I, C'_{2(1)}, \hat{\sigma}_h, \hat{\sigma}_{v(1)}\}$,

$\widehat{\boldsymbol{C}}_{2h} = \{I, \widehat{C}_2, \hat{\sigma}_h, i\}$, $\widehat{\boldsymbol{C}}'_{2h} = \{I, \widehat{C}'_{2(1)}, i, \hat{\sigma}_{v(2)}\}$, $\boldsymbol{C}_{2h} = \{I, C'_{2(1)}, i, \sigma_{v(3)}\}$,

$\widehat{\boldsymbol{C}}_6 = \{I, \widehat{C}_6, C_3, \widehat{C}_2, C_3^2, \widehat{C}_6^5\}$,

$\widehat{\boldsymbol{D}}_3 = \{I, C_3, C_3^2, \widehat{C}'_{2(1)}, \widehat{C}'_{2(2)}, \widehat{C}'_{2(3)}\}$, $\boldsymbol{D}_3 = \{I, C_3, C_3^2, C'_{2(1)}, C'_{2(2)}, C'_{2(3)}\}$,

$\boldsymbol{C}_{3v} = \{I, C_3, C_3^2, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}$, $\widehat{\boldsymbol{C}}_{3v} = \{I, C_3, C_3^2, \hat{\sigma}_{v(1)}, \hat{\sigma}_{v(2)}, \hat{\sigma}_{v(3)}\}$,

$\widehat{\boldsymbol{C}}_{3h} = \{I, C_3, C_3^2, \hat{\sigma}_h, \widehat{S}_3, \widehat{S}_3^5\}$, $\boldsymbol{C}_{3i} = \{I, C_3, C_3^2, S_6, i, S_6^5\}$,

$\widehat{\boldsymbol{D}}_{2h} = \{I, \widehat{C}_2, \widehat{C}'_{2(1)}, C'_{2(2)}, \hat{\sigma}_h, i, \sigma_{v(1)}, \hat{\sigma}_{v(2)}\}$,

$\widehat{\boldsymbol{D}}_6 = \{I, \widehat{C}_6, C_3, \widehat{C}_2, C_3^2, \widehat{C}_6^5, \widehat{C}'_{2(1)}, C''_{2(1)}, \widehat{C}''_{2(2)}, C'_{2(2)}, \widehat{C}'_{2(3)}, C'_{2(3)}\}$,

$\widehat{\boldsymbol{C}}_{6v} = \{I, \widehat{C}_6, C_3, \widehat{C}_2, C_3^2, \widehat{C}_6^5, \sigma_{v(1)}, \hat{\sigma}_{v(1)}, \sigma_{v(2)}, \hat{\sigma}_{v(2)}, \sigma_{v(3)}, \hat{\sigma}_{v(3)}\}$,

$\widehat{\boldsymbol{C}}_{6h} = \{I, \widehat{C}_6, C_3, \widehat{C}_2, C_3^2, \widehat{C}_6^5, \hat{\sigma}_h, S_6, \widehat{S}_3, i, \widehat{S}_3^5, S_6^5\}$,

$\widehat{\boldsymbol{D}}_{3h} = \{I, C_3, C_3^2, \widehat{C}'_{2(1)}, \widehat{C}'_{2(3)}, \hat{\sigma}_h, \widehat{S}_3, \widehat{S}_3^5, \sigma_{v(1)}, \sigma_{v(2)}, \sigma_{v(3)}\}$,

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

Among the subgroups of $\widehat{\boldsymbol{D}}_{6h}$ (order 24), three subgroups of order 12 should be mentioned, since they are concerned with dichotomous properties that are chemically significant. The $\boldsymbol{D}_{3d}$-subgroup (called *the maximal anisoenergetic subgroup*) and its subgroups are related to the fixation of a cyclohexane ring. The fixation is explained by the coset decomposition of eq. 1. The $\widehat{\boldsymbol{D}}_6$-subgroup (called *the maximal chiral subgroup*) and its subgroups are related to the chirality/achirality phenomena. This feature corresponds to the following coset decomposition:

$$\widehat{\boldsymbol{D}}_{6h} = \widehat{\boldsymbol{D}}_6 + i\widehat{\boldsymbol{D}}_6. \tag{3}$$

The $\widehat{\boldsymbol{D}}'_{3h}$-subgroup (called *the maximal pseudo-reflective subgroup*) and its subgroups are related to the nature of internal racemization, which is explained by the following coset decomposition:

$$\widehat{\boldsymbol{D}}_{6h} = \widehat{\boldsymbol{D}}'_{3h} + i\widehat{\boldsymbol{D}}'_{3h}. \tag{4}$$

It should be noted that the pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ is isomorphic to the point group $\boldsymbol{D}_{6h}$ having the corresponding operations:

$$\boldsymbol{D}_{6h} = \{I, C_6, C_3, C_2, C_3^2, C_6^5, C_{2(1)}, C'_{2(1)}, C_{2(2)}, C'_{2(2)}, C_{2(3)}, C'_{2(3)},$$
$$\sigma_h, S_6, S_3, i, S_3^5, S_6^5, \sigma_{v(1)}, \sigma'_{v(1)}, \sigma_{v(2)}, \sigma'_{v(2)}, \sigma_{v(3)}, \sigma'_{v(3)}\},$$

so that each of the subgroups listed above for $\widehat{\boldsymbol{D}}_{6h}$ corresponds to the counterpart subgroup of $\boldsymbol{D}_{6h}$ [23].

2.3 Chirality and Energeticity

In a similar way to the usual point group $\boldsymbol{D}_{6h}$ [23], the subgroups of $\widehat{\boldsymbol{D}}_{6h}$ can be categorized into chiral and achiral subgroups by virtue of proper or improper (pseudo)rotations listed in Table 1.

In contrast to the counterparts of $\boldsymbol{D}_{6h}$, the operations of the pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ are alternatively classified into pseudorotations and usual rotations (Table 1). This feature introduces another category called *energeticity* for classifying the subgroups of $\widehat{\boldsymbol{D}}_{6h}$ [15]. Thus, if a subgroup contains at least one pseudorotation, it is defined as an isoenergetic subgroup; otherwise it is defined as being anisoenergetic. Such an isoenergetic subgroup is designated by a symbol with a hat, while an anisoenergetic subgroup is designated by a symbol without a hat.

By taking the chirality/achirality and the isoenergeticity/anisoenegeticity into account, we obtain four categories of subgroups, as shown in Table 2: chiral-anisoenergetic subgroups (Type IV), achiral-anisoenergetic subgroups (Type III), chiral-isoenergetic subgroups (Type II), and achiral-isoenergetic subgroups. The achiral-isoenergetic subgroups

can be further categorized into two cases (Type I and Type I'). If an achiral-isoenergetic subgroup contains no proper pseudorotations, it is defined as a Type I' subgroup; otherwise, it is defined as a Type I subgroup. Obviously, such a Type I' subgroup contains proper rotations and improper pseudo-rotations (Table 1).

Table 2: Isoenergetic and Anisoenergetic Subgroups of $\widehat{\boldsymbol{D}}_{6h}$ [16]

	chiral	achiral
anisoenergetic	Type IV (Q $\rightleftarrows$ R or $\overline{\text{Q}} \rightleftarrows \overline{\text{R}}$) $\boldsymbol{C}_1, \boldsymbol{C}'_2, \boldsymbol{C}_3, \boldsymbol{D}_3,$	Type III (A $\rightleftarrows$ B) $\boldsymbol{C}_s, \boldsymbol{C}_i, \boldsymbol{C}_{2h}, \boldsymbol{C}_{3v}, \boldsymbol{C}_{3i}, \boldsymbol{D}_{3d},$
isoenergetic	Type II (Q $\rightleftarrows$ Q or $\overline{\text{Q}} \rightleftarrows \overline{\text{Q}}$) $\widehat{\boldsymbol{C}}_2, \widehat{\boldsymbol{C}}'_2, \widehat{\boldsymbol{D}}_2, \widehat{\boldsymbol{C}}_6, \widehat{\boldsymbol{D}}_3, \widehat{\boldsymbol{D}}_6,$	Type I (A $\rightleftarrows$ A) $\widehat{\boldsymbol{C}}_{2v}, \widehat{\boldsymbol{C}}'_{2v}, \widehat{\boldsymbol{C}}_{2h}, \widehat{\boldsymbol{C}}'_{2h}, \widehat{\boldsymbol{D}}_{2h},$ $\widehat{\boldsymbol{C}}_{6v}, \widehat{\boldsymbol{C}}_{6h}, \widehat{\boldsymbol{D}}_{3h}, \widehat{\boldsymbol{D}}_{3d}, \widehat{\boldsymbol{D}}_{6h}.$
		Type I' (Q $\rightleftarrows$ $\overline{\text{Q}}$) $\widehat{\boldsymbol{C}}_s, \widehat{\boldsymbol{C}}'_s, \widehat{\boldsymbol{C}}''_{2v}, \widehat{\boldsymbol{C}}_{3v}, \widehat{\boldsymbol{C}}_{3h}, \widehat{\boldsymbol{D}}'_{3h},$

2.4 Orbits and Coset Representations

The twelve positions (six axial and six equatorial positions) of a cyclohexane skeleton are so equivalent under flexible conditions as to construct an equivalence class called *an orbit*. The orbit is assigned to a coset representation (CR) $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$, which is characterized by a row vector called a fixed-point vector (FPV),

$$FPV = (12, 0, 0, 0, 4, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0), \quad (5)$$

where the elements are aligned in the order of the subgroups listed above. This is identical with the $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-row of the mark table precalculated (Table 1 of Ref. [15]).

3 Mathematical Foundations of Desymmetrization

3.1 Subductions of Coset Representations

The derivation of a high-symmetry cyclohexane derivative can be regarded as a desymmetrization of a cyclohexane skeleton by ligand substitution. As a result, the $\widehat{\boldsymbol{D}}_{6h}$-symmetry of the cyclohexane skeleton is reduced into the corresponding subsymmetry so that the $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-orbit of the twelve positions is divided into several orbits. This desymmetrization is controlled by the subduction of the CR $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$, as shown for general cases [21].

For example, let us consider the design of a $\widehat{\boldsymbol{C}}_{2v}$-derivative. This design process obeys the subduction of $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$ into $\widehat{\boldsymbol{C}}_{2v}$, which can be carried out easily by means of the procedure described in Section 9.2 of my previous book [21]. Thus, the collection of the 1st ($\boldsymbol{C}_1$), 2nd ($\widehat{\boldsymbol{C}}_2$), 5th ($\boldsymbol{C}_s$), 6th ($\widehat{\boldsymbol{C}}_s$), and 11th elements ($\widehat{\boldsymbol{C}}_{2v}$) in the FPV (eq. 5)

gives an FPV of the subduction, i.e. $(12, 0, 4, 0, 0)$. The resulting FPV is multiplied by the inverse mark table of $\widehat{\boldsymbol{C}}_{2v}$ to give

$$(12,0,4,0,0)\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (2,0,2,0,0), \tag{6}$$

where the 5×5 matrix on the left-hand side is the inverse mark table of $\widehat{\boldsymbol{C}}_{2v}$, which is equivalent to that of the usual point group $\boldsymbol{C}_{2v}$ [21]. The row vector on the right-hand side shows the multiplicities of CRs in the order of $\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_1)$, $\widehat{\boldsymbol{C}}_{2v}(/\widehat{\boldsymbol{C}}_2)$, $\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_s)$, $\widehat{\boldsymbol{C}}_{2v}(/\widehat{\boldsymbol{C}}_s)$, and $\widehat{\boldsymbol{C}}_{2v}(/\widehat{\boldsymbol{C}}_{2v})$. It follows that the row vector $(2, 0, 2, 0, 0)$ corresponds to the subduction represented by

$$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s) \downarrow \widehat{\boldsymbol{C}}_{2v} = 2\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_1) + 2\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_s). \tag{7}$$

The subductions of the CR $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$ into other subgroups can be also be precalculated, as shown in Table 3. The data listed in Table 3 constructs the $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-row of the subduction table of $\widehat{\boldsymbol{D}}_{6h}$ [21, 15].
It should be noted that Polya's theorem can be derived by multiplying the USCIs and the coefficients listed in the "sum" column of Table 3 or equivalently, by the addition of the PCIs for all subgroups.

3.2 Sphericity of an Orbit

In general, a $\boldsymbol{G}(/\boldsymbol{G}_i)$-orbit is classified into a homospheric, enantiospheric, or hemispheric case, as summarized in Table 4 [24]. The sphericity is designated more concisely by a dummy variable: $a_{|\boldsymbol{G}|/|\boldsymbol{G}_i|}$ for a homospheric orbit, $c_{|\boldsymbol{G}|/|\boldsymbol{G}_i|}$ for an enantiospheric orbit, and $b_{|\boldsymbol{G}|/|\boldsymbol{G}_i|}$ for a hemispheric orbit, where the subscript $|\boldsymbol{G}|/|\boldsymbol{G}_i|$ represents the size of the $\boldsymbol{G}(/\boldsymbol{G}_i)$-orbit. Thereby, a subduction result is assigned to a product of such dummy variables, which is called *a unit subduced cycle index with chirality fittingness* (USCI-CF). For example, since $\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_1)$ and $\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_s)$ appearing in eq. 7 are respectively enantiospheric and homospheric, the subduction result represented by eq. 7 is assigned to a USCI-CF $a_2^2c_4^2$, as shown in the USCI-CF column of Table 3 (row 18). When such sphericity is not taken into consideration, the corresponding USCI (without chirality fittingness) are obtained, e.g. $s_2^2s_4^2$ for eq. 7. From the subduction results for the other subgroups listed in Table 3, the corresponding USCI-CFs and USCIs can be obtained and listed also in Table 3. All of the USCIs for the usual point group $\boldsymbol{D}_{6h}$ have been reported as a table [23], which is also effective to the isomorphic pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$.

4 Systematic Design of High-Symmetry Cyclohexane Derivatives

4.1 Cyclohexane Derivatives of $\boldsymbol{D}_{3d}$

Let us first consider cyclohexane derivatives of $\boldsymbol{D}_{3d}$-symmetry. The existence or nonexistence of the $\boldsymbol{D}_{3d}$-derivatives can be predicted by examining the corresponding partial

Table 3: Subductions of $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$

subduction			USCI	USCI-CF	sum	eq. no.
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_1$	=	$12\boldsymbol{C}_1(/\boldsymbol{C}_1)$	s_1^{12}	b_1^{12}	$\frac{1}{24}$	(8)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_2$	=	$6\widehat{\boldsymbol{C}}_2(/\boldsymbol{C}_1)$	s_2^6	b_2^6	$\frac{1}{24}$	(9)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}'_2$	=	$6\widehat{\boldsymbol{C}}'_2(/\boldsymbol{C}_1)$	s_2^6	b_2^6	$\frac{1}{8}$	(10)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}'_2$	=	$6\boldsymbol{C}'_2(/\boldsymbol{C}_1)$	s_2^6	b_2^6	$\frac{1}{8}$	(11)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_s$	=	$4\boldsymbol{C}_s(/\boldsymbol{C}_1)+4\boldsymbol{C}_s(/\boldsymbol{C}_s)$	$s_1^4s_2^4$	$a_1^4c_2^4$	$\frac{1}{8}$	(12)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_s$	=	$6\widehat{\boldsymbol{C}}_s(/\boldsymbol{C}_1)$	s_2^6	c_2^6	$\frac{1}{8}$	(13)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}'_s$	=	$6\boldsymbol{C}'_s(/\boldsymbol{C}_1)$	s_2^6	c_2^6	$\frac{1}{24}$	(14)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_i$	=	$6\boldsymbol{C}_i(/\boldsymbol{C}_1)$	s_2^6	c_2^6	$\frac{1}{24}$	(15)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_3$	=	$4\boldsymbol{C}_3(/\boldsymbol{C}_1)$	s_3^4	b_3^4	$\frac{1}{12}$	(16)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_2$	=	$3\widehat{\boldsymbol{D}}_2(/\boldsymbol{C}_1)$	s_4^3	b_4^3	0	(17)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{2v}$	=	$2\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_1)+2\widehat{\boldsymbol{C}}_{2v}(/\boldsymbol{C}_s)$	$s_2^2s_4^2$	$a_2^2c_4^2$	0	(18)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}'_{2v}$	=	$2\widehat{\boldsymbol{C}}'_{2v}(/\boldsymbol{C}_1)+2\widehat{\boldsymbol{C}}'_{2v}(/\boldsymbol{C}_s)$	$s_2^2s_4^2$	$a_2^2c_4^2$	0	(19)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}''_{2v}$	=	$3\widehat{\boldsymbol{C}}''_{2v}(/\boldsymbol{C}_1)$	s_4^3	c_4^3	0	(20)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{2h}$	=	$3\widehat{\boldsymbol{C}}_{2h}(/\boldsymbol{C}_1)$	s_4^3	c_4^3	0	(21)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}'_{2h}$	=	$3\widehat{\boldsymbol{C}}'_{2h}(/\boldsymbol{C}_1)$	s_4^3	c_4^3	0	(22)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}'_{2h}$	=	$2\boldsymbol{C}'_{2h}(/\boldsymbol{C}_1)+2\boldsymbol{C}'_{2h}(/\boldsymbol{C}_s)$	$s_2^2s_4^2$	$a_2^2c_4^2$	0	(23)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_6$	=	$2\widehat{\boldsymbol{C}}_6(/\boldsymbol{C}_1)$	s_6^2	b_6^2	$\frac{1}{12}$	(24)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_3$	=	$2\widehat{\boldsymbol{D}}_3(/\boldsymbol{C}_1)$	s_6^2	b_6^2	0	(25)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{D}_3$	=	$2\boldsymbol{D}_3(/\boldsymbol{C}_1)$	s_6^2	b_6^2	0	(26)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_{3v}$	=	$4\boldsymbol{C}_{3v}(/\boldsymbol{C}_s)$	s_3^4	a_3^4	0	(27)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{3v}$	=	$2\widehat{\boldsymbol{C}}_{3v}(/\boldsymbol{C}_1)$	s_6^2	c_6^2	0	(28)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{3h}$	=	$2\widehat{\boldsymbol{C}}_{3h}(/\boldsymbol{C}_1)$	s_6^2	c_6^2	$\frac{1}{12}$	(29)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{C}_{3i}$	=	$2\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$	s_6^2	c_6^2	$\frac{1}{12}$	(30)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_{2h}$	=	$\widehat{\boldsymbol{D}}_{2h}(/\boldsymbol{C}_1)+\widehat{\boldsymbol{D}}_{2h}(/\boldsymbol{C}_s)$	s_4s_8	a_4c_8	0	(31)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_6$	=	$\widehat{\boldsymbol{D}}_6(/\boldsymbol{C}_1)$	s_{12}	b_{12}	0	(32)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{6v}$	=	$2\widehat{\boldsymbol{C}}_{6v}(/\boldsymbol{C}_s)$	s_6^2	a_6^2	0	(33)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{C}}_{6h}$	=	$\widehat{\boldsymbol{C}}_{6h}(/\boldsymbol{C}_1)$	s_{12}	c_{12}	0	(34)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_{3h}$	=	$2\widehat{\boldsymbol{D}}_{3h}(/\boldsymbol{C}_s)$	s_6^2	a_6^2	0	(35)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}'_{3h}$	=	$\widehat{\boldsymbol{D}}'_{3h}(/\boldsymbol{C}_1)$	s_{12}	c_{12}	0	(36)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_{3d}$	=	$\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$	s_{12}	c_{12}	0	(37)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\boldsymbol{D}_{3d}$	=	$2\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$	s_6^2	a_6^2	0	(38)
$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)\downarrow\widehat{\boldsymbol{D}}_{6h}$	=	$\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$	s_{12}	a_{12}	0	(39)

Table 4: Sphericities of Orbits [24]

G	G_i	sphericity of $G(/G_i)$	chirality fittingness (objects allowed)	USCI-CF	USCI
achiral	achiral	homospheric	achiral	$a_{\|G\|/\|G_i\|}$	$s_{\|G\|/\|G_i\|}$
achiral	chiral	enantiospheric	achiral,[a] chiral[b]	$c_{\|G\|/\|G_i\|}$	$s_{\|G\|/\|G_i\|}$
chiral	chiral	hemispheric	achiral,[c] chiral	$b_{\|G\|/\|G_i\|}$	$s_{\|G\|/\|G_i\|}$

[a] An achiral object is restriced to be chiral. The half and the other half of the orbit are superimposable by a rotoreflection operator of G.
[b] The orbit accommodates the half number ($|G|/2|G_i|$) of chiral objects and the half number of chiral objects of opposite chirality so as to accomplish compensated chiral packing
[c] An achiral object is restriced to be chiral.

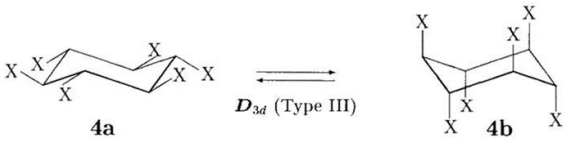

Figure 2: Cyclohexane Derivative of D_{3d}-Symmetry

cycle indices with and without chirality fittingness (PCI-CF and PCI) [21], where the PCI takes account of achiral ligands only, while the PCI-CF takes account of achiral and chiral ligands. They are calculated from the data of Table 3 and the D_{3d}-column of the inverse mark table of $\widehat{D}_{6h}$. Since the latter table is equivalent to that of the usual point group D_{6h} [23], we can obtain the corresponding PCI-CF and PCI as follows:

$$\text{PCI-CF}(D_{3d}) = \frac{1}{2}(a_6^2 - a_{12}) \tag{40}$$

$$\text{PCI}(D_{3d}) = \frac{1}{2}(s_6^2 - s_{12}) \tag{41}$$

We use these equations qualitatively in the present paper, though more quantitative results based on generating functions can be obtained by the introduction of appropriate inventories into these equations [22]. Thus, the PCI-CF (eq. 40) predicts the existence of D_{3d}-derivatives having achiral ligands only, since it contains terms for homospheric orbits (a_6 and a_{12}). This prediction is confirmed by the non-zero nature of the PCI (eq. 41).
Equation 38 in Table 3 shows the appearance of two $D_{3d}(/C_s)$-orbits during the desymmetrization into D_{3d}. Since the $D_{3d}(/C_s)$-orbits are homospheric, they accommodate achiral ligands to give D_{3d}-derivatives. Since the size of each $D_{3d}(/C_s)$-orbit is equal to $|D_{3d}|/|C_s| = 12/2 = 6$, we can select an example having a formula CH_6X_6, as shown in Fig. 2, where the symbol X represents an achiral ligand. Note that the H_6 and the X_6 are

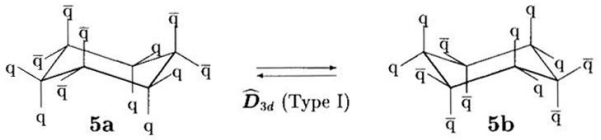

Figure 3: Cyclohexane Derivative of $\widehat{D}_{3d}$-Symmetry

accommodated distinctly by the six-membered $D_{3d}(/C_s)$-orbits in accord with chirality fittingness shown in Table 4.

4.2 Cyclohexane Derivatives of $\widehat{D}_{3d}$

The PCI-CF and the PCI for the $\widehat{D}_{3d}$-symmetry are calculated from the data of Table 3 and the $\widehat{D}_{3d}$-column of the inverse mark table of $\widehat{D}_{6h}$ as follows:

$$\text{PCI-CF}(\widehat{D}_{3d}) = \frac{1}{2}(c_{12} - a_{12}) \tag{42}$$

$$\text{PCI}(\widehat{D}_{3d}) = \frac{1}{2}(s_{12} - s_{12}) = 0 \tag{43}$$

As found in eq. 43, the value of PCI vanishes. It follows that $\widehat{D}_{3d}$-derivatives does not exist if only achiral ligands are taken into consideration. On the other hand, the PCI-CF (eq. 42) indicates the existence of $\widehat{D}_{3d}$-derivatives with chiral ligands.
Equation 37 in Table 3 shows the appearance of a twelve-membered $\widehat{D}_{3d}(/C_1)$-orbit ($|\widehat{D}_{3d}|/|C_1| = 12$) during the desymmetrization into $\widehat{D}_{3d}$. Since the $\widehat{D}_{3d}(/C_1)$-orbit is enantiospheric, it accommodates chiral ligands to bring out a compensated chiral packing in accord with chirality fittingness (Table 4). An example of such a packing is illustrated in Fig. 3, where the symbols q and $\overline{\text{q}}$ represent chiral ligands enantiomeric to each other in isolation.
It should be noted that, strictly speaking, the q and the $\overline{\text{q}}$ should be proligands defined previously by us [25]. However, the use of ligands in place of proligands provides us with no confusion within the scope of this paper.

4.3 Cyclohexane Derivatives of $\widehat{D}'_{3h}$

The PCI-CF and the PCI for the $\widehat{D}'_{3h}$-symmetry are calculated from the data of Table 3 and the $\widehat{D}'_{3h}$-column of the inverse mark table of $\widehat{D}_{6h}$ as follows:

$$\text{PCI-CF}(\widehat{D}'_{3h}) = \frac{1}{2}(c_{12} - a_{12}) \tag{44}$$

$$\text{PCI}(\widehat{D}'_{3h}) = \frac{1}{2}(s_{12} - s_{12}) = 0 \tag{45}$$

The vanished value of the PCI (eq. 45) indicates that $\widehat{D}_{3d}$-derivatives does not exist by considering achiral ligands only. On the other hand, the PCI-CF (eq. 44) indicates the existence of $\widehat{D}'_{3h}$-derivatives with chiral ligands.

According to eq. 36 of Table 3, the resulting $\widehat{\boldsymbol{D}}'_{3h}(/\boldsymbol{C}_1)$-orbit is enantiospheric. Hence the twelve-membered orbit (i.e. $|\widehat{\boldsymbol{D}}'_{3h}|/|\boldsymbol{C}_1| = 12$) accommodates chiral ligands to satisfy a compensated chiral packing in agreement with the chirality fittingness listed in Table 4. An example of such a packing is illustrated in Fig. 4.

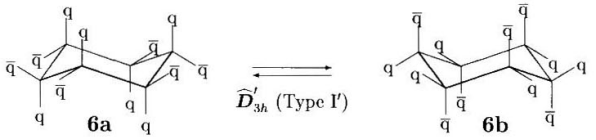

Figure 4: Cyclohexane Derivative of $\widehat{\boldsymbol{D}}'_{3h}$-Symmetry

4.4 Cyclohexane Derivatives of $\widehat{\boldsymbol{D}}_{3h}$

The PCI-CF and the PCI for the $\widehat{\boldsymbol{D}}_{3h}$-symmetry are calculated as follows:

$$\text{PCI-CF}(\widehat{\boldsymbol{D}}_{3h}) = \frac{1}{2}(a_6^2 - a_{12}) \tag{46}$$

$$\text{PCI}(\widehat{\boldsymbol{D}}_{3h}) = \frac{1}{2}(s_6^2 - s_{12}) \tag{47}$$

Thus, eqs. 46 and 47 predict the existence of $\widehat{\boldsymbol{D}}_{3h}$-derivatives having achiral ligands only. Equation 35 in Table 3 shows the appearance of two $\widehat{\boldsymbol{D}}_{3h}(/\boldsymbol{C}_s)$-orbits, both of which are homospheric so as to accommodate achiral ligands (Table 4). Since the size of each $\widehat{\boldsymbol{D}}_{3h}(/\boldsymbol{C}_s)$-orbit is equal to $|\widehat{\boldsymbol{D}}_{3h}|/|\boldsymbol{C}_s| = 12/2 = 6$, we can select an example having a formula CH_6X_6, as shown in Fig. 5.

4.5 Cyclohexane Derivatives of $\widehat{\boldsymbol{C}}_{6h}$

The PCI-CF and the PCI for the $\widehat{\boldsymbol{D}}'_{3h}$-symmetry are calculated in a similar way:

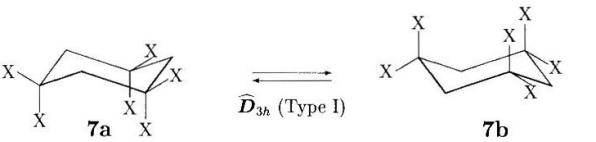

Figure 5: Cyclohexane Derivative of $\widehat{\boldsymbol{D}}_{3h}$-Symmetry

$$\text{PCI-CF}(\widehat{\boldsymbol{C}}_{6h}) = \frac{1}{2}(c_{12} - a_{12}) \tag{48}$$

$$\text{PCI}(\widehat{\boldsymbol{C}}_{6h}) = \frac{1}{2}(s_{12} - s_{12}) = 0 \tag{49}$$

The zero value of the PCI (eq. 49) indicates that $\widehat{\boldsymbol{C}}_{6h}$-derivatives does not exist by considering achiral ligands only. On the other hand, the PCI-CF (eq. 48) indicates the existence of $\widehat{\boldsymbol{C}}_{6h}$-derivatives with chiral ligands.
The subduction shown by eq. 34 of Table 3 indicates that the resulting $\widehat{\boldsymbol{C}}_{6h}(/\boldsymbol{C}_1)$-orbit is twelve-membered ($|\widehat{\boldsymbol{C}}_{6h}|/|\boldsymbol{C}_1| = 12$) and enantiospheric. Hence it accommodates twelve chiral ligands (six q's and six $\overline{\text{q}}$'s) in a compensated chiral packing (Table 4). An example of such a packing is illustrated in Fig. 6.

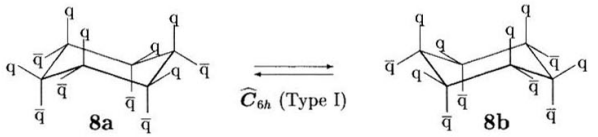

Figure 6: Cyclohexane Derivative of $\widehat{\boldsymbol{C}}_{6h}$-Symmetry

4.6 Cyclohexane Derivatives of $\widehat{\boldsymbol{C}}_{6v}$

The PCI-CF and PCI for $\widehat{\boldsymbol{C}}_{6v}$-symmetry are similarly calculated from the data of Table 3 and the $\widehat{\boldsymbol{C}}_{6v}$-column of the inverse mark table of $\widehat{\boldsymbol{D}}_{6h}$. Thus, we can obtain the PCI-CF and PCI as follows:

$$\text{PCI-CF}(\widehat{\boldsymbol{C}}_{6v}) = \frac{1}{2}(a_6^2 - a_{12}) \tag{50}$$

$$\text{PCI}(\widehat{\boldsymbol{C}}_{6v}) = \frac{1}{2}(s_6^2 - s_{12}) \tag{51}$$

Equations 50 and 51 predict the existence of $\widehat{\boldsymbol{C}}_{6v}$-derivatives having achiral ligands only. According to eq. 33 in Table 3, two $\widehat{\boldsymbol{C}}_{6v}(/\boldsymbol{C}_s)$-orbits appear during the desymmetrization into $\widehat{\boldsymbol{C}}_{6v}$, where the size of each orbit is calculated to be $|\widehat{\boldsymbol{C}}_{6v}|/|\boldsymbol{C}_s| = 12/2 = 6$. Since the $\widehat{\boldsymbol{C}}_{6v}(/\boldsymbol{C}_s)$-orbits are homospheric, they accommodate achiral ligands to give $\widehat{\boldsymbol{C}}_{6v}$-derivatives. A $\widehat{\boldsymbol{C}}_{6v}$-derivative with a formula CH_6X_6 is depicted in Fig. 7, where the H_6 and the X_6 are accommodated distinctly by the six-membered $\widehat{\boldsymbol{C}}_{6v}(/\boldsymbol{C}_s)$-orbits in accord with chirality fittingness shown in Table 4.

4.7 Cyclohexane Derivatives of $\widehat{\boldsymbol{D}}_6$

The PCI-CF and the PCI for the $\widehat{\boldsymbol{D}}_6$-symmetry are calculated from the data of Table 3 and the $\widehat{\boldsymbol{D}}_6$-column of the inverse mark table of $\widehat{\boldsymbol{D}}_{6h}$ as follows:

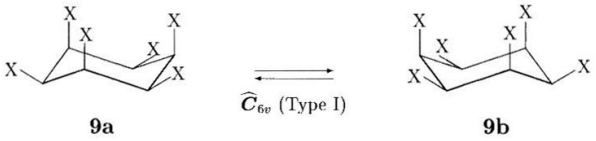

Figure 7: Cyclohexane Derivative of $\widehat{C}_{6v}$-Symmetry

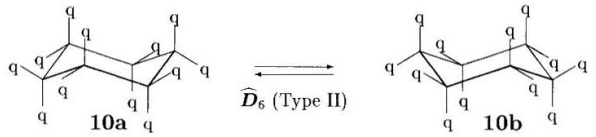

Figure 8: Cyclohexane Derivative of $\widehat{D}_6$-Symmetry

$$\text{PCI-CF}(\widehat{D}_6) = \frac{1}{2}(b_{12} - a_{12}) \tag{52}$$

$$\text{PCI}(\widehat{D}_6) = \frac{1}{2}(s_{12} - s_{12}) = 0 \tag{53}$$

The PCI (eq. 43) vanishes, while the PCI-CF (eq. 42) remains non-zero. It follows that $\widehat{D}_6$-derivatives does not exist by considering achiral ligands only, but they exist by considering chiral ligands along with achiral ones. The twelve chiral ligands (q) in the resulting derivative (**10a**/**10b**) are so equivalent as to construct an orbit governed by a CR $\widehat{D}_6(/C_1)$.

4.8 Cyclohexane Derivatives of D_3

The PCI-CF and the PCI for the D_3-symmetry are calculated as follows:

$$\text{PCI-CF}(D_3) = \frac{1}{4}b_6^2 - \frac{1}{4}b_{12} - \frac{1}{4}a_6^2 - \frac{1}{4}c_{12} + \frac{1}{2}a_{12} \tag{54}$$

$$\text{PCI}(D_3) = \frac{1}{4}s_6^2 - \frac{1}{4}s_{12} - \frac{1}{4}s_6^2 - \frac{1}{4}s_{12} + \frac{1}{2}s_{12} = 0 \tag{55}$$

The PCI-CF (eq. 54) remains non-zero, while the PCI (eq. 55) vanishes. This means that that D_3-derivatives exist by considering chiral ligands along with achiral ones. According to eq. 26 in Table 3, an example is illustrated in Fig. 9, where one hemispheric $D_3(/C_1)$-orbit accommodates six chiral ligands (q) and the other hemispheric $D_3(/C_1)$-orbit accommodates six hydrogens. This packing obeys the chirality fittingness shown in Table 4.

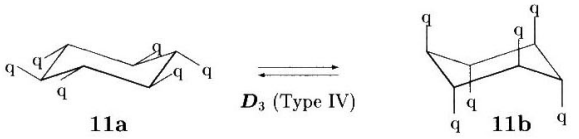

Figure 9: Cyclohexane Derivative of $\boldsymbol{D}_3$-Symmetry

4.9 Cyclohexane Derivatives of $\widehat{\boldsymbol{D}}_3$

The PCI-CF and the PCI for the $\widehat{\boldsymbol{D}}_3$-symmetry are calculated from the data of Table 3 and the $\widehat{\boldsymbol{D}}_3$-column of the inverse mark table of $\widehat{\boldsymbol{D}}_{6h}$ as follows:

$$\text{PCI-CF}(\widehat{\boldsymbol{D}}_3) = \frac{1}{4}b_6^2 - \frac{1}{4}b_{12} - \frac{1}{4}a_6^2 - \frac{1}{4}c_{12} + \frac{1}{2}a_{12} \tag{56}$$

$$\text{PCI}(\widehat{\boldsymbol{D}}_3) = \frac{1}{4}s_6^2 - \frac{1}{4}s_{12} - \frac{1}{4}s_6^2 - \frac{1}{4}s_{12} + \frac{1}{2}s_{12} = 0 \tag{57}$$

The PCI-CF (eq. 56) remains non-zero, while the PCI (eq. 57) vanishes. Hence $\widehat{\boldsymbol{D}}_3$-derivatives exist by considering chiral ligands along with achiral ones. According to eq. 25 in Table 3, an example is illustrated in Fig. 10. This derivation obeys the chirality fittingness shown in Table 4, since one hemispheric $\widehat{\boldsymbol{D}}_3(/\boldsymbol{C}_1)$-orbit accommodates six chiral ligands (q) and the other hemispheric $\widehat{\boldsymbol{D}}_3(/\boldsymbol{C}_1)$-orbit accommodates six hydrogens.

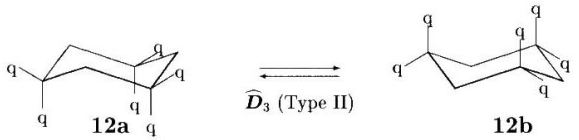

Figure 10: Cyclohexane Derivative of $\widehat{\boldsymbol{D}}_3$-Symmetry

5 Energetic Equivalency

If a derivative has two energetically equivalent (i.e. homomeric or enantiomeric) conformers, it is defined as an isoenergetic derivative; otherwise, it is defined as an anisoenergetic derivative. In general, an isoenergetic derivative is assigned to an isoenergetic subgroup that is designated by a symbol with a hat, while an anisoenergetic derivative is assigned to an anisoenergetic subgroup that is designated by a symbol without a hat (Table 2). The nature of being isoenergetic or anisoenergetic is called *energeticity*, as the nature of being chiral or achiral is called *chirality*. Thus, the energeticity of a group described above

is correlated to the energeticity of a compound. It should be noted that the energeticity stems from the dichotomous nature of the $\widehat{D}_{6h}$-symmetry, as represented by eq. 1.

5.1 Isoenergetic Derivatives

The inverted conformers of an isoenergetic derivative is energetically equal to each other. In other words, they are homomeric or enantiomeric to each other. Such isoenergetic derivatives are classified into Type I, I′, and II (Table 2).

The derivative **5a/5b** of $\widehat{D}_{3d}$-symmetry (Fig. 3) is classified into a Type I case (Table 2). According to the general equation (A $\rightleftarrows$ A), the conformer **5a** of C_{3i} point group is converted into the homomeric conformer **5b** of C_{3i} point group. Note that the pseudo-point group $\widehat{D}_{3d}$ is assigned to the **5a/5b** pair and that the six q's and the six $\overline{\text{q}}$'s are so equivalent as to construct an enantiospheric $\widehat{D}_{3d}(/C_1)$-orbit.

The derivative **7a/7b** of $\widehat{D}_{3h}$-symmetry (Fig. 5) is also classified into a Type I case (Table 2). The conformers (**7a** and **7a**) belonging to C_{3v} point group are interchanged in accord with the general equation (A $\rightleftarrows$ A) to give the pair **7a/7b** of $\widehat{D}_{3h}$-symmetry. The six Xs belong to a homospheric $\widehat{D}_{3h}(/C_s)$-orbit, while the six hydrogens belong to another homospheric $\widehat{D}_{3h}(/C_s)$-orbit.

The derivative **8a/8b** $\widehat{C}_{6h}$-symmetry (Fig. 6) is classified into a Type I case (Table 2). According to the general equation (A $\rightleftarrows$ A), The symmetries of the conformers **8a** and **8b** are decided to be C_{3i}, while that of the **8a/8b** pair is $\widehat{C}_{6h}$-symmetry. Note that the six q's and the six $\overline{\text{q}}$'s are equivalent under flexible conditions so as to construct an enantiospheric $\widehat{C}_{6h}(/C_1)$-orbit.

The derivative **9a/9b** $\widehat{C}_{6v}$-symmetry (Fig. 7) is classified into a Type I case (Table 2). While the pair **9a/9b** belongs to $\widehat{C}_{6v}$-symmetry, the conformers (**9a** and **9b**) belong to C_{3v} point group, where they are interchanged in accord with the general equation (A $\rightleftarrows$ A). The six Xs belong to a homospheric $\widehat{C}_{6v}(/C_s)$-orbit, while the six hydrogens belong to another homospheric $\widehat{C}_{3v}(/C_s)$-orbit.

The $\widehat{D}'_{3h}$-symmtry for **6a/6b** (Fig. 4) is classifed into a Type I′ case, which is represented by the general expression Q $\rightleftarrows$ $\overline{\text{Q}}$, where Q and $\overline{\text{Q}}$ represent a pair of enantiomeric confomers (Table 2).

The symmetry of the pair **10a/10b** is determined to be $\widehat{D}_6$, which is categorized into a Type II case (Table 2). According to the general equation (Q $\rightleftarrows$ Q or $\overline{\text{Q}}$ $\rightleftarrows$ $\overline{\text{Q}}$), the conformational transformation converts the conformer **10a** into its homomeric conformer **10b** (Fig. 8). The conformer **10a** is superimposable to **10b** by appropriate proper rotations of the supergroup $\widehat{D}_{6h}$ or by isometric transformations. This stems from the isoenergetic nature of $\widehat{D}_6$. On the other hand, the chiral nature of the $\widehat{D}_6$-symmetry permits the appearance of the corresponding enantiomeric pair (**10a**/**10b** for Q $\rightleftarrows$ $\overline{\text{Q}}$).

The derivative **12a/12b** of $\widehat{D}_3$ is also classified into a Type II case (Fig. 10). The symmetrical nature can be explained in a similar way to the $\widehat{D}_6$-symmetry described above.

5.2 Anisoenergetic Derivatives

The inverted conformers of an anisoenergetic derivative is not energetically equal to each other. Such isoenergetic derivatives are classified into Type III and IV (Table 2).

Table 5: Chronality of $G(/G_i)$ [15]

G	G_i	chronality of $G(/G_i)$	chronality fittingness (objects allowed)
isoenergetic	isoenergetic	homochronal	isoenergetic
isoenergetic	anisoenergetic	enantiochronal	isoenergetic,[a] anisoenergetic
anisoenergetic	anisoenergetic	hemichronal	isoenergetic,[a] anisoenergetic

[a] The isoenergetic object is desymmetrized into an anisoenergetic one.

The D_{3d}-symmetry of **4a/4b** is anisoenergetic and achiral (Type III). According to the general equation (A $\rightleftarrows$ B), the conformer **4a** of D_{3d} is converted into the conformer **4b** of D_{3d}, where the two conformers are energetically different from each other (Fig. 2). Note that the point group D_{3d} assigned to each of the conformers is identical with the pseudo-point group assigned to the pair of the conformers.

The symmetry of the derivative **11a/11b** is assigned to D_3, which is categorized into a Type IV case. The behavior shown in Fig. 9 stems from the anisoenergetic nature of the D_3-symmetry. Thus, the two conformers are energetically different so that one conformer **11a** has equatorial q's and the other one **11b** has axial q's. Note that each of the conformers belongs to a usual point group of the same kind (C_2'-symmetry). On the other hand, the chiral nature of the C_2'-symmetry appears in the difference between two pairs of conformers, where one pair (**11a/11b**, in general Q $\rightleftarrows$ R; Q and R: chiral) is enantiomeric to the other pair (**$\overline{11a}$/$\overline{11b}$**, in general $\overline{Q} \rightleftarrows \overline{R}$; $\overline{Q}/\overline{R}$: enantiomeric to Q and R).

5.3 Chronality and Pro-anisoenergeticity

The introduction of the isoenergetic/anisoenergetic concept provides us with the chronality concept, which is another criterion for characterizing $G(/G_i)$-orbits of pseudo-point groups (Table 5) [15]. By comparing the isoenergetic/anisoenergetic nature of the local symmetry G_i with that of the global symmetry G, we can determine the chronality of the $G(/G_i)$-orbit, as collected in Table 5. It is easy to determine chronality, since isoenergetic and anisoenergetic groups are differentiated in the present paper by using symbols with and without a hat.

For example, the $\widehat{D}_{6h}(/C_s)$-orbit is enantiochronal, since the glabal symmetry $\widehat{D}_{6h}$ is isoenergetic while the local symmetry C_s is anisoenergetic. The enantiochronality of the $\widehat{D}_{6h}(/C_s)$-orbit means that the 12 ligand positions of cyclohexane are equivalent under flexible conditions, but split into six equatorial and six axial positions under fixed conditions. This desymmetrization process is controlled by the subduction of the CR represented by

$$\widehat{D}_{6h}(/C_s) \downarrow D_{3d} = 2D_{3d}(/C_s), \tag{58}$$

where the symbol D_{3d} represents a point group. In each resulting conformer of the point group D_{3d} (under fixed conditions), the six equatorial ligands construct an orbit governed by $D_{3d}(/C_s)$, while the six axial ligands construct another $D_{3d}(/C_s)$-orbit.

The six carbons of cyclohexane construct an orbit governs by $\widehat{\boldsymbol{D}}_{6h}(/\widehat{\boldsymbol{C}}'_{2v})$, which is homochronal by virtue of the criterion shown in Table 5. The fixation of the cyclohexane ring is represented by the following subduction:

$$\widehat{\boldsymbol{D}}_{6h}(/\widehat{\boldsymbol{C}}'_{2v}) \downarrow \boldsymbol{D}_{3d} = \boldsymbol{D}_{3d}(/\boldsymbol{C}_s). \tag{59}$$

It follows that the six carbons are equivalent even under the fixed condition because they are accommodated in the six-membered $\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$-orbit.

As an analogy to prochirality [26], we can consider *pro-anisoenergeticity*, since the order of the maximal anisoenergetic subgroup $\boldsymbol{D}_{3d}$ in eq. 1 is equal to the half of the order of $\widehat{\boldsymbol{D}}_{6h}$. A pro-anisoenergetic compound is defined as an isoenergetic one having at least one enantiochronal orbit. A set of ligands in such a enantiochronal orbit are equivalent under flexible conditions, but are divided into two halves of ligands under fixed conditions.

The $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-orbit assigned to the twelve ligand positions of cyclohexane is enantiochronal. Hence, cyclohexane itself is isoenergetic and pro-anisoenergetic so that the orbit is desymmetrized under fixed conditions according to the subduction represented by eq. 58. The resulting two orbits are governed by $\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$, where $|\boldsymbol{D}_{3d}|/|\boldsymbol{C}_s| = 12/2 = 6$. This means that one $\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$ corresponds to a set of equatorial ligands and the other $\boldsymbol{D}_{3d}(/\boldsymbol{C}_s)$ corresponds to a set of axial ligands.

In general, an isoenergetic derivative has one or more orbits derived from the $\widehat{\boldsymbol{D}}_{6h}(/\boldsymbol{C}_s)$-orbit of cyclohexane itself. The global symmetry of the derivative is isoenergetic because it is an isoenergetic subgroup of the $\widehat{\boldsymbol{D}}_{6h}$. On the other hand, the local symmetry ($\boldsymbol{C}_1$ or $\boldsymbol{C}_s$) is anisoenergetic because it is a subgroup of the anisoenergetic $\boldsymbol{C}_s$. It follows that each relevant orbit of the isoenergetic derivative is concluded to be enantiochronal. This conclusion is confirmed by the inspection of the subduction data in Table 3. Hence the isoenergetic derivative is pro-anisoenergetic.

For example, the Type I derivative **5a/5b** ($\widehat{\boldsymbol{D}}_{3d}$-symmetry in Fig. 3) has a twelve-membered $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit of six q's and the six $\overline{\text{q}}$'s, which are equivalent under flexible conditions. Since the $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit is enantiochronal, the derivative **5a/5b** is pro-anisoenergetic. The fixation of **5a/5b** is expressed by the equation $\widehat{\boldsymbol{D}}_{3d} \cap \boldsymbol{D}_{3d} = \boldsymbol{C}_{3i}$, where the $\boldsymbol{D}_{3d}$ is the maximal anisoenergetic subgroup for specifying fixed conditions. As the $\widehat{\boldsymbol{D}}_{3d}$-symmetry is fixed into $\boldsymbol{C}_{3i}$, the $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit is subduced according to the following subduction:

$$\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1) \downarrow \boldsymbol{C}_{3i} = 2\boldsymbol{C}_{3i}(/\boldsymbol{C}_1). \tag{60}$$

This subduction can be regarded as the successive desymmetrization of eq. 37 and eq. 30 (Table 3). Each of the two $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbits on the right-hand side of eq. 60 is enantiospheric and accommodates six chiral ligands according to a compensated chiral packing. Thus one $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit in each confomer accommodates the set of equatorial ligands (three q's and three $\overline{\text{q}}$'s), while the other $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit accommodates the set of axial ligands (three q's and three $\overline{\text{q}}$'s). The two $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbits are mixed up into the enantiochronal $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit under flexible conditions.

6 Symmetric Equivalency

6.1 Type I Meso-Derivatives

As implied in the previous discussion, Type I derivatives can be classified into two cases. One case is that each conformer contains achiral ligands only (e.g. **7a/7b** and **9a/9b**), while the other case is that each conformer contains chiral ligands (e.g. **5a/5b** and **8a/8b**; sometimes along with achiral ligands). The latter case should be mentioned from a symmetrical point of view, since it is concerned with a kind of meso-compounds.

The twelve-membered $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit of the Type I derivative **5a/5b** (Fig. 3) accommodates six q's and the six $\overline{\text{q}}$'s, which are equivalent under flexible conditions. The orbit is desymmetrized according to eq. 60 under fixed conditions. One of the resulting $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit in a fixed confomer is enantiospheric, where it accommodates the set of equatorial ligands (three q's and three $\overline{\text{q}}$'s). The other $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit, which accommodates the set of axial ligands (three q's and three $\overline{\text{q}}$'s), is also enantiospheric. As a result, each conformer under fixed conditions (eq. 60) is decided to be a so-called meso-molecule. Since the $\widehat{\boldsymbol{D}}_{3d}(/\boldsymbol{C}_1)$-orbit is also enantiospheric, the derivative **5a/5b** is concluded to be a new kind of meso-compound under flexible conditions.

In a similar way, the Type I derivative **8a/8b** ($\widehat{\boldsymbol{C}}_{6h}$-symmetry in Fig. 6) is fixed according to the following subduction:

$$\widehat{\boldsymbol{C}}_{6h}(/\boldsymbol{C}_1) \downarrow \boldsymbol{C}_{3i} = 2\boldsymbol{C}_{3i}(/\boldsymbol{C}_1). \tag{61}$$

Note that $\widehat{\boldsymbol{C}}_{6h} \cap \boldsymbol{D}_{3d} = \boldsymbol{C}_{3i}$. This subduction can be regarded as the successive desymmetrization of eq. 34 and eq. 30 (Table 3). The right-hand side of eq. 61 predicts the appearance of an enantiospheric $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit of equatorial ligands (three q's and three $\overline{\text{q}}$'s) and another enantiospheric $\boldsymbol{C}_{3i}(/\boldsymbol{C}_1)$-orbit of axial ligands (three q's and three $\overline{\text{q}}$'s). It follows that each conformer due to eq. 61 is also determined to be a so-called meso-molecule and that the derivative **8a/8b** is another example of meso-compound under flexible conditions.

Each of eqs. 60 and 61 can be regarded as the conversion of an enantiochronal orbit into hemichronal orbits from an energetical point of view. As a result, the derivatives **5a/5b** and **8a/8b** are concluded to be pro-anisoenergetic.

6.2 Meso-Character of Type I′ Derivatives

According to the general expression $\text{Q} \rightleftarrows \overline{\text{Q}}$, Type I′ derivatives can always be regarded as meso-compounds because of the interchange between enantiomeric conformers (Q and $\overline{\text{Q}}$) under flexible conditions.

For example, the Type I′ derivative **6a/6b** (Fig. 4) is fixed according to the following subduction:

$$\widehat{\boldsymbol{D}}'_{3h}(/\boldsymbol{C}_1) \downarrow \boldsymbol{D}_3 = 2\boldsymbol{D}_3(/\boldsymbol{C}_1). \tag{62}$$

Note that $\widehat{\boldsymbol{D}}'_{3h} \cap \boldsymbol{D}_{3d} = \boldsymbol{D}_3$. This subduction can be regarded as the successive desymmetrization of eq. 36 and eq. 26 (Table 3). Equation 62 indicates that the enantiospheric $\widehat{\boldsymbol{D}}'_{3h}(/\boldsymbol{C}_1)$-orbit is fixed into two hemispheric $\boldsymbol{D}_3(/\boldsymbol{C}_1)$-orbits. The conformer **6a** contains a $\boldsymbol{D}_3(/\boldsymbol{C}_1)$-orbit having six equatorial chiral ligands of the same chirality ($\overline{\text{q}}$) as well as

another $\boldsymbol{D}_3(/\boldsymbol{C}_1)$-orbit having six axial chiral ligands of the opposite chirality (q). On the other hand the conformer **6b** contains two $\boldsymbol{D}_3(/\boldsymbol{C}_1)$-orbits having interchanged equatorial and axial ligands. Hence the conformational change brings out the internal compensation of optical activity.

6.3 $\widehat{\boldsymbol{D}}_{6h}$ Beyond $\boldsymbol{D}_{6h}$

It should be emphasized that the use of the usual point group $\boldsymbol{D}_{6h}$ should be discontinued even in expedient procedures for explaining the stereochemisty of cyclohexane derivatives. The point group $\boldsymbol{D}_{6h}$ is unsuccessful in characterizing the stereochemical properties of isoenergetic derivatives (i.e. Type I, I′, and II) without any exceptions, although it is isomorphic to the present pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$. Moreover, the point group $\boldsymbol{D}_{6h}$ fails also in characterizing the energetic properties of anisoenergetic derivatives (i.e. Type III and IV) without any exceptions.

As for isoenergetic derivatives, the point group $\boldsymbol{D}_{6h}$ is incapable of explaining fixation into equatorial and axial ligands. As a typical example, we should refer to *cis*-1,2-dimethylcyclohexane based on a simple polygon (planar) formula, which belongs to $\boldsymbol{C}_s$ that is a subgroup of $\boldsymbol{D}_{6h}$. Although the $\boldsymbol{C}_s$ can explain the apparent achirality, it is incapable of explaining fixation into an axial methyl and an equatorial one.

In the present approach based on $\widehat{\boldsymbol{D}}_{6h}$, the symmetry of *cis*-1,2-dimethylcyclohexane is assigned to $\widehat{\boldsymbol{C}}_s$, which is a Type I′ case (Table 2). According to the general expression $\mathrm{Q} \rightleftarrows \overline{\mathrm{Q}}$, the enantiomeric confomers of *cis*-1,2-dimethylcyclohexane (Q and $\overline{\mathrm{Q}}$) appear under fixed conditions. The two methyl ligands construct a $\widehat{\boldsymbol{C}}_s(/\boldsymbol{C}_1)$-orbit, which is enantiospheric and enantiochronal. The enantiosphericity indicates that *cis*-1,2-dimethylcyclohexane is prochiral (as a meso-compound). On the other hand, the enantiochronality indicates that it is pro-anisoenergetic to bring out separation into an axial methyl and an equatorial one under fixed condition.

As for anisoenergetic derivatives, their energetic properties cannot be described by the point group $\boldsymbol{D}_{6h}$. For example, an all-*trans*-1,2,3,4,5,6-hexasubstituted derivative based on a simple polygon (planar) formula belongs to $\boldsymbol{D}_{3d}$ that is a subgroup of $\boldsymbol{D}_{6h}$. Obviously, this polygon formula is incapable of specifying the dynamic nature between the two conformers **4a** and **4b** (Fig. 2).

The present approach treats the pair of the conformers (**4a**/**4b** depicted in Fig. 2) as a Type III derivative. The anisoenergetic nature of **4a**/**4b** is explained by the group $\boldsymbol{D}_{3d}$ that is a subgroup of $\widehat{\boldsymbol{D}}_{6h}$. Although the same symbol $\boldsymbol{D}_{3d}$ is used, the $\boldsymbol{D}_{3d}$ as a subgroup of $\widehat{\boldsymbol{D}}_{6h}$ characterizes the $\boldsymbol{D}_{3d}$-symmetries of both the conformers (**4a** and **4b**) as well as the conformational change between them.

7 Conclusion

A pseudo-point group $\widehat{\boldsymbol{D}}_{6h}$ has been applied to the design of high-symmetry cyclohexane derivatives, which are designated by its subgroups such as $\boldsymbol{D}_{3d}$, $\widehat{\boldsymbol{D}}_{3d}$, $\widehat{\boldsymbol{D}}'_{3h}$, $\widehat{\boldsymbol{D}}_{3h}$, $\widehat{\boldsymbol{C}}_{6h}$, $\widehat{\boldsymbol{C}}_{6v}$, $\widehat{\boldsymbol{D}}_6$, $\boldsymbol{D}_3$, and $\widehat{\boldsymbol{D}}_3$. The existence/nonexistence of these derivatives has been prediced by comparing partial cycle indices with and without chirality fittingness (PCI-CFs and PCIs). Energetical equivalency/nonequivalency for equatorial and axial ligands has been discussed by virtue of CRs, which are classified enantiochronal, homochronal,

and hemichronal ones. Symmetric equivalency/nonequivalency has also been discussed by the sphericities of CRs.

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