Combinatorial Enumeration of Cubane Derivatives as Three-Dimensional Entities. IV. Gross Enumeration by the Extended Superposition Method

Shinsaku Fujita

Shonan Institute of Chemoinformatics and Mathematical Chemistry,

Kaneko 479-7 Ooimachi, Ashigara-Kami-Gun, Kanagawa-Ken,

258-0019 Japan

E-mail: shinsaku_fujita@nifty.com

(Received June 10, 2011)

Abstract

The extended superposition method, which has been developed by us as an extension of the concept of elementary superposition (S. Fujita, *Theor. Chim. Acta*, **82**, 473–498 (1992)), is applied to enumeration of cubane derivatives with chiral and achiral proligands. This method provides us with a tool for evaluating the respective contribution of each USCI-CF (unit subduced-cycle index with chirality fittingness) to the corresponding CI-CF (cycle index with chirality fittingness), which is in turn calculated by means of the proligand method, the markaracter method, the characteristic-monomial method or others. The extended superposition method does not require generating functions but requires cycle indices (CI) for regular and irregular cases, which depend upon permutational features of chiral and/or achiral (pro)ligands. Calculated values by the extended superposition method are clarified to be identical with those obtained in terms of generating functions. Effects of chiral proligands (as three-dimensional structures) on the numbers of cubane derivatives are detailedly compared with those of the corresponding graphs (as two-dimensional constitutions).

1 Introduction

As discussed in Parts I–III of this series reported in this journal, gross enumerations by the proligand method [1–3], the markaracter method [4, 5], and the characteristic monomial method [6–8] are based on generating functions, which are derived from cycle indices (CIs) or cycle indices with chirality fittingness (CI-CFs) during their practical calculations of isomer numbers. Although such calculations using generating functions are convenient to obtain whole results enumerated for every constitutions, there are many cases in which only specified calculations for given constitutions are necessary to be examined.

For the purpose of conducting such specified calculations, we have proposed the concept of *elementary superposition* [9, Chapter 18], which allows us to obtain isomer numbers with given constitutions, where the numbers are itemized with respect to point-group symmetries of isomers. The first version of elementary superposition based on unit subduced cycle indices (USCIs) [10] has been extended to be capable of treating cases in which unit subduced cycle indices with chirality fittingness (USCI-CFs) are applied to enumeration of three-dimensional structural isomers [11]. On a similar line to the degenerate derivation of the markaracter method from the USCI method (cf. Part II of this series), the elementary superposition method for treating USCIs has been degenerated into the superposition method for treating CIs [10], which has been proven to be equivalent to the methods developed by Redfield [12] and Read [13, 14]. An extended version of the superposition method for dealing with CI-CFs has been also developed by starting from USCI-CFs [11]. We here call this version *the extended superposition method*, because this method is capable of treating both chiral and achiral (pro)ligands.

The purpose of the present series is to compare various methods of combinatorial enumeration, where we use the cubane skeleton of high symmetry ($\mathbf{O}_h$) as a common starting structure and we emphasize 3D structures of enumerated isomers as well as those of ligands to be substituted. In this paper, the extended superposition method is applied to isomer enumerations of cubane derivatives, where both achiral and chiral ligands (more abstractly, proligands) are taken into consideration after introducing chirality fittingness. Thereby, the versatility of the extended superposition method is emphasized even in the cubane skeleton of high symmetry ($\mathbf{O}_h$).

2 Methods Based on Generating Functions

This section is devoted to generate cycle indices with chirality fittingness (CI-CFs), which are used for the extended superposition method as well as for other methods based on generating functions. Enumeration data for comparison are also given by using the other methods based on generating functions, although the full data have been reported previously in Part I of this series.

2.1 CI-CFs for Enumerating Cubane Derivatives

Let us consider derivation of 3D structural isomers by starting from a cubane skeleton of $\mathbf{O}_h$-symmetry, where the numbering of the eight positions is shown in **1** (Figure 1).

By applying either one of the proligand method (cf. Part I), the markaracter method (cf. Part II), the characteristic monomial method (cf. Part III), and other methods supported by the USCI approach [9], we are able to obtain the following cycle indices with chirality fittingness (CI-CFs) for calculating the total number of 3D structural isomers (Eq. 1), the number of achiral
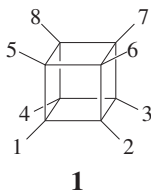
Figure 1: Numbering of the eight positions of cubane (**1**)

derivatives (Eq. 2), and the number of enantiomeric pairs of chiral derivatives (Eq. 3):

$$\text{CI-CF}(\mathbf{P},\$_d) \;=\; \frac{1}{48}b_1^8 + \frac{3}{16}b_2^4 + \frac{1}{6}b_1^2b_3^2 + \frac{1}{8}b_4^2 + \frac{1}{12}c_2^4 + \frac{1}{6}c_2c_6 + \frac{1}{8}a_1^4c_2^2 + \frac{1}{8}c_4^2 \quad (1)$$

$$\text{CI-CF}^{(a)}(\mathbf{P},\$_d) \;=\; \frac{1}{6}c_2^4 + \frac{1}{3}c_2c_6 + \frac{1}{4}a_1^4c_2^2 + \frac{1}{4}c_4^2 \quad\quad\quad\quad\quad\quad (2)$$

$$\text{CI-CF}^{(e)}(\mathbf{P},\$_d) \;=\; \frac{1}{48}b_1^8 + \frac{3}{16}b_2^4 + \frac{1}{6}b_1^2b_3^2 + \frac{1}{8}b_4^2 - \frac{1}{12}c_2^4 - \frac{1}{6}c_2c_6 - \frac{1}{8}a_1^4c_2^2 - \frac{1}{8}c_4^2, \quad (3)$$

where the symbol $\$_d$ denotes a sphericity index, which is selected from a_d for a homospheric case, b_d for a hemispheric case, and c_d for an enantiospheric case. It should be noted that each monomial contained in these CI-CFs is a subduced cycle index with chirality fittingness (SCI-CF), which is generally a product of USCI-CFs in accord with orbits (equivalence classes) of substitution positions of a given skeleton. Because the cubane skeleton (**1**) to be discussed in the present article contains a single orbit of eight substitution positions, each SCI-CF is identical with the corresponding USCI-CF.

2.2   Generating Functions for Enumerating Cubane Derivatives

Suppose that substituents are selected from an inventory of proligands:

$$\mathbf{L} = \{\text{H},\text{A},\text{W},\text{X},\text{Y},\text{Z};\; \text{p},\bar{\text{p}};\; \text{q},\bar{\text{q}}\}, \quad\quad\quad (4)$$

where H, A, W, X, Y, and Z are achiral proligands in isolation, while p, q, $\bar{\text{p}}$, and $\bar{\text{q}}$ are chiral proligands in isolation. The pair of a letter (e.g., p) and its overlined counterpart (e.g., $\bar{\text{p}}$) represents an enantiomeric pair.

First, let us briefly examine the three methods based on generating functions: i.e., Theorem 1 of [1] for the proligand method (cf, Part I), Theorem 1 of Part II for the markaracter method (the CI-CF version of Theorem 5 of [5] for CI), or Theorem 4 of [8] for the characteristic monomial method (cf. Part III). As shown in Prat I of this series, the ligand inventory **L** generates the following inventory functions:

$$a_d \;=\; \text{H}^d + \text{A}^d + \text{W}^d + \text{X}^d + \text{Y}^d + \text{Z}^d \quad\quad\quad\quad\quad (5)$$

$$b_d \;=\; \text{H}^d + \text{A}^d + \text{W}^d + \text{X}^d + \text{Y}^d + \text{Z}^d + \text{p}^d + \bar{\text{p}}^d + \text{q}^d + \bar{\text{q}}^d \quad (6)$$

$$c_d \;=\; \text{H}^d + \text{A}^d + \text{W}^d + \text{X}^d + \text{Y}^d + \text{Z}^d + 2\text{p}^{d/2}\bar{\text{p}}^{d/2} + 2\text{q}^{d/2}\bar{\text{q}}^{d/2}. \quad (7)$$

They are introduced into Eq. 1 to give a generating function:

$$
\begin{aligned}
g \;=\; & H^8 + H^7A + H^7W + H^7X + H^7Y + H^7Z + \frac{1}{2}(H^7p + H^7\overline{p}) \\
& + \frac{1}{2}(H^7q + H^7\overline{q}) + 3H^6A^2 + 3H^6AW + 3H^6AX + 3H^6AY + 3H^6AZ + \cdots \\
& + \frac{3}{2}(H^6Ap + H^6A\overline{p}) + \frac{3}{2}(H^6Aq + H^6A\overline{q}) + 3H^6W^2 + 3H^6WX + \cdots \\
& + \frac{7}{2}(H^5Ap^2 + H^5A\overline{p}^2) + 9H^5Ap\overline{p} + 7(H^5Apq + H^5A\overline{pq}) + \cdots \\
& + 11(H^4A^2p^2 + H^4A^2\overline{p}^2) + 23H^4A^2p\overline{p} + \cdots,
\end{aligned}
\tag{8}
$$

where the coefficient of each term $H^hA^aW^wX^xY^yZ^zp^p\overline{p}^{\overline{p}}q^q\overline{q}^{\overline{q}}$ represents the number of cubane derivatives as 3D-structural isomers having h of H, a of A, w of W, x of X, y of Y, z of Z, p of p, $\overline{p}$ of $\overline{p}$ q of q, and $\overline{q}$ of $\overline{q}$. Such a mode of substitution can be represented by a substitution pattern $[h,a,w,x,y,z;p,\overline{p},q,\overline{q}]$, where we can presume $h \geq a \geq w \geq x \geq y \geq z$; $p \geq q$, $p \geq \overline{p}$, and $q \geq \overline{q}$ without loosing generality.

The isomer numbers can be itemized into achiral and chiral derivatives by using Eqs. 2 and 3. As for practical calculations based on generating functions and results reported in tabular forms, see Parts I and II of this series.

3 Elementary Superpositions

The crux of the extended superposition is to evaluate each monomial (i.e., SCI-CF) contained in a CI-CF independently, where the SCI-CF is in turn derived from USCI-CFs. This independent evaluation is permitted by the concept of elementary superpositions [11].

3.1 Regular Ligand Partitions

The term *regular ligand partition* [11] has been coined to refer to a substitution pattern in which chiral ligands appear pairwise to form an enantiotopic pair, e.g.,

$$
[\theta]_1 = [5,1,0,0,0,0;1,1,0,0],
\tag{9}
$$

which corresponds to the formula $H^5Ap\overline{p}$. Such regular cases require Eqs. 62 and 63 of [11], which are calculated to treat the present regular case of $[\theta]_1$:

$$
\mathbf{H} \;=\; S^{[5]} \otimes S^{[1]} \otimes \widetilde{\mathscr{S}}^{[1]}
\tag{10}
$$
$$
\mathbf{H}' \;=\; S^{[5]} \otimes S^{[1]} \otimes \mathscr{S}^{[1]} \otimes \mathscr{S}^{[1]},
\tag{11}
$$

where the symbol $S^{[n]}$ denotes a symmetric group of degree n, the symbol $\widetilde{\mathscr{S}}^{[n]}$ denotes a symmetric group for treating the pairwise behavior of $p^n\overline{p}^n$, and the symbol $\mathscr{S}^{[n]}$ denotes a symmetric group for treating a separate behavior of p^n and $\overline{p}^n$.

On the basis of Eqs. 10 and 11, extended cycle indices defined by Eqs. 64 and 65 of [11] are calculated as follows to treat the present case of the substitution pattern $[\theta]_1$ (Eq. 9):

$$
\mathrm{CI}(\mathbf{H}, s_d, c_d) \;=\; \frac{1}{120}(s_1^5 + 15s_1s_2^2 + 20s_1^2s_3 + 10s_1^3s_2 + 20s_2s_3 + 30s_1s_4 + 24s_5) \times s_1 \times c_2
$$

$$= \frac{1}{120}(s_1^6 c_2 + 15 s_1^2 s_2^2 c_2 + \cdots) \tag{12}$$

$$\text{CI}(\mathbf{H}', s_d, b_d) = \frac{1}{120}(s_1^5 + 15 s_1 s_2^2 + 20 s_1^2 s_3 + 10 s_1^3 s_2 + 20 s_2 s_3 + 30 s_1 s_4 + 24 s_5) \times s_1 \times b_1^2$$

$$= \frac{1}{120}(s_1^6 b_1^2 + 15 s_1^2 s_2^2 b_1^2 + \cdots), \tag{13}$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity.

The elementary superposition of each monomial (SCI) in the CI-CF (Eq. 1) by one of the extended cycle indices (Eq. 12 or Eq. 13) results in the evaluation of the number of the fixed isomers, where Eq. 12 is applied to each monomial (i.e., each of the top four monomials in Eq. 1) corresponding to an achiral cyclic group (or an improper rotation), while Eq. 13 is applied to each monomial (i.e., each of the last four monomials in Eq. 1) corresponding to a chiral cyclic group (or a proper rotation). In other words, Eq. 12 is applied to each monomial of the CI-CF captaining sphericity indices a_d's and/or c_d's. while Eq. 13 is applied to each monomial captaining sphericity indices b_d's only.

It should be noted that, during the process of the elementary superposition, the cycle structures of monomials in Eq. 12 or Eq. 13 are selected to be consistent with that of the monomial at issue. The $\circledast$ operation has been defined to formulate the procedure described above more concisely, so as to give Theorem 4 (the elementary superposition with chirality fittingness) in [11]. Briefly speaking, the $\circledast$ operation is concerned with the separate applications of Eq. 12 and of Eq. 13, as described above.

As for the monomial b_1^8 in the CI-CF (Eq. 1), the monomial $s_1^6 b_1^2$ of Eq. 13 is selected because s_1 is compatible with b_1. According to Lemma 2 of [11], we can evaluate the following value:

$$\frac{1}{120} \times (1^8 \times 8!) = 336, \tag{14}$$

which shows the contribution of the monomial b_1^8 to the total isomer number to be calculated. The remaining monomials containing b_d are evaluated to give zero values. On the other hand, the monomial $a_1^4 c_2^2$ in the CI-CF (Eq. 1) matches with the monomial $s_1^4 s_2 c_2$ of Eq. 13, because s_1 is compatible with a_1 as well as s_2 is compatible with c_2. According to Lemma 3 of [11], we can evaluate the following value:

$$\frac{1}{120} \times 10 \times (1^4 \times 4!) \times (2^2 \times 2!) = 16. \tag{15}$$

The remaining monomials containing a_d and/or c_d are evaluated to give zero values. Thereby, we obtain the following row vector,

$$(336, 0, 0, 0, 0, 0, 16, 0), \tag{16}$$

in which each term represents the number of fixed isomers with respect to the corresponding cyclic group (or to the corresponding $\mathbf{Q}$-conjugacy class). Such a row vector is here called *a fixed ligand vector*.

Then, Theorem 6 (the superposition with chirality fittingness) of [11] is applied to the vector (Eq. 16) and the CI-CF (Eq. 1) to evaluate the number ($B_{[\theta]_1}$) of isomers having the formula $H^5 App\overline{p}$ or the partition $[\theta]_1$:

$$B_{[\theta]_1} = \frac{1}{48} \times 336 + \frac{1}{8} \times 16 = 7 + 2 = 9. \tag{17}$$

The value $B_{[\theta]_1} = 9$ is equal to the coefficient of the term $H^5Ap\bar{p}$ in the right-hand side of the generating function (Eq. 8).

On a similar line, the elementary superposition of Eq. 12 (no effect of Eq. 13) onto the CI-CF$^{(a)}$ represented by Eq. 2, so as to give the number $(B_{[\theta]_1}^{(a)})$ of achiral derivatives:

$$B_{[\theta]_1}^{(a)} = \frac{1}{4} \times 16 = 4, \tag{18}$$

where the value 16 is concerned with the monomial $a_1^4 c_2^2$ of the CI-CF$^{(a)}$ and obtained in a similar way to Eq. 15.

The elementary superposition of Eqs. 12 and 13 onto the CI-CF$^{(e)}$ (Eq. 3) gives the number $(B_{[\theta]_1}^{(e)})$ of enantiomeric pairs of chiral derivatives:

$$B_{[\theta]_1}^{(e)} = \frac{1}{48} \times 336 - \frac{1}{8} \times 16 = 7 - 2 = 5, \tag{19}$$

which is obtained by changing the plus sign of Eq. 17 into minus. Obviously, we have:

$$B_{[\theta]_1}^{(a)} + B_{[\theta]_1}^{(e)} = B_{[\theta]_1}. \tag{20}$$

3.2 Irregular Ligand Partitions

Such a ligand partition as represented by

$$[\theta]_2 = [5,1,0,0,0,0;1,0,1,0], \tag{21}$$

which corresponds to the formula H^5Apq, is referred to as an *irregular ligand partition* according to [11]. Because this partition is concerned with a chiral case, only $\mathbf{H}'$ is used to examine elementary superposition. Hence, Eq. 13, which can be also used to treat the present irregular case, is superposed onto Eq. 1, where the monomial b_1^8 of Eq. 1 is compatible with the monomial $s_1^6 b_1^2$ of Eq. 13 to give

$$\frac{1}{120} \times (1^8 \times 8!) = 336. \tag{22}$$

Because the other monomials of Eq. 13 give zero values, we obtain the following fixed ligand vector as a row vector,

$$(336,0,0,0,0,0,0,0), \tag{23}$$

in which each term represents the number of fixed isomers with respect to the corresponding cyclic group (or to the corresponding $\mathbf{Q}$-conjugacy class). Then, Theorem 6 (the superposition with chirality fittingness) of [11] is applied to the vector (Eq. 23) and the CI-CF (Eq. 1), so as to evaluate the number $(B_{[\theta]_2})$ of isomers having the formula H^5Apq or the partition $[\theta]_2$:

$$B_{[\theta]_2} = \frac{1}{48} \times 336 = 7. \tag{24}$$

Strictly speaking, the value $B_{[\theta]_2} = 7$ corresponds to the formula of H^5Apq. Obviously, the same calculation should be done for the formula $H^5A\overline{pq}$ (or $[5,1,0,0,0,0;0,1,0,1]$). It follows that this value corresponds to the term $7(H^5Apq + H^5A\overline{pq})$ in the right-hand side of the generating function (Eq. 8). This means that there are 14 enantiomeric pairs because of $14 \times \frac{1}{2}(H^5Apq +$

$H^5A\overline{pq}$). Note that each pair of enantiomers, e.g., $H^5Apq/H^5A\overline{pq}$, is counted once so that the combined term $\frac{1}{2}(H^5Apq + H^5A\overline{pq})$ corresponds to one pair of enantiomers.

When Eq. 13 is superposed onto Eq. 2, there emerge no monomials to be considered. Hence, the number $(B^{(a)}_{[\theta]_2})$ of achiral derivatives is evaluated to be zero:

$$B^{(a)}_{[\theta]_2} = 0. \tag{25}$$

Eq. 13 is superposed onto Eq. 3, so as to give the half number $(B^{(e)}_{[\theta]_2})$ of enantiomeric pairs of chiral derivatives:

$$B^{(e)}_{[\theta]_2} = \frac{1}{48} \times 336 = 7, \tag{26}$$

which is equal to Eq. 24 because of Eq. 25. Note that this value should be duplicated to give 14 enantiomeric pairs because of $14 \times \frac{1}{2}(H^5Apq + H^5A\overline{pq})$.

In order to check the validity of such duplication for the number of enantiomeric pairs, let us next examine another case of an irregular ligand partition:

$$[\theta]_3 = [5,1,0,0,0,0;2,0,0,0], \tag{27}$$

which corresponds to the formula H^5Ap^2 (or $H^5A\overline{p}^2$). Eq. 63 of [11] is used to treat such an irregular case:

$$\mathbf{H}' = S^{[5]} \otimes S^{[1]} \otimes \mathscr{S}^{[2]}, \tag{28}$$

where the symbol $S^{[n]}$ denotes a symmetric group of degree n and the symbol $\mathscr{S}^{[n]}$ denotes a symmetric group for treating a separate behavior of p^n and $\overline{p}^n$.

On the basis of Eq. 28, an extended cycle index defined by Eq. 65 of [11] is calculated as follows to treat the present irregular case:

$$
\begin{aligned}
\mathrm{CI}(\mathbf{H}', s_d, b_d) &= \frac{1}{120}(s_1^5 + 15s_1s_2^2 + 20s_1^2s_3 + 10s_1^3s_2 + 20s_2s_3 + 30s_1s_4 + 24s_5) \\
&\quad \times s_1 \times \frac{1}{2}(b_1^2 + b_2) \\
&= \frac{1}{120} \times \frac{1}{2} \times (s_1^6 b_1^2 + 15s_1^2 s_2^2 b_1^2 + \cdots + s_1^6 b_2 + 15s_1^2 s_2^2 b_2 + \cdots), \tag{29}
\end{aligned}
$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity.

The monomial b_1^8 in the CI-CF (Eq. 1) is compatible to the monomial $s_1^6 b_1^2$ of Eq. 29. Hence the corresponding elementary superposition is calculated as follows:

$$\frac{1}{120} \times \frac{1}{2} \times (1^8 \times 8!) = 168. \tag{30}$$

The remaining monomials are evaluated to give zero values. Thereby, we obtain the following fixed ligand vector:

$$(168,0,0,0,0,0,0,0), \tag{31}$$

each term of which represents the number of fixed isomers with respect to the corresponding cyclic group (or to the corresponding $\mathbf{Q}$-conjugacy class). Then, Theorem 6 (the superposition with chirality fittingness) of [11] is applied to the vector (Eq. 31) and the CI-CF (Eq. 1) to evaluate the number $(B_{[\theta]_3})$ of isomers having the formula H^5Ap^2 or the partition $[\theta]_3$:

$$B_{[\theta]_3} = \frac{1}{48} \times 168 = \frac{7}{2}. \tag{32}$$

This value corresponds to the term $\frac{7}{2}(H^5Ap^2 + H^5A\bar{p}^2)$ which appears in in the right-hand side of the generating function (Eq. 8). This means that there are 7 enantiomeric pairs because the term should be considered to be $7 \times \frac{1}{2}(H^5Apq + H^5A\overline{pq})$.

4 Elementary Superpositions vs. Generating Functions

This section is devoted to compare elementary superpositions with generating functions as tools of evaluating fixed ligand vectors.

4.1 Fixed Ligand Vectors Due to Elementary Superpositions

As an illustrative example, let us examine a regular ligand partition represented as follows:

$$[\theta]_4 = [4, 2, 0, 0, 0, 0; 1, 1, 0, 0], \tag{33}$$

which corresponds to the formula $H^4A^2p\bar{p}$. Such a regular case requires Eqs. 62 and 63 of [11], which are calculated to treat the present regular case of $[\theta]_4$:

$$\mathbf{H} = \mathbf{S}^{[4]} \otimes \mathbf{S}^{[2]} \otimes \widetilde{\mathscr{S}}^{[1]} \tag{34}$$
$$\mathbf{H'} = \mathbf{S}^{[4]} \otimes \mathbf{S}^{[2]} \otimes \mathscr{S}^{[1]} \otimes \mathscr{S}^{[1]}, \tag{35}$$

where the symbols are used in the same meanings as presented in Eqs. 10 and 11. On the basis of Eqs. 34 and 35, extended cycle indices defined by Eqs. 64 and 65 of [11] are calculated as follows to treat the present case of $[\theta]_4$:

$$\begin{aligned}
\mathrm{CI}(\mathbf{H}, s_d, c_d) &= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \frac{1}{2}(s_1^2 + s_2) \times c_2 \\
&= \frac{1}{24} \times \frac{1}{2}(\cdots + 3s_2^3 c_2 + 7s_1^4 s_2 c_2 + \cdots) \tag{36} \\
\mathrm{CI}(\mathbf{H'}, s_d, b_d) &= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \frac{1}{2}(s_1^2 + s_2) \times b_1^2 \\
&= \frac{1}{24} \times \frac{1}{2}(\cdots + s_1^6 b_1^2 + \cdots), \tag{37}
\end{aligned}$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity. Note that the term $7s_1^4 s_2 c_2$ in Eq. 36 is generated from $(6s_1^2 s_2)(s_1^2)(c_2)$ plus $(s_1^4)(s_2)(c_2)$.

According to Lemma 2 or 3 of [11], the elementary superposition of each monomial in the CI-CF (Eq. 1) by either one of the extended cycle indices (Eq. 36 or Eq. 37) results in the evaluation of the number of the fixed isomers:

$$s_1^6 b_1^2 \text{ (Eq. 37) onto } b_1^8: \quad \frac{1}{24} \times \frac{1}{2} \times (1^8 \times 8!) = 840 \tag{38}$$

$$s_2^3 c_2 \text{ (Eq. 36) onto } c_2^4: \quad \frac{1}{24} \times \frac{1}{2} \times (2^4 \times 4!) \times 3 = 24 \tag{39}$$

$$s_1^4 s_2 c_2 \text{ (Eq. 36) onto } a_1^4 c_2^2: \quad \frac{1}{24} \times \frac{1}{2} \times (1^4 \times 4!) \times (2^2 \times 2!) \times 7 = 28. \tag{40}$$

The remaining monomials are evaluated to give zero values. Thereby, we obtain the following fixed ligand vector:

$$(840, 0, 0, 0, 24, 0, 28, 0). \tag{41}$$

Then, Theorem 6 of [11] is applied to the vector (Eq. 41) and the CI-CF (Eq. 1) to evaluate the number ($B_{[\theta]_4}$) of isomers having the formula $H^4A^2p\overline{p}$ or the partition $[\theta]_4$:

$$B_{[\theta]_4} = \frac{1}{48} \times 840 + \frac{1}{12} \times 24 + \frac{1}{8} \times 28 = \frac{35}{2} + 2 + \frac{7}{2} = 23. \qquad (42)$$

The value $B_{[\theta]_1} = 23$ is equal to the coefficient of the term $H^4A^2p\overline{p}$ in the right-hand side of the generating function (Eq. 8).

On a similar line, the elementary superposition of Eq. 36 (no effect of Eq. 37) onto the CI-CF$^{(a)}$ (Eq. 2), so as to give the number ($B_{[\theta]_4}^{(a)}$) of achiral derivatives:

$$B_{[\theta]_4}^{(a)} = \frac{1}{6} \times 24 + \frac{1}{4} \times 28 = 4 + 7 = 11. \qquad (43)$$

On the other hand, the elementary superposition of Eqs. 36 and 37 onto the CI-CF$^{(e)}$ (Eq. 3) gives the number ($B_{[\theta]_4}^{(e)}$) of enantiomeric pairs of chiral derivatives:

$$B_{[\theta]_4}^{(e)} = \frac{1}{48} \times 840 - \frac{1}{12} \times 24 - \frac{1}{8} \times 28 = \frac{35}{2} - 2 - \frac{7}{2} = 12. \qquad (44)$$

Among 23 derivatives (Eq. 42) of the formula $H^4A^2p\overline{p}$ ([4,2,0,0;1,1,0,0]), 11 achiral derivatives calculated as Eq. 43 are illustrated in Fig. 2. Among the 11 achiral derivatives illustrated in Fig. 2, each isolated derivative (e.g., **2**) is characterized by a Type IV stereoisogram [15]. On the other hand, each pair surrounded by a frame (e.g., **3** and **4**) is in an *RS*-diastereomeric relationship. Such an *RS*-diastereomeric relationship is characterized by a Type V stereoisogram, which represents a generalized case of pseudoasymmetry [15].

Twelve enantiomeric pairs of chiral derivatives calculated as Eq. 44 are illustrated in Fig. 3. Among the 12 enantiomeric pairs of chiral derivatives (Fig. 3), two pairs surrounded by each frame (e.g., **13a/13b** and **14a/14b**) are stereoisomeric (more specifically speaking, *RS*-stereoisomeric) to each other, where they are characterized by a Type III stereoisogram [15]. On the other hand, each enantiomeric pair surrounded by a frame (e.g., **21a/21b**) is characterized by a Type II stereoisogram [15].

4.2 Fixed Ligand Vectors Due to Generating Functions

The CI-CF (Eq. 1) is characterized by the formal row vector of USCI-CFs (unit subduced cycle indices with chirality fittingness):

$$(b_1^8, b_2^4, b_1^2b_3^2, b_4^2, c_2^4, c_2c_6, a_1^4c_2^2, c_4^2), \qquad (45)$$

which appear in the $\mathbf{O}_h(/\mathbf{C}_{3v})$-row of the non-dominant USCI-CF table discussed in Part II of this series, i.e., b_1^8 for $\mathbf{C}_1$, b_2^4 for $\mathbf{C}_2$ and $\mathbf{C}_2'$, $b_1^2b_3^2$ for $\mathbf{C}_3$, b_4^2 for $\mathbf{C}_4$, c_2^4 for $\mathbf{C}_s$ and $\mathbf{C}_i$, c_2c_6 for $\mathbf{C}_{3i}$, $a_1^4c_2^2$ for $\mathbf{C}_s'$, and c_4^2 for $\mathbf{S}_4$.

An alternative way of calculating a fixed ligand vector is to introduce Eqs. 5–7 into the USCI-CFs listed in Eq. 45. The resulting generating functions contain values as the coefficients of monomials to be considered. Among them, non-zero terms necessary to the present case are listed as follows:

$$b_1^8: \quad 840H^4A^2p\overline{p} \qquad (46)$$

$$c_2^4: \quad 24H^4A^2p\overline{p} \qquad (47)$$

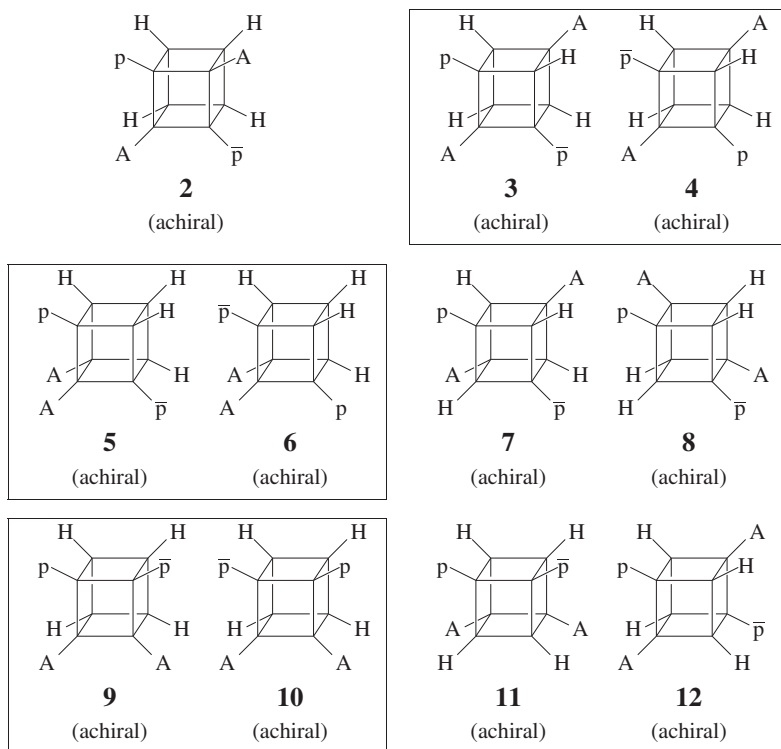$$a_1^4c_2^2: \quad 28H^4A^2p\overline{p} \qquad (48)$$

Figure 2: Achiral cubane derivatives with $H^4A^2p\bar{p}$ ([4,2,0,0;1,1,0,0])

Thereby, we obtain the following fixed ligand vector,

$$(840, 0, 0, 0, 24, 0, 28, 0), \tag{49}$$

which is identical with Eq. 41, so that the same result as Eq. 42 is alternatively obtained.

5 Ligands as 3D Structures vs. as Graphs

5.1 Stereoisomeric Chiral Proligands

From a stereochemical point of view, the derivatives of the formula $H^4A^2p\bar{p}$ have stereoisomers of the formula $H^4A^2p^2$ (or $H^4A^2\bar{p}^2$), which is represented by an irregular ligand partition:

$$[\theta]_5 = [4, 2, 0, 0, 0, 0; 2, 0, 0, 0]. \tag{50}$$

According to Eq. 63 of [11], we obtain the following equation:

$$\mathbf{H}' = S^{[4]} \otimes S^{[2]} \otimes \mathscr{S}^{[2]}, \tag{51}$$
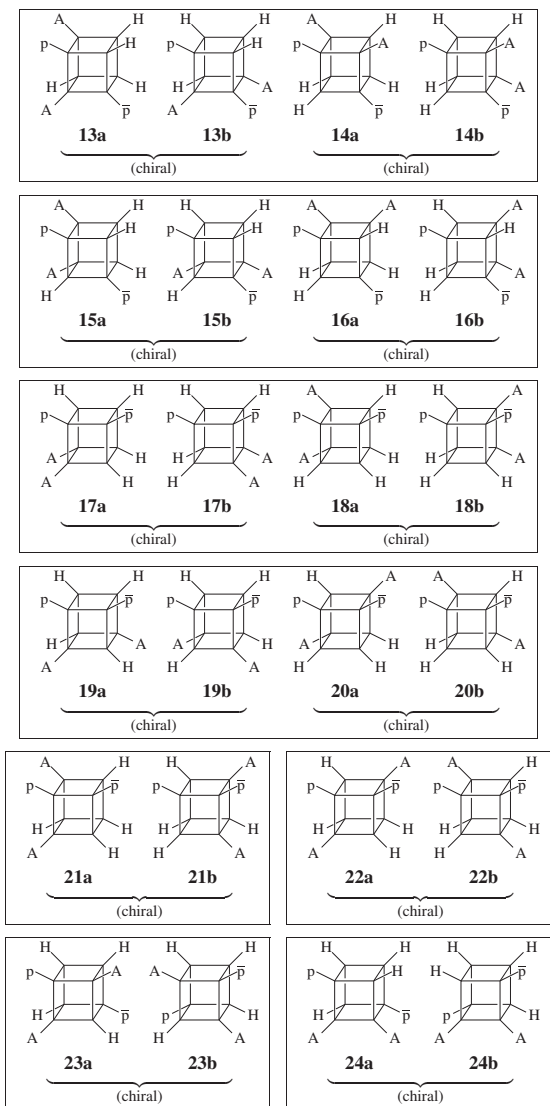
Figure 3: Chiral cubane derivatives with $H^4A^2p\bar{p}$ ([4,2,0,0;1,1,0,0])

where the symbols are used in the same meanings as presented in Eqs. 10 and 11. On the basis of Eq. 51, an extended cycle index defined by Eq. 65 of [11] is calculated as follows to treat the present case of $[\theta]_5$:

$$
\begin{aligned}
\mathrm{CI}(\mathbf{H}', s_d, b_d) &= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \frac{1}{2}(s_1^2 + s_2) \times \frac{1}{2}(b_1^2 + b_2) \\
&= \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2}(s_1^6 b_1^2 + 3s_2^3 b_2 + \cdots),
\end{aligned}
\tag{52}
$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity.

According to Lemma 2 of [11], the elementary superposition of each monomial in the CI-CF (Eq. 1) by the extended cycle index (Eq. 52) results in the evaluation of the number of the fixed isomers:

$$
s_1^6 b_1^2 \text{ (Eq. 52) onto } b_1^8: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (1^8 \times 8!) = 420
\tag{53}
$$

$$
s_2^3 b_2 \text{ (Eq. 52) onto } b_2^4: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (2^4 \times 4!) \times 3 = 12.
\tag{54}
$$

The remaining monomials are evaluated to give zero values. Thereby, we obtain the following fixed ligand vector as a row vector,

$$
(420, 12, 0, 0, 0, 0, 0, 0).
\tag{55}
$$

Then, Theorem 6 of [11] is applied to the vector (Eq. 55) and the CI-CF (Eq. 1) to evaluate the number ($B_{[\theta]_5}$) of isomers having the formula $H^4 A^2 p^2$ or the partition $[\theta]_5$:

$$
B_{[\theta]_5} = \frac{1}{48} \times 420 + \frac{3}{16} \times 12 = \frac{35}{4} + \frac{9}{4} = 11.
\tag{56}
$$

The value $B_{[\theta]_5} = 11$ is equal to the coefficient of the term $11(H^4 A^2 p^2 + H^4 A^2 \bar{p}^2)$ in the right-hand side of the generating function (Eq. 8). Note that the partition $[\theta]_5$ is paired with the partition $[\theta]_5' = [4,2,0,0,0,0;0,2,0,0]$ corresponding to $H^4 A^2 \bar{p}^2$. This means the presence of 22 enantiomeric pairs because of $11 \times \frac{1}{2}(H^4 A^2 p^2 + H^4 A^2 \bar{p}^2)$. Obviously, we obtain $B_{[\theta]_5}^{(a)} = 0$ for the number of achiral derivatives and $B_{[\theta]_5}^{(e)} = 11$ for the number of enantiomeric pairs.

Among the 22 enantiomeric pairs $H^4 A^2 p^2 / H^4 A^2 \bar{p}^2$, 8 pairs are illustrated in Fig. 4, where they are collected to show their stereoisomeric relationships to achiral cubane derivatives of $H^4 A^2 p \bar{p}$ collected in Fig. 2. Structural formulas surrounded in each frame are stereoisomeric to each other. More strictly speaking, they construct a degenerate quadruplet of RS-stereoisomers, which is specified by a Type II stereoisogram [15].

Among the 22 enantiomeric pairs $H^4 A^2 p^2 / H^4 A^2 \bar{p}^2$, the remaining 14 pairs are illustrated in Fig. 5, where they are collected to show their stereoisomeric relationships to enantiomeric pairs of cubane derivatives of $H^4 A^2 p \bar{p}$, which are collected in Fig. 3. Structural formulas surrounded in each frame are stereoisomeric to each other. More strictly speaking, they construct a (degenerate) quadruplet of RS-stereoisomers, which is specified by a Type III (or Type II) stereoisogram [15].

5.2 Chiral Proligands as Graphs

When the derivatives of the formula $H^4 A^2 p \bar{p}$ and $H^4 A^2 p^2$ (or $H^4 A^2 \bar{p}^2$) are considered to be stereoisomers, the proligands p and $\bar{p}$ are regarded as a graph which has 2D constitutions, where
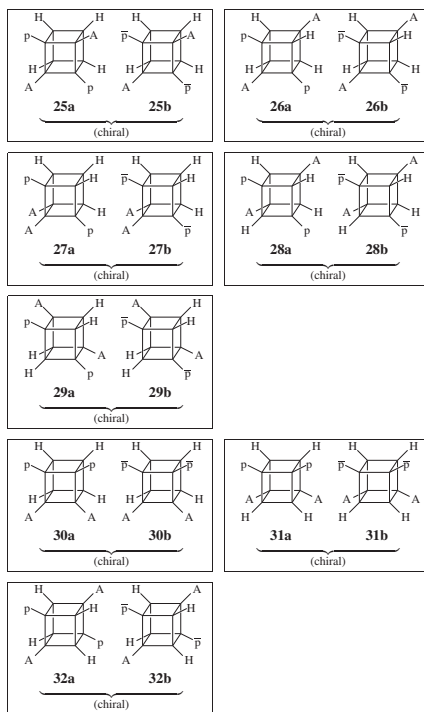
Figure 4: Enantiomeric pairs of chiral cubane derivatives with $H^4A^2p^2$ ([4,2,0,0;2,0,0,0]) and $H^4A^2\overline{p}^2$ ([4,2,0,0;0,2,0,0]). To be continued.

the symbol $\hat{p}$ denotes such a graph corresponding to p and $\overline{p}$. Then, let us count derivatives of the formula $H^4A^2\hat{p}^2$, which corresponds to a regular ligand partition:

$$[\theta]_6 = [4,2,2,0,0,0;0,0,0,0], \tag{57}$$

because the graph $\hat{p}$ can be regarded as an achiral proligand. To treat proligands as graphs, Eqs. 62 and 63 of [11] are degenerated to give the following group:

$$\mathbf{H} = \mathbf{H}' = S^{[4]} \otimes S^{[2]} \otimes S^{[2]}, \tag{58}$$

where the symbols are used in the same meanings as presented in Eqs. 10 and 11. On the basis of Eq. 58, extended cycle indices defined by Eqs. 64 and 65 of [11] are calculated to give a degenerate CI as follows:

$$\begin{aligned}
\mathrm{CI}(\mathbf{H}, s_d) &= \mathrm{CI}(\mathbf{H}', s_d) \\
&= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \left(\frac{1}{2}(s_1^2 + s_2)\right)^2
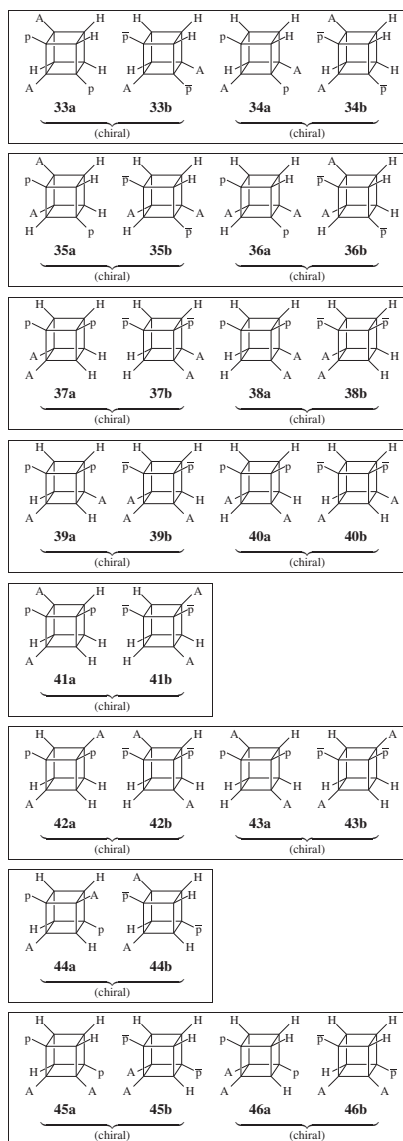\end{aligned}$$

Figure 5: Enantiomeric pairs of chiral cubane derivatives with $H^4A^2p^2$ ([4,2,0,0;2,0,0,0]) and $H^4A^2\bar{p}^2$ ([4,2,0,0;0,2,0,0]). Continued.

$$\begin{aligned}
&= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \frac{1}{2} \times \frac{1}{2}(s_1^4 + 2s_1^2 s_2 + s_2^2) \\
&= \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2}(s_1^8 + 3s_2^4 + 16s_1^4 s_2^2 + \cdots),
\end{aligned} \tag{59}$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity. Note that the term $16s_1^4 s_2^2$ is generated by $(s_1^4)(s_2^2) + (6s_1^2 s_2)(2s_1^2 s_2) + (3s_2^2)(s_1^4)$.

According to Lemmas 2 and 3 of [11], the elementary superposition of each monomial in the CI-CF (Eq. 1) by the extended cycle index (Eq. 59) results in the evaluation of the number of the fixed isomers:

$$s_1^8 \text{ (Eq. 59) onto } b_1^8: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (1^8 \times 8!) = 420 \tag{60}$$

$$s_2^4 \text{ (Eq. 59) onto } b_2^4: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (2^4 \times 4!) \times 3 = 12 \tag{61}$$

$$s_2^4 \text{ (Eq. 59) onto } c_2^4: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (2^4 \times 4!) \times 3 = 12 \tag{62}$$

$$s_1^4 s_2^2 \text{ (Eq. 59) onto } a_1^4 c_2^2: \quad \frac{1}{24} \times \frac{1}{2} \times \frac{1}{2} \times (1^4 \times 4!) \times (2^2 \times 2!) \times 16 = 32. \tag{63}$$

The remaining monomials are evaluated to give zero values. Thereby, we obtain the following fixed ligand vector as a row vector,

$$(420, 12, 0, 0, 12, 0, 32, 0). \tag{64}$$

Then, Theorem 6 of [11] is applied to the vector (Eq. 64) and the CI-CF (Eq. 1) to evaluate the number $(B_{[\theta]_6})$ of isomers having the formula $H^4 A^2 \hat{p}^2$ or the partition $[\theta]_6$:

$$B_{[\theta]_6} = \frac{1}{48} \times 420 + \frac{3}{16} \times 12 + \frac{1}{12} \times 12 + \frac{1}{8} \times 32 = \frac{35}{4} + \frac{9}{4} + 1 + 4 = 16. \tag{65}$$

Comparison between Figs. 2 and 4 provides 8 sets of stereoisomers, i.e.,

{**2**; **25a/25b**}, {**3**, **4**; **26a/26b**}, {**5**, **6**; **27a/27b**}, {**7**; **28a/28b**},
{**8**; **29a/29b**}, {**9**, **10**; **30a/30b**}, {**11**; **31a/31b**}, and {**12**; **32a/32b**}.

On the other hand, comparison between Figs. 3 and 5 provides 8 sets of stereoisomers, i.e.,

{**13a/13b**, **14a/14b**; **33a/33b**, **34a/34b**}, {**15a/15b**, **16a/16b**; **35a/35b**, **36a/36b**},
{**17a/17b**, **18a/18b**; **37a/37b**, **38a/38b**}, {**19a/19b**, **20a/20b**; **39a/39b**, **40a/40b**},
{**21a/21b**; **41a/41b**}, {**22a/22b**; **42a/42b**, **43a/43b**},
{**23a/23b**; **44a/44b**}, {**24a/24b**; **45a/45b**, **46a/46b**}.

Hence, there totally appear 16 sets of stereoisomers in accord with the value calculated by Eq. 65. These results clearly demonstrate effects without and with chirality fittingness, i.e., graphs vs. 3D structures for proligands.

6 Preliminary Desymmetrizations of Skeletons

When a starting skeleton has a high symmetry as shown in the present case **1** (Figure 1) of O_h, it is sometimes troublesome to verify enumeration results. Preliminary desymmetrization
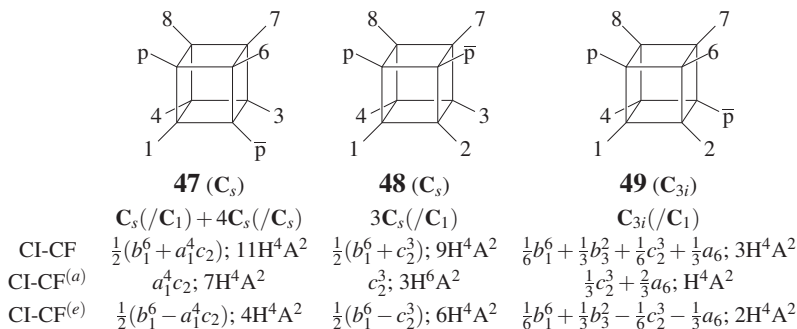
	47 ($\mathbf{C}_s$)	**48** ($\mathbf{C}_s$)	**49** ($\mathbf{C}_{3i}$)
	$\mathbf{C}_s(/\mathbf{C}_1) + 4\mathbf{C}_s(/\mathbf{C}_s)$	$3\mathbf{C}_s(/\mathbf{C}_1)$	$\mathbf{C}_{3i}(/\mathbf{C}_1)$
CI-CF	$\frac{1}{2}(b_1^6 + a_1^4 c_2)$; 11H^{4}A^2	$\frac{1}{2}(b_1^6 + c_2^3)$; 9H^{4}A^2	$\frac{1}{6}b_1^6 + \frac{1}{3}b_3^2 + \frac{1}{6}c_2^3 + \frac{1}{3}a_6$; 3H^{4}A^2
CI-CF$^{(a)}$	$a_1^4 c_2$; 7H^{4}A^2	c_2^3; 3H^{6}A^2	$\frac{1}{3}c_2^3 + \frac{2}{3}a_6$; H^{4}A^2
CI-CF$^{(e)}$	$\frac{1}{2}(b_1^6 - a_1^4 c_2)$; 4H^{4}A^2	$\frac{1}{2}(b_1^6 - c_2^3)$; 6H^{4}A^2	$\frac{1}{6}b_1^6 + \frac{1}{3}b_3^2 - \frac{1}{6}c_2^3 - \frac{1}{3}a_6$; 2H^{4}A^2

Figure 6: Cubane skeletons substituted preliminarily by p and $\bar{\text{p}}$

of the skeleton provides us with a convenient way of doing such verification, where partially substituted skeletons are taken into consideration. To check the data illustrated in Figs. 2 and 3, let us start from three skeletons (**47–49**) shown in Fig. 6, in which p and $\bar{\text{p}}$ are preliminarily substituted.

Point-group symmetries for **47–49** are shown in Fig. 6. By the substitution of the proligands p and $\bar{\text{p}}$, the remaining six positions of each desymmetrized skeleton are restricted to be divided into several orbits (equivalence classes), which are controlled by coset representations of its point-group symmetry. For example, the six positions of **47** are divided into five orbits:

$$\{3, 8\}, \{1\}, \{4\}, \{6\}, \text{ and } \{7\}. \tag{66}$$

which are controlled by a set of coset representations:

$$\mathbf{C}_s(/\mathbf{C}_1) + 4\mathbf{C}_s(/\mathbf{C}_s). \tag{67}$$

Thereby, a CI-CF for total enumeration is calculated as follows:

$$\text{CI-CF}(\mathbf{C}_s, \$) = \frac{1}{2}(b_1^6 + a_1^4 c_2), \tag{68}$$

which is listed in the bottom part of Fig. 6. Note that the monomial (SCI-CF) b_1^6 is calculated from USCI-CFs of the 5 component orbits, i.e., $(b_1^2)(b_1)(b_1)(b_1)(b_1)$, while the monomial (SCI-CF) $a_1^4 c_2$ stems from $(c_2)(a_1)(a_1)(a_1)(a_1)$. Similarly, the CI-CF$^{(a)}$ for enumerating achiral derivatives and the CI-CF$^{(e)}$ for enumerating enantiomeric pairs are calculated as shown in the bottom part of Fig. 6. This procedure is repeated to examine **48** and **49**, giving CI-CFs, CI-CF$^{(a)}$s, and CI-CF$^{(e)}$s, which are also collected in the bottom part of Fig. 6.

Because p and $\bar{\text{p}}$ are already placed, four H's and two A's are taken into consideration as achiral proligands so that Eqs. 62 and 63 of [11] are degenerated to give the following group:

$$\mathbf{H} = \mathbf{H}' = S^{[4]} \otimes S^{[2]}, \tag{69}$$

where the symbols are used in the same meanings as presented in Eqs. 10 and 11. On the basis of Eq. 69, extended cycle indices defined by Eqs. 64 and 65 of [11] are calculated to give a

degenerate CI as follows:

$$
\begin{aligned}
\mathrm{CI}(\mathbf{H}, s_d) &= \mathrm{CI}(\mathbf{H}', s_d) \\
&= \frac{1}{24}(s_1^4 + 6s_1^2 s_2 + 3s_2^2 + 8s_1 s_3 + 6s_4) \times \frac{1}{2}(s_1^2 + s_2) \\
&= \frac{1}{24} \times \frac{1}{2}(s_1^6 + 3s_2^3 + 7s_1^4 s_2 + \cdots),
\end{aligned} \tag{70}
$$

where monomials unnecessary in the following discussion are omitted for the sake of brevity.

According to Lemmas 2 and 3 of [11], the elementary superposition of each monomial in the CI-CF of **47** (Eq. 68 or in the bottom part of Fig. 6) by the extended cycle index (Eq. 70) results in the evaluation of the number of the fixed isomers:

$$s_1^6 \text{ (Eq. 70) onto } b_1^6 : \qquad \frac{1}{24} \times \frac{1}{2} \times (1^6 \times 6!) = 15 \tag{71}$$

$$s_1^4 s_2 \text{ (Eq. 70) onto } a_1^4 c_2 : \qquad \frac{1}{24} \times \frac{1}{2} \times (1^4 \times 4!) \times (2 \times 1!) \times 7 = 7 \tag{72}$$

Then, Theorem 6 of [11] is used to give

$$\frac{1}{2} \times 15 + \frac{1}{2} \times 7 = 11 \tag{73}$$

which denotes the total number of cubane derivatives of $H^4 A^2$ (or fully $H^4 A^2 p\bar{p}$) by starting from the p,$\bar{p}$-substituted skeleton **47**. This value is alternatively obtained by introducing

$$a_d = b_d = c_d = H^d + A^d \tag{74}$$

into the CI-CF of **47** (Eq. 68 or in Fig. 6), where the resulting generating function contains the term $11H^4 A^2$ as indicating after the CI-CF at issue in Fig. 6. Similarly, the applications of the elementary superposition method or the generating function method to the CI-CF$^{(a)}$ and CI-CF$^{(e)}$ provide the corresponding values for **47**, as shown in Fig. 6. This set of procedures is repeated to examine **48** and **49**, where each calculation result is shown also in the bottom part of Fig. 6 in the form of the coefficient of the term $H^4 A^2$.

The data illustrated in Figs. 2 and 3 are verified by the itemized calculations shown in the bottom part of Fig. 6 as follows:

1. As for **47**, 7 achiral derivatives are found to be {**2, 3, 4, 5, 6, 7, 8**} of Fig. 2, while 4 enantiomeric pairs are found to be {**13a/13b, 14a/14b, 15a/15b, 16a/16b**} of Fig. 3. Totally, there are 11 derivatives based on **47** as a p,$\bar{p}$-skeleton, where the value is consistent with the total number 11 calculated.

2. As for **48**, 3 achiral derivatives correspond to {**9, 10, 11**} of Fig. 2, while 6 enantiomeric pairs correspond to {**17a/17b, 18a/18b, 19a/19b, 20a/20b, 21a/21b, 22a/22b**} of Fig. 3. Totally, there are 9 derivatives, which are consistent with the total number 9 calculated.

3. As for **49**, one achiral derivative is {**12**} of Fig. 2 while two enantiomeric pairs are found to be {**23a/23b, 24a/24b**} of Fig. 3. Totally, there are 3 derivatives, which are consistent with the total number 3 calculated.

7 Conclusions

The extended superposition method, which has been developed as an application of elementary superposition [11], is applied to enumeration of cubane derivatives with chiral and achiral proligands. This method provides us with a tool for evaluating the respective contribution of each USCI-CF (unit subduced-cycle index with chirality fittingness) to the corresponding CI-CF (cycle index with chirality fittingness), which is calculated by means of the proligand method (Part I of this series), the markaracter method (Part II), the characteristic-monomial method (Part III) or others. The extended superposition method does not require generating functions but requires cycle indices (CI) for regular and irregular cases, which depend upon permutational features of chiral and/or achiral (pro)ligands. Calculated values by the extended superposition method are clarified to be identical with those obtained in terms of generating functions, which are calculated by using the proligand method (Part I), the markaracter method (Part II), and the characteristic monomial method (Part III).

References

[1] S. Fujita, *Theor. Chem. Acc.*, **113**, 73–79 (2005).

[2] S. Fujita, *Theor. Chem. Acc.*, **113**, 80–86 (2005).

[3] S. Fujita, *Theor. Chem. Acc.*, **115**, 37–53 (2006).

[4] S. Fujita, *Theor. Chim. Acta*, **91**, 291–314 (1995).

[5] S. Fujita, *Theor. Chim. Acta*, **91**, 315–332 (1995).

[6] S. Fujita, *Bull. Chem. Soc. Jpn.*, **71**, 1587–1596 (1998).

[7] S. Fujita, *Theor. Chem. Acc.*, **99**, 224–230 (1998).

[8] S. Fujita, *J. Chem. Inf. Comput. Sci.*, **40**, 1101–1112 (2000).

[9] S. Fujita, "Symmetry and Combinatorial Enumeration in Chemistry," Springer-Verlag, Berlin-Heidelberg (1991).

[10] S. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 2770–2775 (1990).

[11] S. Fujita, *Theor. Chim. Acta*, **82**, 473–498 (1992).

[12] J. H. Redfield, *Am. J. Math.*, **49**, 433–455 (1927).

[13] R. C. Read, *J. London Math. Soc.*, **34**, 417–436 (1959).

[14] R. C. Read, *Canad. J. Math.*, **20**, 808–841 (1968).

[15] S. Fujita, *J. Org. Chem.*, **69**, 3158–3165 (2004).