Enumeration of Three-Dimensional Structures Derived from a Dodecahedrane Skeleton under a Restriction Condition. II. The Restricted-Partial-Cycle-Index (RPCI) Method Based on Restricted Subduced Cycle Indices

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The restricted-partial-cycle-index (RPCI) method for combinatorial enumeration under the restriction of no adjacency of ligands has been developed as a restricted version of the partial-cycle-index (PCI) method of the unit-subduced-cycle-index (USCI) approach (S. Fujita, "Symmetry and Combinatorial Enumeration in Chemistry," Springer-Verlag (1991)). To take account of the restriction condition, (unrestricted) subduced cycle indices with chirality fittingness (SCI-CFs) of the USCI approach are converted into restricted subduced cycle indices with chirality fittingness (RSCI-CFs). Then, restricted partial cycle indices with chirality fittingness (RPCI-CFs) are derived from the RSCI-CFs, just as partial cycle indices with chirality fittingness (PCI-CFs) are derived from the SCI-CFs in the USCI approach. The resulting RPCI-CFs provide generating functions for restricted enumerations. The RPCI method using such RPCI-CFs is applied to enumeration of dodecahedrane derivatives under the restriction of no adjacency of ligands. Several enumerated derivatives are depicted and their symmetries are discussed to comprehend stereochemical properties such as pseudoasymmetry, sphericity, and prochirality.

1 Introduction

In the preceding Part I of this series, we have reported the restricted-fixed-point-matrix (RFPM) method for counting isomers under a restriction condition of no-adjacency of ligands, where restricted subduced cycle indices with and without chirality fittingness (RSCI-CFs and RSCIs) play a crucial role for determining the restriction condition. The RSCI-CFs (or RSCIs) have been combined with the fixed-point-matrix (FPM) method of the unit-subduced-cycle-index (USCI) approach [1,2] so as to develop the RFPM method. Because the USCI approach provides us with the partial-cycle-index (PCI) method as another reliable method for combinatorial enumeration [1], our next target is to extend the PCI method by adopting such RSCI-CFs (or RSCIs), so as to develop the restricted-partial-cycle-index (RPCI) method for counting isomers under the re-

striction condition.

As a continuation of Part I of this series, we will examine the problem of restricted substitution, where bulky substituents such as *tert*-butyl ligands occupy non-adjacent sites of a dodecahedrane skeleton.

2 The RPCI Method

2.1 Restricted Subduced Cycle Indices

The numbering of 20 vertices in a dodecahedron skeleton is shown in Figure 1 by using a projection diagram (1) and a Schlegel diagram (2).

Because ligand substitution causes desymmetrization of a given skeleton, each orbit (equivalence class) of substitution sites in the skeleton is divided into a set of suborbits, which is characterized by a unit subduced cycle index with ((USCI-CF)

Figure 1. Numbering of a dodecahedrane skeleton (projection diagram (1) and Schlegel diagram (2)).

and without chirality fittingness (USCI). Such USCI-CFs (or USCIs) are pre-calculated by considering the subduction of coset representations and are collected as tabular forms [1]. When two or more orbits of substitution sites participate in the ligand substitution, relevant USCI-CFs (or USCIs) are multiplied to give subdued cycle indices with (SCI-CFs) or without chirality (SCIs). Because USCIs, SCI-CFs, etc. are degenerate forms of USCI-CFs, SCI-CFs, etc., we use the latter hereafter as representations of the terms with and without CF.

The 20 vertices of the dodecahedrane skeleton (1) construct an orbit, which is governed by the coset representation $\mathbf{I}_h / (\mathbf{C}_{3v})$. Because of the presence of a single orbit, the USCI-CF (reported in [3]) can be used as SCI-CFs, which are collected in the SCI-CF-column of Table 1.

Suppose that *tert*-butyl ligands (X 's as achiral substituents) and *sec*-butyl ligands ($p/\bar{p}$ as an enantiomeric pair of chiral ligands) are placed on the vertices of the dodecahedrane skeleton (c1) under the restriction of no adjacent occupation. By the concepts of territory indicators and territory discriminants (cf. Part I), SCI-CFs are converted into restricted subdued cycle indices with chirality fittingness (RSCI-CFs), as collected in the RSCI-CF-column of Table 1.

The algebraic procedure for converting SCI-CFs into RSCI-CFs is omitted here, because it has been discussed in Part I of this series. Instead, we examine the resulting RSCI-CFs diagrammatically for the purpose of understanding the meaning of the conversions collected in Table 1. For example, the $\mathbf{C}_{2v}$ -row of Table 1 indicates the SCI-CF of $\mathbf{C}_{2v}$ to be $a_2^4 c_4^3$. Each sphericity index a_2 corresponds to a two-membered homospheric orbit, while each sphericity index c_4 corresponds to a four-membered enantiospheric orbit, as formulated in [1].

The two-fold axis of the $\mathbf{C}_{2v}$ -group is selected to run through the midpoints of the edges $\{1,8\}$ and $\{13,20\}$. By inspecting

the dodecahedrane skeleton c1, the SCI-CF $a_2^4 c_4^3$ for the $\mathbf{C}_{2v}$ -group corresponds to the following mode of division:

$$a_2^4 : \underline{A_1 = \{1,8\}}, \underline{A_2 = \{6,10\}}, \\ A_3 = \{11,15\}, \underline{A_4 = \{13,20\}} \quad (1)$$

$$c_4^3 : A_5 = \{2,5,7,9\}, A_6 = \{12,14,16,19\}, \\ A_7 = \{3,4,17,18\} \quad (2)$$

Because the underlined suborbits (A_1 , A_4 , and A_7) already contain adjacent sites, they are rejected before detailed examination. Among the remaining suborbits, an appropriate set of suborbits is selected so as to satisfy the restriction condition by virtue of the scheme described in Part I of this series, where territory indicators and territory discriminants are used as clues for such selection based on the restriction condition. As an extreme case, for example, each of the remaining suborbits (A_2 , A_3 , A_5 , or A_6) itself meets the restricted condition and can be adopted as a selected set.

Such a selected set is characterized by a monomial appearing in the corresponding RSCI-CF, as shown in the $\mathbf{C}_{2v}$ -row of Table 1. As a result, the selected sets for the $\mathbf{C}_{2v}$ -group are shown in Figure 2. For example, the monomial $2a_2$ corresponds to fixed 3D-structures **3** and **4**, which use A_2 and A_3 , respectively. Because they are homospheric, they are capable of accommodating two achiral ligands (X^2) in agreement with chirality fittingness [1]. The two structures **3** and **4** are identical with each other under the action of $\mathbf{I}_h$.

On the other hand, the monomial $2c_4$ corresponds to fixed 3D-structures **5** and **6**, which use A_5 and A_6 , respectively. Because they are enantiospheric, they are capable of accommodating four achiral ligands (X^4) or two pairs of chiral ligands ($\bar{p}$) in agreement with chirality fittingness [1]. The latter mode of accommodation causes pseudoasymmetry, which will be discussed later.

The monomials $2a_2 c_4$ and c_4^2 are respectively concerned with two suborbits as shown by **7–9** in Figure 2.

Totally, Figure 2 shows all of the fixed points (fixed structures of $\mathbf{C}_{2v}$) under the restriction condition, so that the numbers of them (i.e., marks) are characterized by the RSCI-CF for $\mathbf{C}_{2v}$, i.e., $1 + 2a_2 + 2c_4 + 2a_2 c_4 + c_4^2$. The RSCI-CFs for the other subgroups of $\mathbf{I}_h$ can be discussed in a similar way. This means that the RSCI-CFs are capable of substituting for the corresponding SCI-CFs in the processes of evaluating marks under the restriction condition. In other words, the RSCI-CFs

Figure 2. 3D Structures fixed by the subduction into C_{2v} under the restriction condition of no adjacency. They corresponds to the RSCI-CF for C_{2v} , i.e., $1 + 2a_2 + 2c_4 + 2a_2c_4 + c_4^2$.

serve as a substantial and just enough part of the SCI-CFs, when we consider enumeration under the restriction condition.

2.2 Restricted Partial Cycle Indices

As shown in Def. 16.3 of Ref [1], usual (or unrestricted) SCI-CFs of the USCI approach are transformed into partial cycle indices with chirality fittingness (PCI-CFs), which provide us with the PCI method for combinatorial enumeration. The SCI-CFs can be replaced by the RSCI-CFs, because the latter are generated as a substantial part of the former. Hence, the RSCIs are transformed into restricted partial cycle indices (RPCIs) by using the inverse matrix M_G^{-1} of the mark table M_G of G :

Definition 1(RPCI-CFs) Restricted partial cycle indices with chirality fittingness (RPCI-CFs) are defined as follows:

$$\overline{\text{PCI-CF}}(G_i; \$_d) = \sum_{j=1}^s \bar{m}_{ji} \overline{\text{SCI-CF}}(G_j; \$_d) \quad (3)$$

for $i = 1, 2, \dots, s$, where $\bar{m}_{ji}$ represents the ji -element of the inverse matrix M_G^{-1} , i.e., the element which appears at the intersection of the i -th column and the j -th row. The symbol

$\$_d$ represents a sphericity index a_d for a homospheric orbit, an index b_d for a hemispheric orbit, or an index c_d for an enantiospheric orbit.

The usual PCIs described in Theorem 16.3 of Ref [1], are easily replaced by the RPCIs defined by Def. 1. Thereby, a theorem based on the RPCIs (Def. 1) is obtained in a similar way to Theorem 16.3 [1] based on the PCIs.

The RSCI-CFs collected in Table 1 are aligned to give a row vector, which is formally multiplied by the inverse matrix $M_{I_h}^{-1}$ (Table 2 of [3]). This multiplication process gives the same result as eq 3 (Def. 1). Thereby, we are able to obtain the following set of RPCI-CFs:

$$\begin{aligned} \overline{\text{PCI-CF}}(C_1; \$_d) &= \frac{5}{4}b_1^2 + \frac{11}{2}b_1^3 + \frac{151}{12}b_1^4 + \frac{239}{15}b_1^5 + \dots \end{aligned} \quad (4)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_2; \$_d) &= \frac{3}{2}b_2 + \frac{9}{2}b_2^2 + 3b_2^3 + \frac{1}{4}b_2^4 - \frac{1}{4}b_2^5 + \dots \end{aligned} \quad (5)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_s; \$_d) &= \frac{1}{2}a_1^2 - a_1a_3 - a_2 - a_3 - \frac{1}{2}a_3^2 + \dots \end{aligned} \quad (6)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_i; \$_d) &= \frac{1}{2}a_6 - \frac{1}{2}a_2c_4 + \frac{1}{2}c_2^2 + \frac{1}{2}c_2^3 + \dots \end{aligned} \quad (7)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_3; \$_d) &= 2b_1b_3^2 + b_1^2b_3 + \frac{1}{2}b_1^2b_3^2 - \frac{1}{4}b_2 + \dots \end{aligned} \quad (8)$$

$$\overline{\text{PCI-CF}}(D_2; \$_d) = 0 \quad (9)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_{2v}; \$_d) &= a_2 + a_2c_4 + c_4 + \frac{1}{2}c_4^2 - \frac{1}{2}c_8 \end{aligned} \quad (10)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(C_{2h}; \$_d) &= a_2c_4 + c_4 + \frac{1}{2}c_4^2 - \frac{1}{2}c_8 - a_6 \end{aligned} \quad (11)$$

$$\overline{\text{PCI-CF}}(C_s; \$_d) = \frac{1}{2}b_5 - \frac{1}{2}a_5 \quad (12)$$

$$\begin{aligned} \overline{\text{PCI-CF}}(D_3; \$_d) &= \frac{1}{2}b_2 + \frac{1}{2}b_6 - \frac{1}{2}a_2 - \frac{1}{2}a_6 \end{aligned} \quad (13)$$

Table 1. SCI-CFs and RSCI-CFs for the $I_h(/C_{3v})$ -Orbit

G_j ($\subset I_h$)	SCI-CF [3]	RSCI-CF $\overline{\text{SCI-CF}}(G_j; \$_d)$
C_1	b_1^{20}	$1 + 20b_1 + 160b_1^2 + 660b_1^3 + 1510b_1^4 + 1912b_1^5 + 1240b_1^6 + 320b_1^7 + 5b_1^8$
C_2	b_2^{10}	$1 + 8b_2 + 18b_2^2 + 12b_2^3 + b_2^4$
C_s	$a_1^4 c_2^8$	$1 + 4a_1 + 4a_1^2 + 6c_2 + 20a_1c_2 + 16a_1^2c_2 + 10c_2^2 + 12a_1^2c_2^2 + 24a_1c_2^2 + 8a_1c_2^3 + 6c_2^3 + c_2^4$
C_i	c_2^{10}	$1 + 10c_2 + 30c_2^2 + 30c_2^3 + 5c_2^4$
C_3	$b_1^2 b_3^6$	$1 + 2b_1 + b_1^2 + 6b_3 + 10b_1b_3 + 4b_1^2b_3 + 8b_1b_3^2 + 7b_3^2 + 2b_1^2b_3^2$
D_2	b_4^5	$1 + 2b_4 + b_4^2$
C_{2v}	$a_2^4 c_4^3$	$1 + 2a_2 + 2c_4 + 2a_2c_4 + c_4^2$
C_{2h}	$a_2^2 c_4^4$	$1 + 2a_2 + 2c_4 + 2a_2c_4 + c_4^2$
C_5	b_5^4	$1 + 2b_5$
D_3	$b_2 c_6^3$	$1 + b_2 + b_6$
C_{3v}	$a_1^2 a_3^2 c_6^2$	$1 + 2a_1 + a_1^2 + 2a_3 + 2a_1a_3 + a_3^2$
C_{3i}	$c_2 c_6^3$	$1 + 3c_6 + c_2 + 2c_2c_6$
D_{2h}	$a_3^3 c_8$	$1 + c_8$
D_5	b_{10}^2	1
C_{5v}	a_5^4	$1 + 2a_5$
C_{5i}	c_{10}^2	1
T	$b_4^2 b_{12}$	$1 + 2b_4 + b_4^2$
D_{3d}	$a_2 a_6 c_{12}$	$1 + a_2 + a_6$
D_{5d}	a_{10}^2	1
T_h	$c_8 a_{12}$	$1 + c_8$
I	b_{20}	1
I_h	a_{20}	1

$$\overline{\text{PCI-CF}}(C_{3v}; \$_d) = a_1 + \frac{1}{2}a_1^2 + a_3 + a_1a_3 + \frac{1}{2}a_3^2 - \frac{1}{2}a_2 - \frac{1}{2}a_6 \quad (14)$$

$$\overline{\text{PCI-CF}}(C_{3i}; \$_d) = \frac{3}{2}c_6 + \frac{1}{2}c_2 + c_2c_6 - \frac{1}{2}a_2 - \frac{1}{2}a_6 - c_8 \quad (15)$$

$$\overline{\text{PCI-CF}}(D_{2h}; \$_d) = 0 \quad (16)$$

$$\overline{\text{PCI-CF}}(D_5; \$_d) = 0 \quad (17)$$

$$\overline{\text{PCI-CF}}(C_{5v}; \$_d) = a_5 \quad (18)$$

$$\overline{\text{PCI-CF}}(C_{5i}; \$_d) = 0 \quad (19)$$

$$\overline{\text{PCI-CF}}(T; \$_d) = b_4 + \frac{1}{2}b_4^2 - \frac{1}{2}c_8 \quad (20)$$

$$\overline{\text{PCI-CF}}(D_{3d}; \$_d) = a_2 + a_6 \quad (21)$$

$$\overline{\text{PCI-CF}}(D_{5d}; \$_d) = 0 \quad (22)$$

$$\overline{\text{PCI-CF}}(T_h; \$_d) = c_8 \quad (23)$$

$$\overline{\text{PCI-CF}}(I; \$_d) = 0 \quad (24)$$

$$\overline{\text{PCI-CF}}(I_h; \$_d) = 1 \quad (25)$$

where the symbol $\$ _d$ represents a_d , b_d , or c_d .

2.3 Restricted Enumeration

Suppose that a set of ligands is selected from a ligand inventory L :

$$L = \{H, X, p, \bar{p}\}, \quad (26)$$

and that they are placed on the 20 vertices of the dodecahedrane skeleton (1) under the restriction condition of no adjacency. The symbol X denotes a *tert*-butyl ligand as an achiral ligand and a pair of p and $\bar{p}$ represents an enantiomeric pair of *sec*-butyl ligands. Then, the following inventory functions:

$$a_d = X^d \quad (27)$$

$$b_d = X^d + p^d + \bar{p}^d \quad (28)$$

$$c_d = X^d + 2p^{d/2}\bar{p}^{d/2} \quad (29)$$

are introduced into the RPCI-CFs (eqs 4–25). Note that the right-hand side of each inventory function does not contain 1^d (or H^d) because the RSCI-CFs (or the RPCI-CFs) have already evaluated such substitutions as vacant vertices. The resulting equations are expanded to give the following generating functions:

$$\begin{aligned} f_{C_1} = & 3X^3 + 8X^4 + 13X^5 + 7X^6 + X^7 \\ & + p\bar{p} + 67p^2\bar{p}^2 + 198p^3\bar{p}^3 + p^4\bar{p}^4 \\ & + \frac{5}{2}(Xp + X\bar{p}) + \frac{1}{2}(p^2 + \bar{p}^2) + 5(p^3 + \bar{p}^3) \\ & + 10(p^4 + \bar{p}^4) + \frac{31}{2}(p^5 + \bar{p}^5) \\ & + \frac{17}{2}(p^6 + \bar{p}^6) + \dots \end{aligned} \quad (30)$$

$$f_{C_2} = X^2 + 3X^4 + 2X^6 + 7p^2\bar{p}^2 + \frac{3}{2}(p^2 + \bar{p}^2) + 4(p^4 + \bar{p}^4) + \frac{5}{2}(p^6 + \bar{p}^6) + \dots \quad (31)$$

$$f_{C_s} = X^2 + 4X^3 + 4X^4 + 5X^5 + 3X^6 + 2X^7 + 3p\bar{p} + 7p^2\bar{p}^2 + 12p^3\bar{p}^3 + 2p^4\bar{p}^4 + 24p\bar{p}X^3 + \dots \quad (32)$$

$$f_{C_i} = p^2\bar{p}^2 + 3p^3\bar{p}^3 + 2X^2p^3\bar{p}^3 + 5X^2p^2\bar{p}^2 + 2X^2p\bar{p} + 3X^4p\bar{p} + X^4p^2\bar{p}^2 \quad (33)$$

$$f_{C_3} = X^3 + X^4 + X^5 + X^6 + 2X^7 + \frac{1}{2}(p + \bar{p}) + 2p^3\bar{p}^3 + \frac{1}{2}(Xp + X\bar{p}) + \frac{3}{2}(p^3 + \bar{p}^3) + \dots \quad (34)$$

$$f_{D_2} = 0 \quad (35)$$

$$f_{C_{2v}} = X^2 + X^4 + X^6 + 2p^2\bar{p}^2 + 2X^2p^2\bar{p}^2 + 2X^4p^2\bar{p}^2 + p^4\bar{p}^4 \quad (36)$$

$$f_{C_{2h}} = X^4 + 2p^2\bar{p}^2 + 2X^2p^2\bar{p}^2 + 2X^4p^2\bar{p}^2 + p^4\bar{p}^4 \quad (37)$$

$$f_{C_5} = \frac{1}{2}(p^5 + \bar{p}^5) \quad (38)$$

$$f_{D_3} = \frac{1}{2}(p^2 + \bar{p}^2) + \frac{1}{2}(p^6 + \bar{p}^6) \quad (39)$$

$$f_{C_{3v}} = X + X^3 + X^4 \quad (40)$$

$$f_{C_{3i}} = X^6 + p\bar{p} + 3p^3\bar{p}^3 + 2X^2p^3\bar{p}^3 + 2X^6p\bar{p} + 2p^4\bar{p}^4 \quad (41)$$

$$f_{D_{2h}} = 0 \quad (42)$$

$$f_{D_3} = 0 \quad (43)$$

$$f_{C_{3v}} = X^5 \quad (44)$$

$$f_{C_{3i}} = 0 \quad (45)$$

$$f_T = X^4 + (p^4 + \bar{p}^4) + (X^4p^4 + X^4\bar{p}^4) + \frac{1}{2}(p^8 + \bar{p}^8) \quad (46)$$

$$f_{D_{3d}} = X^2 + X^6 \quad (47)$$

$$f_{D_{3d}} = 0 \quad (48)$$

$$f_{T_h} = X^8 + 2p^4\bar{p}^4 \quad (49)$$

$$f_I = 0 \quad (50)$$

$$f_{I_h} = 1, \quad (51)$$

where the coefficient of each monomial $X^x p^p \bar{p}^{\bar{p}}$ for the G_i - symmetry represents the number of dodecahedrane derivatives of G_i which has x of X, p of p, and $\bar{p}$ of $\bar{p}$ as substituents under the restriction condition.

3 Drawing Derivatives Enumerated

3.1 Achiral Derivatives

The generating function $f_{C_{2v}}$ (eq 36) shows that there are one isomer with X^2 (**10**), one isomer with X^4 (**11**), one isomer with X^6 (**12**), two isomers with $p^2\bar{p}^2$ (**13** and **14**), two isomers with $X^2p^2\bar{p}^2$ (**15** and **16**), two isomers with $X^4p^2\bar{p}^2$ (**17** and **18**), and one isomer with $p^4\bar{p}^4$ (**19**), as shown in Figure 3. where an open circle represents a *tert*-butyl ligand (X), while black and gray solid circles represent an enantiomeric pair of *sec*-butyl ligands (p and $\bar{p}$).

The C_{2v} - derivatives with achiral ligands only (Figure 3) can be related to the fixed structures shown in Figure 2 as follows:

1. The one isomer with X^2 (**10**) corresponds to the fixed 3D-structures (**3** and **4**) which coincide with each other under the action I_h to give **10** as a single derivative.
2. The one isomer with X^4 (**11**) corresponds to the fixed 3D-structures (**5** and **6**) which coincide with each other under the action I_h to give **11** as a single derivative.
3. On the other hand, the one isomer with X^6 (**12**) corresponds to the fixed 3D-structures (**7** and **8**) which coincide with each other under the action I_h to give **12** as a single derivative.

The C_{2v} - derivatives with chiral and achiral ligands in Figure 3 can be also related to the fixed structures shown in Figure 2 by virtue of chirality fittingness [1]:

1. Each of the two isomers with $p^2\bar{p}^2$ (**13** and **14**) corresponds to the fixed 3D-structures (**5** and **6**) which coincide with each other under the action I_h to give **13** or **14** as a single derivative. Compare **13** (and **14**) with c11. The

Figure 3. C_{2v} -Derivatives of dodecahedrane counted under the restriction condition of no adjacency, where a circle represents a *tert*-butyl ligand (X), while black and gray solid circles represent a enantiomeric pair of *sec*-butyl ligands (p and $\bar{p}$).

two p's and the two $\bar{p}$'s occupy the four-membered enantiospheric orbit in accord with chirality fittingness. The relationship between **13** and **14** is diastereomeric so as to be an extended case of pseudoasymmetry.

- Each of the two isomers with $X^2p^2\bar{p}^2$ (**15** and **16**) corresponds to the fixed 3D-structures (**7** and **8**) which coincide with each other under the action I_h . Compare **15**(and **16**) with **12** to examine the effect of chirality fittingness.
- Each of the two isomers with $X^4p^2\bar{p}^2$ (**17** and **18**) corresponds to the fixed 3D-structure (**9**). Note that the two four-membered orbits are enantiospheric, as accommodating X^4 and $p^2\bar{p}^2$ according to c_4^2 . The relationship between **17** and **18** is diastereomeric so as to be an extended case of pseudoasymmetry.
- The one isomer with $p^4\bar{p}^4$ (**19**) corresponds to the fixed 3D-structures (**9**), in which the four p's and the four $\bar{p}$'s are considered to give two sets of $p^2\bar{p}^2$, which occupy the two four-membered enantiospheric orbits in accord with chirality fittingness.

It should be noted that the related derivatives with X^8 (**9**, the open circles represent achiral ligands (X's)) does not belong to C_{2v} but to T_h . This behavior is understandable by examining the PCI-CF for C_{2v} , (eq 10), where the last two terms $\frac{1}{2}c_4^2 - \frac{1}{2}c_8$

Figure 4. C_{2h} -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

in the right-hand side nullify X^8 by introducing $c_4 = X^4$ and $c_8 = X^8$ (or fully $c_4 = 1 + X^4 + 2p^2\bar{p}^2$ and $c_8 = 1 + X^8 + 2p^4\bar{p}^4$) in accord with the inclusion-exclusion principle.

The generating function $f_{C_{2h}}$ (eq 37) shows that there are one X^4 -isomer (**20**), two $p^2\bar{p}^2$ -isomer (**21** and **22**), two $X^2p^2\bar{p}^2$ -isomer (**23** and **24**), two $X^4p^2\bar{p}^2$ -isomer (**25** and **26**), and one $p^4\bar{p}^4$ -isomer (**27**), as shown in Figure 4.

Note that the two-fold axis of the C_{2h} -group is selected to run through the midpoints of the two remote edges {1,8} and {13,20}, while the horizontal mirror plane contains the other two remote edges {3,4} and {17,18}. The monomials contained in the RSCI-CF for C_{2h} (Table 1) or in the RPCI-CF (eq 11) show the following correspondences: c_4 to **20**, **21**, and **22**; a_2c_4 to **23** and **24**; as well as c_4^2 to **25**, **26**, and **27**.

The relationship between **21** and **22**, between **23** and **24**, or between **25** and **26** is diastereomeric so as to exhibit extended pseudoasymmetric features. That is to say, the exchange between one half of the chiral substituents (black solid circles) and the other half (gray solid circles) in **21**, **23**, or **25** generates **22**, **24**, or **26**, because the two halves are related geometrically to construct an enantiospheric orbit.

On the other hand, the exchange between one half of the chiral substituents (black solid circles) and the other half (gray solid circles) in **27** generates **27** itself. It follows that **27** can be regarded as an extended meso-type compound, although the

Figure 5. D_{3d} -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

Figure 6. T_h -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

two halves are also related geometrically to construct an enantiospheric orbit.

The generating function $f_{D_{3d}}$ (eq 47) shows the presence of one X^2 -isomer (**28**) and one X^6 -isomer (**29**), as shown in Figure 5.

The three-fold axis of the D_{3d} -group runs through the vertices 1 and 20. The three dihedral two-fold axes (perpendicular to the three-fold axis) run respectively through the midpoints of the two remote edges {3,4} and {17,18}, through the midpoints of the two remote edges {6,7} and {11,12}, and through the midpoints of the two remote edges {9,10} and {14,15}. Each of the three dihedral mirror plane contains the three-fold axis and one edge {1,2}, {1,5}, or {1,8}. The X^2 -isomer (**28**) and the X^6 -isomer (**29**) correspond respectively to a_2 and a_g , which are contained in the RSCI-CF for D_{3d} (Table 1) or in the RPCI-CF (eq 21).

The generating function f_{T_h} (eq 49) shows the presence of one X^8 -isomer (**30**) and two $p^4 \bar{p}^4$ -isomers (**31** and **32**), as shown in Figure 6. They correspond to c_8 , which is contained in the RSCI-CF for T_h (Table 1) or in the RPCI-CF (eq 23). The relationship between **31** and **32** is diastereomeric so as to exhibit extended pseudoasymmetric features.

It should be noted here that, geometrically speaking, the symmetry of **31** (or **32**) is not T_h , when $p/\bar{p}$ represents a pair of chiral *sec*-butyl ligand. Because the *sec*-butyl ligand belongs to C_1 in isolation, it is incompatible with the local symmetry

Figure 7. D_3 -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

(C_3) of the $T_h/(C_3)$ -orbit (corresponding to the sphericity index c_8 in the SCI-CF). Thereby, the symmetry of **31** (or **32**) is reduced into D_{2h} , where the eight sites constructs a $D_{2h}/(C_1)$ -orbit, which can accommodate the *sec*-butyl ligands of C_1 . This type of incompatibility has been discussed in terms of *mismatched molecules* in Section 21.4 of [1]. To avoid this type of incompatibility, we have proposed the concepts of proligands and promolecules [1]. Thus, the symmetry of **31** (or **32**) is concluded to be T_h as a promolecule, when p and $\bar{p}$ are regarded as proligands.

3.2 Chiral Derivatives

In the present enumeration, a pair of enantiomeric derivatives is counted once, where the number of such pairs appears as a multiple of such a term as $\frac{1}{2}(p^2 + \bar{p}^2)$.

For example, the generating function f_{D_3} (eq 39) shows that there are one enantiomeric pair of isomers of $\frac{1}{2}(p^2 + \bar{p}^2)$ (**33**) and one enantiomeric pair of isomers of $\frac{1}{2}(p^6 + \bar{p}^6)$ (**34**), as depicted in Figure 7.

Note that **33** (**33**) is a mismatched molecule, where *sec*-butyl ligands of C_1 occupy the two $D_3/(C_3)$ -sites so that the D_3 -symmetry of **33** as a promolecule is geometrically reduced into C_2 . Even geometrically speaking, in contrast, the D_3 -symmetry of **34** (**34**) as a promolecule remains to be D_3 , because the C_1 -symmetry of a *sec*-butyl ligand matches the local symmetry (C_1) of the $D_3/(C_1)$ -orbit. As for the relationship between **33** (**33**) and **28**, it should be added that the D_{3d} -symmetry of **28** as a promolecule remains to be D_{3d} geometrically, because the C_{3v} -symmetry of a *tert*-butyl ligand matches the local symmetry (C_{3v}) of the $D_{3d}/(C_{3v})$ -orbit in **28**.

On the basis of the data of the generating function f_T (eq 46), Figure 8 depicts T -derivatives of dodecahedrane.

Figure 8. **T** -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

There exists one pair of X^4 -derivatives ($\mathbf{35} / \overline{\mathbf{35}}$); the symmetry of each member is **T** as a promolecule and as a geometric 3D-structure, because the C_{3v} -symmetry of a *tert*-butyl ligand matches the local symmetry of the **T**/(C_3) -orbit in $\mathbf{35}$ ($C_{3v} \supset C_3$). Note that the C_{3v} -symmetry (achiral) of the *tert*-butyl ligand in isolation is restricted into C_3 (chiral) when the ligand is incorporated in $\mathbf{35}$.

The monomial $(p^4 + \bar{p}^4)$ in eq 46 should be interpreted as being $2 \times \frac{1}{2}(p^4 + \bar{p}^4)$, so that there are two pairs of **T**-derivatives ($\mathbf{36} / \overline{\mathbf{36}}$ and $\mathbf{37} / \overline{\mathbf{37}}$). Both the pairs ($\mathbf{36} / \overline{\mathbf{36}}$ and $\mathbf{37} / \overline{\mathbf{37}}$) are mismatched molecules so that they belong to **T** as promolecules (C_3 as the local symmetry) while they belong to D_2 as geometric 3D-structures (C_1 as the local symmetry) because *sec*-butyl ligands belong to C_1 in isolation.

On the same line, the monomial $(X^4 p^4 + X^4 \bar{p}^4)$ in eq 46

should be interpreted as being $2 \times \frac{1}{2}(X^4 p^4 + X^4 \bar{p}^4)$, so that there are two pairs of **T**-derivatives ($\mathbf{38} / \overline{\mathbf{38}}$ and $\mathbf{39} / \overline{\mathbf{39}}$). Both the pairs ($\mathbf{38} / \overline{\mathbf{38}}$ and $\mathbf{39} / \overline{\mathbf{39}}$) are concluded to be mismatched molecules by the same discussion as described above.

The monomial $\frac{1}{2}(p^8 + \bar{p}^8)$ in eq 46 indicates the presence of one pair of **T**-derivatives ($\mathbf{40} / \overline{\mathbf{40}}$). The eight chiral ligands p 's (or $\bar{p}$'s) of the same chirality in $\mathbf{40}$ (or $\overline{\mathbf{40}}$) are divided into two halves (the one half of four p 's (or $\bar{p}$'s) at the vertices 5, 9, 12, and 16 vs. the other half of four p 's (or $\bar{p}$'s) at the vertices 2, 7, 14, and 19), each of which is governed by the coset representation **T**/(C_3). The **T** -symmetry of $\mathbf{40}$ (or $\overline{\mathbf{40}}$) as a promolecule is geometrically reduced into D_2 , because *sec*-butyl ligands of C_1 (p 's or $\bar{p}$'s) occupy the two **T**/(C_3) -orbits (as a promolecule), which are reduced into the D_2 /(C_1) -orbits (as a molecule).

3.3 Prochirality and RS-Stereogenicity

As recently discussed in detail by us [4], the conventional concepts of "prochirality" and "stereogenicity" should be abandoned, because geometrical features and permutational features are mixed up in the conventional usage of these concepts. Instead, the purely geometric concept of *prochirality* (Chapter 10 of [1], [5]) and the purely permutational concept of *RS-stereogenicity* [6] should be used in an integrated fashion for the purpose of comprehending stereochemistry [7,8].

The several derivatives depicted above provide us with an illustrative set of prochiral molecules in such a purely geometric meaning. For example, the four achiral ligands (X 's) of the C_{2v} -derivative ($\mathbf{11}$) shown in Figure 3 construct a four-membered orbit governed by the coset representation C_{2v} /(C_1). This orbit is enantiospheric and corresponds to c_4 , because the global symmetry C_{2v} is achiral and the local symmetry C_1 is chiral ($(|C_{2v}| / |C_1| = 4 / 1 = 4)$). In a chiral condition (e.g., an attack of a chiral reagent), the enantiospheric orbit is divided into two halves, i.e., one half of two X 's at the vertices 2 and 7 and the other half of two X 's at the vertices 5 and 9. This means that one of the two halves is predominantly attacked to give a derivative of either chirality. In other words, the C_{2v} -derivative ($\mathbf{11}$) is prochiral so as to have potentiality of giving chiral derivatives. Thus the enantiosphericity is directly linked to the prochirality of purely geometric meaning. The two halves (totally four sites) are in an enantiotopic relationship, which is an extension of the conventional concept "enantiotopic" between two sites.

The chiral ligands (two p 's and two $\bar{p}$'s) of the C_{2v} -derivative (**13**) shown in Figure 3 construct an enantiospheric orbit governed by the coset representation $C_{2v}/(C_1)$ (corresponding to c_4). In a chiral condition (e.g., an attack of a chiral reagent) the enantiospheric orbit is divided into two halves, i.e., one half of two $\bar{p}$'s at the vertices 2 and 7 and the other half of two p 's at the vertices 5 and 9. Hence, the above-mentioned discussion holds true in this case.

We have proposed the concept of *stereoisograms* to discuss chirality (as a purely geometrical concept) and *RS*-stereogenicity (as a purely permutational concept) in an integrated fashion [6]. The merit of the introduction of stereoisograms has been emphasized by explaining a typical pseudoasymmetry of two diastereomeric tetrahedral molecules $CXYp\bar{p}$ (X, Y : achiral ligands; and $p/\bar{p}$: a pair of enantiomeric ligands), where the permutation of p and $\bar{p}$ causes interconversion of the two diastereomers while the reflection causes no such interconversion.

The stereoisomeric cases described above as extended pseudoasymmetric cases, i.e., **13/14**, **17/18**, **21/22**, **23/24**, **25/26**, and **31/32**, can be discussed by means of stereoisograms, which treat geometric features and permutational ones in a conceptually different but integrated fashion.

4 Conclusion

The restricted-partial-cycle-index (RPCI) method for combinatorial enumeration under the restriction of no adjacency of ligands has been developed by starting from the partial-cycle-index (PCI) method of the unit-subduced-cycle-index (USCI) approach [1]. Thus, restricted partial cycle indices with chirality fittingness (RPCI-CFs) are derived from restricted subduced cycle indices with chirality fittingness (RSCI-CFs) just

as partial cycle indices with chirality fittingness (PCI-CFs) are derived from subduced cycle indices with chirality fittingness (SCI-CFs). Such RSCI-CFs are derived from subduced cycle indices with chirality fittingness (SCI-CFs), where the SCI-CFs are combined with territory indicators to give territory discriminants, which are treated by considering the restriction condition so as to generate RSCI-CFs. The restricted-partial-cycle-index (RPCI) method is regarded as a restricted version of the PCI method of the USCI approach [1]. The RPCI method is applied to enumeration of sterically hindered derivatives of dodecahedrane.

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