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

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: November 1, 2011; Accepted for publication: June 26, 2012; Advance publication: September 22, 2012)

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 restriction condition.

As a continuation of Part I of this series, we will examine the problem of restricted substitution, where bulky substituents such as tert-buty lligands 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)
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 subduced 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 \( I_5 / \{ C_{2h} \} \). 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/\( \overline{p} \)) 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 subduced cycle indices (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 \( C_{2s} \)-row of Table 1 indicates the SCI-CF of \( C_{2v} \) to be \( a_2^2c_4^3 \). 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 \( C_{2v} \) 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 \( a_2^2c_4^3 \) for the \( C_{2v} \)-group corresponds to the following mode of division:

\[
a_2^2: \quad A_4 = \{4,8\}, A_2 = \{6,10\}, \\
a_3 = \{11,15\}, A_4 = \{13,20\}
\]

\[
c_4^3: \quad A_4 = \{2,5,7,9\}, A_6 = \{12,14,16,19\}, \\
A_4 = \{3,4,17,18\}
\]

Because the underlined suborbits (\( A_6 \), \( A_4 \), and \( A_4 \)) 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 (\( A_2 \), \( A_2 \), \( A_4 \), or \( A_4 \)) 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 \( C_{2v} \)-row of Table 1. As a result, the selected sets for the \( C_{2v} \)-group are shown in Figure 2. For example, the monomial \( 2a_4 \) corresponds to fixed 3D-structures 3 and 4, which use \( A_4 \) and \( A_4 \), 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 \( I_5 \).

On the other hand, the monomial \( 2c_4 \) corresponds to fixed 3D-structures 5 and 6, which use \( A_4 \) and \( A_4 \), respectively. Because they are enantiospheric, they are capable of accommodating four achiral ligands (\( X^4 \)) or two pairs of chiral ligands (\( \overline{p} \)) in agreement with chirality fittingness [1]. The latter mode of accommodation causes pseudoasymmetry, which will be discussed later.

The monomials \( 2a_4c_4 \) 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 \( C_{2v} \)) under the restriction condition, so that the numbers of them (i.e., marks) are characterized by the RSCI-CF for \( C_{2v} \), i.e., \( 1 + 2a_4 + 2c_4 + 2a_4c_4 + c_4^2 \). The RSCI-CFs for the other subgroups of \( I_5 \) 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
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 $M^{-1}$ of the mark table $M$ of $G$:

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

$$
\text{PCI-CF}(G_i; S_j) = \sum_{p=1}^{L} n_p \text{SCI-CF}(G_i; S_j)
$$

for $i=1,2,\ldots,s$, where $n_p$ represents the $ji$-element of the inverse matrix $M^{-1}$, i.e., the element which appears at the intersection of the $i$-th column and the $j$-th row. The symbol $S_j$ represents a sphericity index $a_j$ for a homospheric orbit, an index $b_j$ for a hemispheric orbit, or an index $c_j$ for an entantiospheric 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 $M^{-1}$ (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:

$$
\text{PCI-CF}(G_i; S_j) = \frac{5}{4} b_1^3 + \frac{11}{2} b_1^2 + \frac{151}{12} b_1 + \frac{239}{15} b_1 + \cdots
$$

(4)

$$
\text{PCI-CF}(G_i; S_j) = \frac{3}{2} b_2^2 + \frac{9}{2} b_2 + 3 b_1 + \frac{1}{4} b_1 - \frac{1}{4} b_1 + \cdots
$$

(5)

$$
\text{PCI-CF}(G_i; S_j) = \frac{1}{2} a_2 - a_1 - a_1 - \frac{1}{2} a_1 + \cdots
$$

(6)

$$
\text{PCI-CF}(G_i; S_j) = \frac{1}{2} a_2 - a_1 - a_1 - \frac{1}{2} c_1 + \cdots
$$

(7)

$$
\text{PCI-CF}(G_i; S_j) = 2 b_2 h_2 + b_2 h_1 + \frac{1}{2} h_2 h_1 - \frac{1}{4} h_2 + \cdots
$$

(8)

$$
\text{PCI-CF}(D_i; S_j) = 0
$$

(9)

$$
\text{PCI-CF}(G_i; S_j) = a_2 + a_1 c_4 + c_4 + \frac{1}{2} c_4 - \frac{1}{2} c_4
$$

(10)

$$
\text{PCI-CF}(G_i; S_j) = a_2 c_4 + c_4 + \frac{1}{2} c_4 - \frac{1}{2} c_4 - a_1
$$

(11)

$$
\text{PCI-CF}(G_i; S_j) = \frac{1}{2} b_2 - \frac{1}{2} a_2
$$

(12)

$$
\text{PCI-CF}(D_i; S_j) = \frac{1}{2} b_2 + \frac{1}{2} a_2 - \frac{1}{2} a_2 - \frac{1}{2} a_2
$$

(13)
where the symbol $S_{j}$ represents $a_{j}$, $b_{j}$, or $c_{j}$.

### 2.3 Restricted Enumeration

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

$$L = \{H, X, p, \overline{p}\},$$

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 $\overline{p}$ represents an enantiomeric pair of sec-butyl ligands. Then, the following inventory functions:

$$a_{d} = X^{4}$$

$$b_{d} = X^{4} + \overline{p}^{4} + \overline{p}^{4}$$

$$c_{d} = X^{4} + 2p^{4} + \overline{p}^{4}$$

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:

$$f_{c} = 3X^{4} + 8X^{4} + 13X^{4} + 7X^{4} + X^{4} + p\overline{p} + 67p\overline{p} + 198p\overline{p} + \overline{p}^{4}$$

$$+ \frac{5}{2}(Xp + X\overline{p}) + \frac{1}{2}(p^{4} + \overline{p}^{4}) + 5(p^{4} + \overline{p}^{4})$$

$$+ 10(p^{4} + \overline{p}^{4}) + \frac{31}{2}(p^{4} + \overline{p}^{4})$$

$$+ \frac{17}{2}(p^{4} + \overline{p}^{4}) + \cdots$$

### Table 1. SCI-CFs and RSCI-CFs for the $I_{b}(C_{2v})$-Orbit

<table>
<thead>
<tr>
<th>$G_{j}$</th>
<th>SCI-CF</th>
<th>RSCI-CF</th>
<th>SCI-CF(Gj, $S_{j}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{1}$</td>
<td>$b_{1}^{2}$</td>
<td>1 + 20b_{1} + 160b_{1}^{2} + 660b_{1}^{3} + 1510b_{1}^{4} + 1912b_{1}^{5} + 1240b_{1}^{6} + 320b_{1}^{7} + 5b_{1}^{8}</td>
<td>$PCI-CF(T_{V};S_{j}) = b_{j} + \frac{1}{2}b_{j}^{2} - \frac{1}{2}c_{j}$</td>
</tr>
<tr>
<td>$C_{2}$</td>
<td>$b_{10}^{10}$</td>
<td>1 + 8b_{2} + 18b_{2}^{2} + 12b_{2}^{3} + b_{2}^{4}</td>
<td>$PCI-CF(D_{4h};S_{j}) = a_{j} + a_{j}$</td>
</tr>
<tr>
<td>$C_{3}$</td>
<td>$a_{2}^{14}$</td>
<td>1 + 4a_{1} + 4a_{1}^{2} + 6a_{2}^{2} + 20a_{1}a_{2} + 16a_{1}a_{2}</td>
<td>$PCI-CF(D_{4h};S_{j}) = 0$</td>
</tr>
<tr>
<td>$C_{4}$</td>
<td>$c_{2}^{10}$</td>
<td>1 + 10c_{2} + 30c_{2}^{2} + 30c_{2}^{3} + 5c_{2}^{4}</td>
<td>$PCI-CF(T_{h};S_{j}) = c_{j}$</td>
</tr>
<tr>
<td>$C_{5}$</td>
<td>$b_{2}b_{3}^{6}$</td>
<td>1 + 2b_{1} + b_{1}^{2} + 6b_{3} + 10b_{1}b_{3} + 4b_{1}b_{3} + 8b_{1}b_{3}^{2} + 7b_{3}^{2} + 2b_{1}b_{3}^{2}</td>
<td>$PCI-CF(I_{h};S_{j}) = 0$</td>
</tr>
<tr>
<td>$D_{2}$</td>
<td>$b_{2}^{4}$</td>
<td>1 + 2b_{1} + b_{1}^{2}</td>
<td>$PCI-CF(I_{h};S_{j}) = 1$</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$a_{2}^{4}$</td>
<td>1 + 2a_{2} + 2a_{2}^{2} + 2a_{2}^{4}</td>
<td></td>
</tr>
<tr>
<td>$C_{2h}$</td>
<td>$a_{2}^{4}$</td>
<td>1 + 2a_{2} + 2a_{2}^{2} + 2a_{2}^{4}</td>
<td></td>
</tr>
<tr>
<td>$C_{5}$</td>
<td>$b_{2}^{4}$</td>
<td>1 + 2b_{5}</td>
<td></td>
</tr>
<tr>
<td>$D_{3}$</td>
<td>$b_{2}b_{3}^{4}$</td>
<td>1 + 2b_{2} + b_{2}^{2}</td>
<td></td>
</tr>
<tr>
<td>$C_{3v}$</td>
<td>$a_{2}^{4}$</td>
<td>1 + 2a_{1} + a_{1}^{2} + 2a_{3} + 2a_{1}a_{3}</td>
<td></td>
</tr>
<tr>
<td>$C_{3i}$</td>
<td>$c_{2}^{4}$</td>
<td>1 + 3c_{2} + c_{2}^{2} + 2c_{2}c_{6}</td>
<td></td>
</tr>
<tr>
<td>$D_{4h}$</td>
<td>$a_{2}^{4}$</td>
<td>1 + c_{8}</td>
<td></td>
</tr>
<tr>
<td>$D_{5}$</td>
<td>$b_{2}^{4}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$C_{5v}$</td>
<td>$a_{2}^{4}$</td>
<td>1 + 2a_{5}</td>
<td></td>
</tr>
<tr>
<td>$C_{5i}$</td>
<td>$c_{2}^{4}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>$b_{2}b_{3}^{2}$</td>
<td>1 + 2b_{2} + b_{2}^{2}</td>
<td></td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>$a_{2}a_{12}^{4}$</td>
<td>1 + a_{2} + a_{6}</td>
<td></td>
</tr>
<tr>
<td>$D_{2d}$</td>
<td>$a_{2}^{4}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$T_{h}$</td>
<td>$a_{3}a_{12}$</td>
<td>1 + c_{8}</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>$b_{20}$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$I_{h}$</td>
<td>$a_{20}$</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

DOI: 10.2477/jccj.2011-0020

143
where the coefficient of each monomial $X^i p^j p^k$ for the $G_i$-symmetry represents the number of dodecahedral derivatives of $G_i$ which has $x$ of $X$, $p$ of $p$, and $p$ of $p$ as substituents under the restriction condition.

3 Drawing Derivatives Enumerated

3.1 Achiral Derivatives

The generating function $f_{c_{2i}}$ (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 $p^2 p^2$ (13 and 14), two isomers with $X^2 p^2 p^2$ (15 and 16), two isomers with $X^4 p^2 p^2$ (17 and 18), and one isomer with $p^4 p^4$ (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 $p$).

The $C_{2i}$-derivatives with achiral ligands only (Figure 3) can be related to the fixed structures shown in Figure 2 by virtue of chirality fittingness [1]:

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 $I_k$ 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 $I_k$ 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 $I_k$ to give 12 as a single derivative.

The $C_{2i}$-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 $p^2 p^2$ (13 and 14) corresponds to the fixed 3D-structures (5 and 6) which coincide with each other under the action $I_k$ to give 13 or 14 as a single derivative. Compare 13 (and 14) with c11. The
two p’s and the two 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.

2. Each of the two isomers with 222Xpp (15 and 16) corresponds to the fixed 3D-structure (7 and 8) which coincide with each other under the action \( h_1 \). Compare 15 (and 16) with 12 to examine the effect of chirality fittingness.

3. Each of the two isomers with 422Xpp (17 and 18) corresponds to the fixed 3D-structure (9). Note that the two four-membered orbits are enantiospheric, as accommodating 4X and 22pp according to 24c. The relationship between 17 and 18 is diastereomeric so as to exhibit extended pseudoasymmetric features.

4. The one isomer with 44pp (19) corresponds to the fixed 3D-structures (9), in which the four p’s and the four p’s are considered to give two sets of 2p^1p^1, which occupy the two four-membered enantiospheric orbits in accord with chirality fittingness.

It should be noted that the related derivatives with X^b (9, the open circles represent achiral ligands (X’s)) does not belong to \( C_{2v} \), but to \( T_4 \). This behavior is understandable by examining the PCI-CF for \( C_{2v} \) (eq 10), where the last two terms \( \frac{1}{2}c_4^2 - \frac{1}{2}c_8 \) in the right-hand side nullify \( X^b \) by introducing \( c_4 = X^a \) and \( c_8 = X^b \) (or fully \( c_4 = 1 + X^a + 2p^1p^1 \) and \( c_8 = 1 + X^b + 2p^1p^1 \)) in accord with the inclusion-exclusion principle.

The generating function \( f_{c_4} \) (eq 37) shows that there are one \( X^a \)-isomer (20), two \( p^1p^1 \)-isomer (21 and 22), two \( X^a p^1p^1 \)-isomer (23 and 24), two \( X^a p^1p^1 \)-isomer (25 and 26), and one \( p^1p^1 \)-isomer (27), as shown in Figure 4.

Note that the two-fold axis of the \( C_{2a} \)-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 \( C_{2a} \) (Table 1) or in the RPCI-CF (eq 11) show the following correspondences: \( c_4 \) to 20, 21, and 22; \( a_5c_4 \) 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 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 \( \overline{p} \)).

Figure 4. \( C_{2a} \)-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 $f_{b_n}$ (eq 47) shows the presence of one $X^2$ -isomer (28) and one $X^3$ -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 $X^3$ -isomer (29) correspond respectively to $a_2$ and $a_3$, which are contained in the RSCI-CF for $D_{3d}$ (Table 1) or in the RPCI-CF (eq 21).

The generating function $f_{a_1}$ (eq 49) shows the presence of one $X^2$ -isomer (30) and two $p^p\bar{p}$ -isomers (31 and 32), as shown in Figure 6. They correspond to $c_1$, which is contained in the RSCI-CF for $T_d$ (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 $T_d$, 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

\[ (C_1) \]

of the $T_d$/$(C_1)$ -orbit (corresponding to the sphericity index $c_1$ in the SCI-CF). Thereby, the symmetry of 31 (or 32) is reduced into $D_{2d}$, where the eight sites constructs a $D_{2d}$/$(C_1)$ -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 $T_d$ 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 $\frac{1}{2}(p^3 + \bar{p}^3)$. For example, the generating function $f_{a_1}$ (eq 39) shows that there are one enantiomeric pair of isomers of $\frac{1}{2}(p^3 + \bar{p}^3)$ (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 $D_5$/$(C_5)$ -sites so that the $D_5$ -symmetry of 33 as a promolecule is geometrically reduced into $C_1$. 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 ($C_5$) of the $D_5$/$(C_5)$ -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 $C_{3d}$ -symmetry of a tert-butyl ligand matches the local symmetry ($C_{3d}$) of the $D_{3d}$/$(C_{3d})$ -orbit in 28.

On the basis of the data of the generating function $f_{a_1}$ (eq 46), Figure 8 depicts $T$-derivatives of dodecahedrane.

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

Figure 6: $T_d$ -Derivatives of dodecahedrane counted under the restriction condition of no adjacency.

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

(\[ (C_1) \]) of the $T_d$/$(C_1)$ -orbit (corresponding to the sphericity index $c_1$ in the SCI-CF). Thereby, the symmetry of 31 (or 32) is reduced into $D_{2d}$, where the eight sites constructs a $D_{2d}$/$(C_1)$ -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 $T_d$ 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 $\frac{1}{2}(p^3 + \bar{p}^3)$. For example, the generating function $f_{a_1}$ (eq 39) shows that there are one enantiomeric pair of isomers of $\frac{1}{2}(p^3 + \bar{p}^3)$ (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 $D_5$/$(C_5)$ -sites so that the $D_5$ -symmetry of 33 as a promolecule is geometrically reduced into $C_1$. 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 ($C_5$) of the $D_5$/$(C_5)$ -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 $C_{3d}$ -symmetry of a tert-butyl ligand matches the local symmetry ($C_{3d}$) of the $D_{3d}$/$(C_{3d})$ -orbit in 28.

On the basis of the data of the generating function $f_{a_1}$ (eq 46), Figure 8 depicts $T$-derivatives of dodecahedrane.
There exists one pair of $X^4$-derivatives ($\frac{35}{35}$); the symmetry of each member is $T$ as a promolecule and as a geometric 3D-structure, because the $3v_C$-symmetry of a tert-butyl ligand matches the local symmetry of the $3v_C$-orbit in $\frac{35}{35}$ ($3v_C \supset CC$). Note that the $3v_C$-symmetry (achiral) of the tert-butyl ligand in isolation is restricted into $3C$ as the local symmetry when the ligand is incorporated in $\frac{35}{35}$.

The monomial $\frac{1}{2}(p^4 + \overline{p}^4)$ in eq 46 should be interpreted as being $2 \times \frac{1}{2}(X^4p^4 + X^4\overline{p}^4)$, so that there are two pairs of $T$-derivatives ($\frac{36}{36}$ and $\frac{37}{37}$). Both the pairs ($\frac{38}{38}$ and $\frac{39}{39}$) are concluded to be mismatched molecules by the same discussion as described above.

The monomial $\frac{1}{2}(p^4 + \overline{p}^4)$ in eq 46 indicates the presence of one pair of $T$-derivatives ($\frac{40}{40}$). The eight chiral ligands $p$'s (or $\overline{p}$'s) of the same chirality in $\frac{40}{40}$ are divided into two halves (the one half of four $p$'s (or $\overline{p}$'s) at the vertices 5, 9, 12, and 16 vs. the other half of four $p$'s (or $\overline{p}$'s) at the vertices 2, 7, 14, and 19), each of which is governed by the coset representation $T/(C_4)$. The $T$-symmetry of $\frac{40}{40}$ as a promolecule is geometrically reduced into $D_2$, because sec-butyl ligands of $C_4$ (p's or $\overline{p}$'s) occupy the two $T/(C_4)$-orbits (as a promolecule), which are reduced into the $D_2/(C_4)$-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 $2v_C$-derivative ($\frac{11}{35}$) shown in Figure 3 construct a four-membered orbit governed by the coset representation $T/(C_4)$ of $C_4$. Note that the $C_n$ -symmetry (achiral) of the tert-butyl ligand in isolation is restricted into $C_4$ (chiral) when the ligand is incorporated in $\frac{35}{35}$.

The monomial $(p^4 + \overline{p}^4)$ in eq 46 should be interpreted as being $2 \times \frac{1}{2}(p^4 + \overline{p}^4)$, so that there are two pairs of $T$-derivatives ($\frac{36}{36}$ and $\frac{37}{37}$). Both the pairs ($\frac{36}{36}$ and $\frac{37}{37}$) are mismatched molecules so that they belong to $T$ as promolecules ($C_4$ 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 $C_4$ in isolation.

On the same line, the monomial $(X^4p^4 + X^4\overline{p}^4)$ in eq 46 should be interpreted as being $2 \times \frac{1}{2}(X^4p^4 + X^4\overline{p}^4)$, so that there are two pairs of $T$-derivatives ($\frac{38}{38}$ and $\frac{39}{39}$). Both the pairs ($\frac{38}{38}$ and $\frac{39}{39}$) are concluded to be mismatched molecules by the same discussion as described above.

The monomial $\frac{1}{2}(p^4 + \overline{p}^4)$ in eq 46 indicates the presence of one pair of $T$-derivatives ($\frac{40}{40}$). The eight chiral ligands $p$'s (or $\overline{p}$'s) of the same chirality in $\frac{40}{40}$ are divided into two halves (the one half of four $p$'s (or $\overline{p}$'s) at the vertices 5, 9, 12, and 16 vs. the other half of four $p$'s (or $\overline{p}$'s) at the vertices 2, 7, 14, and 19), each of which is governed by the coset representation $T/(C_4)$. The $T$-symmetry of $\frac{40}{40}$ as a promolecule is geometrically reduced into $D_2$, because sec-butyl ligands of $C_4$ (p's or $\overline{p}$'s) occupy the two $T/(C_4)$-orbits (as a promolecule), which are reduced into the $D_2/(C_4)$-orbits (as a molecule).
The chiral ligands (two p’s and two \( \overline{p}’s \)) 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 \( c_1 \)). 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 \( \overline{p}’s \) 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 \( CXyp\overline{p} \) (X, Y: achiral ligands; and p/\( \overline{p} \): a pair of enantiomeric ligands), where the permutation of p and \( \overline{p} \) 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 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.

References