Systematic Enumeration of Nonrigid Isomers with Given Ligand Symmetries

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A new method for enumerating nonrigid isomers with rotatable ligands has been developed so as to take the symmetries of the ligands into consideration. The method has been based on extended partial cycle indices and has been applied to the enumeration of methyl ether derivatives, tetramethylallene derivatives, and 2,2-dimethylpropane derivatives. These results have been compared with the enumeration results of the corresponding promolecules. The factorization of terms in generating functions has been discussed so that the new method is capable of examining the relationship between promolecules and molecules quantitatively.

1. INTRODUCTION

Combinatorial enumeration of isomers is one of the most attractive problems in which group theory plays an important role. Methods of solving such problems are classified into three categories in terms of the equivalence classes used in their basic formulation.

Methods of the first category are based on conjugacy classes as equivalence classes. This means that they take individual elements of a group into main consideration. In other words, they ignore the subgroups of the group in the mathematical formulation of them. As a result, they are limited to the combinatorial enumeration of isomers with given formulas (or mathematically with given weights). It follows that they are incapable of enumeration concerning isomer symmetries. Pólya's theorem[1] and an equivalent counterpart known as Redfield's group-reduced distribution[2] are representative, giving enumeration results in the form of generating functions. Their chemical applications have been already discussed in the original paper.[1] The Redfield−Read superposition theorem[2−4] and the related s-function method[5] are also used but are less familiar than the generating-function methods described above. Its applicability to chemical problems has been discussed by Davidson.[6] Ruch's method was based on double-coset decompositions[7,8] and was originally aimed at chemical applications. Chemical aspects and applications of these methods have been summarized in excellent reviews[9−12] and books.[13,14]

We have recently developed a new method classified in the second category, since this starts from **Q**-conjugacy classes as equivalence classes. This method is based on characteristic monomials,[15−20] which are in turn derived from the subduction of **Q**-conjugacy representations. Since this method also ignores the subgroups of the group in its formulation, it is concerned only with the formulas of isomers.

Methods of the third category are based on conjugate subgroups as equivalence classes. They are capable of enumerating isomers with respect to formulas as well as to symmetries, because the symmetries of isomers to be enumerated are ascribed to such subgroups. The methods by Sheehan[21] and by Hässelbarth[22] are grounded on tables of marks, which come from Burnside.[23] The method by Kerber and Thürlings[24] uses tables of marks and double cosets to produce generating functions. The method by Brocas[25] is founded on double cosets and framework groups, the latter of which were originated by Pople.[26] The method by Mead[27] uses tables of marks and double cosets. The method by Lloyd[28] is based on marks of permutation groups. The SCI method developed by us[29] is a generating-function method based on subduced cycle indices (SCIs) and mark tables, the former of which are derived from the subduction of coset representations. The PCI method by us[30] is also a generating-function method using partial cycle indices (PCIs), which are also derived from the subduction of coset representations. The elementary-superposition method developed by us[31] is based on the concept of the elemental superposition, which has been proposed to discuss desymmetrization processes[32] and has been applied to SCIs. The partial-superposition method by us[30,31] is also based on the elemental superposition, which is applied to PCIs. The latter four methods are collectively called "the USCI approach", since they start from unit subduced cycle indices (USCIs) obtained by the subduction of coset representations.

Since the methods of the three categories have been mainly applied to the enumeration of rigid molecules, the next step has been to enumerate nonrigid molecules with rotatable ligands. To do this task, the extension of conceptual framework has been necessary. Thus, the concept of "coronas" has been introduced by Pólya[1,14] and combined with the methods of the first category to solve such enumeration problems of nonrigid isomers. The concept is essentially equivalent to wreath products, which have been used to count stereoisomers and positional isomers in a generalized wreath product method.[33] These methods have been restricted within the enumeration of nonrigid isomers with given formulas but not with symmetries because of their origin of the first category.

Among the methods of the third category, the SCI method of the USCI approach has been applied to the enumeration of nonrigid isomers with given formulas and given symmetries.[32−34] This enumeration is further sophisticated in terms of the concept of promolecules,[36,37] which have been

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defined as skeletons substituted by proligands (structureless ligands with chirality/achirality). Although the relationship between promolecules and molecules has been treated rather qualitatively, this sophistication has clarified that the itemization on symmetries has been concerned with promolecules but not with molecules themselves. In other words, the itemization on symmetries has been concerned with proligands, but not with ligands, though even such itemization has provided us with a useful categorization of molecules. More precisely speaking, the symmetries of ligands enumerated have not belonged to the level of point groups but have been concerned only with the chirality/achirality of the ligands, as found by the careful inspection of the previous formulations.[34,35]

As clarified by the preceding paragraphs, the main target of this paper is to give a new method for enumeration of nonrigid isomers, which is an extention of the PCI method. Thereby, the symmetries of ligands can be considered to cover the level of their point groups. Further, the new method will be shown to be capable of examining the relationship between promolecules and molecules quantitatively through the factorization of terms appearing in generating functions.

2. NONRIGID ISOMER ENUMERATION

2.1. Mathematical Foundations. Let **H** be a point group assigned to a rotatable ligand (or substituent). The positions of the rotatable ligand are represented by

$$\Delta = \{\delta_1, \delta_2, ..., \delta_{|\Delta|}\} \tag{1}$$

which are governed by a set of coset representations

$$\sum_{l=1}^{t} \gamma_l \mathbf{H}(/\mathbf{H}_l) \tag{2}$$

where the size of the set Δ is represented by

$$|\Delta| = \sum_{l=1}^{t} \gamma_l |\mathbf{H}|/|\mathbf{H}_l| \tag{3}$$

The local symmetry $\mathbf{H}_l$ related to $\mathbf{H}(/\mathbf{H}_l)$ is selected from a nonredundant set of subgroups of **H**:

$$\mathrm{SSG}_{\mathbf{H}} = \{\mathbf{H}_1, \mathbf{H}_2, ..., \mathbf{H}_t\} \tag{4}$$

Suppose that the positions of Δ are replaced by a set of atoms selected from the following set:

$$\mathbf{X} = \{X_1, X_2, ..., X_{|\mathbf{X}|}\} \tag{5}$$

The resulting ligand corresponds to the weight (formula) represented by

$$W_{[\nu]} = X_1^{\nu_1} X_2^{\nu_2} \cdots X_{|\mathbf{X}|}^{\nu_{|\mathbf{X}|}} \tag{6}$$

where $[\nu]$ is a partition of $|\Delta|$, i.e.

$$[\nu]: \ \nu_1 + \nu_2 + \cdots + \nu_{|\mathbf{X}|} = |\Delta| \tag{7}$$

For the sake of simplicity, we use the symbol $[\nu_1, \nu_2, ..., \nu_{|\mathbf{X}|}]$ to refer to the concrete partition for a ligand. Our first problem is to obtain the number ($A_{m\nu}$) of ligands with the weight $W_{[\nu]}$ and a given symmetry $\mathbf{H}_m$ ($\subset\mathbf{H}$).

Let $\mathrm{ZI}(\mathbf{H}_m; s_{d_{mn}})$ be a subduced cycle index (SCI) concerning the subgroup $\mathbf{H}_m$. For this case, the SCI is equal to the product of the unit subduced cycle indices (USCIs), i.e.

$$\sum_{l=1}^{t} \gamma_l \mathbf{H}(/\mathbf{H}_l) \downarrow \mathbf{H}_m \tag{8}$$

Thereby, we define the partial cycle index (PCI) for $\mathbf{H}_m$ in light of Definition 16.3 (eq 16.28) of ref 32 as follows

$$\mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}}) = \sum_{m=1}^{t} \bar{m}_{ml}^{(\mathbf{H})} \mathrm{ZI}(\mathbf{H}_m; s_{d_{mn}}) \tag{9}$$

for $m = 1, 2, ..., t$, where $\bar{m}_{ml}^{(\mathbf{H})}$ is the ml-element of the inverse mark table (M^{-1}) for **H**. A generating function for the number ($A_{m\nu}$) of ligands with the weight $W_{[\nu]}$ and the symmetry $\mathbf{H}_m$ is represented by

$$\sum_{[\nu]} A_{m\nu} W_\nu = \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}}) \tag{10}$$

where the dummy variables in the right-hand side are replaced by atom inventories

$$s_{d_{mn}} = X_1^{s_{dmn}} + X_2^{s_{dmn}} + \cdots + X_{|\mathbf{X}|}^{s_{dmn}} \tag{11}$$

Let **G** be a point group assigned to a skeleton, the positions of which are represented by

$$\Omega = \{\omega_1, \omega_2, ..., \omega_{|\Omega|}\} \tag{12}$$

which are governed by a set of coset representations

$$\sum_{i=1}^{s} \alpha_i \mathbf{G}(/\mathbf{G}_i) \tag{13}$$

where the size of the set Ω (i.e., the number of the positions) is represented by

$$|\Omega| = \sum_{i=1}^{s} \alpha_i |\mathbf{G}|/|\mathbf{G}_i| \tag{14}$$

The local symmetry $\mathbf{G}_i$ related to $\mathbf{G}(/\mathbf{G}_i)$ is selected from a nonredundant set of subgroups of **G**

$$\mathrm{SSG}_{\mathbf{G}} = \{\mathbf{G}_1, \mathbf{G}_2, ..., \mathbf{G}_s\} \tag{15}$$

Suppose that each position (ω) of Ω is replaced by a ligand with the weight $W_{[\nu]}^{(\omega)}$ (eq 6) and the symmetry $\mathbf{H}_m$, where $\mathbf{H}_m$ runs over an achiral subset ($\mathbf{H}^{(a)}$) and over a chiral one ($\mathbf{H}^{(c)}$) of $\mathrm{SSG}_{\mathbf{H}}$, and $W_{[\nu]}^{(\omega)}$ runs over the partition $[\nu]$ to give a total weight

$$W_{[\nu']} = \prod_{\omega} W_{[\nu]}^{(\omega)} = X_1^{\nu'_1} X_2^{\nu'_2} \cdots X_{|\mathbf{X}|}^{\nu'_{|\mathbf{X}|}} \tag{16}$$

where $[\nu']$ represents a partition of $|\Delta|\cdot|\Omega|$, i.e.

$$[\nu']: \ \nu'_1 + \nu'_2 + \cdots + \nu'_{|\mathbf{X}|} = |\Delta|\cdot|\Omega| \tag{17}$$

For the sake of simplicity, we use the symbol $[\nu'_1, \nu'_2, ..., \nu'_{|\mathbf{X}|}]$ to refer to the concrete partition for an isomer. Then, our next problem is to obtain the number ($B_{i\nu'}$) of such

isomers with the weight $W_{[\nu']}$ as well as with a given symmetry $\mathbf{G}_i$.

We define the partial cycle index with chirality fittingness (PCIC) for $\mathbf{G}_i$ in light of Definition 19.6 (eq 19.55) of ref 32 as follows

$$\mathrm{PCIC}(\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) = \sum_{j=1}^{s} \bar{m}_{jk}^{(\mathbf{G})} \mathrm{ZIC}(\mathbf{G}_j; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) \quad (18)$$

for $i = 1, 2, ..., s$, where $\mathrm{ZIC}(\mathbf{G}_j; s_{d_{jk}})$ is a subduced cycle index with chirality fittingness (SCI-CF) concerning the subgroup $\mathbf{G}_i$. The symbol $\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]$ is used to indicate that ligand symmetries are selected from $\mathbf{H}^{(a)}$ and $\mathbf{H}^{(c)}$. When either $\mathbf{H}^{(a)}$ or $\mathbf{H}^{(c)}$ is selected, the symbol $\mathbf{G}_i[\mathbf{H}^{(a)}]$ or $\mathbf{G}_i[\mathbf{H}^{(c)}]$ is also permitted.

A generating function for the number ($B_{i\nu'}$) of isomers with the weight $W_{[\nu']}$ and the symmetry $\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]$ is represented by

$$\sum_{[\nu']} B_{i\nu'} W_{[\nu']} = \mathrm{PCIC}(\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) \quad (19)$$

where the dummy variables on the right-hand side are replaced by ligand inventories

$$a_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(a)}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \quad (20)$$

$$b_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(a)}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) + 2 \sum_{\mathbf{H}_m \in \mathbf{H}^{(c)}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \quad (21)$$

$$c_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(a)}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) + 2 \sum_{\mathbf{H}_m \in \mathbf{H}^{(c)}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \quad (22)$$

In a special case where only one achiral subgroup $\mathbf{H}_m$ is considered, the ligand inventories take simpler forms as follows:

$$a_{d_{jk}} = b_{d_{jk}} = c_{d_{jk}} = \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \quad (23)$$

When only one chiral subgroup is taken into consideration, such ligand inventories as

$$a_{d_{jk}} = 0 \quad (24)$$

$$b_{d_{jk}} = c_{d_{jk}} = 2\mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \quad (25)$$

are selected. The right-hand sides of the ligand inventories represented by eqs 20−22 (or eq 23 or eqs 24 and 25) can be replaced by eq 9 after the introduction of the atom inventory represented by eq 11, and then introduced into eq 19. On the other hand, an alternative procedure is available. The ligand inventories (eqs 20−22 or eq 23 or eqs 24 and 25) can be introduced into eq 19 to give a partial cycle index of an extended type

$$\mathrm{PCI}'(\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]; s_d) = \mathrm{PCIC}(\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) \quad (26)$$

into which the atom inventory (eq 11) is introduced afterward.

It should be noted here that the method described above is regarded as a generalization of Fujita's SCI method for enumerating nonrigid isomers.[34,35] Suppose that $\mathbf{H}^{(a)}$ in eq 18 represents the set of all achiral subgroups of $\mathbf{H}$ while $\mathbf{H}^{(c)}$ represents the set of all chiral subgroups of $\mathbf{H}$. Then, eq 18 provides PCIs concerning all of the subgroups of $\mathbf{H}$. This means that the PCIs give results equivalent to the ones obtained from SCIs in the SCI method.[34,35] On the other hand, the formulation described in eq 26 can only be derived from the present PCI method, but not from the SCI method.

Moreover, Pólya's corona[1,14] can be easily derived from the extended PCIs (eq 26) in which $\mathbf{H}^{(a)}$ plus $\mathbf{H}^{(c)}$ in eq 18 represent the set of all subgroups of $\mathbf{H}$. By summing up them over all the subgroups of $\mathbf{G}$ (i.e., $\mathbf{G}_i$ for $i = 1, 2, ..., s$), we have a cycle index as follows

$$\sum_{i=1}^{s} \mathrm{PCI}'(\mathbf{G}_i[\mathbf{H}^{(a)}; \mathbf{H}^{(c)}]; s_d) \quad (27)$$

which can be proven to be equivalent to Pólya's corona. Note that the inverse process is impossible; that is to say, the PCIs (eq 26) cannot be derived from Pólya's corona because of the shortage of information on the group−subgroup relationship.

2.2. Enumeration of Substituted Methyl Ligands. Let us first consider ligands based on a methyl ligand,[38] where the three hydrogen atoms are replaced by a set of atoms selected from X, Y, and Z. We treat the enumeration of such substituted methyl ligands in light of the PCI method.[32] Since the methyl hydrogens are governed by a coset representation $\mathbf{C}_{3v}(/\mathbf{C}_s)$, we obtain the set of subduced cycle indices (SCIs) as being (s_1^3, s_1s_2, s_3, s_3), which is formally multiplied by the inverse of the mark table of $\mathbf{C}_{3v}$ to give the following PCIs for every subgroup of $\mathbf{C}_{3v}$[39,40]

$$\mathrm{PCI}(\mathbf{C}_1; s_d) = \frac{1}{6}s_1^3 - \frac{1}{2}s_1s_2 - \frac{1}{6}s_3 + \frac{1}{2}s_3 = \frac{1}{6}s_1^3 - \frac{1}{2}s_1s_2 + \frac{1}{3}s_3 \quad (28)$$

$$\mathrm{PCI}(\mathbf{C}_s; s_d) = s_1s_2 - s_3 \quad (29)$$

$$\mathrm{PCI}(\mathbf{C}_{3v}; s_d) = s_3 \quad (30)$$

where $\mathrm{PCI}(\mathbf{C}_3; s_d)$ is omitted since it vanishes. The atom inventory of this enumeration is calculated to be

$$s_d = X^d + Y^d + Z^d \quad (31)$$

which is introduced into each of eqs 28−30. The resulting equations are expanded to give generating functions

$$f_{\mathbf{C}_1} = XYZ \quad (32)$$

$$f_{\mathbf{C}_s} = X^2Y + X^2Z + XY^2 + XZ^2 + Y^2Z + YZ^2 \quad (33)$$

$$f_{\mathbf{C}_{3v}} = X^3 + Y^3 + Z^3 \quad (34)$$

The coefficient of the term $X^xY^yZ^z$ in each generating function indicates the number of isomeric ligands with the formula $X^xY^yZ^z$ and the symmetry at issue. To illustrate this enumeration, Figure 1 shows an XYZ, $\mathbf{C}_1$-, an X^2Y, $\mathbf{C}_s$-, and an X^3,

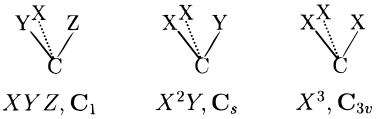


Figure 1. Methyl ligands.

$\mathbf{C}_{3v}$-isomer. The remaining isomers can be generated by the permutations of X, Y, and Z.

2.3. Enumeration of Derivatives of Dimethyl Ether. Dimethyl ether is considered to be a $\mathbf{C}_{2v}$-skeleton having two methyl ligands. Then, a derivative of dimethyl ether is considered to be generated by substituting the methyl ligands for appropriate substituted methyl ligands. Since the two positions of the skeleton to be substituted are ascribed to the coset representation $\mathbf{C}_{2v}(/\mathbf{C}_s)$, we obtain the set of subduced cycle indices with chirality fittingness (SCI-CFs) by applying Definition 19.7 of ref 32 to this enumeration, i.e., $(b_1^2, b_2, a_1^2, c_2, a_2)$.[41] This alignment is regarded as a formal row vector and multiplied by the inverse of the mark table of $\mathbf{C}_{2v}$ to give the following PCI-CFs for every subgroup of $\mathbf{C}_{2v}$

$$\mathrm{PCIC}(\mathbf{C}_1; a_d, b_d, c_d) = \frac{1}{4}b_1^2 - \frac{1}{4}b_2 - \frac{1}{4}a_1^2 - \frac{1}{4}c_2 + \frac{1}{2}a_2 \tag{35}$$

$$\mathrm{PCIC}(\mathbf{C}_2; a_d, b_d, c_d) = \frac{1}{2}b_2 - \frac{1}{2}a_2 \tag{36}$$

$$\mathrm{PCIC}(\mathbf{C}_s; a_d, b_d, c_d) = \frac{1}{2}a_1^2 - \frac{1}{2}a_2 \tag{37}$$

$$\mathrm{PCIC}(\mathbf{C}_s'; a_d, b_d, c_d) = \frac{1}{2}c_2 - \frac{1}{2}a_2 \tag{38}$$

$$\mathrm{PCIC}(\mathbf{C}_{2v}; a_d, b_d, c_d) = a_2 \tag{39}$$

where the symbols for ligand symmetries are omitted for the sake of simplicity.

Let us now consider the $\mathbf{C}_1$-ligand collected in Figure 1. As found easily in eq 32, there is one $\mathbf{C}_1$-ligand with the formula *XYZ*. Hence, the ligand inventories (eqs 24 and 25) are calculated for this case as follows

$$a_d = 0 \tag{40}$$

$$b_d = c_d = 2\left(\frac{1}{6}s_d^3 - \frac{1}{2}s_d s_{2d} + \frac{1}{3}s_{3d}\right) = 2(XYZ)^d \tag{41}$$

where eq 31 has been used in advance. They are introduced into eqs 35−39 to give the following generating functions for every subgroup

$$f_{\mathbf{C}_2[\mathbf{C}_1]} = f_{\mathbf{C}_s'[\mathbf{C}_1]} = \frac{1}{2}(2(XYZ)^2) = X^2Y^2Z^2 \tag{42}$$

where $f_{\mathbf{C}_1[\mathbf{C}_1]}$, $f_{\mathbf{C}_s[\mathbf{C}_1]}$, and $f_{\mathbf{C}_{2v}[\mathbf{C}_1]}$ are omitted since they vanish. The coefficient of the term $X^2Y^2Z^2$ on the right-hand side of eq 42 indicates that there is one isomer with $X^2Y^2Z^2$ and $\mathbf{C}_2$-$[\mathbf{C}_1]$-symmetry. On the other hand, the coefficient of the term $X^2Y^2Z^2$ on the right-hand side of eq 42 indicates that there is one isomer with $X^2Y^2Z^2$ and $\mathbf{C}_s'[\mathbf{C}_1]$-symmetry. These isomers are depicted in Figure 2.

Let us next consider $\mathbf{C}_s$-ligands based on CH_3. Equation 23 is calculated by starting from eq 29 to give the ligand

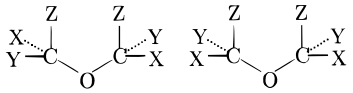


Figure 2. $X^2Y^2Z^2$-derivatives of dimethyl ether.

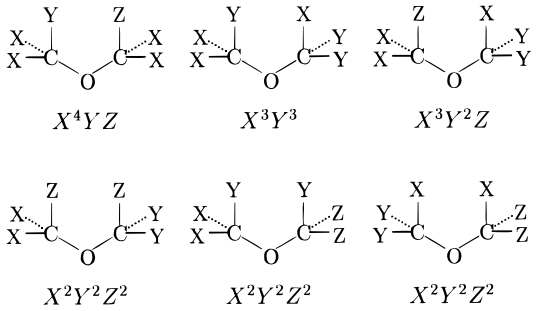


Figure 3. $\mathbf{C}_s[\mathbf{C}_s]$-derivatives of dimethyl ether.

inventories for this case:

$$a_d = b_d = c_d = s_d s_{2d} - s_{3d} \tag{43}$$

They are equal to one another, since only achiral ligands are taken into consideration. They are introduced into eqs 35−39 to give partial cycle indices of an extended type

$$\mathrm{PCI}'(\mathbf{C}_s[\mathbf{C}_s]; s_d) = \frac{1}{2}(s_1 s_2 - s_3)^2 - \frac{1}{2}(s_2 s_4 - s_6)$$
$$= \frac{1}{2}(s_1^2 s_2^2 - 2s_1 s_2 s_3 + s_3^2 - s_2 s_4 + s_6) \tag{44}$$

$$\mathrm{PCI}'(\mathbf{C}_{2v}[\mathbf{C}_s]; s_d) = s_2 s_4 - s_6 \tag{45}$$

where PCI′s for $\mathbf{C}_1[\mathbf{C}_s]$, $\mathbf{C}_2[\mathbf{C}_s]$, and $\mathbf{C}_s'[\mathbf{C}_s]$ are omitted since they vanish to zero. Note that the ligand inventory represented by eq 43 has been introduced into eqs 35−39 without the precedent introduction of eq 31. The atom inventory (eq 31) is introduced afterward into eqs 44 and 45 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions:

$$f_{\mathbf{C}_s[\mathbf{C}_s]} = (X^4YZ + XY^4Z + XYZ^4) + (X^3Y^3 + Y^3Z^3 + X^3Z^3) + (X^3Y^2Z + X^3YZ^2 + X^2Y^3Z + X^2YZ^3 + XY^3Z^2 + XY^2Z^3) + 3X^2Y^2Z^2 \tag{46}$$

$$f_{\mathbf{C}_{2v}[\mathbf{C}_s]} = X^4Y^2 + X^4Z^2 + X^2Y^4 + X^2Z^4 + Y^4Z^2 + Y^2Z^4 \tag{47}$$

As found easily in eq 46, there are four types of terms for $\mathbf{C}_s[\mathbf{C}_s]$-isomers, i.e., [4, 1, 1]-type (X^4YZ, etc., in the first parentheses), [3, 3, 0]-type (X^3Y^3, etc., in the second parentheses), [3, 2, 1]-type (X^3Y^2Z, etc., in the third parentheses), and [2, 2, 2]-type ($X^2Y^2Z^2$). The four types of isomers are illustrated in Figure 3, in which a representative for each of the first three types is depicted along with all of the three isomers for the last type. All of the terms appearing in eq 47 belong to the [4, 2, 0]-type. The six isomers corresponding to the terms are depicted in Figure 4.

To obtain the ligand inventories for $\mathbf{C}_{3v}$-ligands, eq 30 is introduced into eq 23. Thereby, we arrive at the ligand

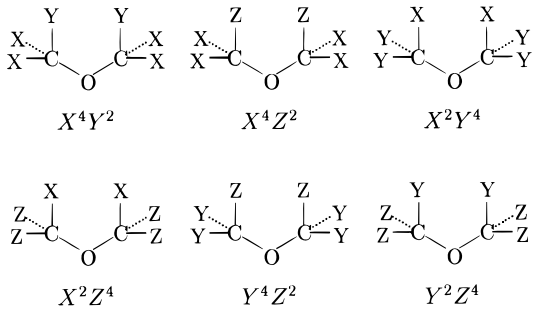


Figure 4. $\mathbf{C}_{2v}[\mathbf{C}_s]$-derivatives of dimethyl ether.

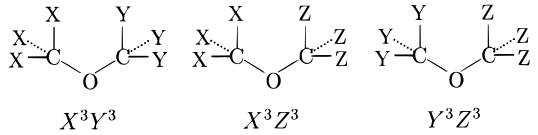


Figure 5. $\mathbf{C}_s[\mathbf{C}_{3v}]$-derivatives of dimethyl ether.

inventories represented by

$$a_d = b_d = c_d = s_{3d} \tag{48}$$

They are also equal to one another, since only achiral ligands are taken into consideration. These inventories are introduced into eqs 35−39, giving partial cycle indices of an extended type

$$\mathrm{PCI}'(\mathbf{C}_s[\mathbf{C}_{3v}]; s_d) = \frac{1}{2}s_3^2 - \frac{1}{2}s_6 \tag{49}$$

$$\mathrm{PCI}'(\mathbf{C}_{2v}[\mathbf{C}_{3v}]; s_d) = s_6 \tag{50}$$

where $\mathrm{PCI}'(\mathbf{C}_1[\mathbf{C}_{3v}]; s_d)$, $\mathrm{PCI}'(\mathbf{C}_2[\mathbf{C}_{3v}]; s_d)$, and $\mathrm{PCI}'(\mathbf{C}_s'[\mathbf{C}_{3v}]; s_d)$ are omitted since they vanish. Then, the atom inventory (eq 31) is introduced into eqs 49 and 50 of nonzero expression, which are expanded to give the following generating functions:

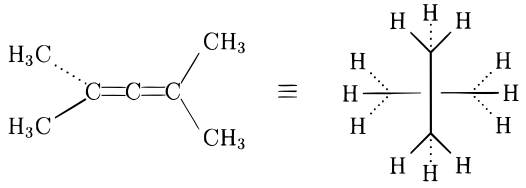
$$f_{\mathbf{C}_s[\mathbf{C}_{3v}]} = X^3Y^3 + X^3Z^3 + Y^3Z^3 \tag{51}$$

$$f_{\mathbf{C}_{2v}[\mathbf{C}_{3v}]} = X^6 + Y^6 + Z^6 \tag{52}$$

Equation 51 indicates that there are three $\mathbf{C}_s[\mathbf{C}_{3v}]$-derivatives of [3, 3, 0]-type. These derivatives are illustrated in Figure 5. On the other hand, eq 52 indicates that there are three $\mathbf{C}_{2v}[\mathbf{C}_{3v}]$-derivatives of [6, 0, 0]-type. Their symmetries essentially correspond to the symmetry of dimethyl ether itself.

2.4. Enumeration of Derivatives of Tetramethylallenes. Tetramethylallene (**1**) is a molecule of $\mathbf{D}_{2d}$-symmetry if we take account of the highest attainable symmetry. In light of the present methodology, tetramethylallene is regarded as a tetramethyl derivative of a promolecule of $\mathbf{D}_{2d}$-symmetry. For the convenience of drawing, we adopt the convention of drawing tetramethylallene shown in Figure 6, where the molecule is depicted as **2** by the inspection along the S_4-axis.

A derivative of tetramethylallene is considered to be generated by placing substituted methyl ligands on the four positions of an allene skeleton. Since the four positions of the skeleton are ascribed to the coset representation



1 **2**

Figure 6. Convention for drawing tetramethylallene.

$\mathbf{D}_{2d}(/\mathbf{C}_s)$, we obtain the set of SCI-CFs by applying Definition 19.7 of ref 32 to the present case, i.e., (b_1^4, b_2^2, b_2^2, $a_1^2c_2$, c_4, a_2^2, b_4, a_4).[41] This alignment is regarded as a formal row vector and multiplied by the inverse of the mark table of $\mathbf{D}_{2d}$ to give the following PCI-CFs for every subgroup of $\mathbf{D}_{2d}$

$$\mathrm{PCIC}(\mathbf{C}_1; a_d, b_d, c_d) = \frac{1}{8}b_1^4 - \frac{1}{8}b_2^2 - \frac{1}{4}b_2^2 - \frac{1}{4}a_1^2c_2 + \frac{1}{4}a_2^2 + \frac{1}{4}b_4 \tag{53}$$

$$\mathrm{PCIC}(\mathbf{C}_2; a_d, b_d, c_d) = \frac{1}{4}b_2^2 - \frac{1}{4}c_4 - \frac{1}{4}a_2^2 - \frac{1}{4}b_4 + \frac{1}{4}a_4 \tag{54}$$

$$\mathrm{PCIC}(\mathbf{C}_2'; a_d, b_d, c_d) = \frac{1}{2}b_2^2 - \frac{1}{2}b_4 \tag{55}$$

$$\mathrm{PCIC}(\mathbf{C}_s; a_d, b_d, c_d) = \frac{1}{2}a_1^2c_2 - \frac{1}{2}a_2^2 \tag{56}$$

$$\mathrm{PCIC}(\mathbf{S}_4; a_d, b_d, c_d) = \frac{1}{2}c_4 - \frac{1}{2}a_4 \tag{57}$$

$$\mathrm{PCIC}(\mathbf{C}_{2v}; a_d, b_d, c_d) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4 \tag{58}$$

$$\mathrm{PCIC}(\mathbf{D}_2; a_d, b_d, c_d) = \frac{1}{2}b_4 - \frac{1}{2}a_4 \tag{59}$$

$$\mathrm{PCIC}(\mathbf{D}_{2d}; a_d, b_d, c_d) = a_4 \tag{60}$$

where the symbols for ligand symmetries are omitted for the sake of simplicity.

Let us consider $\mathbf{C}_1$-ligands on the allene skeleton, where we can use the ligand inventories represented by eqs 40 and 41. These are introduced into eqs 53−60 to give the following generating functions for every subgroup

$$f_{\mathbf{C}_1[\mathbf{C}_1]} = f_{\mathbf{C}_2'[\mathbf{C}_1]} = f_{\mathbf{S}_4[\mathbf{C}_1]} = f_{\mathbf{D}_2[\mathbf{C}_1]} = X^4Y^4Z^4 \tag{61}$$

where the generating functions of zero value (for $\mathbf{C}_2[\mathbf{C}_1]$, $\mathbf{C}_s[\mathbf{C}_1]$, $\mathbf{C}_{2v}[\mathbf{C}_1]$, and $\mathbf{D}_{2d}[\mathbf{C}_1]$) are omitted. The coefficient of the term $X^4Y^4Z^4$ on the right-hand side of each nonzero equation indicates that there is one isomer with $X^4Y^4Z^4$ and the symmetry at issue ($\mathbf{C}_1[\mathbf{C}_1]$, $\mathbf{C}_2'[\mathbf{C}_1]$, $\mathbf{S}_4[\mathbf{C}_1]$, or $\mathbf{D}_2[\mathbf{C}_1]$). These isomers are depicted in Figure 7, where each isomer consists of four ligands selected from the *XYZ*, $\mathbf{C}_1$-ligand (Figure 1) and its enantiomeric ligand.

Let us next consider $\mathbf{C}_s$-ligands based on CH_3, where we use the ligand inventories described above (eq 43). These are introduced into eqs 53−60 to give partial cycle indices

of an extended type

$$\mathrm{PCI}'(\mathbf{C}_1[\mathbf{C}_s];\, s_d) = \frac{1}{8}(s_1 s_2 - s_3)^4 - \frac{1}{8}(s_2 s_4 - s_6)^2 - \frac{1}{4}(s_1 s_2 - s_3)^2(s_2 s_4 - s_6) + \frac{1}{4}(s_4 s_8 - s_{12}) \quad (62)$$

$$\mathrm{PCI}'(\mathbf{C}'_2[\mathbf{C}_s];\, s_d) = \frac{1}{2}(s_2^2 s_4^2 - 2 s_2 s_4 s_6 + s_6^2 - s_4 s_8 + s_{12}) \quad (63)$$

$$\mathrm{PCI}'(\mathbf{C}_s[\mathbf{C}_s];\, s_d) = \frac{1}{2}(s_1^2 s_2^2 - 2 s_1 s_2 s_3 + s_3^2 - s_2 s_4 + s_6)(s_2 s_4 - s_6) \quad (64)$$

$$\mathrm{PCI}'(\mathbf{C}_{2v}[\mathbf{C}_s];\, s_d) = \frac{1}{2}(s_2^2 s_4^2 - 2 s_2 s_4 s_6 + s_6^2 - s_4 s_8 + s_{12}) \quad (65)$$

$$\mathrm{PCI}'(\mathbf{D}_{2d}[\mathbf{C}_s];\, s_d) = s_4 s_8 - s_{12} \quad (66)$$

where $\mathrm{PCI}'(\mathbf{C}_2[\mathbf{C}_s];\, s_d)$, $\mathrm{PCI}'(\mathbf{S}_4[\mathbf{C}_s];\, s_d)$, and $\mathrm{PCI}'(\mathbf{D}_2[\mathbf{C}_s];\, s_d)$ vanish.

Then, the atom inventory (eq 31) is introduced into eqs 62−66 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions:

$$f_{\mathbf{C}_1[\mathbf{C}_s]} = (X^7Y^4Z + X^7YZ^4 + \cdots) + (X^7Y^3Z^2 + X^7Y^2Z^3 + \cdots) + (X^6Y^5Z + X^6YZ^5 + \cdots) + 2(X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 5(X^6Y^3Z^3 + X^6Y^3Z^3 + \cdots) + 5(X^5Y^5Z^2 + X^5Y^2Z^5 + \cdots) + 6(X^5Y^4Z^3 + X^5Y^3Z^4 + \cdots) + 9X^4Y^4Z^4 \quad (67)$$

$$f_{\mathbf{C}'_2[\mathbf{C}_s]} = (X^8Y^2Z^2 + X^2Y^8Z^2 + \cdots) + (X^6Y^6 + X^6Z^6 + \cdots) + (X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 3X^4Y^4Z^4 \quad (68)$$

$$f_{\mathbf{C}_s[\mathbf{C}_s]} = (X^8Y^3Z + X^8YZ^3 + \cdots) + (X^7Y^5 + X^7Z^5 + \cdots) + (X^7Y^4Z + X^7YZ^4 + \cdots) + 2(X^7Y^3Z^2 + X^7Y^2Z^3 + \cdots) + 2(X^6Y^5Z + X^6YZ^5 + \cdots) + 3(X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 2(X^6Y^3Z^3 + X^3Y^6Z^3 + \cdots) + 2(X^5Y^5Z^2 + X^5Y^2Z^5 + \cdots) + 3(X^5Y^4Z^3 + X^5Y^3Z^4 + \cdots) + 3X^4Y^4Z^4 \quad (69)$$

$$f_{\mathbf{C}_{2v}[\mathbf{C}_s]} = (X^8Y^2Z^2 + X^2Y^8Z^2 + \cdots) + (X^6Y^6 + X^6Z^6 + \cdots) + (X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 3X^4Y^4Z^4 \quad (70)$$

$$f_{\mathbf{D}_{2d}[\mathbf{C}_s]} = X^8Y^4 + X^8Z^4 + X^4Y^8 + X^4Z^8 + Y^8Z^4 + Y^4Z^8 \quad (71)$$

To illustrate the results shown in eq 67, Figure 8 depicts five $\mathbf{C}_1[\mathbf{C}_s]$, $X^6Y^3Z^3$-derivatives. The number (five) of derivatives is found as a coefficient of the term $X^6Y^3Z^3$ appearing in eq 67. The results represented by eq 68 (for $\mathbf{C}'_2[\mathbf{C}_s]$) are exemplified by Figure 9, which depicts one $X^8Y^2Z^2$-, one X^6Y^6-, one $X^6Y^4Z^2$, and three $X^4Y^4Z^4$-isomers. To exemplify the results given by eq 69 (for $\mathbf{C}_s[\mathbf{C}_s]$), the derivatives corresponding to the term $X^6Y^4Z^2$ are drawn in Figure 10.

2.5. Enumeration of Derivatives of 2,2-Dimethylpropane. 2,2-Dimethylpropane or tetramethylmethane (**3**) (Figure 11) belongs to $\mathbf{T}_d$-symmetry as a conformer in the highest attainable symmetry. We adopt a projection through the S_4-axis to draw derivatives, e.g., **4** for 2,2-dimethylpropane

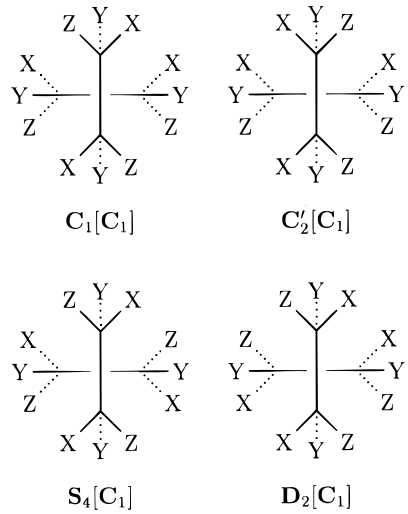


Figure 7. $X^4Y^4Z^4$-derivatives of tetramethylallene.

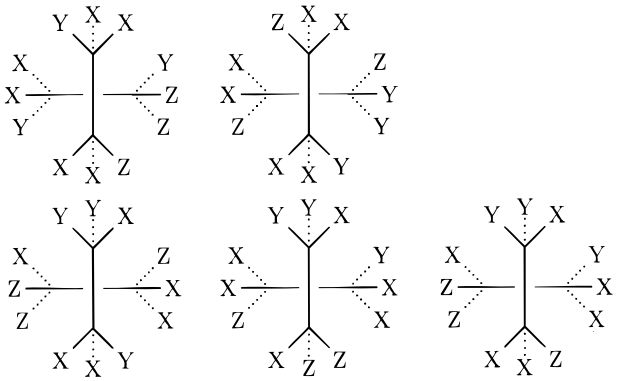


Figure 8. Five $\mathbf{C}_1[\mathbf{C}_s]$, $X^6Y^3Z^3$-derivatives of tetramethylallene.

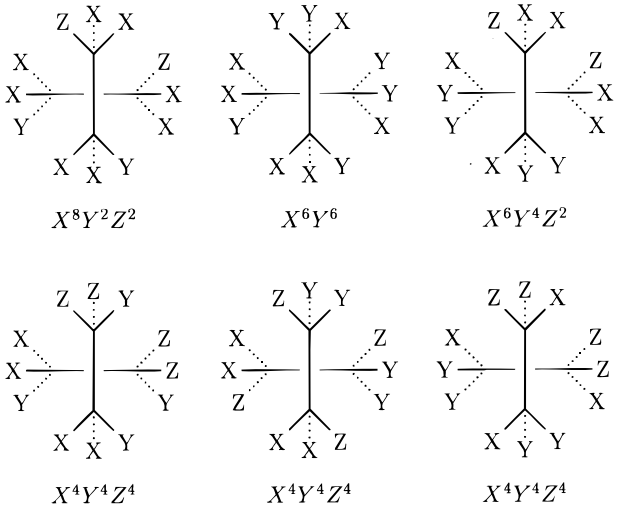


Figure 9. $\mathbf{C}'_2[\mathbf{C}_s]$-derivatives of tetramethylallene.

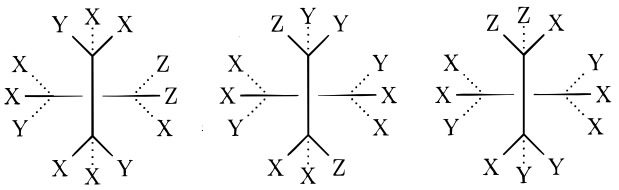
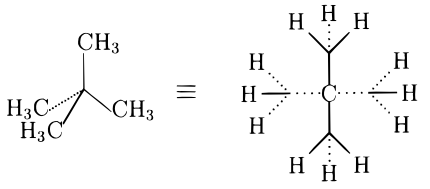


Figure 10. Three $\mathbf{C}_s[\mathbf{C}_s]$, $X^6Y^4Z^2$-derivatives of tetramethylallene.



3 **4**

Figure 11. Convention for drawing 2,2-dimethylpropane.

itself. This projection is parallel to the one indicated for tetramethylallene (**2**).

A derivative of 2,2-dimethylpropane is considered to be generated by placing substituted methyl ligands on the four positions of a methane skeleton. The four positions of the skeleton construct an orbit governed by the coset representation $\mathbf{T}_d(/\mathbf{C}_{3v})$. Note that the local symmetry of the orbit $\mathbf{C}_{3v}$ is equal to the full symmetry of an unsubstituted methyl ligand. In accord with the coset representation $\mathbf{T}_d(/\mathbf{C}_{3v})$, the corresponding set of SCI-CFs is obtained to be (b_1^4, b_2^2, $a_1^2c_2$, b_1b_3, c_4, b_4, a_2^2, a_1a_3, a_4, b_4, a_4) by using Definition 19.7 of ref 32.[41] This formal row vector is multiplied by the inverse of the mark table of $\mathbf{T}_d$ to give the following PCI-CFs for every subgroup of $\mathbf{T}_d$

$$\mathrm{PCIC}(\mathbf{C}_1; a_d, b_d, c_d) = \frac{1}{24}b_1^4 - \frac{1}{8}b_2^2 - \frac{1}{4}a_1^2c_2 - \frac{1}{6}b_1b_3 + \frac{1}{12}b_4 + \frac{1}{4}a_2^2 + \frac{1}{2}a_1a_3 + \frac{1}{6}b_4 - \frac{1}{2}a_4 \quad (72)$$

$$\mathrm{PCIC}(\mathbf{C}_2; a_d, b_d, c_d) = \frac{1}{4}b_2^2 - \frac{1}{4}c_4 - \frac{1}{4}b_4 - \frac{1}{4}a_2^2 + \frac{1}{2}a_4 \quad (73)$$

$$\mathrm{PCIC}(\mathbf{C}_s; a_d, b_d, c_d) = \frac{1}{2}a_1^2c_2 - \frac{1}{2}a_2^2 - a_1a_3 + a_4 \quad (74)$$

$$\mathrm{PCIC}(\mathbf{C}_3; a_d, b_d, c_d) = \frac{1}{2}b_1b_3 - \frac{1}{2}a_1a_3 - \frac{1}{2}b_4 + \frac{1}{2}a_4 \quad (75)$$

$$\mathrm{PCIC}(\mathbf{S}_4; a_d, b_d, c_d) = \frac{1}{2}c_4 - \frac{1}{2}a_4 \quad (76)$$

$$\mathrm{PCIC}(\mathbf{D}_2; a_d, b_d, c_d) = \frac{1}{6}b_4 - \frac{1}{2}a_4 - \frac{1}{6}b_4 + \frac{1}{2}a_4 = 0 \quad (77)$$

$$\mathrm{PCIC}(\mathbf{C}_{2v}; a_d, b_d, c_d) = \frac{1}{2}a_2^2 - \frac{1}{2}a_4 \quad (78)$$

$$\mathrm{PCIC}(\mathbf{C}_{3v}; a_d, b_d, c_d) = a_1a_3 - a_4 \quad (79)$$

$$\mathrm{PCIC}(\mathbf{D}_{2d}; a_d, b_d, c_d) = a_4 - a_4 = 0 \quad (80)$$

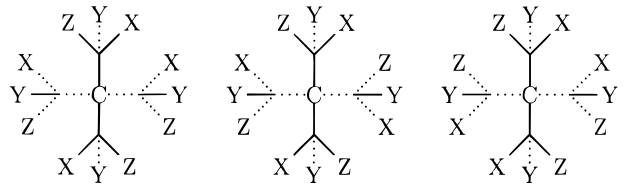
$$\mathrm{PCIC}(\mathbf{T}; a_d, b_d, c_d) = \frac{1}{2}b_4 - \frac{1}{2}a_4 \quad (81)$$

$$\mathrm{PCIC}(\mathbf{T}_d; a_d, b_d, c_d) = a_4 \quad (82)$$

where the symbols for ligand symmetries are omitted for the sake of simplicity.

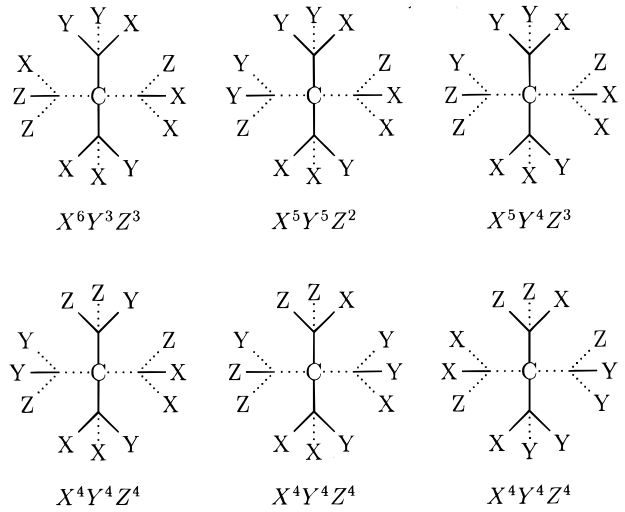
Suppose that $\mathbf{C}_1$-ligands derived from a methyl ligand are placed on the four positions of the methane skeleton. The ligand inventories represented by eqs 40 and 41 are introduced into eqs 72−82 to give the following generating functions for every subgroup

$$f_{\mathbf{C}_3[\mathbf{C}_1]} = f_{\mathbf{S}_4[\mathbf{C}_1]} = f_{\mathbf{T}[\mathbf{C}_1]} = X^4Y^4Z^4 \quad (83)$$



$\mathbf{C}_3[\mathbf{C}_1]$ $\mathbf{S}_4[\mathbf{C}_1]$ $\mathbf{T}[\mathbf{C}_1]$

Figure 12. $X^4Y^4Z^4$-derivatives of 2,2-dimethylpropane.



$X^6Y^3Z^3$ $X^5Y^5Z^2$ $X^5Y^4Z^3$

$X^4Y^4Z^4$ $X^4Y^4Z^4$ $X^4Y^4Z^4$

Figure 13. $\mathbf{C}_1[\mathbf{C}_s]$-derivatives of 2,2-dimethylpropane.

where the generating functions of zero value for the remaining subgroups of $\mathbf{T}_d[\mathbf{C}_1]$ are omitted. The coefficient of the term $X^4Y^4Z^4$ on the right-hand side of each nonzero equation indicates that there is one isomer of $\mathbf{C}_3[\mathbf{C}_1]$-, $\mathbf{S}_4[\mathbf{C}_1]$-, or $\mathbf{T}[\mathbf{C}_1]$-symmetry. They are depicted in Figure 12, where each ligand is the *XYZ*, $\mathbf{C}_1$-ligand (Figure 1) or its enantiomeric counterpart.

To place $\mathbf{C}_s$-ligands on the four positions of the methane skeleton, the ligand inventories represented by eq 43 are introduced into eqs 72−82. Thereby we obtain partial cycle indices of an extended type

$$\mathrm{PCI}'(\mathbf{C}_1[\mathbf{C}_s]; s_d) = \frac{1}{24}(s_1s_2 - s_3)^4 + \frac{1}{8}(s_2s_4 - s_6)^2 - \frac{1}{4}(s_1s_2 - s_3)^2(s_2s_4 - s_6) + \frac{1}{3}(s_1s_2 - s_3)(s_3s_6 - s_9) - \frac{1}{4}(s_4s_8 - s_{12}) \quad (84)$$

$$\mathrm{PCI}'(\mathbf{C}_s[\mathbf{C}_s]; s_d) = \frac{1}{2}(s_1s_2 - s_3)^4(s_2s_4 - s_6) - \frac{1}{2}(s_2s_4 - s_6)^2 - (s_1s_2 - s_3)(s_3s_6 - s_9) + (s_4s_8 - s_{12}) \quad (85)$$

$$\mathrm{PCI}'(\mathbf{C}_{2v}[\mathbf{C}_s]; s_d) = \frac{1}{2}(s_2^2\,s_4^2 - 2s_2s_4s_6 + s_6^2 - s_4s_8 + s_{12}) \quad (86)$$

$$\mathrm{PCI}'(\mathbf{C}_{3v}[\mathbf{C}_s]; s_d) = (s_1s_2 - s_3)(s_3s_6 - s_9) - (s_4s_8 - s_{12}) \quad (87)$$

$$\mathrm{PCI}'(\mathbf{T}_d[\mathbf{C}_s]; s_d) = s_4s_8 - s_{12} \quad (88)$$

where the PCI′s for $\mathbf{C}_2[\mathbf{C}_s]$, $\mathbf{C}_3[\mathbf{C}_s]$, $\mathbf{S}_4[\mathbf{C}_s]$, $\mathbf{D}_2[\mathbf{C}_s]$, $\mathbf{D}_{2d}[\mathbf{C}_s]$,

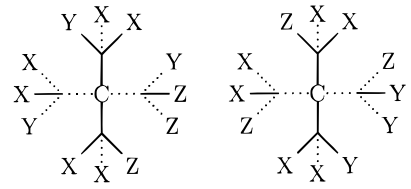
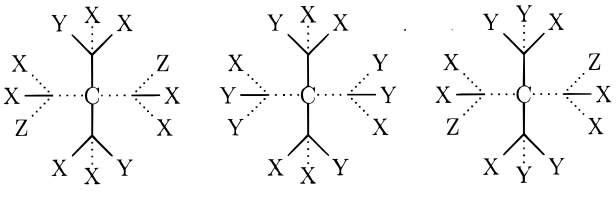


Figure 14. $\mathbf{C}_s[\mathbf{C}_s]$, $X^6Y^3Z^3$-derivatives of 2,2-dimethylpropane.



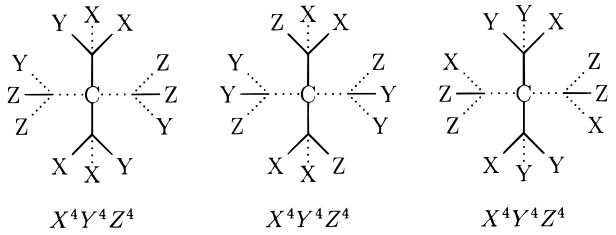


Figure 15. $\mathbf{C}_{2v}[\mathbf{C}_s]$-derivatives of 2,2-dimethylpropane.

and $\mathbf{T}[\mathbf{C}_s]$ are omitted since they are equal to zero. The atom inventory (eq 31) is introduced into eqs 84−88 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions:

$$f_{\mathbf{C}_1[\mathbf{C}_s]} = (X^6Y^3Z^3 + X^3Y^6Z^3 + \cdots) + (X^5Y^5Z^2 + X^5Y^2Z^5 + \cdots) + (X^5Y^4Z^3 + X^5Y^3Z^4 + \cdots) + 3X^4Y^4Z^4 \quad (89)$$

$$f_{\mathbf{C}_s[\mathbf{C}_s]} = (X^7Y^4Z + X^7YZ^4 + \cdots) + (X^7Y^3Z^2 + X^7Y^2Z^3 + \cdots) + (X^6Y^5Z + X^6YZ^5 + \cdots) + 2(X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 2(X^6Y^3Z^3 + X^3Y^6Z^3 + \cdots) + 2(X^5Y^5Z^2 + X^5Y^2Z^5 + \cdots) + 3(X^5Y^4Z^3 + X^5Y^3Z^4 + \cdots) \quad (90)$$

$$f_{\mathbf{C}_{2v}[\mathbf{C}_s]} = (X^8Y^2Z^2 + X^2Y^8Z^2 + \cdots) + (X^6Y^6 + X^6Z^6 + \cdots) + 2(X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) + 3X^4Y^4Z^4 \quad (91)$$

$$f_{\mathbf{C}_{3v}[\mathbf{C}_s]} = (X^8Y^3Z + X^8YZ^3 + \cdots) + (X^7Y^5 + X^7Z^5 + \cdots) + (X^7Y^3Z^2 + X^7Y^2Z^3 + \cdots) + (X^6Y^5Z + X^6YZ^5 + \cdots) + (X^6Y^4Z^2 + X^6Y^2Z^4 + \cdots) \quad (92)$$

$$f_{\mathbf{T}_d[\mathbf{C}_s]} = X^8Y^4 + X^8Z^4 + X^4Y^8 + X^4Z^8 + Y^8Z^4 + Y^4Z^8 \quad (93)$$

To exemplify the results given by eq 89 ($\mathbf{C}_1[\mathbf{C}_s]$), Figure 13 shows one $X^6Y^3Z^2$-, one $X^5Y^5Z^2$-, one $X^5Y^4Z^3$-, and three $X^4Y^4Z^4$-isomers. The $X^6Y^3Z^3$-term appearing in eq 90 ($\mathbf{C}_s[\mathbf{C}_s]$) corresponds to two $\mathbf{C}_s[\mathbf{C}_s]$, $X^6Y^3Z^3$-derivatives depicted in Figure 14. To illustrate the results given in eq 91 ($\mathbf{C}_{2v}[\mathbf{C}_s]$), Figure 15 depicts one $X^8Y^2Z^2$-, one X^6Y^6-, one $X^6Y^4Z^2$-, and three $X^4Y^4Z^4$-isomers. Figure 16 illustrates the results given by eq 92 ($\mathbf{C}_{3v}[\mathbf{C}_s]$).

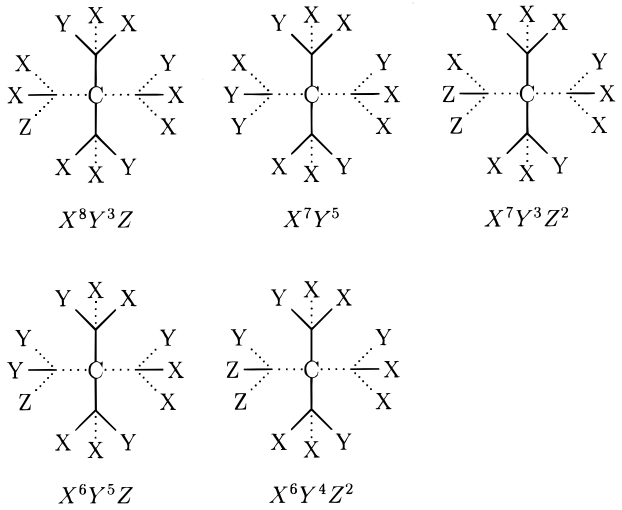


Figure 16. $\mathbf{C}_{3v}[\mathbf{C}_s]$-derivatives of 2,2-dimethylpropane.

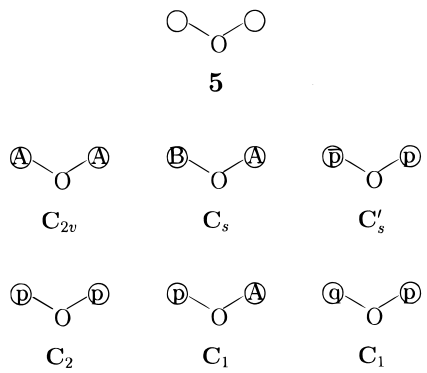


Figure 17. Skeleton and promolecules for derivatives of dimethyl ether.

3. PROMOLECULE ENUMERATION

3.1. Promolecules for the Derivation of Dimethy Ether. To examine the derivation of dimethyl ether more clearly, we examine promolecules derived from a skeleton **5** (Figure 17). The two positions (○) of the skeleton take a pair of proligands selected from achiral proligands (A and B), chiral proligands (p and q) and their enantiomers ($\bar{\text{p}}$ and $\bar{\text{q}}$). The ligand inventories of this case are obtained to be

$$a_d = A^d + B^d \quad (94)$$

$$b_d = A^d + B^d + p^d + \bar{p}^d + q^d + \bar{q}^d \quad (95)$$

$$c_d = A^d + B^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} \quad (96)$$

Since the two positions of the skeleton (**5**) are ascribed to the coset representation $\mathbf{C}_{2v}(/\mathbf{C}_s)$, the PCIs (eqs 35−39) also hold true for this case. Hence the inventories (eqs 94−96) are introduced into eqs 35−39 to give the following generating functions for every subgroup of $\mathbf{C}_{2v}$:

$$f_{\mathbf{C}_1} = \frac{1}{2}(Ap + A\bar{p}) + \frac{1}{2}(Bp + B\bar{p}) + \frac{1}{2}(Aq + A\bar{q}) + \frac{1}{2}(Bq + B\bar{q}) + \frac{1}{2}(pq + \overline{pq}) + \frac{1}{2}(p\bar{q} + \bar{p}q) \quad (97)$$

$$f_{\mathbf{C}_2} = \frac{1}{2}(p^2 + \bar{p}^2) + \frac{1}{2}(q^2 + \bar{q}^2) \quad (98)$$

$$f_{\mathbf{C}_s} = AB \quad (99)$$

$$f_{\mathbf{C}_s'} = p\bar{p} + q\bar{q} \quad (100)$$

$$f_{\mathbf{C}_{2v}} = A^2 + B^2 \quad (101)$$

It should be noted that the paired term ($Ap + A\bar{p}$) indicates a pair of enantiomeric promolecules, Ap and A$\bar{\text{p}}$ ($\mathbf{C}_1$); the term ($pq + \overline{pq}$) indicates another pair of enantiomeric promolecules, pq and $\overline{\text{pq}}$ ($\mathbf{C}_1$); and the term ($p^2 + \bar{p}^2$) corresponds to a further pair of enantiomeric promolecules, p^2 and $\bar{\text{p}}^2$ ($\mathbf{C}_2$). The coefficient ($^1/_2$) before each of the paired terms comes from the present convention that a pair of enantiomeric promolecules is counted once. The term $p\bar{p}$ is assigned to an achiral promolecule, p$\bar{\text{p}}$ ($\mathbf{C}_s'$), which represents the internal compensation of local chirality (so-called meso-form). Representative promolecules based on the skeleton (**5**) are depicted in Figure 17.

3.2. Promolecules for Tetramethylallene and 2,2-Dimethylpropane. In the previous paper,[36] we have enumerated promolecules derived from an allene skeleton by using the SCI method. Equivalent results of enumeration can be obtained by using the PCI method in which the PCI-CFs obtained above (eqs 53−60) are applied to the present enumeration of promolecules without any modification. When achiral ligands (A, B, C, and D) and chiral ligands (p, q, r, s, and their enantiomers) are taken into consideration, the ligand inventories are obtained to be

$$a_d = A^d + B^d + C^d + D^d \quad (102)$$

$$b_d = A^d + B^d + C^d + D^d + p^d + \bar{p}^d + q^d + \bar{q}^d r^d + \bar{r}^d s^d + \bar{s}^d \quad (103)$$

$$c_d = A^d + B^d + C^d + D^d + 2p^{d/2}\bar{p}^{d/2} + 2q^{d/2}\bar{q}^{d/2} + 2r^{d/2}\bar{r}^{d/2} + 2s^{d/2}\bar{s}^{d/2} \quad (104)$$

These inventories are introduced into the PCI-CFs (eqs 53−60), and the resulting equations are expanded to give generating functions for every subsymmetry of $\mathbf{D}_{2d}$. The results are equivalent to Figure 5 of ref 36. Several promolecules necessary for the later discussions are listed in Figure 18.

Promolecules derived from a methane skeleton are enumerated by the present PCI method, where the PCI-CFs obtained above (eqs 72−82) are applied to the present case. One of the merits of the present method is such common usage of PCI-CFs in enumerating nonrigid molecules and promolecules, though equivalent results have been obtained by using the SCI method.[36] The ligand inventories (eqs 102−104) are introduced into the PCI-CFs (eqs 72−82). The resulting equations are expanded to give generating functions for every subsymmetry of $\mathbf{D}_2$. The results are equivalent to Table 1 and Figure 2 of ref 36. Several promolecules necessary for the later discussions are listed in Figure 19.

4. DISCUSSION

4.1. Factorization of Terms for Derivatives of Dimethyl Ethers. Since the present method is closely associated with the concept of promolecules, each term of a generating function can be easily factorized in light of the types of promolecules. This feature is one of the merits of the present approach.

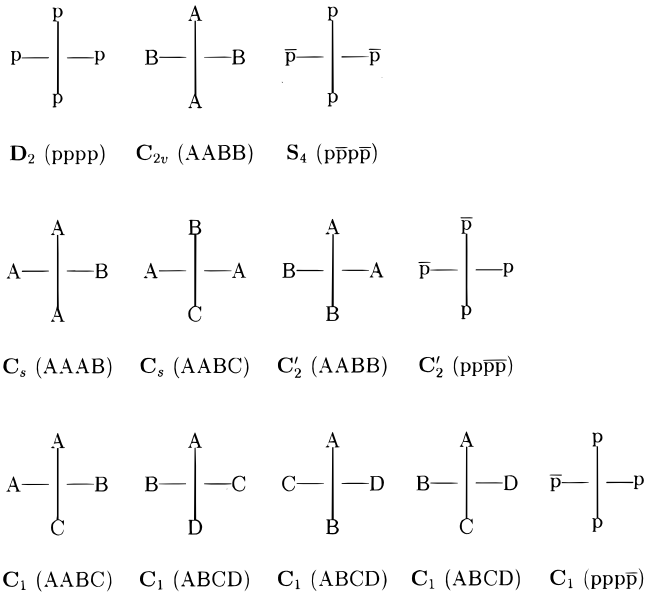


Figure 18. Several promolecules for allene derivatives.

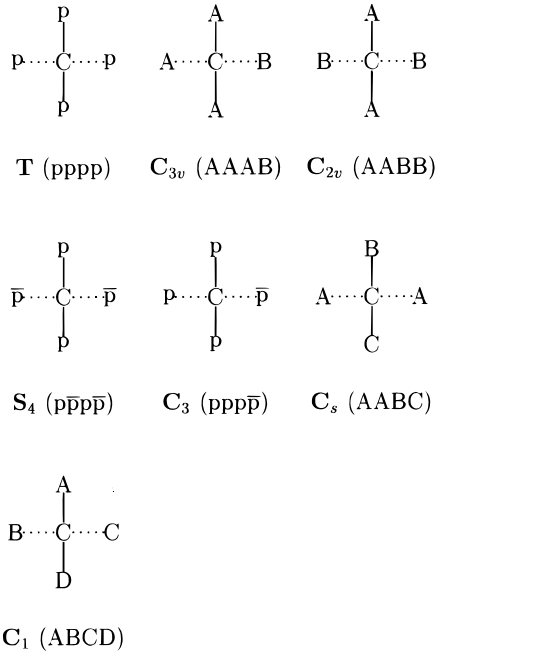


Figure 19. Several promolecules for methane derivatives.

For example, the $X^2Y^2Z^2$-molecules depicted in Figure 2 are ascribed to the promolecules listed in Figure 17, i.e., p−O−p and p−O−$\bar{\text{p}}$, which contain a chiral proligand p or its enantiomeric proligand $\bar{\text{p}}$. This means that the term $X^2Y^2Z^2$ is factorized into $XYZ \times XYZ$, each factor of which corresponds to a chiral XYZ-ligand or its enantiomeric ligand, as found in Figure 2.

On the other hand, the terms for the $\mathbf{C}_s[\mathbf{C}_s]$-derivatives of dimethyl ether collected in Figure 3 are factorized as follows: $X^4YZ = X^2Y \times X^2Z$, $X^3Y^3 = X^2Y \times XY^2$, $X^3Y^2Z = X^2Z \times XY^2$, and $X^2Y^2Z^2 = X^2Z \times Y^2Z = X^2Y \times YZ^2 = XY^2 \times XZ^2$, each factor of which takes the form of the partition [2, 1, 0]. These modes of factorization are ascribed to the

Table 1. Factorization of Terms for $\mathbf{C}_1[\mathbf{C}_s]$ for Tetramethylallene

symmetry	term	factors	promolecule
$\mathbf{C}_1[\mathbf{C}_s]$	X^7Y^4Z	$(X^2Y)^2 \times XY^2 \times X^2Z$	AABC
	$X^7Y^3Z^2$	$X^2Y \times XY^2 \times (X^2Z)^2$	AABC
	X^6Y^5Z	$X^2Y \times (XY^2)^2 \times X^2Z$	AABC
	$2X^6Y^4Z^2$	$(X^2Y)^2 \times XY^2 \times XZ^2$	AABC
		$(X^2Y)^2 \times X^2Z \times Y^2Z$	AABC
	$5X^6Y^3Z^3$	$(X^2Y)^2 \times YZ^2 \times X^2Z$	AABC
		$X^2Y \times (X^2Z)^2 \times Y^2Z$	AABC
		$3X^2Y \times X^2Z \times XY^2 \times XZ^2$	ABCD
	$5X^5Y^5Z^2$	$(X^2Y)^2 \times XY^2 \times YZ^2$	AABC
		$(XY^2)^2 \times X^2Y \times XZ^2$	AABC
		$3X^2Y \times X^2Z \times XY^2 \times Y^2Z$	ABCD
	$6X^5Y^4Z^3$	$(X^2Y)^2 \times XZ^2 \times Y^2Z$	AABC
		$(XY^2)^2 \times X^2Z \times XZ^2$	AABC
		$(X^2Z)^2 \times XY^2 \times Y^2Z$	AABC
		$3X^2Y \times X^2Z \times XY^2 \times YZ^2$	ABCD
	$9X^4Y^4Z^4$	$3X^2Y \times X^2Z \times YZ^2 \times Y^2Z$	ABCD
		$3X^2Y \times XY^2 \times XZ^2 \times YZ^2$	ABCD
		$3XY^2 \times Y^2Z \times XZ^2 \times X^2Z$	ABCD

Table 2. Factorization of Terms for $\mathbf{C}'_2[\mathbf{C}_s]$ for Tetramethylallene

symmetry	term	factors	promolecule
$\mathbf{C}_1[\mathbf{C}_s]$	$X^8Y^2Z^2$	$(X^2Y)^2 \times (X^2Z)^2$	AABB
	X^6Y^6	$(X^2Y)^2 \times (XY^2)^2$	AABB
	$X^6Y^4Z^2$	$(X^2Z)^2 \times (XY^2)^2$	AABB
	$3X^4Y^4Z^4$	$(X^2Y)^2 \times (XZ^2)^2$	AABB
		$(X^2Z)^2 \times (Y^2Z)^2$	AABB
		$(XY^2)^2 \times (XZ^2)^2$	AABB

$\mathbf{C}_s$-promolecule A−O−B listed in Figure 17, since such [2, 1, 0]-ligands represent achiral ligands belonging to $\mathbf{C}_s$ (Figure 1). The three modes of factorization of the term $X^2Y^2Z^2$ correspond to the presence of three $X^2Y^2Z^2$-isomers, as found in the bottom row of Figure 3.

The terms for the $\mathbf{C}_{2v}[\mathbf{C}_s]$-derivatives of dimethyl ether collected in Figure 4 are factorized into $X^4Y^2 = (X^2Y)^2$, $X^4Z^2 = (X^2Z)^2$, etc., each pair of factors of which takes the square form of the partition [2, 1, 0]. These modes of factorization are ascribed to the $\mathbf{C}_{2v}$-promolecule A−O−A listed in Figure 17.

4.2. Factorization of Terms for Derivatives of Tetramethylallene. The factorization of each term appearing in eq 67 (for $\mathbf{C}_1[\mathbf{C}_s]$) is shown in Table 1, where it is conducted in accord with the promolecules of AABC- or ABCD-type having $\mathbf{C}_1$-symmetry (Figure 18).

The derivatives listed in Figure 8 correspond to the factorization of $5X^6Y^3Z^3$ shown in Table 1. The first derivative in the top row of Figure 8 corresponds to the factorization of the term into $(X^2Y)^2 \times YZ^2 \times X^2Z$, while the second derivative is associated with the factorization $X^2Y \times (X^2Z)^2 \times Y^2Z$. Each of the factors corresponds to the formula of a respective ligand. Thus, it takes the form represented by the partition [2, 1, 0] for a $\mathbf{C}_s$-ligand, an example of which is listed in Figure 1 as an X^2Y-ligand. Each of the derivatives is ascribed to the $\mathbf{C}_1$-promolecule of AABC-type listed in Figure 18.

The three $X^6Y^3Z^3$-derivatives in the bottom row of Figure 8 correspond to $X^2Y \times X^2Z \times XY^2 \times XZ^2$ (Table 1). They are ascribed to the three $\mathbf{C}_1$-promolecules of ABCD-type listed in Figure 18.

The derivatives collected in Figure 9 correspond to the data shown in Table 2, which involves the factorization of each term appearing in eq 68 (for $\mathbf{C}'_2[\mathbf{C}_s]$). The factorization shown in Table 2 shows that these molecules of $\mathbf{C}'_2[\mathbf{C}_s]$-symmetry are ascribed to the $\mathbf{C}'_2$-promolecule of AABB-type listed in Figure 18.

Table 3. Factorization of Terms for $\mathbf{C}_s[\mathbf{C}_s]$ for Tetramethylallene

symmetry	term	factors	promolecule
$\mathbf{C}_s[\mathbf{C}_s]$	X^8Y^3Z	$(X^2Y)^3 \times X^2Z$	AAAB
	X^7Y^5	$(X^2Y)^3 \times XY^2$	AAAB
	X^7Y^4Z	$(X^2Y)^2 \times XY^2 \times X^2Z$	AABC
	$2X^7Y^3Z^2$	$(X^2Y)^3 \times XZ^2$	AAAB
		$X^2Y \times XY^2 \times (X^2Z)^2$	AABC
	$2X^6Y^5Z$	$(X^2Y)^3 \times Y^2Z$	AAAB
		$X^2Y \times (XY^2)^2 \times X^2Z$	AABC
	$3X^6Y^4Z^2$	$(X^2Y)^3 \times YZ^2$	AAAB
		$(X^2Y)^2 \times XY^2 \times XZ^2$	AABC
		$(X^2Y)^2 \times X^2Z \times Y^2Z$	AABC
	$2X^6Y^3Z^3$	$(X^2Y)^2 \times YZ^2 \times X^2Z$	AABC
		$X^2Y \times (X^2Z)^2 \times Y^2Z$	AABC
	$2X^5Y^5Z^2$	$(X^2Y)^2 \times XY^2 \times YZ^2$	AABC
		$(XY^2)^2 \times X^2Y \times XZ^2$	AABC
	$3X^5Y^4Z^3$	$(X^2Y)^2 \times XZ^2 \times Y^2Z$	AABC
		$(XY^2)^2 \times X^2Z \times XZ^2$	AABC
		$(X^2Z)^2 \times XY^2 \times Y^2Z$	AABC

Table 4. Factorization of Terms for $\mathbf{C}_1[\mathbf{C}_s]$ for 2,2-Dimethylpropane

symmetry	term	factors	promolecule
$\mathbf{C}_1[\mathbf{C}_s]$	$X^6Y^3Z^3$	$X^2Y \times X^2Z \times XY^2 \times XZ^2$	ABCD
	$X^5Y^5Z^2$	$X^2Y \times X^2Z \times XY^2 \times Y^2Z$	ABCD
	$X^5Y^4Z^3$	$X^2Y \times X^2Z \times XY^2 \times YZ^2$	ABCD
	$3X^4Y^4Z^4$	$X^2Y \times X^2Z \times YZ^2 \times Y^2Z$	ABCD
		$X^2Y \times XY^2 \times XZ^2 \times YZ^2$	ABCD
		$XY^2 \times Y^2Z \times XZ^2 \times X^2Z$	ABCD

The factorization of each term appearing in eq 69 (for $\mathbf{C}_s[\mathbf{C}_s]$) is shown in Table 3, where it is conducted in accord with the promolecules of AAAB- or AABC-type having $\mathbf{C}_s$-symmetry (Figure 18). Among the three $X^6Y^4Z^2$-derivatives listed in Figure 10, the first one belongs to the AAAB-type while the others belong to the AABC-type. This result is in agreement with the data concerning the term $X^6Y^4Z^2$ shown in Table 3.

All of the $X^4Y^4Z^4$-derivatives of tetramethylallene shown in Figure 7 correspond to the factorization into $(XYZ)^4$, each factor of which is ascribed to a chiral proligand (p) or its enantiomeric counterpart ($\bar{\text{p}}$). As a result, they correspond to the promolecules listed in Figure 18 as follows: the $\mathbf{C}_1[\mathbf{C}_1]$-derivative of Figure 7 to the $\mathbf{C}_1$-promolecule (ppp$\bar{\text{p}}$), the $\mathbf{C}'_2[\mathbf{C}_1]$-derivative to the $\mathbf{C}'_2$-promolecule (pppp), the $\mathbf{S}_4[\mathbf{C}_1]$-derivative to the $\mathbf{S}_4$-promolecule (p$\bar{\text{p}}$p$\bar{\text{p}}$), and the $\mathbf{D}_2[\mathbf{C}_1]$-derivative to the $\mathbf{D}_2$-promolecule (pppp).

On the other hand, the factorization of the term of $X^4Y^4Z^4$ for $\mathbf{C}_1[\mathbf{C}_s]$-molecules produces three combinations of factors, as found in Table 1. Each of these combinations corresponds to the three $\mathbf{C}_1$-promolecules of ABCD-type listed in Figure 18.

The three $X^4Y^4Z^4$-derivatives of tetramethylallene listed in the bottom row of Figure 9 are ascribed to the $\mathbf{C}'_2$-promolecule of AABB-type (Figure 18). The corresponding factorization is found in Table 2.

4.3. Factorization of Terms for Derivatives of 2,2-Dimethylpropane. To discuss the $\mathbf{C}_1[\mathbf{C}_s]$-derivatives depicted in Figure 13, the factorization of each term appearing in eq 89 is shown in Table 4, where it is conducted in accord with the promolecules of ABCD-type having $\mathbf{C}_1$-symmetry (Figure 19). This corresponds to the fact that chiral (pro)-molecules based on a methane skeleton contain four ligands

Table 5. Factorization of Terms for $\mathbf{C}_s[\mathbf{C}_s]$ for 2,2-Dimethylpropane

symmetry	term	factors	promolecule
$\mathbf{C}_s[\mathbf{C}_s]$	X^7Y^4Z	$(X^2Y)^2 \times XY^2 \times X^2Z$	AABC
	$X^7Y^3Z^2$	$X^2Y \times XY^2 \times (X^2Z)^2$	AABC
	X^6Y^5Z	$X^2Y \times (XY^2)^2 \times X^2Z$	AABC
	$2X^6Y^4Z^2$	$(X^2Y)^2 \times XY^2 \times XZ^2$	AABC
		$(X^2Y)^2 \times X^2Z \times Y^2Z$	AABC
	$2X^6Y^3Z^3$	$(X^2Y)^2 \times YZ^2 \times X^2Z$	AABC
		$X^2Y \times (X^2Z)^2 \times Y^2Z$	AABC
	$2X^5Y^5Z^2$	$(X^2Y)^2 \times XY^2 \times YZ^2$	AABC
		$(XY^2)^2 \times X^2Y \times XZ^2$	AABC
	$3X^5Y^4Z^3$	$(X^2Y)^2 \times XZ^2 \times Y^2Z$	AABC
		$(XY^2)^2 \times X^2Z \times XZ^2$	AABC
		$(X^2Z)^2 \times XY^2 \times Y^2Z$	AABC

Table 6. Factorization of Terms for $\mathbf{C}_{2v}[\mathbf{C}_s]$ for 2,2-Dimethylpropane

symmetry	term	factors	promolecule
$\mathbf{C}_{2v}[\mathbf{C}_s]$	$X^8Y^2Z^2$	$(X^2Y)^2 \times (X^2Z)^2$	AABB
	X^6Y^6	$(X^2Y)^2 \times (XY^2)^2$	AABB
	$X^6Y^4Z^2$	$(X^2Z)^2 \times (XY^2)^2$	AABB
	$3X^4Y^4Z^4$	$(X^2Y)^2 \times (YZ^2)^2$	AABB
		$(X^2Z)^2 \times (Y^2Z)^2$	AABB
		$(XY^2)^2 \times (XZ^2)^2$	AABB

Table 7. Factorization of Terms for $\mathbf{C}_{3v}[\mathbf{C}_s]$ for 2,2-Dimethylpropane

symmetry	term	factors	promolecule
$\mathbf{C}_{3v}[\mathbf{C}_s]$	X^8Y^3Z	$(X^2Y)^3 \times X^2Z$	AAAB
	X^7Y^5	$(X^2Y)^3 \times XY^2$	AAAB
	$X^7Y^3Z^2$	$(X^2Y)^3 \times XZ^2$	AAAB
	X^6Y^5Z	$(X^2Y)^3 \times Y^2Z$	AAAB
	$X^6Y^4Z^2$	$(X^2Y)^3 \times YZ^2$	AAAB

of different kinds. Note that each factor listed in Table 4 takes the form of the partition [2, 1, 0] for a $\mathbf{C}_s$-ligand, an example of which is listed in Figure 1 as an X^2Y-ligand.

The factorization of each term appearing in eq 90 ($\mathbf{C}_s[\mathbf{C}_s]$) is shown in Table 5, where it is conducted in accord with the promolecules of AABC-type having $\mathbf{C}_s$-symmetry (Figure 19). The two $X^6Y^3Z^3$-molecules with $\mathbf{C}_s[\mathbf{C}_s]$-symmetry depicted in Figure 14 illustrate the data in Table 5.

The factorization of each term appearing in eq 91 ($\mathbf{C}_{2v}[\mathbf{C}_s]$) is shown in Table 6. All of the results are in agreement with the promolecules of AABB-type having $\mathbf{C}_{2v}$-symmetry (Figure 19). The six molecules with $\mathbf{C}_{2v}[\mathbf{C}_s]$-symmetry depicted in Figure 15 illustrate the data in Table 6, though their formulas are different from one another.

The factorization of each term appearing in eq 92 ($\mathbf{C}_{3v}[\mathbf{C}_s]$) is shown in Table 7. The five molecules with $\mathbf{C}_{3v}[\mathbf{C}_s]$-symmetry depicted in Figure 16 illustrate the data in Table 7, though their formulas are different from one another. They are in accord with the promolecules of AAAB-type having $\mathbf{C}_{3v}$-symmetry (Figure 19).

The $X^4Y^4Z^4$-derivatives of 2,2-dimethylpropane shown in Figure 12 correspond to the factorization into $(XYZ)^4$. The derivatives listed in Figure 12 correspond to the promolecules shown in Figure 19 as follows: the $\mathbf{C}_3[\mathbf{C}_1]$-derivative to the $\mathbf{C}_3$-promolecule (ppp$\bar{\text{p}}$), the $\mathbf{S}_4[\mathbf{C}_1]$-derivative to the $\mathbf{S}_4$-promolecule (p$\bar{\text{p}}$p$\bar{\text{p}}$), and the $\mathbf{T}[\mathbf{C}_1]$-derivative to the $\mathbf{T}$-promolecule (pppp). It should be noted that the $\mathbf{C}_3[\mathbf{C}_1]$-derivative of 2,2-dimethylpropane (Figure 12) is related to the $\mathbf{C}_1[\mathbf{C}_1]$-derivative of tetramethylallene (Figure 7), both $\mathbf{C}_2'[\mathbf{C}_1]$- and $\mathbf{S}_4[\mathbf{C}_1]$-derivatives of tetramethylallene (Figure 7) are related to the $\mathbf{S}_4[\mathbf{C}_1]$-derivative 2,2-dimethylpropane (Figure 12), and the $\mathbf{T}[\mathbf{C}_1]$-derivative of 2,2-dimethylpropane (Figure 12) is related to the $\mathbf{D}_2[\mathbf{C}_1]$-derivative of tetramethylallene (Figure 7).

The factorization of the term of $X^4Y^4Z^4$ for $\mathbf{C}_1[\mathbf{C}_s]$-molecules produces three combinations of factors, as found in Table 4. Note that each of these combinations corresponds to one $\mathbf{C}_1$-promolecule of ABCD-type shown in Figure 19. The concrete forms of these derivatives are found in the bottom row of Figure 13. Compare these combinations with the ones listed in the bottom of Table 1.

The three $X^4Y^4Z^4$-derivatives of 2,2-dimethylpropane listed in the bottom row of Figure 15 are ascribed to the $\mathbf{C}_{2v}$-promolecule of AABB-type (Figure 19). The corresponding factorization is found in Table 6. Compare the $\mathbf{C}_{2v}[\mathbf{C}_s]$, $X^4Y^4Z^4$-derivatives of 2,2-dimethylpropane (Figure 15) with $\mathbf{C}_2'[\mathbf{C}_s]$, $X^4Y^4Z^4$-derivatives of tetramethylallene (Figure 9). The relationship between them comes from the fact that the C_2-axis and the dihedral $\mathbf{C}_2'$-axis of the point group $\mathbf{D}_{2d}$ (tetramethylallene) coincide with each other so as to give the C_2-axis of the point group $\mathbf{T}_d$ (2,2-dimethylpropane) during the symmetrization.

5. CONCLUSION

A new method for enumerating nonrigid isomers with rotatable ligands has been developed so as to take account of the symmetries of the ligands. The method is an extention of the partial-cycle-index method so that it is applicable to the enumeration of isomers as molecules and as promolecules. The factorization of terms in generating functions has been discussed. Thereby, the method is shown to be capable of examining the relationship between promolecules and molecules quantitatively.

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(38) We use the word "methyl ligand" in place of "methyl group" because the word "group" is used as a mathematical term in this paper.
(39) The inverses of the mark tables have been reported in Appendix B of ref 32.
(40) The USCI tables have been reported in Appendix D of ref 32.
(41) The USCI-CF tables have been reported in Appendix E of ref 32.

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