Combinatorial Enumeration of Nonrigid Isomers with Given Ligand Symmetries on the Basis of Promolecules with A Subsymmetry of $D_{\infty h}$

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Received July 21, 1999

To enumerate nonrigid isomers with given ligand symmetries on the basis of a $\mathbf{D}_{\infty h}$ skeleton, the concept of extended partial cycle indices (extended PCIs) proposed newly has been combined with the concept of promolecules proposed previously. The infinite nature of the $\mathbf{D}_{\infty h}$-group is concealed by adopting the factor group of finite order, $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ ($=\mathbf{K}$). Thus, the partial cycle indices with chirality fittingness (PCI-CFs) for the factor group **K** are calculated and combined with the PCIs for ligand symmetries so as to give the extended PCIs for various itemized enumurations. This method has been successfully applied to the enumeration of ethane derivatives, where the full enumeration based on **K** has been compared with partial enumerations based on **K** as well as with those based on the factor group $\mathbf{C}_{\infty h}/\mathbf{C}_{\infty}$ ($=\mathbf{K}_3 \subset \mathbf{K}$). Each term of the resulting generating functions has been factorized into a pair of factors to represent ligand constitutions. Thereby, the depiction of resulting molecules can be conducted systematically so as to provide the maps of ethane derivatives corresponding to all of the substitution types.

1. INTRODUCTION

Combinatorial enumeration of isomers has been one of the dominant chemical fields in which group theory plays an important role.[1,2] Pólya's theorem[3,4] and related group-theoretical tools have been widely used in such chemical combinatorics, as summarized in excellent reviews[5−8] and books.[1,2,4,9−11] They have been originally applied to the enumeration of rigid isomers.[12,13] As a matter of course, they can be applied to the enumeration of such nonrigid isomers as ethane derivatives, if the conformation of such a nonrigid skeleton as ethane is considered to be fixed so as to give a staggered conformer of $\mathbf{D}_{3d}$-symmetry or an eclipsed one of $\mathbf{D}_{3h}$-symmetry. This methodology, however, provides the number of conformers but not the number of isomers. For example, the anti and gauche forms of 1,2-dichloroethane, which are distinct conformers under the action of $\mathbf{D}_{3d}$-symmetry, both correspond to one isomer (1,2-dichloroethane) as a compound if we take account of the number of dichloroethanes (e.g., 1,2-dichloroethane and 1,1-dichloroethane) without considering their conformations.

The ring-flipping of a cyclohexane ring causes another type of isomerism involving conformers. The enumerations of such cyclohexane isomers have been studied by means of a kind of extended groups with ring-flipping operators or equivalents.[14−16]

In order to enumerate nonrigid molecules with rotatable ligands, Pólya's theorem has been combined with the concept of "coronas".[3,4] The coronas are essentially equivalent to wreath products, which have been used to count stereoisomers and positional isomers in a generalized wreath product method.[17] An alternative method has been based on the concept of the full covering group,[18] which is combined with Pólya's theorem to enumerate ethane derivatives. These methods have been restricted within the enumeration of nonrigid isomers with given formulas but not with symmetries. This is because there have been no convenient methods for characterizing the symmetries of non-rigid isomers under unfixed conditions. For example, the anti form of 1,2-dichloroethane has been ascribed to the point group $\mathbf{C}_s$ as a fixed conformer, but in turn the symmetry of rotatable 1,2-dichloroethane has not been specified in terms of the conventional point-group theory.

We have developed the subduced-cycle-index (SCI) method for the enumeration of rigid isomers.[19] The SCI method has merit over Pólya's theorem and others so that enumeration results based on the SCI method are itemized with respect to molecular formulas as well as to symmetries. For example, the SCI method has been able to predict that there are two $\mathbf{C}_1$-isomers, one $\mathbf{C}_2$-isomer, four $\mathbf{C}_s$-isomers, and two $\mathbf{C}_{2v}$-isomers for dichloroadamantanes ($C_{10}H_{14}Cl_2$).[20] Thus, the result has clarified both the formulas and symmetries of the isomers.[21] On the other hand, Pólya's theorem and the related methods have given only the gross number, i.e., nine for the isomers of dichloroadamantanes.[20]

The SCI method has later been applied to the enumeration of non-rigid isomers with given formulas and symmetries, where the merit described above has been maintained, but only "in part".[22−24] The enumeration of non-rigid isomers by the SCI method has presumed a model in which a set of ligands occupies the positions of a skeleton belonging to a given symmetry. However, the symmetry of each ligand in the model has been taken into consideration only in the form of chirality/achirality, though the full symmetry of the ligand has been considered during the process of the enumeration. For example, this method has predicted that there are one $\mathbf{C}_{2v}$-isomer (i.e., $C(CH_3)_2(CH_2X)_2$) and one $\mathbf{C}_{3v}$-isomer (i.e., $C(CH_3)_3(CHX_2)$) for disubstituted derivatives ($C_5H_{10}X_2$) of tetramethylmethane.[22] Note that the symmetries $\mathbf{C}_{2v}$ and $\mathbf{C}_{3v}$

10.1021/ci990074y CCC: $19.00
Published on Web 01/28/2000

are concerned with the skeletal symmetries but not with the ligand symmetries for CH_3, CH_2X, and CHX_2.

This situation has been revealed more clearly by adopting the concept of promolecules,[25] where an alternative model (promolecule) is presumed so that a set of proligands (structureless three-dimensional objects with chirality/achirality) occupies the positions of a skeleton belonging to a given symmetry. A simple method in which ligands have been enumerated with respect only to chirality/achirality has been developed as an application of characteristic monomials.[26] By virtue of these treatments, the above-described isomers $C(CH_3)_2(CH_2X)_2$ and $C(CH_3)_3(CHX_2)$ have been represented by the formulas CA_2B_2 and CA_3D, where the ligands CH_3, CH_2X, and CHX_2 have been replaced by the proligands A, B, and D. Then, the resulting promolecules CA_2B_2 and CA_3D have been recognized to belong to $\mathbf{C}_{2v}$ and $\mathbf{C}_{3v}$. Thus, the word "in part" at the top of the preceding paragraph means that the ligand symmetries have been not fully treated, though the skeleton symmetries have been taken into full consideration in the form of the symmetries of the promolecules.

To apply the concept of promolecules to the enumeration of ethane derivatives, we have treated a promolecule of $\mathbf{D}_{\infty h}$, the order of which is infinite.[27] We have been able to conceal the infinite nature of the group $\mathbf{D}_{\infty h}$ by introducing a factor group $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$. Thereby, we apply the SCI method for enumerating nonrigid isomers to the enumeration of ethane derivatives[27] and later to the enumeration of ferrocene derivatives.[26] These enumerations have also laid stress on the chirality/achirality of each ligand, but not on its full symmetry, though skeleton symmetries, in turn, have been taken into full consideration. It follows that a more elaborate enumeration is desirable, where the point group of the ligand is taken into full consideration.

The target of the present work is to develop a more elaborate method for enumerating nonrigid isomers associated with a promolecule of $\mathbf{D}_{\infty h}$, where the partial-cycle-index (PCI) method[28] will be shown to be more suitable for such enumerations than the SCI method. Afterward, the factorization of terms in resulting generating functions will be discussed to reveal the relationship between promolecules and molecules.

2. RESULTS

2.1. Mathematical Foundations. Let $\mathbf{H}$ be a point group assigned to a rotatable ligand (or substituent). Suppose the positions (Δ) of the rotatable ligand are divided into orbits (sets of equivalent positions) that are governed by a set of coset representations, $\sum_{l=1}^{t}\gamma_l\mathbf{H}(/\mathbf{H}_l)$. From a given set ($\mathbf{X}$) of atoms, an appropriate atom set containing ν_1X_1, ν_2X_2, ..., and $\nu_{|\mathbf{X}|}X_{|\mathbf{X}|}$ is selected to be placed on the positions (Δ), giving a substituted ligand. The mode of the selection corresponds to the partition $[\nu_1, \nu_2, ..., \nu_{|\mathbf{X}|}]$ (=$[\nu]$), where we have nonnegative integers satisfying

$$\nu_1 + \nu_2 + \cdots + \nu_{|\mathbf{X}|} = |\Delta| \tag{1}$$

Then, the substituted ligand has the weight (formula) represented by

$$W_{[\nu]} = X_1^{\nu 1} X_2^{\nu 2} \cdots X_{|\mathbf{X}|}^{\nu|\mathbf{X}|} \tag{2}$$

For example, a methyl ligand belongs to the point group $\mathbf{H} = \mathbf{C}_{3v}$, where the set of its three hydrogens constructs an orbit Δ governed by the coset representation $\mathbf{C}_{3v}(/\mathbf{C}_s)$. The symbol $\mathbf{C}_{3v}(/\mathbf{C}_s)$ indicates that the global symmetry of the methyl ligand is $\mathbf{C}_{3v}$ while the local symmetry for each hydrogen is $\mathbf{C}_s$. When two hydrogens of the methyl are replaced by two Xs, we have a ligand represented by CHX_2. This means that we select 2X and H from $\mathbf{X} = \{X, H\}$ ($X_1 = X$ and $X_2 = H$, and $\nu_1 = 2$ and $\nu_2 = 1$ for eq 1) and that the weight (eq 2) is determined to be $W_{[21]} = X^2H^1$.

The resulting ligand CHX_2 is determined to belong to the point group $\mathbf{C}_s$. The two X's construct an orbit governed by $\mathbf{C}_s(/\mathbf{C}_1)$, while the one hydrogen constructs a one-membered orbit governed by $\mathbf{C}_s(/\mathbf{C}_s)$. The process of converting CH_3 into CHX_2 is regarded as the desymmetrization from $\mathbf{C}_{3v}$ to $\mathbf{C}_s$, which is ascribed to the subduction represented by

$$\mathbf{C}_{3v}(/\mathbf{C}_s) \downarrow \mathbf{C}_s = \mathbf{C}_s(/\mathbf{C}_s) + \mathbf{C}_s(/\mathbf{C}_1)$$

The process described in this paragraph can be generalized as follows so as to be applied to cases in which Δ is divided into several orbits.

For the group $\mathbf{H}$, we have precalculated the subduction into the subgroup, i.e., $\mathbf{H}(\mathbf{H}_l) \downarrow \mathbf{H}_m$, which are transformed to the corresponding unit subduced cycle index (USCI). They are tabulated in the form of a subduction table and a USCI table for the group $\mathbf{H}$.[29] The USCIs are collected according to the subduction

$$\sum_{l=1}^{t}\gamma_l\mathbf{H}(/\mathbf{H}_l) \downarrow \mathbf{H}_m \tag{3}$$

to give a subduced cycle index (SCI) for the subgroup $\mathbf{H}_m$, which is represented by the symbol $\mathrm{ZI}(\mathbf{H}_m; s_{d_{mn}})$. Thereby, we arrive at the partial cycle index (PCI) for $\mathbf{H}_m$ as follows[30]

$$\mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}}) = \sum_{m=1}^{t}\bar{m}_{ml}^{(\mathbf{H})}\mathrm{ZI}(\mathbf{H}_m; s_{d_{mn}}) \tag{4}$$

for $m = 1, 2, ..., t$, where $\bar{m}_{ml}^{(\mathbf{H})}$ is the ml-element of the inverse mark table (M^{-1}) for $\mathbf{H}$.

Let $A_{m\nu}$ be the number of ligands with the weight $W_{[\nu]}$ and a given symmetry $\mathbf{H}_m$ ($\subset\mathbf{H}$). A generating function for given $A_{m\nu}$ is represented by

$$\sum_{[\nu]}A_{m\nu}\mathrm{W}_{\nu} = \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}}) \tag{5}$$

where the dummy variables in the PCI are replaced by atom inventories

$$s_{d_{mn}} = X_1^{s_{dmn}} + X_2^{s_{dmn}} + \cdots + X_{|\mathbf{X}|}^{s_{dmn}} \tag{6}$$

Let us consider a skeleton of $\mathbf{D}_{\infty h}$-symmetry. The skeleton is considered to belong to the factor group of order 4 represented by

$$\mathbf{K} = \mathbf{D}_{\infty h}/\mathbf{C}_{\infty} = \{\mathbf{C}_{\infty}, \mathbf{C}_{\infty}C_2, \mathbf{C}_{\infty}\sigma_v, \mathbf{C}_{\infty}\sigma_h\} \tag{7}$$

where the generator of $\mathbf{C}_{\infty}$ is an infinite rotation axis through the long axis of the skeleton.[27] Note that $\mathbf{K}$ is isomorphic to

the point group $\mathbf{C}_{2v}$ and contains the subgroups represented by

$$\mathbf{K}_1 = \mathbf{C}_\infty/\mathbf{C}_\infty = \{\mathbf{C}_\infty\} \tag{8}$$

$$\mathbf{K}_2 = \mathbf{D}_\infty/\mathbf{C}_\infty = \{\mathbf{C}_\infty, \mathbf{C}_\infty C_2\} \tag{9}$$

$$\mathbf{K}_3 = \mathbf{C}_{\infty v}/\mathbf{C}_\infty = \{\mathbf{C}_\infty, \mathbf{C}_\infty \sigma_v\} \tag{10}$$

$$\mathbf{K}_4 = \mathbf{C}_{\infty h}/\mathbf{C}_\infty = \{\mathbf{C}_\infty, \mathbf{C}_\infty \sigma_h\} \tag{11}$$

$$\mathbf{K}_5 = \mathbf{K} \tag{12}$$

The two positions of the skeleton (Ω) construct a two-membered orbit, which is governed by the coset representation $\mathbf{K}(/\mathbf{K}_3)$, where we have $|\Omega| = |\mathbf{K}|/|\mathbf{K}_3| = 2$. Since the skeleton of the factor group $\mathbf{K}$ can be regarded as a rigid object, the partial cycle index with chirality fittingness (PCI-CF) defined for rigid molecules is applicable to the present $\mathbf{K}$-skeleton.[31] Thereby, we have the PCI-CF (denoted by the symbol PCIC) for $\mathbf{K}_i$ as follows

$$\mathrm{PCIC}(\mathbf{K}_i; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) = \sum_{j=1}^{s} \bar{m}_{jk}^{(\mathbf{K})} \mathrm{ZIC}(\mathbf{K}_j; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) \tag{13}$$

for $i = 1, 2, ..., s$, where $\mathrm{ZIC}(\mathbf{K}_j; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}})$ is a subduced cycle index with chirality fittingness (SCI-CF) for the subgroup $\mathbf{K}_j$. The SCI-CF shown in eq 13 has been originally aimed at cases in which ligand inventories ($a_{d_{jk}}$, $b_{d_{jk}}$, and $C_{d_{jk}}$) are concerned with the chirality/achirality of ligands (see def 3 of ref 27). However, they are applicable to the present case if appropriate ligand inventories are used so as to take ligand symmetries (not chirality/achirality) into full consideration.

Supposed that a ligand with the weight $W_{[\nu]}^{(\omega)}$ (eq 2) and the symmetry $\mathbf{H}_m^{(\omega)}$ is placed on a position ω of Ω to give a total weight

$$W_{[\nu']} = \prod_{\omega} W_{[\nu]}^{(\omega)} = X_1^{\nu'_1} X_2^{\nu'_2} \cdots X_{|\mathbf{X}|}^{\nu'_{|\mathbf{X}|}} \tag{14}$$

where $[\nu'_1, \nu'_2, \cdots, \nu'_{|\mathbf{X}|}]$ (=$[\nu']$) represents a partition of $|\Delta| \cdot |\Omega|$, where we have

$$\nu'_1 + \nu'_2 + \cdots + \nu'_{|\mathbf{X}|} = |\Delta| \cdot |\Omega| \tag{15}$$

Let $B_{i\nu'}$ be the number of such isomers with the weight $W_{[\nu']}$ as well as with a given symmetry $\mathbf{K}_i$, where $\mathbf{H}_m^{(\omega)}$ is selected an achiral subset ($\mathbf{H}^{(\mathrm{a})}$) and/or a chiral one ($\mathbf{H}^{(\mathrm{c})}$) of $\mathbf{H}$. The symmetry of a resulting isomer is represented by the symbol $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]$. The dummy variables in the PCI in eq 13 are replaced by ligand inventories

$$a_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(\mathrm{a})}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \tag{16}$$

$$b_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(\mathrm{a})}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) + 2 \sum_{\mathbf{H}_m \in \mathbf{H}^{(\mathrm{c})}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \tag{17}$$

$$c_{d_{jk}} = \sum_{\mathbf{H}_m \in \mathbf{H}^{(\mathrm{a})}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) + 2 \sum_{\mathbf{H}_m \in \mathbf{H}^{(\mathrm{c})}} \mathrm{PCI}(\mathbf{H}_m; s_{d_{mn}d_{jk}}) \tag{18}$$

Thereby, we obtain extended partial cycle indices (extended PCIs) for every symmetry $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]$ as follows

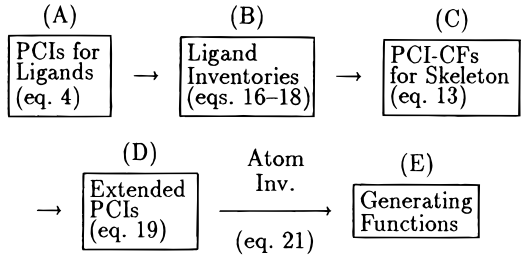


Figure 1. Procedure for enumeration.

$$\overline{\mathrm{PCI}}(\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]; s_{d_{mn}d_{jk}}) = \mathrm{PCIC}(\mathbf{K}_i; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) \tag{19}$$

where the dummy variables $a_{d_{jk}}$, $b_{d_{jk}}$, and $c_{d_{jk}}$ are replaced by another set of dummy variables, $s_{d_{mn}d_{jk}}$. The symbol $\overline{\mathrm{PCI}}$ is used to designate such extended PCIs. As a result, a generating function for $B_{i\nu'}$ isomers with the weight $W_{[\nu']}$ and the symmetry $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]$ is represented by

$$\sum_{[\nu']} B_{i\nu'} W_{[\nu']} = \overline{\mathrm{PCI}}(\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]; s_{d_{mn}d_{jk}}) \tag{20}$$

where the dummy variables in the extended PCIs are replaced by extended atom inventories

$$s_{d_{mn}d_{jk}} = X_1^{s_{d_{mn}d_{jk}}} + X_2^{s_{d_{mn}d_{jk}}} + \cdots + X_{|\mathbf{X}|}^{s_{d_{mn}d_{jk}}} \tag{21}$$

The symbol $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}]$ is used to indicate that ligand symmetries are selected from $\mathbf{H}^{(\mathrm{a})}$ and $\mathbf{H}^{(\mathrm{c})}$. When either $\mathbf{H}^{(\mathrm{a})}$ or $\mathbf{H}^{(\mathrm{c})}$ is selected, the symbol $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}]$ or $\mathbf{K}_i[\mathbf{H}^{(\mathrm{c})}]$ is also permitted. Further, the symbol $\mathbf{K}_i[\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}; \mathbf{H}^{(\mathrm{a}')}, \mathbf{H}^{(\mathrm{c}')}]$ is used to designate cases to which different sets of ligand symmetries, $\{\mathbf{H}^{(\mathrm{a})}, \mathbf{H}^{(\mathrm{c})}\}$ and $\{\mathbf{H}^{(\mathrm{a}')}, \mathbf{H}^{(\mathrm{c}')}\}$, are applied.

Figure 1 summarizes the present procedure of deriving generating functions for isomer enumeration. The ligand inventories (Figure 1B, eqs 16−18) are polynomials of dummy variables (s_d). The introduction of the ligand inventories into the PCI-CFs for the skeleton (Figure 1C, eq 13) produces the extended PCIs (Figure 1D, eq 19), which are also polymomials of dummy variables (s_d). It should be emphasized here that the generation of generating functions (Figure 1E) is carried out in the last step by the introduction of atom inventories such as eq 21 into the extended PCIs. This feature is in sharp contrast to that of the previous method,[27] in which the generation of generating functions is carried out in an intermediate step corresponding to Figure 1B or C.

2.2. Factor Groups for $\mathbf{D}_{\infty h}$. In the present enumeration, we do not deal with the $\mathbf{D}_{\infty h}$-group directly, but adopt a factor group $\mathbf{D}_{\infty h}/\mathbf{C}_\infty$ (=$\mathbf{K}$) instead. This treatment becomes more effective by combining the concept of promolecules, though the mathematical formulation described in the preceding section does not explicitly presume intermediate promolecules. This is because each subgroup ($\mathbf{K}_1$, $\mathbf{K}_2$, $\mathbf{K}_3$, $\mathbf{K}_4$, or $\mathbf{K}_5$) of the factor group can be assigned to an appropriate promolecule derived from a $\mathbf{D}_{\infty h}$-skeleton. There are six types of such promolecules,[27] which are depicted in Figure 2, where the symbols A and B represent achiral proligands and the symbols p and q represent chiral proligands. A symbol with an overline (e.g., $\bar{\mathrm{p}}$) is used to represent the enantiomeric counterpart of a proligand without an overline (e.g., p).

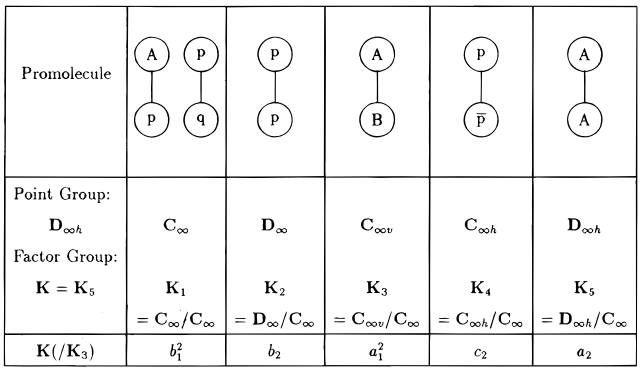


Figure 2. Promolecules of $\mathbf{D}_{\infty h}$ and subgroups of factor group **K**.

2.3. Full Enumeration of Ethane Derivatives. The full enumeration of ethane derivatives follows the procedure shown in Figure 1. Since the PCI-CFs for the **K**-skeleton can be commonly used for the present cases of enumeration (Figure 1C), they are calculated in advance in subsection 2.3.1.

2.3.1. PCI-CFs for K-Skeleton. Since the two positions of the **K**-skeleton are ascribed to the coset representation $\mathbf{K}(/\mathbf{K}_3)$, we obtain the set of subduced cycle indices with chirality fittingness (SCI-CFs) by using the data collected in Table III of ref 27, i.e., $(b_1^2, b_2, a_1^2, c_2, a_2)$, which are cited in the bottom of Figure 2. This formal row vector is multiplied by the inverse of the mark table of **K**

$$M_{(\mathbf{K})}^{-1} = (\bar{m}_{jk}^{(\mathbf{K})}) = \begin{pmatrix} {}^1/_4 & 0 & 0 & 0 & 0 \\ -{}^1/_4 & {}^1/_2 & 0 & 0 & 0 \\ -{}^1/_4 & 0 & {}^1/_2 & 0 & 0 \\ -{}^1/_4 & 0 & 0 & {}^1/_2 & 0 \\ {}^1/_2 & -{}^1/_2 & -{}^1/_2 & -{}^1/_2 & 1 \end{pmatrix} \quad (22)$$

in accord with eq 13 to give the following PCI-CFs for every subgroup of **K**:

$$\mathrm{PCIC}(\mathbf{K}_1; a_d, b_d, c_d) = \frac{1}{4}b_1^2 - \frac{1}{4}b_2 - \frac{1}{4}a_1^2 - \frac{1}{4}c_2 + \frac{1}{2}a_2 \quad (23)$$

$$\mathrm{PCIC}(\mathbf{K}_2; a_d, b_d, c_d) = \frac{1}{2}b_2 - \frac{1}{2}a_2 \quad (24)$$

$$\mathrm{PCIC}(\mathbf{K}_3; a_d, b_d, c_d) = \frac{1}{2}a_1^2 - \frac{1}{2}a_2 \quad (25)$$

$$\mathrm{PCIC}(\mathbf{K}_4; a_d, b_d, c_d) = \frac{1}{2}c_2 - \frac{1}{2}a_2 \quad (26)$$

$$\mathrm{PCIC}(\mathbf{K}; a_d, b_d, c_d) = a_2 \quad (27)$$

It should be noted that the dummy variables a_d, b_d, and c_d are, respectively, related to homospheric hemispheric, and enantiopheric orbits.[24]

2.3.2. PCIs for Methyl Ligands. A methyl ligand has three hydrogens that are governed by a coset representation $\mathbf{C}_{3v}(/\mathbf{C}_s)$. Hence, we obtain the set of subduced cycle indices (SCIs), s^3_1, s_1s_2, s_3, s_3), which is equal to the set of USCIs for $\mathbf{C}_{3v}(/\mathbf{C}_s)$. This alignment is formally multiplied by the inverse of the mark table of $\mathbf{C}_{3v}$ to give the following PCIs for every subgroup of $\mathbf{C}_{3v}$:

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

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

$$\mathrm{PCI}(\mathbf{C}_3; s_{d'}) = \frac{1}{2}s_3 - \frac{1}{2}s_3 = 0 \quad (30)$$

$$\mathrm{PCI}(\mathbf{C}_{3v}; s_{d'}) = s_3 \quad (31)$$

Note that the $\mathrm{PCI}(\mathbf{C}_3; s_{d'})$ (eq 30) vanishes to zero in agreement with the fact that there exist no $\mathbf{C}_3$-ligands under the present conditions of enumeration.

2.3.3. Ligand Inventories and Extended PCIs. All Ligand Symmetries. Let us now consider all of the subgroups of $\mathbf{C}_{3v}$ as ligand symmetries. This means that we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ for the achiral subgroups and $\mathbf{H}^{(c)} = \{\mathbf{C}_1, \mathbf{C}_3\}$ for the chiral subgroups. As a result, we have the corresponding ligand inventories

$$a_d = \mathrm{PCI}(\mathbf{C}_s; s_{dd'}) + \mathrm{PCI}(\mathbf{C}_{3v}; s_{dd'}) = s_ds_{2d} \quad (32)$$

$$b_d = c_d = \mathrm{PCI}(\mathbf{C}_s; s_{dd'}) + 2\mathrm{PCI}(\mathbf{C}_1; s_{dd'}) + \mathrm{PCI}(\mathbf{C}_{3v}; s_{dd'}) + 2\mathrm{PCI}(\mathbf{C}_3; s_{dd'}) = {}^1/_3s_d^3 + {}^2/_3s_{3d} \quad (33)$$

by applying eqs 16−18 to the present case. In light of eq 19, these ligand inventories are introduced into eqs 23−27 to give

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}, \mathbf{H}^{(c)}]; s_d) = \frac{1}{36}(s_1^3 + 2s_3 - 3s_1s_2)(s_1^3 + 2s_3 + 3s_1s_2) - \frac{1}{6}(s_2^3 + 2s_6 - 3s_2s_4) \quad (34)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_2[\mathbf{H}^{(a)}, \mathbf{H}^{(c)}]; s_d) = \frac{1}{6}(s_2^3 + 2s_6 - 3s_2s_4) \quad (35)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}, \mathbf{H}^{(c)}]; s_d) = \frac{1}{2}(s_1^2 s_2^2 - s_2s_4) \quad (36)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_4[\mathbf{H}^{(a)}, \mathbf{H}^{(c)}]; s_d) = \frac{1}{6}(s_2^3 + 2s_6 - 3s_2s_4) \quad (37)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_4[\mathbf{H}^{(a)}, \mathbf{H}^{(c)}]; s_d) = s_2s_4 \quad (38)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \{\mathbf{C}_1, \mathbf{C}_3\}$.

Suppose that six atoms are selected from the set represented by

$$\mathbf{X} = \{U, V, W, X, Y, Z\} \quad (39)$$

Then, an atom inventory is calculated to be

$$s_d = U^d + V^d + W^d + X^d + Y^d + Z^d \quad (40)$$

This inventory is introduced into the extended PCIs represented by eqs 34−38. After the expansion of the resulting equations, we have the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)},\mathbf{H}^{(c)}]} = (U^4VW + U^4VX + \cdots) + (U^3V^2W + U^3V^2X + \cdots) + 4(U^3VWX + U^3VWY + \cdots) + 4(U^2V^2WX + U^2V^2WY + \cdots) + 10(U^2VWXY + U^2VXYZ + \cdots) + 20UVWXYZ \quad (41)$$

$$f_{\mathbf{K}_2[\mathbf{H}^{(a)},\mathbf{H}^{(c)}]} = (U^2V^2W^2 + U^2V^2X^2 + ...) \quad (42)$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)},\mathbf{H}^{(c)}]} = (U^5V + U^5W + \cdots) \quad (43)$$

$$+ (U^4V^2 + U^4W^2 + \cdots) + (U^4VW + U^4VX + \cdots) + 2(U^3V^3 + U^3W^3 + \cdots) + 2(U^3V^2W + U^3V^2X + \cdots) + 3(U^2V^2W^2 + U^2V^2X^2 + \cdots) + 2(U^2V^2WX + U^2V^2WY + \cdots) \quad (44)$$

$$f_{\mathbf{K}_4[\mathbf{H}^{(a)},\mathbf{H}^{(c)}]} = (U^2V^2W^2 + U^2V^2X^2 + \cdots) \quad (45)$$

$$f_{\mathbf{K}_5[\mathbf{H}^{(a)},\mathbf{H}^{(c)}]} = (U^6 + V^6 + \cdots) + (U^4V^2 + U^4W^2 + \cdots) \quad (46)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \{\mathbf{C}_1, \mathbf{C}_3\}$. Each of the equations is concerned with the symmetry, $\mathbf{K}_1$, $\mathbf{K}_2$, $\mathbf{K}_3$, $\mathbf{K}_4$, or $\mathbf{K}_5$ (=$\mathbf{K}$). The coefficient of the term $U^uV^vW^wX^xY^yZ^z$ (or the partition [u, v, w, x, y, z]) in each equation represents the number of isomers with the formula $U^uV^vW^wX^xY^yZ^z$ for the respective symmetry. It should be noted that a set of terms (monomials) in each pair of parentheses have the same coefficient, since the variables U to Z can be permuted without changing the respective generating functions. Hence, we adopt as a representative a term $U^uV^vW^wX^xY^yZ^z$ that satisfies $u \geq v \geq w \geq x \geq y \geq z$ for simplicity sake. For example, the term U^4VW or the partition [4, 1, 1, 0, 0, 0] is selected from a set of U^4VW (or [4, 1, 1, 0, 0, 0]), U^4VX (or [4, 1, 0, 1, 0, 0]), U^4VY (or [4, 1, 0, 0, 1, 0]), etc.

The results represented by eqs 41−46 are equivalent to the ones reported in ref 27 (eq 36), though the latter were given in the form of a matrix calculated by the SCI method. It should be noted that, as the result of adopting all ligand symmetries, these enumeration results are not itemized with respect to ligand symmetries. In other words, only the chirality/achirality of each ligand is taken into consideration.

Chiral Ligand Symmetries. To obtain itemized enumerations with respect to ligand symmetries, let us next consider the chiral subgroups of $\mathbf{C}_{3v}$. This means that we place $\mathbf{H}^{(a)} = \varnothing$ and $\mathbf{H}^{(c)} = \{\mathbf{C}_1, \mathbf{C}_3\}$. The enumeration is equivalent to the one in which only the $\mathbf{C}_1$-subgroup is taken into consideration, since eq 30 for $\mathbf{C}_3$ vanishes into zero. Obviously, isomers to be enumerated in this condition are categorized into p−q, p−p, or p−$\bar{\text{p}}$ shown in Figure 2.

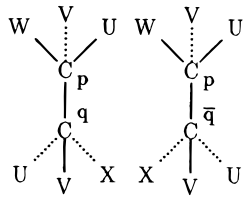


Figure 3. Diastereomers with $\mathbf{K}_1[\mathbf{C}_1]$ and U^2V^2WX.

By using eq 28, we have the corresponding ligand inventories as follows:

$$a_d = 0 \quad (47)$$

$$b_d = c_d = 2\left(\frac{1}{6}s_d^3 - \frac{1}{2}s_ds_{2d} + \frac{1}{3}s_{3d}\right) = \frac{1}{3}(s_d^3 - 3s_ds_{2d} + 2s_{3d}) \quad (48)$$

They are introduced into eqs 23−27 to give the following extended PCIs for every subgroup

$$\overline{\text{PCI}}(\mathbf{K}_1[\mathbf{C}_1]; s_d) = \frac{1}{36}(s_1^3 - 3s_1s_2 + 2s_3)^2 - \frac{1}{6}(s_2^3 - 3s_2s_4 + 2s_6) \quad (49)$$

$$\overline{\text{PCI}}(\mathbf{K}_2[\mathbf{C}_1]; s_d) = \frac{1}{6}(s_2^3 - 3s_2s_4 + 2s_6) \quad (50)$$

$$\overline{\text{PCI}}(\mathbf{K}_3[\mathbf{C}_1]; s_d) = 0 \quad (51)$$

$$\overline{\text{PCI}}(\mathbf{K}_4[\mathbf{C}_1]; s_d) = \frac{1}{6}(s_2^3 - 3s_2s_4 + 2s_6) \quad (52)$$

$$\overline{\text{PCI}}(\mathbf{K}_5[\mathbf{C}_1]; s_d) = 0 \quad (53)$$

where the symbol $[\mathbf{C}_1]$ for the ligand symmetry is in place of $[\mathbf{H}^{(c)}]$.

Let us select six atoms from the set $\mathbf{X}$ (eq 39). Then, the atom inventory (eq 40) is introduced into the extended PCIs of nonzero value (eqs 49−53). After the expansion of the resulting equations, we have the following generating functions:

$$f_{\mathbf{K}_1[\mathbf{C}_1]} = 2(U^2V^2WX + U^2V^2WY + \cdots) + 6(U^2VWXY + U^2VXYZ + \cdots) + 20UVWXYZ \quad (54)$$

$$f_{\mathbf{K}_2[\mathbf{C}_1]} = (U^2V^2W^2 + U^2V^2X^2 + \cdots) \quad (55)$$

$$f_{\mathbf{K}_3[\mathbf{C}_1]} = 0 \quad (56)$$

$$f_{\mathbf{K}_4[\mathbf{C}_1]} = (U^2V^2W^2 + U^2V^2X^2 + \cdots) \quad (57)$$

$$f_{\mathbf{K}_5[\mathbf{C}_1]} = 0 \quad (58)$$

According to the term U^2V^2WX in eq 54 (for $\mathbf{K}_1$-symmetry), there are two molecules of U^2V^2WX, as found in Figure 3. Although the term U^2V^2WX is factorized into $UVW \times UVX$ in a single manner, the present enumeration

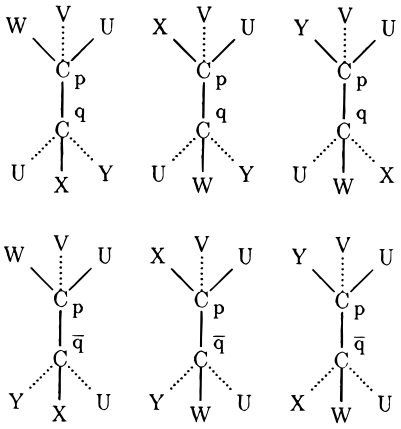


Figure 4. Diastereomers with $\mathbf{K}_1[\mathbf{C}_1]$ and U^2VWXY.

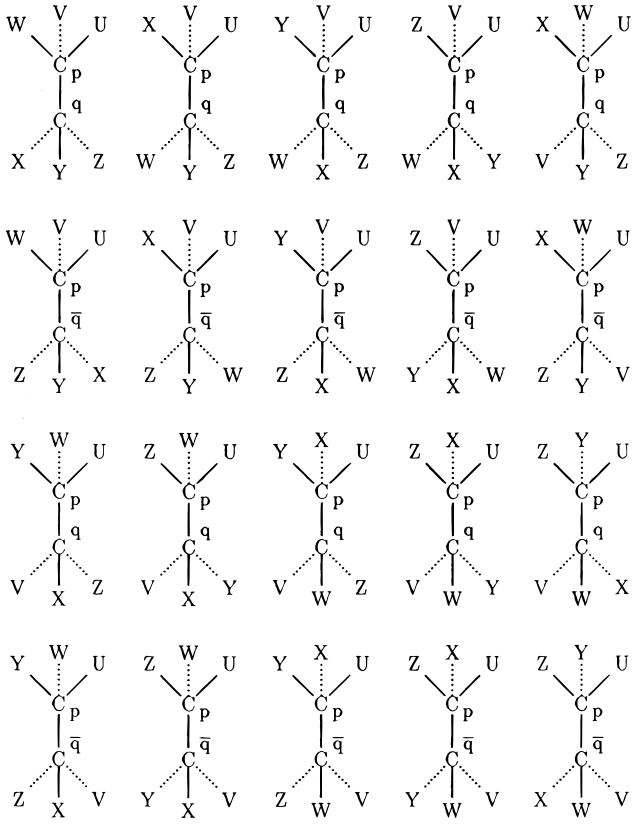
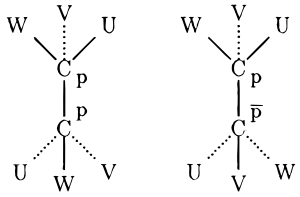


Figure 5. Diastereomers with $\mathbf{K}_1[\mathbf{C}_1]$ and $UVWXYZ$.

predicts the presence of two isomers. Stereochemically speaking, the two molecules are diastereomeric to each other, as indicated by the symbols, p−q and p−$\bar{q}$, written on respective ethane carbons. Since each of these molecules is chiral, a pair of enantiomers (e.g., a pair of p−q and $\bar{p}$−$\bar{q}$ or a pair of p−$\bar{q}$ and $\bar{p}$−q) is counted once in the present enumeration. Figure 3 illustrates an arbitrary enantiomer selected from a pair of enantiomers corresponding to one diastereomer.

The coefficient of the term U^2VWXY in eq 54 indicates that there appear six molecules of U^2VWXY. They are depicted in Figure 4 in agreement with the factorization into $UVW \times UXY$, $UVX \times UWY$, and $UVY \times UWX$, each of which corresponds to a pair of diastereomers (the first row and the second row).

There are 20 molecules of $UVWXYZ$ as indicated by the coefficient of the term $UVWXYZ$ appearing in eq 54. Since



$\mathbf{K}_2[\mathbf{C}_1]$ (chiral) $\mathbf{K}_4[\mathbf{C}_1]$ (achiral)

Figure 6. Derivatives with $U^2V^2W^2$.

the term is factorized in 10 ways ($UVW \times XYZ$, $UVX \times WYZ$, $UVY \times WXZ$, $UVZ \times WXY$, $UWX \times VYZ$, $UWY \times VXZ$, $UWZ \times VXY$, $UXY \times VWZ$, $UXZ \times VWY$, and $UYZ \times VWX$), 10 pairs of diastereomers are present, as found in Figure 5. The molecules of the first row are diasteromeric to those of the second row. Similarly, the third and the fourth rows indicate pairs of diasteromers.

The coefficient of the term $U^2V^2W^2$ in eq 55 shows that there is one molecule with $U^2V^2W^2$ and $\mathbf{K}_2[\mathbf{C}_1]$. This molecule is chiral, and an arbitrary enantiomer is depicted in Figure 6 (left).

On the other hand, the same term in eq 57 indicates the presence of one molecule with $U^2V^2W^2$ and $\mathbf{K}_4[\mathbf{C}_1]$, as depicted also in Figure 6 (right). This molecule is achiral and has a so-called meso-configuration.

Achiral Ligand Symmetries. Let us next consider all the achiral subgroups of $\mathbf{C}_{3v}$. Then, we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \varnothing$. By virtue of the data collected in Figure 2, derivatives enumerated in this condition belong to the A−B or A−A type. The PCI for $\mathbf{C}_s$ (eq 29) and the one for $\mathbf{C}_{3v}$ (eq 31) are summed up to give the corresponding ligand inventories:

$$a_d = b_d = c_d = s_d s_{2d} \tag{59}$$

They are introduced into eqs 23−27 to give the following extended PCIs for every subgroup

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}]; s_d) = 0 \tag{60}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_2[\mathbf{H}^{(a)}]; s_d) = 0 \tag{61}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}]; s_d) = \frac{1}{2}(s_1^2 s_2^2 - s_2 s_4) \tag{62}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_4[\mathbf{H}^{(a)}]; s_d) = 0 \tag{63}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_5[\mathbf{H}^{(a)}]; s_d) = s_2 s_4 \tag{64}$$

Suppose a set of six atoms is selected from the set $\mathbf{X}$ (eq 39). Then, the atom inventory (eq 40) is introduced into the extended PCIs of nonzero value (eqs 62−64). After the expansion of the resulting equations, we have the following

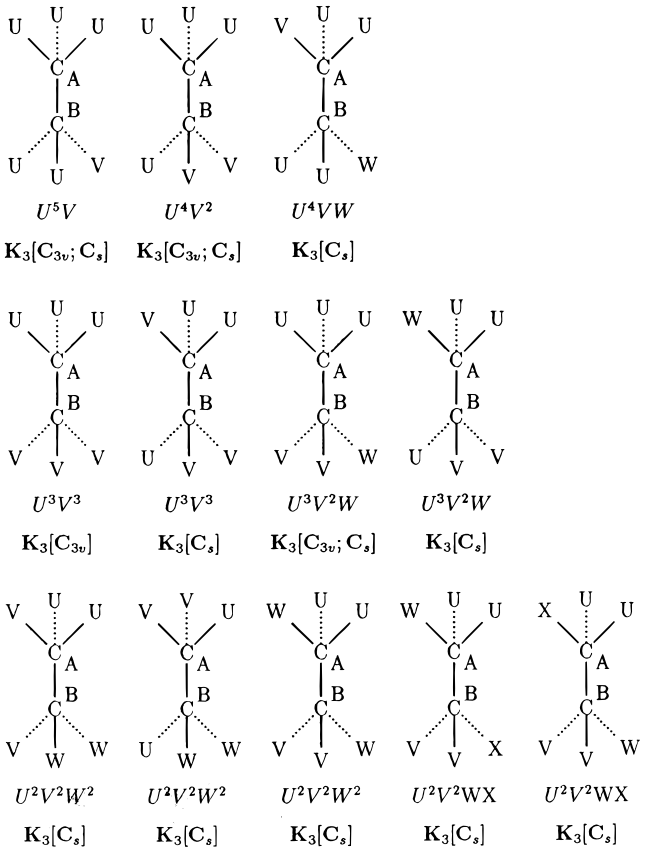


Figure 7. Derivatives with $\mathbf{K}_3[\mathbf{H}^{(a)}; \mathbf{H}^{(a')}]$.

generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)}]} = 0 \tag{65}$$

$$f_{\mathbf{K}_2[\mathbf{H}^{(a)}]} = 0 \tag{66}$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)}]} = (U^5V + U^5W + \cdots) + (U^4V^2 + U^4W^2 + \cdots) + (U^4VW + U^4VX + \cdots) + 2(U^3V^3 + U^3W^3 + \cdots) + 2(U^3V^2W + U^3V^2X + \cdots) + 3(U^2V^2W^2 + U^2V^2X^2 + \cdots) + 2(U^2V^2WX + U^2V^2WY + \cdots) \tag{67}$$

$$f_{\mathbf{K}_4[\mathbf{H}^{(a)}]} = 0 \tag{68}$$

$$f_{\mathbf{K}_5[\mathbf{H}^{(a)}]} = (U^6 + V^6 + \cdots) + (U^4V^2 + U^4W^2 + \cdots) \tag{69}$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \varnothing$.

By the inspection of the coefficients of respective terms in eq 67, we predict that there are one U^5V-isomer, one U^4V^2-isomer, one U^4VW-isomer, two U^3V^3-isomers, two U^3V^2W-isomers, three $U^2V^2W^2$-isomers, and two U^2V^2WX-isomers, all of which belong to $\mathbf{K}_3[\mathbf{H}^{(a)}]$-symmetry. They are depicted in Figure 7, where the symbol $\mathbf{K}_3[\mathbf{C}_{3v}; \mathbf{C}_s]$, for example, represents that the molecule contains a $\mathbf{C}_{3v}$-ligand and a $\mathbf{C}_s$-ligand. An abbreviated form $\mathbf{K}_3[\mathbf{C}_s]$ is used in place of the symbol $\mathbf{K}_3[\mathbf{C}_s; \mathbf{C}_s]$.

On the other hand, eq 57 indicates that there are one U^6-molecule and one U^4V^2-molecule, both of which belong to $\mathbf{K}_5[\mathbf{H}^{(a)}]$. They are depicted also in Figure 8.

$\mathbf{C}_s$-Ligand Symmetries. Let us consider the $\mathbf{C}_s$-subgroup of $\mathbf{C}_{3v}$, where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ and $\mathbf{H}^{(c)} = \{\varnothing\}$. This

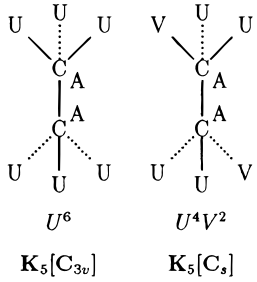


Figure 8. Derivatives with $\mathbf{K}_5[\mathbf{H}^{(a)}]$.

enumeration is also concerned with the A−B and the A−A type shown in Figure 2, but gives more specific data than the preceding enumeration. By using the PCI shown in eq 29, the corresponding ligand inventories are calculated for this case to be

$$a_d = b_d = c_d = s_d s_{2d} - s_{3d} \tag{70}$$

They are introduced into eqs 23−27 to give extended PCIs:

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{C}_s]; s_d) = 0 \tag{71}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_2[\mathbf{C}_s]; s_d) = 0 \tag{72}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{C}_s]; s_d) = \frac{1}{2}(s_1 s_2 - s_3)^2 - \frac{1}{2}(s_2 s_4 - s_6) = \frac{1}{2}(s_1^2 s_2^2 - 2s_1 s_2 s_3 + s_3^2 - s_2 s_4 + s_6) \tag{73}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_4[\mathbf{C}_s]; s_d) = 0 \tag{74}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_5[\mathbf{C}_s]; s_d) = s_2 s_4 - s_6 \tag{75}$$

The atom inventory (eq 40) is introduced into eqs 73 and 75 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions

$$f_{\mathbf{K}_1[\mathbf{C}_s]} = 0 \tag{76}$$

$$f_{\mathbf{K}_2[\mathbf{C}_s]} = 0 \tag{77}$$

$$f_{\mathbf{K}_3[\mathbf{C}_s]} = (U^4VW + U^4VX + \cdots) + (U^3V^3 + U^3W^3 + \cdots) + (U^3V^2W + U^3V^2X + \cdots) + 3(U^2V^2W^2 + U^2V^2X^2 + \cdots) + 2(U^2V^2WX + U^2V^2WY + \cdots) \tag{78}$$

$$f_{\mathbf{K}_4[\mathbf{C}_s]} = 0 \tag{79}$$

$$f_{\mathbf{K}_5[\mathbf{C}_s]} = (U^4V^2 + U^4W^2 + \cdots) \tag{80}$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ and $\mathbf{H}^{(c)} = \varnothing$.

The coefficients of respective terms in eq 78 indicate that there are one U^4VW-isomer, one U^3V^3-isomer, one U^3V^2W-isomer, three $U^2V^2W^2$-isomers, and two U^2V^2WX-isomers, all of which belong to $\mathbf{K}_2[\mathbf{H}^{(a)}]$-symmetry. They have already been depicted in Figure 7, where they are designated by the symbol $\mathbf{K}_3[\mathbf{C}_s]$.

The term U^4V^2 in eq 80 indicates the presence of one U^4V^2-molecule of $\mathbf{K}_5[\mathbf{C}_s]$, which has been depicted in Figure 8.

C_{3v}-Ligand Symmetries. To consider the $\mathbf{C}_{3v}$-subgroup of $\mathbf{C}_{3v}$, we place $\mathbf{H}^{(a)} = \{\mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \varnothing$. This enumeration is again concerned with the A−B and the A−A type shown in Figure 2, where the proligands A and B are replaced by ligands of $\mathbf{C}_{3v}$-symmetry. The PCI for $\mathbf{C}_{3v}$ (eq 31) is used to calculate the corresponding ligand inventories for this case:

$$a_d = b_d = c_d = s_{3d} \tag{81}$$

They are introduced into eqs 23−27 to give extended PCIs:

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{C}_{3v}]; s_d) = 0 \tag{82}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_2[\mathbf{C}_{3v}]; s_d) = 0 \tag{83}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{C}_{3v}]; s_d) = \frac{1}{2}(s_3^2 - s_6) \tag{84}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_4[\mathbf{C}_{3v}]; s_d) = 0 \tag{85}$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_5[\mathbf{C}_{3v}]; s_d) = s_6 \tag{86}$$

The atom inventory (eq 40) is introduced into eqs 84 and 86 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)}]} = 0 \tag{87}$$

$$f_{\mathbf{K}_2[\mathbf{H}^{(a)}]} = 0 \tag{88}$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)}]} = (U^3V^3 + U^3W^3 + \cdots) \tag{89}$$

$$f_{\mathbf{K}_4[\mathbf{H}^{(a)}]} = 0 \tag{90}$$

$$f_{\mathbf{K}_5[\mathbf{H}^{(a)}]} = (U^6 + V^6 + \cdots) \tag{91}$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c)} = \varnothing$.

The inspection of the coefficients of respective terms in eq 89 indicates the presence of one U^3V^3-isomer. It has already been depicted in Figure 7, being the molecules with $\mathbf{K}_3[\mathbf{C}_{3v}]$. On the other hand, the term U^6 in eq 91 indicates the presence of one U^6-molecule of $\mathbf{K}_5[\mathbf{C}_{3v}]$, which has been depicted in Figure 8.

2.4. Partial Enumeration of Ethane Derivatives Based on the $\mathbf{K}_3$-Skeleton. The partial enumeration of ethane derivatives also follows the procedure shown in Figure 1. Since the PCI-CFs for the $\mathbf{K}_3$-skeleton can be commonly used for the present enumeration (Figure 1C), they are calculated in advance in subsection 2.4.1.

2.4.1. PCI-CFs for $\mathbf{K}_3$-Skeleton. In order to conduct further sophisticated enumerations, we consider the factor group $\mathbf{K}_3$ of order 2, which consists of the subgroups

$$\mathbf{K}_1 = \{\mathbf{C}_\infty\} \tag{92}$$

$$\mathbf{K}_3 = \{\mathbf{C}_\infty, \mathbf{C}_\infty\sigma_v\} \tag{93}$$

The $\mathbf{K}_3$-group corresponds to the promolecules of A−B, while the $\mathbf{K}_1$-subgroup is associated with A−p and p−q, as shown in Figure 2. Note that the set $\mathbf{H}^{(a)}$ for A of A−B and the set $\mathbf{H}^{(a)'}$ for B should satisfy $\mathbf{H}^{(a)} \cap \mathbf{H}^{(a)'} = \varnothing$ in order to give correct results. Since only one chiral group $\mathbf{C}_1$ is available for ligands, we have no cases in which $\mathbf{H}^{(c)}$ for p and $\mathbf{H}^{(c)'}$ for q satisfy $\mathbf{H}^{(c)} \cap \mathbf{H}^{(c)'} = \varnothing$. It follows that derivatives of p−q type are excluded as a matter of course in the enumeration based on the factor group $\mathbf{K}_3$. The corresponding inverse of the mark table is listed in Table 1.

Table 1. Inverse of Mark Table for $\mathbf{K}_3$

	$\mathbf{K}_3(/\mathbf{K}_1)$	$\mathbf{K}_3(/\mathbf{K}_3)$
$\mathbf{K}_1$	1/2	0
$\mathbf{K}_3$	−1/2	1

Table 2. USCI-CF Table for $\mathbf{K}_3$

	$\mathbf{K}_1$	$\mathbf{K}_3$
$\mathbf{K}_3(/\mathbf{K}_1)$	b_1^2	c_2
$\mathbf{K}_3(/\mathbf{K}_3)$	b_1	a_1

Each proligand in a promolecule belonging to $\mathbf{K}_3$-symmetry constructs a one-membered orbit ascribed to the coset representation $\mathbf{K}_3(/\mathbf{K}_3)$. Since $\mathbf{K}_3(/\mathbf{K}_3)$ is homospheric, it is assigned to the USCI-CF represented by a_1, as found in the USCI-CF table for $\mathbf{K}_3$ (Table 2). For the criterion to determine the sphericity of factor groups, see ref 27.

We regard both of the proligands as the positions of substitution (α and β). By using the $\mathbf{K}_3(/\mathbf{K}_3)$-row of Table 2, we obtain the set of subduced cycle indices with chirality fittingness (SCI-CFs), i.e., $(b_1^{(\alpha)} b_1^{(\beta)}, a_1^{(\alpha)} a_1^{(\beta)})$. This formal row vector is multiplied by the inverse of the mark table of $\mathbf{K}_3$ (Table 1) in accord with eq 13 to give the following PCI-CFs for every subgroup of $\mathbf{K}_3$:

$$\mathrm{PCIC}(\mathbf{K}_1; a_d, b_d, c_d) = \frac{1}{2}(b_1^{(\alpha)} b_1^{(\beta)} - a_1^{(\alpha)} a_1^{(\beta)}) \tag{94}$$

$$\mathrm{PCIC}(\mathbf{K}_3; a_d, b_d, c_d) = a_1^{(\alpha)} a_1^{(\beta)} \tag{95}$$

It should be noted that eqs 94 and 95 for the factor group $\mathbf{K}_3$ presume different sets of PCIs (i.e., ligand inventories) for the respective orbits, whereas the preceding treatments for the factor group $\mathbf{K}$ presume the same set of PCIs for all the participant orbits. Such distinction of PCIs is a new matter, but, mathematically speaking, it can be regarded as a generalization of the distinction of weights described for obligatory minimum valencies in Chapter 14 of ref 24.

2.4.2. Ligand Inventories and Extended PCIs for $\mathbf{K}_3$. Achiral and Chiral Ligand Symmetries. Let us now consider the enumeration of derivatives of A−p type, where A (on the position α) is replaced by an achiral ligand selected from $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and p (on the position β) is replaced by a chiral ligand selected from $\mathbf{H}^{(c)} = \{\mathbf{C}_1\}$.

For the position α, eq 59 is adopted as the ligand inventories, i.e.

$$a_d^{(\alpha)} = b_d^{(\alpha)} = c_d^{(\alpha)} = (s_d s2d - s_{3d}) + s_{3d} = s_d s_{2d} \tag{96}$$

On the other hand, the ligand inventories, eqs 47 and 48, are used for the position β, i.e.

$$a_d^{(\beta)} = 0 \tag{97}$$

$$b_d^{(\beta)} = c_d^{(\beta)} = \frac{1}{3}(s_d^3 - 3s_d s_{2d} + 2s_{3d}) \tag{98}$$

The two sets of ligand inventories are introduced into eqs 94 and 95 to give

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = \frac{1}{6}(s_1^3 - 3s_1s_2 + 2s_3)s_1s_2 \quad (99)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = 0 \quad (100)$$

The atom inventory (eq 40) is introduced into eq 99 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = (U^4VW + U^4VX + \cdots) + (U^3V^2W + U^3V^2X + \cdots) + 4(U^3VWX + U^3VWY + \cdots) + 2(U^2V^2WX + U^2V^2WY + \cdots) + 4(U^2VWXY + U^2VWXZ + \cdots) \quad (101)$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = 0 \quad (102)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s, \mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c')} = \{\mathbf{C}_1\}$.

By means of the coefficients of the terms appearing eq 101, we can predict that there are one U^4VW-isomer (the first row), one U^3V^2W-isomer (the first row), four U^3VWX-isomers (the second row), two U^2V^2WX-isomers (the third row), and four U^2VWXY-isomers (the fourth row), all of which are illustrated in the row indicated in the respective parentheses in Figure 9. Since all of these molecules are chiral, an arbitrary enantiomer of each molecule is depicted.

C_s- and C_1-Ligand Symmetries. A more specific enumeration concerning $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ (on the position β) and $\mathbf{H}^{(c')} = \{\mathbf{C}_1\}$ (on the position β) can be conducted in a similar way. For the position α, eq 70 is adopted as the ligand inventories, i.e.

$$a_d^{(\alpha)} = b_d^{(\alpha)} = c_d^{(\alpha)} = s_d s_{2d} - s_{3d} \quad (103)$$

On the other hand, the ligand inventories represented by eqs 97 and 98 are used for the position β. The two sets of ligand inventories are introduced into eqs 94 and 95 to give

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = \frac{1}{6}(s_1^3 - 3s_1s_2 + 2s_3)(s_1s_2 - s_3) \quad (104)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = 0 \quad (105)$$

The atom inventory (eq 40) is introduced into eq 104 of nonzero expression, which is expanded to give the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = (U^3V^2W + U^3V^2X + \cdots) + 3(U^3VWX + U^3VWY + \cdots) + 2(U^2V^2WX + U^2V^2WY + \cdots) + 4(U^2VWXY + U^2VWXZ + \cdots) \quad (106)$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = 0 \quad (107)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ and $\mathbf{H}^{(c')} = \{\mathbf{C}_1\}$.

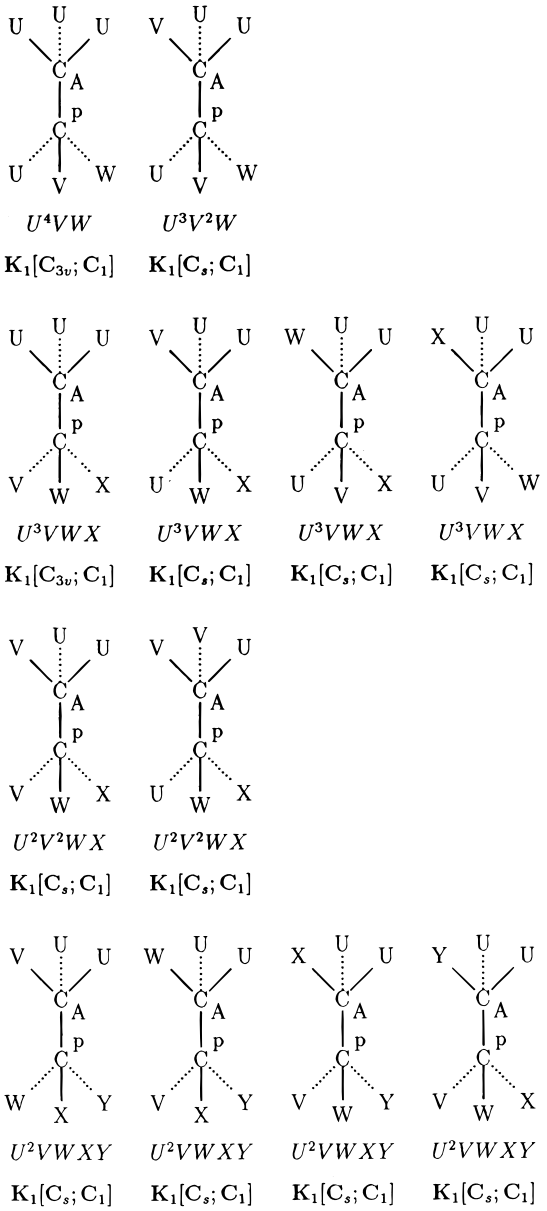


Figure 9. Derivatives with $\mathbf{K}_1[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]$.

The coefficients of the terms appearing in eq 111 predict the presence of one U^4VW-isomer (the first row) and one U^3VWX-isomer (the second row), all of which have been illustrated in Figure 9.

C_{3v}- and C_1-Ligand Symmetries. Another specific enumeration of $\mathbf{H}^{(a)} = \{\mathbf{C}_{3v}\}$ (on the position α) and $\mathbf{H}^{(c)} = \{\mathbf{C}_1\}$ (on the position β) can be conducted in a similar way. For the position α, eq 81 is adopted as the ligand inventories, i.e.

$$a_d^{(\alpha)} = b_d^{(\alpha)} = c_d^{(\alpha)} = s_{3d} \quad (108)$$

On the other hand, the ligand inventories represented by eqs 97 and 98 are used for the position β. The two sets of ligand inventories are introduced into eqs 94 and 95 to give

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = \frac{1}{6}(s_1^3 - 3s_1s_2 + 2s_3)s_3 \quad (109)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}; \mathbf{H}^{(c')}]; s_d) = 0 \quad (110)$$

Table 3. Factorization for $\mathbf{K}_1$-Derivatives

	all ligands eq 41	$[\mathbf{C}_{3v}, \mathbf{C}_s; \mathbf{C}_1]$ eq 101	$[\mathbf{C}_1; \mathbf{C}_1]$ eq 54	$[\mathbf{C}_{3v}; \mathbf{C}_1]$ eq 111	$[\mathbf{C}_s; \mathbf{C}_1]$ eq 106
U^4VW	1	1	0	1 $U^3 \times UVW$	0
U^3V^2W	1	1	0	0	1 $U^2V \times UVW$
U^3VWX	4	4	0	1 $U^3 \times VWX$	3 $U^2V \times UWX$ $U^2W \times UVX$ $U^2X \times UVW$
U^2V^2WX	4	2	2 $2UVW \times UVX$	0	2 $U^2V \times$ VWX $UV^2 \times UWX$
U^2VWXY	10	4	6 $2UVW \times UXY$ $2UVX \times UWY$ $2UWX \times UVY$	0	4 $U^2V \times WXY$ $U^2W \times VXY$ $U^2X \times VWY$ $U^2Y \times VWX$
$UVWXYZ$	20	0	20 $2UVX \times WYZ$ $2UVY \times WXZ$ $2UVZ \times WXY$ $2UWX \times VYZ$ $2UWY \times VXZ$ $2UWZ \times VXY$ $2UXY \times VWZ$ $2UXZ \times VWY$ $2UYZ \times VWX$	0	0

The atom inventory (eq 40) is introduced into eq 109 of nonzero expression, which is expanded to give the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = (U^4VW + U^4VX + \cdots) + (U^3VWX + U^3VWY + \cdots) \quad (111)$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)};\mathbf{H}^{(c')}]} = 0 \quad (112)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_{3v}\}$ and $\mathbf{H}^{(c')} = \{\mathbf{C}_1\}$.

The coefficients of the terms appearing in eq 111 predict the presence of one U^4VW-isomer (the first row) and one U^3VWX-isomer (the second row), all of which have been illustrated in Figure 9.

$\mathbf{C}_s$ and $\mathbf{C}_{3v}$ Ligand Symmetries. Let us consider the enumeration of derivatives of A−B type, where A (on the position α) is replaced by an achiral ligand selected from $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ and B (on the position β) is repaced by another achiral ligand selected from $\mathbf{H}^{(a')} = \{\mathbf{C}_{3v}\}$.

For the position α, eq 70 is adopted as the ligand inventories, i.e.

$$a_d^{(\alpha)} = b_d^{(\alpha)} = c_d^{(\alpha)} = s_d s_{2d} - s_{3d} \quad (113)$$

On the other hand, the ligand inventories represented by eq 59 are used for the position β i.e.

$$a_d^{(\beta)} = b_d^{(\beta)} = c_d^{(\beta)} = s_{3d} \quad (114)$$

The two sets of ligand inventories are introduced into eqs 94 and 95 to give

$$\overline{\mathrm{PCI}}(\mathbf{K}_1[\mathbf{H}^{(a)}; \mathbf{H}^{(a)'}]; s_d) = 0 \quad (115)$$

$$\overline{\mathrm{PCI}}(\mathbf{K}_3[\mathbf{H}^{(a)}; \mathbf{H}^{(a)'}]; s_d) = (s_1 s_2 - s_3) s_3 \quad (116)$$

The atom inventory (eq 40) is introduced into eq 116 of nonzero expression. By expanding the resulting equations, we obtain the following generating functions

$$f_{\mathbf{K}_1[\mathbf{H}^{(a)};\mathbf{H}^{(a')}]} = 0 \quad (117)$$

$$f_{\mathbf{K}_3[\mathbf{H}^{(a)};\mathbf{H}^{(a')}]} = (U^5V + U^5W + \cdots) + (U^4V^2 + U^4W^2 + \cdots) + (U^3V^2W + U^3V^2X + \cdots) \quad (118)$$

where we place $\mathbf{H}^{(a)} = \{\mathbf{C}_s\}$ and $\mathbf{H}^{(a')} = \{\mathbf{C}_{3v}\}$.

The coefficients of respective terms in eq 118 indicate that there are one U^5V-isomer, one U^4V^2-isomer, and one U^3V^2W-isomer. They have already been depicted in Figure 7, as indicated by the symbol $\mathbf{K}_3[\mathbf{C}_{3v}; \mathbf{C}_s]$.

3. DISCUSSION

3.1. Factorization for $\mathbf{K}_1$-Derivatives. The numbers of $\mathbf{K}_1$-derivatives under various conditions are found in the respective generating functions as the coefficients of terms (monomials) contained: i.e., in eq 41 (for all ligands), eq 101 (for $\mathbf{K}_1[\mathbf{C}_{3v}, \mathbf{C}_s; \mathbf{C}_1]$), eq 54 (for $\mathbf{K}_1(\mathbf{C}_1; \mathbf{C}_1]$), eq 111 (for $\mathbf{K}_1[\mathbf{C}_{3v}; \mathbf{C}_1]$), and eq 106 (for $\mathbf{K}1[\mathbf{C}_s; \mathbf{C}_1]$). They are collected in Table 3, where each number represents the coefficient of the term appearing in the corresponding generating functions. Each coefficient of eq 41 is equal to the one obtained by eq 54 plu eq 111 plus eq 106, as found easily by the inspection of Table 3. On the other hand, the number foir eq 101 is equal to the sum of eq 111 plus eq 106. These facts show the validity of the present itemized enumerations.

As shown in Figure 2, a $\mathbf{K}_1$-derivative corresponds to a promolecule of A−p type or of p−q type. In agreement with this categorization, $\mathbf{K}_1[\mathbf{C}_{3v}; \mathbf{C}_1]$-derivatives and $\mathbf{K}_1[\mathbf{C}_s; \mathbf{C}_1]$-derivatives are ascribed to the promolecule of A−p type, while $\mathbf{K}_1[\mathbf{C}_1; \mathbf{C}_1]$-derivatives are assigned to the promolecule

Table 4. Factorization for $\mathbf{K}_3$-Derivatives

	all ligands eq 41	[$\mathbf{C}_{3v}$, $\mathbf{C}_s$] eq 67	[$\mathbf{C}_s$; $\mathbf{C}_s$] eq 78	[$\mathbf{C}_{3v}$; $\mathbf{C}_{3v}$] eq 89	[$\mathbf{C}_{3v}$; $\mathbf{C}_s$] eq 118
U^5V	1	1	0	0	1 $U^3 \times U^2V$
U^4V^2	1	1	0	0	1 $U^3 \times UV^2$
U^4VW	1	1	1 $U^2V \times U^2W$	0	0
U^3V^3	2	2	1 $U^2V \times UV^2$	1 $U^3 \times V^3$	0
U^3V^2W	2	2	1 $U^2W \times UV^2$	0	1 U^3 x V^2W
$U^2V^2W^2$	3	3	3 $U^2V \times V^2W$ $UV^2 \times UW^2$ $U^2W \times V^2W$	0	0
U^2V^2WX	2	2	2 $U^2W \times V^2X$ $U^2X \times V^2W$	0	0

of p−q type. Since methyl ligands of $\mathbf{C}_{3v}$-symmetry take U^3, etc. (partition [3, 0, 0, 0, 0, 0]), those of $\mathbf{C}_s$-symmetry take U^2V, etc. (partition [2, 1, 0, 0, 0, 0]), and those of $\mathbf{C}_1$-symmetry take *UVW*, etc. (partition [1, 1, 1, 0, 0, 0]), each of the terms collected in Table 3 can be factorized according to the modes of ligand symmetries. The results are shown in the [$\mathbf{C}_1$; $\mathbf{C}_1$]-column (eq 54), the [$\mathbf{C}_{3v}$; $\mathbf{C}_1$])-column (eq 111), and the $\mathbf{C}_s$; $\mathbf{C}_1$]-column (eq 106), each of which contains the factorization of the terms corresponding to the respective enumeration conditions.

The modes of factorization contained in the [$\mathbf{C}_1$; $\mathbf{C}_1$]-column have been depicted as the concrete structures in Figures 3, 4, and 5. On the other hand, the modes of factorization for the [$\mathbf{C}_{3v}$; $\mathbf{C}_1$])-column and the [$\mathbf{C}_s$; $\mathbf{C}_1$]-column have been illustrated in Figure 9. It should be emphasized that such factorization facilitates the systematic depiction of resulting molecules to a great degree.

3.2. Factorization for $\mathbf{K}_3$-Derivatives. The numbers of $\mathbf{K}_3$-derivatives calculated by the respective generating functions are collected in Table 4. Each coefficient of eq 41 (for all ligands) is equal to the one obtained by eq 67 (for achiral ligands), since a $\mathbf{K}_3$-derivative is generated by two achiral methyl ligands. It is obviously equal to the sum obtained by eq 78 (the combination of two $\mathbf{C}_s$-ligands) plus eq 89 (the combination of two $\mathbf{C}_{3v}$-ligands) plus eq 118 (the combination of a $\mathbf{C}_{3v}$- and a $\mathbf{C}_s$-ligand). These results again show the validity of the present itemized enumerations.

As shown in Figure 2, a $\mathbf{K}_3$-derivative corresponds to a promolecule of A−B type. Each of the terms collected in Table 4 can be factorized according to the modes of ligand symmetries, as shown in the [$\mathbf{C}_s$; $\mathbf{C}_s$]-column (eq 78), the [$\mathbf{C}_{3v}$; $\mathbf{C}_{3v}$])-column (eq 89), and the [$\mathbf{C}_{3v}$; $\mathbf{C}_s$]-column (eq 118). Note that methyl ligands of C_{3v}-symmetry take U^3, etc. (partition [3,0, 0, 0, 0, 0]), those of C_s-symmetry take U^2V, etc. (partition [2, 1, 0, 0, 0, 0]), and those of $\mathbf{C}_1$-symmetry take *UVW*, etc. (partition [1, 1, 1, 0, 0, 0]). The modes of factorization collected in Table 4 have been depicted as the concrete structures in Figure 7.

3.3. Factorization for the Other Symmetries. Figure 2 indicates that $\mathbf{K}_2$-derivatives are ascribed to the promolecule of p−p type, in which two chiral ligands of the same symmetry (p) are attached to the $\mathbf{D}_{\infty h}$-skeleton. The full enumeration (eq 42) and the partial enumeration concerning $\mathbf{C}_1$-ligands (eq 55) show that there is one $U^2V^2W^2$-isomer belonging to $\mathbf{K}_2[\mathbf{C}_1]$-symmetry. According to the type p−p, the monomial $U^2V^2W^2$ is factorized into even parts, i.e., *UVW* and *UVW*, which are identical with each other to represent a $\mathbf{C}_1$-ligand. Thereby, the corresponding concrete molecules can be depicted, as found in Figure 6 (left). Obviously the molecule of type p−p is chiral so as to give the enantiomeric molecule $\bar{p}$−$\bar{p}$.

$\mathbf{K}_4$-derivatives are ascribed to the promolecule of p−$\bar{p}$ type, as found in Figure 2. The presence of one $U^2V^2W^2$-isomer for $\mathbf{K}_4$-symmetry is indicated by the full enumeration (eq 45) and also by the partial enumeration for $\mathbf{C}_1$-ligands (eq 57). The factorization of the term $U^2V^2W^2$ according to the type p−$\bar{p}$ gives the same result as the $\mathbf{K}_2$-symmetry, i.e., $UVW \times UVW$. However, these factors represent a pair of enantiomeric ligands, as shown in Figure 6 (right). This molecule represents a so-called meso-compound, in which the effect of two chiral ligands vanishes to zero in terms of proligand representation, p and $\bar{p}$.

A $\mathbf{K}_5$-derivative represents the symmetry of ethane itself and ascribed to the promolecule of A−A type (Figure 2). The full enumeration (eq 46) indicates that there are one U^6-isomer and one U^4V^2-isomer. More specifically, the partial enumeration for $\mathbf{C}_s$-ligands (eq 80) shows that the U^4V^2-isomer belongs to $\mathbf{K}_5[\mathbf{C}_s]$-symmetry, while the partial enumeration concerning $\mathbf{C}_{3v}$-ligands (eq 91) reveals that the U^6-isomer is ascribed to $\mathbf{K}_5[\mathbf{C}_{3v}]$-symmetry. Since the term U^6 is factorized into even parts, i.e., $U^3 \times U^3$, the concrete structure can be easily depicted, as found in Figure 8 (left). On the other hand, the factors $U^2V \times U^2V$ derived from the term U^4V^2 correspond to the molecule shown in the right of Figure 8.

4. CONCLUSION

The concept of extended partial cycle indices (extended PCIs) has been proposed to give generating functions for enumerating non-rigid isomers with given ligand symmetries. This has been combined with the concept of promolecules proposed previously[25,27] so that the terms appearing in the generating functions are factorized into a pair of factors to represent ligand constitutions. Thereby, the depiction of resulting molecules can be conducted systematically. This

method has been succesfully applied to the enumeration of ethane derivatives.

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CI990074Y