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A Simple Method for Enumeration of Non-Rigid Isomers. An Application of Characteristic Monomials

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A new and simple procedure for counting isomers derived from non-rigid parent molecules has been developed by the combination of the promolecule concept with the characteristic-monomial method. This procedure has been applied to the enumeration of diphenylmethanes, 2,2-diphenylpropanes, and 2,2-dimethylpropanes, after the characteristic monomial tables for the point groups $\mathbf{C}_{2v}$ and $\mathbf{C}_{3v}$ have been prepared.

The concept of "coronas" has been introduced by Pólya[1,2] to solve enumeration problems of non-rigid molecules due to rotations around bonds. This is essentially equivalent to the concept of wreath products, which has been used to count stereo and positional isomers in a generalized wreath product method.[3] These methods and related topics have been reviewed extensively in books[2,4] and reviews.[5—8] Since these methods have taken account of molecular formulas only, more elaborate methods have been desired so that we are able to count isomers in itemized manners with respect to molecular formulas as well as to spatial symmetries. For this purpose, we have reported the enumeration of non-rigid molecules by means of unit subduced cycle indices (USCIs),[9—11] in which it is possible to count isomers with given formulas and given symmetries. We have further modified this enumeration after we proposed the concept of promolecules.[12,13] Although the enumeration methods based on the USCI approach have given satisfactory results, they contain a tedious step for calculating figure inventories ascribed to each ligand. It is desirable that this step be replaced by a simpler procedure.

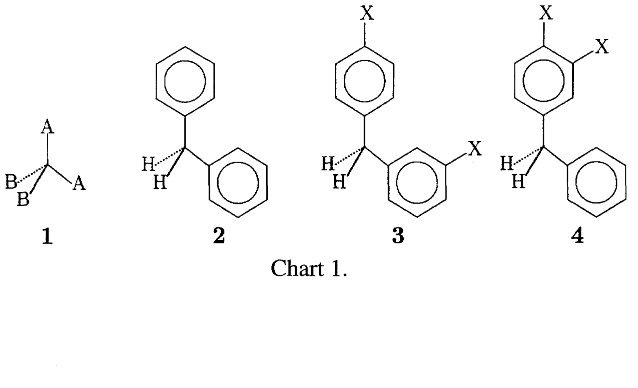
We have recently proposed the concept of characteristic monomials and reported its application to isomer enumeration.[14—18] This method (the characteristic-monomial method) has been shown to be effective also for the enumeration of achiral and chiral isomers.[19] This means that the method can obviously be applied to the enumeration of achiral and chiral ligands, if necessary characteristic monomial tables are prepared. Since the above figure inventories for ligands are concerned with the chirality/achirality of the ligands, it is a natural idea to apply the characteristic-monomial method to calculating such inventories.

As clarified by the preceding paragraphs, the targets of this paper are to prepare further characteristic monomial tables for enumerating ligands and to show that the characteristic-monomial method can be used as a simple and convenient procedure for calculating figure inventories.

Results and Discussion

1 Theoretical Formulation. In the light of the promolecule concept,[12,13] a derivative is considered to be generated by replacing proligands of a promolecule (of symmetry $\mathbf{G}$) with appropriate ligands. Such a promolecule is in turn regarded as a hypothetical molecule by placing proligands on the vertices of a skeleton of a given symmetry $\mathbf{G}'$ ($\mathbf{G} \subset \mathbf{G}'$). Note that each ligand belongs to a point group $\mathbf{H}$ while each proligand is considered to have chirality or achirality. For example, diphenylmethane (**2** in Chart 1) is generated from a promolecule of $\mathbf{C}_{2v}$ symmetry (**1**), where an achiral proligand A is replaced by a phenyl group and an achiral proligand B is replaced by a hydrogen atom. The promolecule (**1**) is in turn generated from a tetrahedral skeleton of $\mathbf{T}_d$ symmetry, where the symmetry $\mathbf{C}_{2v}$ of the promolecule is a subgroup of the symmetry $\mathbf{T}_d$ of the skeleton. It should be noted that the proligands A and B in the promolecule (**1**) have no rotatable nature, while the phenyl group in the molecule (**2**) is rotatable as a ligand.

Let us consider the enumeration of isomers having $\mathbf{G}_i$-symmetry by starting from a $\mathbf{G}$ promolecule ($\mathbf{G}_i \subset \mathbf{G}$), where each formula ($W_\theta$) is calculated by considering ligands rather than proligands.[10] For example, molecules **3** and **4** are isomers of formula X^2. They are conceptually considered to be derivatives of the promolecule **1**, i.e the former with 4-X-phenyl and 3-X-phenyl and the latter with 3,4-X_2-phenyl and



1 **2** **3** **4**

Chart 1.

phenyl. Our problem is to obtain the number of such isomers with a formula W_θ (e.g. X^2) and a $\mathbf{G}_i$-symmetry. Note that they are not regarded as derivatives of diphenylmethane (**2**) in the present paper.

Theorem 1 described in Appendix 2 of Ref. 10 gives a method for enumerating isomers with W_θ-formula and $\mathbf{G}_i$-symmetry. This theorem requires the preceding calculation of $\sigma_{\theta j}$, which is the number of derivatives with weight (W_θ) that are invariant on the operation of $\mathbf{G}_j$ (for $j = 1, 2\cdots, c_{\mathbf{G}}$). Lemma 3[10] gives a method for the calculation of such $\sigma_{\theta j}$, which is given by the following generating functions:

$$\sum_{\theta} \sigma_{\theta j} W_\theta = ZI(\mathbf{G}_j; \$_{d_{jk}}^{(i\alpha)}) \tag{1}$$

for $j = 1, 2\cdots, c_{\mathbf{G}}$. Here every variable of the right-hand side is substituted by figure-inventories:

$$a_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \varkappa_{\xi a} (\omega_{\xi}^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = a, \tag{2}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \varkappa_{\xi a} (\omega_{\xi}^{(i\alpha)})^{d_{jk}} + 2\sum_{\xi} \varkappa_{\xi c} (\omega_{\xi}^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = b, \tag{3}$$

$$c_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \varkappa_{\xi a} (\omega_{\xi}^{(i\alpha)})^{d_{jk}} + 2\sum_{\xi} \varkappa_{\xi c} (\omega_{\xi}^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = c, \tag{4}$$

where each $\omega_{\xi}^{(i\alpha)}$ represents the formula of a ligand:

$$\omega_{\xi}^{(i\alpha)} = \sum_{l}^{|\mathbf{X}|} X_l^{n_l}. \tag{5}$$

The superscript $(i\alpha)$ represents that the corresponding term is associated with the $(i\alpha)$-orbit. In the previous methods,[9,10] the figure inventories ($a_{d_{jk}}^{(i\alpha)}$, $b_{d_{jk}}^{(i\alpha)}$, and $c_{d_{jk}}^{(i\alpha)}$) are calculated by using $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$, which are in turn represented by

$$\varkappa_{\xi a} = \sum_{\substack{p=1 \\ \overline{improper}}}^{c_{\mathbf{H}^{(i\alpha)}}} B_{\xi p}^{(i\alpha)}, \tag{6}$$

$$\varkappa_{\xi c} = \sum_{\substack{p=1 \\ \overline{proper}}}^{c_{\mathbf{H}^{(i\alpha)}}} B_{\xi p}^{(i\alpha)}. \tag{7}$$

Equations 6 and 7 require the values $B_{\xi p}^{(i\alpha)}$, which are in turn obtained from the symmetry-itemized enumeration of ligands. The calculation of $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$ by Eqs. 6 and 7 is a complicated step, as found in the examples described in Ref. 10.

Since $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$ are respectively concerned with achiral ligands and chiral ones, the figure inventory, $a_{d_{jk}}^{(i\alpha)}$ (Eq. 2), can be regarded as a generating function for giving the number of achiral ligands with every molecular formula, if each d_{jk} is equal to unity. The other figure inventory, $b_{d_{jk}}^{(i\alpha)}$ (Eq. 3) or $c_{d_{jk}}^{(i\alpha)}$ (Eq. 4), is also regarded as a generating function involving the number of achiral ligands plus chiral ones. These discussions mean that $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$ can be obtained by using the characteristic-monomial method described in Ref. 19.

By applying Theorem 5 of Ref. 19 to the present enumeration, we find that a generating function for calculating $\varkappa_{\xi a}$ is equivalent to the one for enumerating achiral ligands by starting from a proligand of $\mathbf{H}^{(i\alpha)}$-symmetry as follows:

$$\sum_{\xi} \varkappa_{\xi a} \omega_{\xi}^{(i\alpha)} = CI^{(a)}(\mathbf{H}^{(i\alpha)}; s_d), \tag{8}$$

where the cycle index $CI^{(a)}$ is represented by

$$CI^{(a)}(\mathbf{H}^{(i\alpha)}; s_d) = \sum_{j=1}^{s} N_j^{(a)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}, \tag{9}$$

and the inventories are represented by

$$s_d = \sum_{l=1}^{\nu} X_l^d. \tag{10}$$

On the other hand, a generating function for calculating $\varkappa_{\xi c}$ is equivalent to the one for enumerating achiral and chiral ligands:

$$\sum_{\xi} \varkappa_{\xi c} \omega_{\xi}^{(i\alpha)} = CI^{(m)}(\mathbf{H}^{(i\alpha)}; s_d), \tag{11}$$

where the cycle index $CI^{(m)}$ is represented by

$$CI^{(m)}(\mathbf{H}^{(i\alpha)}; s_d) = \sum_{j=1}^{s} N_j^{(m)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}. \tag{12}$$

2 Enumeration of Diphenylmethane Derivatives. Let us replace each proligand A of the promolecule **1** by a phenyl group with mX and nY ($m+n = 5$). Then, we count isomers with $X^m Y^n$ ($m+n = 10$ for two phenyl groups) and with a given symmetry. Since a phenyl group belongs to $\mathbf{C}_{2v}$-symmetry, a character (markaracter)[20] is calculated to be (5,1,5,1), each integer of which is the number of fixed positions during the operations of a respective subgroup of $\mathbf{C}_{2v}$-symmetry. This row vector is multiplied by the inverse of the $\mathbf{Q}$-conjugacy character table[15] for $\mathbf{C}_{2v}$ to give the following equation:

$$(5,1,5,1)\begin{pmatrix} \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} \\ \frac{1}{4} & -\frac{1}{4} & \frac{1}{4} & -\frac{1}{4} \\ \frac{1}{4} & -\frac{1}{4} & -\frac{1}{4} & \frac{1}{4} \end{pmatrix} = (3,0,2,0). \tag{13}$$

The resulting row vector means that the five positions of a phenyl group are governed by $\mathbf{Q}$-conjugacy representations,[14—18] $3A_1+2B_1$. This can be related to the coset representations governing the positions ($2\mathbf{C}_{2v}(/\mathbf{C}_s)+\mathbf{C}_{2v}(/\mathbf{C}_{2v})$ described in Ref. 10) in the light of the markaracter table for $\mathbf{C}_{2v}$ (Table 1):

$$2\mathbf{C}_{2v}(/\mathbf{C}_s) + \mathbf{C}_{2v}(/\mathbf{C}_{2v}) = 3A_1 + 2B_1. \tag{14}$$

Characteristic monomials prepared for $\mathbf{C}_{2v}$ (Table 2) are collected in accord with $3A_1+2B_1$ to give cycle indices, $CI^{(a)}$

Table 1. Markaracters for $\mathbf{C}_{2v}$

$\mathbf{C}_{2v}$	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}'_s$	Reduction
$\mathbf{C}_{2v}(/\mathbf{C}_1)$	4	0	0	0	$A_1 + A_2 + B_1 + B_2$
$\mathbf{C}_{2v}(/\mathbf{C}_2)$	2	2	0	0	$A_1 + A_2$
$\mathbf{C}_{2v}(/\mathbf{C}_s)$	2	0	2	0	$A_1 + B_1$
$\mathbf{C}_{2v}(/\mathbf{C}'_s)$	2	0	0	1	$A_1 + B_2$
$\mathbf{C}_{2v}(/\mathbf{C}_{2v})$	1	1	1	1	A_1

Table 2. Characteristic Monomials for $\mathbf{C}_{2v}$

$\mathbf{C}_{2v}$	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}'_s$	Remarks
A_1	s_1	s_1	s_1	s_1	$\mathbf{C}_{2v}(/\mathbf{C}_{2v})$
A_2	s_1	s_1	$s_1^{-1}s_2$	$s_1^{-1}s_2$	$\mathbf{C}_{2v}(/\mathbf{C}_2)-\mathbf{C}_{2v}(/\mathbf{C}_{2v})$
B_1	s_1	$s_1^{-1}s_2$	s_1	$s_1^{-1}s_2$	$\mathbf{C}_{2v}(/\mathbf{C}_s)-\mathbf{C}_{2v}(/\mathbf{C}_{2v})$
B_2	s_1	$s_1^{-1}s_2$	$s_1^{-1}s_2$	s_1	$\mathbf{C}_{2v}(/\mathbf{C}'_s)-\mathbf{C}_{2v}(/\mathbf{C}_{2v})$
N_j	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	Achiral isomers and enantiomeric pairs
$N_j^{(m)}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	Achiral and chiral isomers
$N_j^{(e)}$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{4}$	Enantiomeric pairs ($N_j^{(m)}-N_j$)
$N_j^{(a)}$	0	0	$\frac{1}{2}$	$\frac{1}{2}$	Achiral isomers ($N_j-N_j^{(e)}$)

(Eq. 8) and $CI^{(m)}$ (Eq. 12). Since the term for $\mathbf{C}_1$ (or $\mathbf{C}_s$) is calculated to be $(s_1)^3(s_1)^2 = s_1^5$ and the term for $\mathbf{C}_2$ (or $\mathbf{C}'_s$) is calculated to be $(s_1)^3(s_1^{-1}s_2)^2 = s_1s_2^2$, the cycle indices are obtained as follows:

$$CI^{(a)}(\mathbf{C}_{2v}; s_d) = \frac{1}{2}s_1^5 + \frac{1}{2}s_1s_2^2, \tag{15}$$

$$CI^{(m)}(\mathbf{C}_{2v}; s_d) = \frac{1}{2}s_1^5 + \frac{1}{2}s_1s_2^2, \tag{16}$$

where the coefficients are respectively selected from the $N_j^{(a)}$-row and the $N_j^{(m)}$-row of Table 2. Then, the following inventory,

$$s_d = X^d + Y^d, \tag{17}$$

is introduced into the cycle indices. Thereby, we have

$$\begin{aligned} f^{(a)} = f^{(m)} &= \frac{1}{2}(X+Y)^5 + \frac{1}{2}(X+Y)(X^2+Y^2)^2 \\ &= X^5 + 3X^4Y + 6X^3Y^2 + 6X^2Y^3 + 3XY^4 + Y^5. \end{aligned} \tag{18}$$

The right-hand side for $f^{(a)}$ is a generating function for calculating $\varkappa_{\xi a}$, while the one for $f^{(m)}$ is a generating function for calculating $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$. Hence, the figure-inventories (Eqs. 2, 3, and 4) are calculated for the present enumeration:

$$a_d = b_d = c_d = (X^5)^d + 3(X^4Y)^d + 6(X^3Y^2)^d + 6(X^2Y^3)^d + 3(XY^4)^d + (Y^5)^d. \tag{19}$$

The orbit of two As in the promolecule (**1**) is governed by the coset representation, $\mathbf{C}_{2v}(/\mathbf{C}_s)$. From the data of unit subduced cycle indices (USCIs) for $\mathbf{C}_{2v}$ (the $\mathbf{C}_{2v}(/\mathbf{C}_s)$ row of Table 1 in Ref. 10), we obtain the following generating functions for calculating $\sigma_{\theta j}$ (Eq. 1) for diphenylmethanes.

$$\mathbf{C}_1 : b_1^2 = (X^5 + 3X^4Y + 6X^3Y^2 + 6X^2Y^3 + 3XY^4 + Y^5)^2 \tag{20}$$

$$\mathbf{C}_2 : b_2 = X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10} \tag{21}$$

$$\mathbf{C}_s : a_1^2 = (X^5 + 3X^4Y + 6X^3Y^2 + 6X^2Y^3 + 3XY^4 + Y^5)^2 \tag{22}$$

$$\mathbf{C}'_s : c_2 = X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10} \tag{23}$$

$$\mathbf{C}_{2v} : a_2 = X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10} \tag{24}$$

The generating functions are expanded to give the values $\sigma_{\theta j}$, which are aligned to form a matrix. Then, the resulting matrix is multiplied by the inverse of the mark table of the $\mathbf{C}_{2v}$-group to give

$$\begin{array}{l} \begin{array}{r} \\ X^{10}, Y^{10} \\ X^9Y, XY^9 \\ X^8Y^2, X^2Y^8 \\ X^7Y^3, X^3Y^7 \\ X^6Y^4, X^4Y^6 \\ X^5Y^5 \end{array} \begin{array}{c} \begin{array}{ccccc} \mathbf{C}_1 & \mathbf{C}_2 & \mathbf{C}_s & \mathbf{C}'_s & \mathbf{C}_{2v} \end{array} \\ \left(\begin{array}{ccccc} 1 & 1 & 1 & 1 & 1 \\ 6 & 0 & 6 & 0 & 0 \\ 21 & 3 & 21 & 3 & 3 \\ 48 & 0 & 48 & 0 & 0 \\ 78 & 6 & 78 & 6 & 6 \\ 92 & 0 & 92 & 0 & 0 \end{array}\right) \\ (\sigma_{\theta j}) \end{array} \\ \times \underbrace{\left(\begin{array}{ccccc} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{array}\right)}_{\text{inverse}} \\ = \begin{array}{r} \\ X^{10}, Y^{10} \\ X^9Y, XY^9 \\ X^8Y^2, X^2Y^8 \\ X^7Y^3, X^3Y^7 \\ X^6Y^4, X^4Y^6 \\ X^5Y^5 \end{array} \begin{array}{c} \begin{array}{ccccc} \mathbf{C}_1 & \mathbf{C}_2 & \mathbf{C}_s & \mathbf{C}'_s & \mathbf{C}_{2v} \end{array} \\ \left(\begin{array}{ccccc} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 9 & 0 & 3 \\ 0 & 0 & 24 & 0 & 0 \\ 0 & 0 & 36 & 0 & 6 \\ 0 & 0 & 46 & 0 & 0 \end{array}\right) \end{array} \end{array} \tag{25}$$

The matrix in the right-hand side of Eq. 25 gives the number of isomers with X^mY^n and with a given symmetry ($\mathbf{C}_1$, $\mathbf{C}_2$, $\mathbf{C}_s$, $\mathbf{C}'_s$, or $\mathbf{C}_{2v}$) at the corresponding intersection. Note than an X^mY^n term gives the same result as an X^nY^m term. To illustrate this enumeration, Fig. 1 shows nine $\mathbf{C}_s$-isomers with X^2Y^8 ($Y = H$). Each of the six isomers at the first and second rows contains an unsubstituted phenyl group and a di-substituted phenyl group, while each of the three isomers at the bottom row contains two mono-substituted phenyl groups of different kinds. On the other hand, Fig. 2 shows three $\mathbf{C}_{2v}$-isomers with X^2Y^8 ($Y = H$), each of which contains

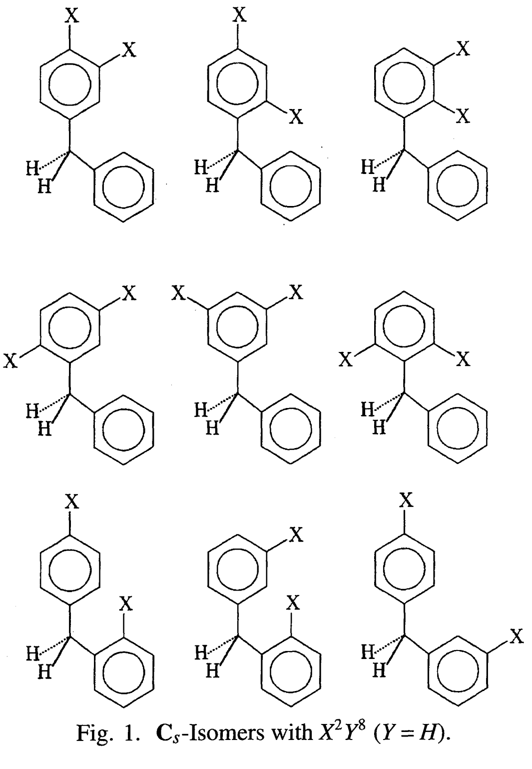


Fig. 1. $\mathbf{C}_s$-Isomers with X^2Y^8 ($Y = H$).

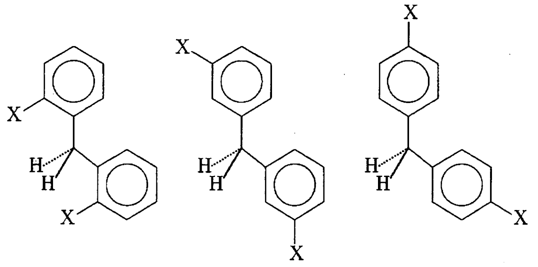


Fig. 2. $\mathbf{C}_{2v}$-Isomers with X^2Y^8 $(Y = H)$.

two mono-substituted phenyl groups of the same kind.

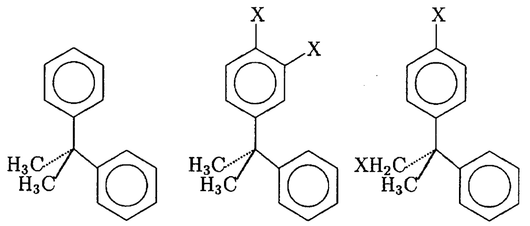
3 Enumeration of 2,2-Diphenylpropane Derivatives. Let us consider derivatives of 2,2-diphenylpropane (**5**). These derivatives are generated by the proligand approach, where we replace each proligand A of the promolecule **1** by a phenyl group with mX and nY $(m+n=5)$ and each proligand B by a methyl group with $m'X$ and $n'Y$ $(m'+n'=3)$. Then, we count isomers with X^mY^n ($m+n = 16$ for each 2,2-diphenylpropane derivative) and a given symmetry ($\mathbf{C}_1$, $\mathbf{C}_2$, $\mathbf{C}_s$, $\mathbf{C}_s'$, or $\mathbf{C}_{2v}$). For example, compounds **6** and **7** are X^2Y^8-isomers ($Y = H$ in Chart 2). This enumeration is a reinvestigation of the example described in Ref. 10 in the light of the present approach. The phenyl group can be treated by the method described in the preceding subsection. The methyl group belongs to $\mathbf{C}_{3v}$-symmetry, where the three positions (hydrogens) construct an orbit governed by the coset representation $\mathbf{C}_{3v}(/\mathbf{C}_s)$. For the treatment of the point group $\mathbf{C}_{3v}$, we prepare the corresponding markaracter table (Table 3) and the characteristic monomial table (Table 4).

Since the coset representation $\mathbf{C}_{3v}(/\mathbf{C}_s)$ for a methyl group is reduced into A_1+E (Table 3), characteristic monomials for $\mathbf{C}_{3v}$ (Table 2) are collected in accord with this reduction to give $CI^{(a)}$ (Eq. 8) and $CI^{(m)}$ (Eq. 12).

$$CI^{(a)}(\mathbf{C}_{3v}; s_d) = s_1 s_2, \tag{26}$$

$$CI^{(m)}(\mathbf{C}_{3v}; s_d) = \frac{1}{6}s_1^3 + \frac{1}{2}s_1 s_2 + \frac{1}{3}s_3, \tag{27}$$

into which the inventory (Eq. 17) is introduced. Thereby, we have



5 **6** **7**

Chart 2.

Table 3. Markaracters for $\mathbf{C}_{3v}$

$\mathbf{C}_{3v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_3$	Reduction
$\mathbf{C}_{3v}(/\mathbf{C}_1)$	6	0	0	A_1+A_2+2E
$\mathbf{C}_{3v}(/\mathbf{C}_s)$	3	1	0	A_1+E
$\mathbf{C}_{3v}(/\mathbf{C}_3)$	2	0	2	A_1+A_2
$\mathbf{C}_{3v}(/\mathbf{C}_{3v})$	1	1	1	A_1

Table 4. Characteristic Monomials for $\mathbf{C}_{3v}$

$\mathbf{C}_{3v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_3$	Remarks
A_1	s_1	s_1	s_1	$\mathbf{C}_{3v}(/\mathbf{C}_{3v})$
A_2	s_1	$s_1^{-1}s_2$	s_1	$\mathbf{C}_{3v}(/\mathbf{C}_3)-\mathbf{C}_{3v}(/\mathbf{C}_{3v})$
E	s_1^2	s_2	$s_1^{-1}s_3$	$\mathbf{C}_{3v}(/\mathbf{C}_s)-\mathbf{C}_{3v}(/\mathbf{C}_{3v})$
N_j	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{3}$	Achiral isomers and enantiomeric pairs
$N_j^{(m)}$	$\frac{1}{3}$	0	$\frac{2}{3}$	Achiral and chiral isomers
$N_j^{(e)}$	$\frac{1}{6}$	$-\frac{1}{2}$	$-\frac{1}{3}$	Enantiomeric pairs $(N_j^{(m)}-N_j)$
$N_j^{(a)}$	0	1	0	Achiral isomers $(N_j-N_j^{(e)})$

$$\begin{aligned} f^{(a)} &= (X+Y)(X^2+Y^2) \\ &= X^3+X^2Y+XY^2+Y^3 \end{aligned} \tag{28}$$

$$\begin{aligned} f^{(m)} &= \frac{1}{6}(X+Y)^3+\frac{1}{2}(X+Y)(X^2+Y^2)+\frac{1}{3}(X^3+Y^3) \\ &= X^3+X^2Y+XY^2+Y^3. \end{aligned} \tag{29}$$

The right-hand sides are generating functions for calculating $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$. Obviously, they are common for $f^{(a)}$ and $f^{(m)}$. Hence, the figure-inventories (Eqs. 2, 3, and 4) are calculated for the present enumeration:

$$a_d = b_d = c_d = (X^3)^d + (X^2Y)^d + (XY^2)^d + (Y^3)^d. \tag{30}$$

This equation is identical with Eq. 11 of Ref. 10. Thus, the present proceduce for obtaining such figure-inventories is shown to be remarkably simpler than the one described in the previous paper.[10]

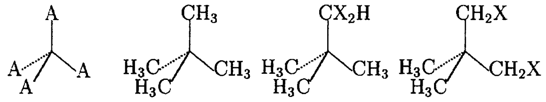
4 Enumeration of 2,2-Dimethylpropane Derivatives. Let us consider derivatives of 2,2-dimethylpropane (**9**), where we replace each proligand A of the promolecule **8** by a methyl group with lX, mY, and nZ $(l+m+n=3)$. Then, we count isomers with $X^lY^mZ^n$ ($l+m+n = 12$ for each 2,2-dimethylpropane derivative) and a given symmetry, as exemplified by compounds **10** and **11** in Chart 3 ($X^2Y^{10}Z^0$-isomers, $Y = H$). This enumeration is a reinvestigation of the example described in Ref. 10 in the light of the present approach. This enumeration means that methyl ligands may be chiral ones when substituted by XYZ.

Since the methyl group can be treated by the same method as described in the preceding subsection, Eqs. 26 and 27 are used as cycle indices, into which the inventory

$$s_d = X^d + Y^d + Z^d \tag{31}$$

is introduced. Thereby, we have

$$\begin{aligned} f^{(a)} &= (X+Y+Z)(X^2+Y^2+Z^2) \\ &= X^3+X^2Y+XY^2+Y^3+X^2Z+XZ^2+Y^2Z+YZ^2+Z^3, \end{aligned} \tag{32}$$



8 **9** **10** **11**

Chart 3.

$$f^{(m)}=\frac{1}{6}(X+Y+Z)^3+\frac{1}{2}(X+Y+Z)(X^2+Y^2+Z^2)\frac{1}{3}(X^3+Y^3+Z^3)$$
$$=X^3+X^2Y+XY^2+Y^3+X^2Z+XZ^2+Y^2Z+YZ^2+Z^3+2XYZ. \qquad (33)$$

The right-hand side of $f^{(a)}$ is a generating function for calculating $\varkappa_{\xi a}$, while $f^{(m)}$ is the one for calculating $\varkappa_{\xi a}$ and $\varkappa_{\xi c}$. The difference between them is the term *XYZ*, which represents a chiral methyl ligand. Thereby, the figure-inventories (Eqs. 2, 3, and 4) are calculated for the present enumeration:

$$a_d=(X^3)^d+(X^2Y)^d+(XY^2)^d+(Y^3)^d+(X^2Z)^d+(XZ^2)^d+(Y^2Z)^d$$
$$+(YZ^2)^d+(Z^3)^d, \qquad (34)$$

$$b_d=c_d=(X^3)^d+(X^2Y)^d+(XY^2)^d+(Y^3)^d+(X^2Z)^d+(XZ^2)^d$$
$$+(Y^2Z)^d+(YZ^2)^d+(Z^3)^d+2(XYZ)^d. \qquad (35)$$

These equations are identical with Eqs. 23 to 25 of Ref. 10. Thus, even in cases where chiral ligands are involved, the present proceduce for obtaining such figure-inventories is shown to be remarkably simpler than the one described in the previous paper.[10]

Conclusion

The combination of the promolecule concept with the characteristic-monomial method has provided us with a simple procedure for counting isomers derived from non-rigid parent molecules. This procedure has been applied to the enumeration of diphenylmethanes. Re-examination concerning 2, 2-diphenylpropanes and 2,2-dimethylpropanes has been accomplished, giving equivalent results to those described in a previous work.[10]

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