

Characteristic Monomial Tables for Enumeration of Achiral and Chiral Isomers

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The characteristic monomial table of an achiral group is applied to combinatorial enumeration of the following types: (1) achiral isomers and enantiomeric pairs, (2) achiral isomers and chiral isomers, (3) enantiomeric pairs, and (4) achiral isomers. The cycle index of each case is obtained by using the same set of subduced cycle indices derived from characteristic monomials, where the coefficients of the subduced cycle indices are given in advance.

Chemical combinatorics is one of the main fields of chemistry that utilize the group theory as an essential tool. In particular, Pólya's theorem, which is based on permutation groups or representations, has been widely used for various problems of counting isomers.[1—5] For example, Pólya's theorem has been applied to the enumeration of optical isomers, after the distinct definitions of isomers as equivalence classes.[6—11] In the continuation of such approaches based on permutation groups or representations, mark tables containing marks for coset representations[12—24] have found their applications to chemical combinatorics.

On the other hand, there exist many other fields of chemistry utilizing another type of group theory, which is based on point groups and linear representations. Thus, character tables containing characters for irreducible representations[25—32] have been applied to various problems in theoretical, physical, inorganic, and organic chemistry.

We have tried to apply the latter type of group theory to chemical combinatorics that has not been its original territory. This effort has been started from the construction of symmetry adapted functions[33] and the alternative formulation of Pólya's theorem, both of which have come from the USCI (unit-subduced-cycle-index) approach developed by us.[34] Thus, we have recently proposed the concepts of markaracter (mark-character) and of **Q**-conjugacy characters to disucuss characters and marks on a common basis,[35,36] where we are able to use characteristic monomials in place of USCIs.[37] In order to show the scope and limitations of the characteristic-monomial approach, the present report deals with the enumeration of optical isomers and related problems.

1 Characteristic Monomials for Achiral and Chiral Point Groups

Let us consider an achiral point group **G**. All of the proper rotations of **G** construct a subgroup $\mathbf{G}^{(m)}$ of **G**. The taget of this section is to clarify the relashionship between the **Q**-conjugacy character table of $\mathbf{G}^{(m)}$ and that of **G** as well as the relashionship between the characteristic monominal table of $\mathbf{G}^{(m)}$ and that of **G**.

When we select an improper rotation σ as a representative, we have the following coset decomposition:

$$\mathbf{G} = \mathbf{G}^{(m)} + \mathbf{G}^{(m)}\sigma. \tag{1}$$

Obviously $\mathbf{G}^{(m)}$ is a normal subgroup of **G** and satisfies $|\mathbf{G}| = 2|\mathbf{G}^{(m)}|$. Let Γ_i ($i = 1, 2, \cdots, s$) be the irreducible representations of $\mathbf{G}^{(m)}$. Then, we have $\Gamma_i^{\uparrow\mathbf{G}}$ as an induced representation of $\mathbf{G}^{(m)}$ into **G**:

$$\Gamma_i^{\uparrow\mathbf{G}}(x) = \begin{pmatrix} \Gamma_i(x) & 0 \\ 0 & \Gamma_i(\sigma^{-1}x\sigma) \end{pmatrix} = \begin{pmatrix} \Gamma_i(x) & 0 \\ 0 & \Gamma_i^{\sigma}(x) \end{pmatrix} \tag{2}$$

$$\Gamma_i^{\uparrow\mathbf{G}}(x\sigma) = \begin{pmatrix} 0 & \Gamma_i(x) \\ \Gamma_i(\sigma^{-1}x\sigma) & 0 \end{pmatrix} = \begin{pmatrix} 0 & \Gamma_i(x) \\ \Gamma_i^{\sigma}(x) & 0 \end{pmatrix} \tag{3}$$

for $x \in \mathbf{G}$ and $\sigma \in \mathbf{G}^{(m)}\sigma$, where the symbol Γ_i^{σ} denotes a conjugate representation of Γ_i within **G**. That is to say, we have

$$\Gamma_i^{\sigma}(x) = \Gamma_i(\sigma^{-1}x\sigma). \tag{4}$$

The irreducible representation Γ_i for the group $\mathbf{G}^{(m)}$ is matured or unmatured, if the criterion described in a previous paper[38] is applied to this case. The maturity of irreducible representations is closely related to the behavior of **Q**-conjugacy representations. More precisely speaking, an appropriate set of unmatured irreducible representations constructs a **Q**-conjugacy representation, which is matured due to the definition described previously.[39] On the other hand, the induced representation $\Gamma_i^{\uparrow\mathbf{G}}$ (Eqs. 2 and 3) may be matured or unmatured according to the properties of the original irreducible representation Γ_i and to the induction process.

Example 1. Let us consider irreducible representations of the point groups **T** and $\mathbf{T}_d$ from the viewpoint of maturity. Since the point group **T** is an unmatured group, its character table is different from its **Q**-conjugacy character table. Table 1 shows the character table of **T**. The representations A (a totally symmetric irreducible representation) and T are matured representations. The representations E_a and

Table 1. Character Table for **T**

	$\mathbf{K}_1$ I	$\mathbf{K}_2$ $3C_2$	$\mathbf{K}_{31}$ $4C_3$	$\mathbf{K}_{32}$ $4C_3^2$
A	1	1	1	1
$E_{(a)}$	1	1	ω	ω^2
$E_{(b)}$	1	1	ω^2	ω
T	3	-1	0	0

$\omega = \cos(2\pi/3)+i\sin(2\pi/3)$.

E_b are both unmatured, but they are added to give a matured representation, as shown in the **Q**-conjugacy chacter table of **T** (Table 2). Note the relationship $\omega+\omega^2 = -1$.

On the other hand, the character table for the point gourp $\mathbf{T}_d$ (Table 3) is identical with the **Q**-conjugacy character table, since all the irreducible representations of the group are matured.

The induction process is usually discussed by comparing between two character tables (e.g., Tables 1 and 3). For example, the totally symmetric irreducible representation A of **T** is induced into $\mathbf{T}_d$ to give $A^{\uparrow\mathbf{T}_d}$, which is reduced to two matured irreducible representations of $\mathbf{T}_d$, i.e. A_1 and A_2. In a similar way, we have $T^{\uparrow\mathbf{T}_d} = T_1+T_2$. Thus, a matured representation of **T** is induced into an induced representation of $\mathbf{T}_d$, which is in turn reducible to two matured irreducible representations. Obviously, we can obtain the subductions of the resulting induced representation, $T_1{\downarrow}\mathbf{T} = T_2{\downarrow}\mathbf{T} = T$.

The unmatured irreducible representation E_a (one of the irreducible representations denoted by the Mulliken notation E) is induced in agreement with the equation, $E_a^{\uparrow\mathbf{T}_d} = E$. In a similar way, we have $E_b^{\uparrow\mathbf{T}_d} = E$. Obviously, we obtain $E{\downarrow}\mathbf{T} = E_a+E_b$.

Let us alternatively consider the above induction process by comparing between two **Q**-conjugacy character tables (e.g., Tables 2 and 3). The matured **Q**-conjugacy representation E obtained by adding E_a and E_b is induced into a representation of degree four, which is reduced in accord with $E^{\uparrow\mathbf{T}_d} = 2E$. Thus, a matured representation of **T** is induced into an induced representation of $\mathbf{T}_d$, which is in turn reducible to two matured irreducible representations. Obviously, we have the subduction of the resulting representation, i.e., $E{\downarrow}\mathbf{T} = E\ (=E_a+E_b)$.

Table 2. **Q**-Conjugacy Character Table for **T**

	$\mathbf{K}_1$ $\downarrow\mathbf{C}_1$ I	$\mathbf{K}_2$ $\downarrow\mathbf{C}_2$ $3C_2$	$\mathbf{K}_3$ $\downarrow\mathbf{C}_3$ $4C_3, 4C_3^2$
A	1	1	1
$E\ (=E_{(a)}+E_{(b)})$	2	2	-1
T	3	-1	0

Table 3. Character (**Q**-Conjugacy Character) Table for $\mathbf{T}_d$

	$\downarrow\mathbf{C}_1$ I	$\downarrow\mathbf{C}_2$ $3C_2$	$\downarrow\mathbf{C}_s$ $6\sigma_d$	$\downarrow\mathbf{C}_3$ $8C_3$	$\downarrow\mathbf{S}_4$ $6S_4$
A_1	1	1	1	1	1
A_2	1	1	-1	1	-1
E	2	2	0	-1	0
T_1	3	-1	-1	0	1
T_2	3	-1	1	0	-1

This example can be extended into general cases, as shown in Appendix A. The examination of the repspective cases can be summarized into a simple theorem concerning **Q**-conjugacy representations.

Theorem 1. *Each* **Q**-*conjugacy representation of* **G** *is subduced into* $\mathbf{G}^{(m)}$ *to give a* **Q**-*conjugacy representation of* $\mathbf{G}^{(m)}$.

Since a set of characteristic monomials is assigned to each **Q**-conjugacy representation, Theorem 1 gives a corollary.

Corollary 1. *A set of characteristic monomials for each* **Q**-*conjugacy representation of* **G** *is identical with the corresponding set of characteristic monomials for* $\mathbf{G}^{(m)}$.

Suppose that a **Q**-conjugacy representation Φ_i for **G** corresponds to the following characteristic monomials:

$$Z(\Phi_i^{\downarrow\mathbf{C}_{n_j}};\, s_d) = \prod^{d|n_j} s_d^{\nu_{id}}, \tag{5}$$

where C_{n_j} denotes a cyclic subgroup of order n_j and the symbol $d|n_j$ indicates that the natural number d runs over the divisors of the natural number n_j. It should be noted the numbering index (subscript) i is changed so as to involve such representations as Φ_{ig} and Φ_{iu} in a single alignment with a single subscript.

Theorem 1 shows that the subduced representation $\Phi_i^{\downarrow\mathbf{G}^{(m)}}$ is a **Q**-conjugacy representation of $\mathbf{G}^{(m)}$. According to Corollary 1, Eq. 5 is converted into

$$Z(\Gamma_i^{\downarrow\mathbf{C}_{n_j}};\, s_d) = Z((\Phi_i^{\downarrow\mathbf{G}^{(m)}})^{\downarrow\mathbf{C}_{n_j}};\, s_d) = Z(\Phi_i^{\downarrow\mathbf{C}_{n_j}};\, s_d) = \prod^{d|n_j} s_d^{\nu_{id}}, \tag{6}$$

where $\mathbf{C}_{n_j}$ denotes a chiral cyclic subgroup of order n_j and the symbol $d|n_j$ indicates that the natural number d runs over the divisors of the natural number n_j.

Example 2. Table 4 collects characteristic monomials for $\mathbf{T}_d$, while Table 5 collects characteristic monomials for **T**. All of the monomials satisfy Corollary 1, as shown in the following explanation.

The irreducible representation A_1, which is also a **Q**-conjugacy representation of $\mathbf{T}_d$, is restricted into **T** to give the irreducible representation A, which is also a **Q**-conjugacy representation. The characteristic monomials in the A_1 row of Table 4 are identical with those in the A row of Table 5 by focusing on the $\downarrow\mathbf{C}_1$, $\downarrow\mathbf{C}_2$, and $\downarrow\mathbf{C}_3$ columns. The irreducible representation A_2 is also restricted into **T** to give the same irreducible representation A and gives the same results as the A_1 does. The set of A_1 and A_2 is an example of Case 2 (see Appendix) inducing a matured representation into a matured one.

The irreducible representation E of $\mathbf{T}_d$ is restricted into **T** to give two irreducible representations (unmatured representations), which are summed up into a **Q**-conjugacy representation E (a matured representation). The comparison between the E row of Table 4 and that of Table 5 indicates that this case isan example of Case 2 (see Appendix) inducing

Table 4. Characteristic Monomial Table for $\mathbf{T}_d$

	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{C}_3$	$\downarrow\mathbf{S}_4$	Remarks
A_1	s_1	s_1	s_1	s_1	s_1	
A_2	s_1	s_1	$s_1^{-1}s_2$	s_1	$s_1^{-1}s_2$	
E	s_1^2	s_1^2	s_2	$s_1^{-1}s_3$	s_2	
T_1	s_1^3	$s_1^{-1}s_2^2$	$s_1^{-1}s_2^2$	s_3	$s_1s_2^{-1}s_4$	
T_2	s_1^3	$s_1^{-1}s_2^2$	s_1s_2	s_3	$s_1^{-1}s_4$	
N_j	$\frac{1}{24}$	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{1}{4}$	Achiral isomers and enatiomeric pairs
$N_j^{(m)}$	$\frac{1}{12}$	$\frac{1}{4}$	0	$\frac{2}{3}$	0	Achiral isomers and chiral isomers
$N_j^{(e)}$	$\frac{1}{24}$	$\frac{1}{8}$	$-\frac{1}{4}$	$\frac{1}{3}$	$-\frac{1}{4}$	Enantiomeric pairs
$N_j^{(a)}$	0	0	$\frac{1}{2}$	0	$\frac{1}{2}$	Achiral isomers

Table 5. Characteristic Monomials for $\mathbf{T}$

$\mathbf{T}$	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_3$
A	s_1	s_1	s_1
E	s_1^2	s_1^2	$s_1^{-1}s_3$
T	s_1^3	$s_1^{-1}s_2^2$	s_3
N_j	$\frac{1}{12}$	$\frac{1}{4}$	$\frac{2}{3}$

an unmatured representation into a matured one.

The irreducible representations, T_1 and T_2, give the same irreducible representation T during the restriction of $\mathbf{T}_d$ into $\mathbf{T}$. All of the participating representations are matured. The comparison between the T_1 and T_2 row of Table 4 and the T row of Table 5 shows that the set of T_1 and T_2 is an example of Case 2 (see Appendix) starting from a matured representation.

Example 3. Table 6 collects characteristic monomials for $\mathbf{T}_h$. All of the monomials satisfy Corollary 1 by comparing the table with Table 5 for $\mathbf{T}$.

The two irreducible representations involved in the $\mathbf{Q}$-conjugacy representation E_g as well as the two irreducible representations involved in the $\mathbf{Q}$-conjugacy representation E_u are obtained by the induction of the two irreducible representation constructing E. The comparison between the participating rows of Table 6 and that of Table 5 indicates that this case is an example of Case 2 (see Appendix) inducing an unmatured representation into an unmatured one.

2 Combinatorial Enumeration

2.1 Enumeration of Achiral Isomers and Enantiomeric Pairs. Although the enumeration described in this subsection will be reported elsewhere in detail with proofs,[37] a brief description and an illustrative example are necessary to give further reults described in the following subsections. The number of achiral isomers plus enantiomeric pairs is calculated by taking account of an achiral point group $\mathbf{G}$, where an enantiomeric pair is regarded as one isomer as well as an achiral isomer is counted as one isomer. This means that an isomer described in the present section corresponds to an equivalence class with respect to all of the symmetry operations of $\mathbf{G}$.

Let us consider a skeleton with n positions. Suppose that the skeleton is controled by the point group $\mathbf{G}$, which has a non-redundant set of dominant subgroups,

$$SCSG_{\mathbf{G}} = \{\mathbf{C}_{n_1}, \mathbf{C}_{n_2}, \cdots, \mathbf{C}_{n_s}\}. \tag{7}$$

The n positions of the skeleton are characterized by a permutation representation, $\mathbf{P}$ ($n = |\mathbf{P}|$). Suppose that the permutation representation $\mathbf{P}$ is transformed into a matrix representation. Then, the latter representation is represented by a linear combination of $\mathbf{Q}$-conjugacy representations, $\hat{\Theta}_i$ ($i = 1, 2, \cdots, s$), i.e.,

$$\mathbf{P} = \sum_{i=1}^{s} a_i \hat{\Theta}_i, \tag{8}$$

where each multiplicity a_i is a non-negative integer.[37] The

Table 6. Characteristic Monomials for $\mathbf{T}_h$

$\mathbf{T}_h$	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{C}_i$	$\downarrow\mathbf{C}_3$	$\downarrow\mathbf{S}_6$	Remarks
A_g	s_1	s_1	s_1	s_1	s_1	s_1	
A_u	s_1	s_1	$s_1^{-1}s_2$	$s_1^{-1}s_2$	s_1	$s_1^{-1}s_2$	
E_g	s_1^2	s_1^2	s_1^2	s_1^2	$s_1^{-1}s_3$	$s_1^{-1}s_3$	
E_u	s_1^2	s_1^2	$s_1^{-2}s_2^2$	$s_1^{-2}s_2^2$	$s_1^{-1}s_3$	$s_1s_2^{-1}s_3^{-1}s_6$	
T_g	s_1^3	$s_1^{-1}s_2^2$	$s_1^{-1}s_2^2$	s_1^3	s_3	s_3	
T_u	s_1^3	$s_1^{-1}s_2^2$	s_1s_2	$s_1^{-3}s_2^3$	s_3	$s_3^{-1}s_6$	
N_j	$\frac{1}{24}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{24}$	$\frac{1}{3}$	$\frac{1}{3}$	Achiral isomers and enatiomeric pairs
$N_j^{(m)}$	$\frac{1}{12}$	$\frac{1}{4}$	0	0	$\frac{2}{3}$	0	Achiral isomers and chiral isomers
$N_j^{(e)}$	$\frac{1}{24}$	$\frac{1}{8}$	$-\frac{1}{8}$	$-\frac{1}{24}$	$\frac{1}{3}$	$-\frac{1}{3}$	Enantiomeric pairs
$N_j^{(a)}$	0	0	$\frac{1}{4}$	$\frac{1}{12}$	0	$\frac{2}{3}$	Achiral isomers

multiplicities are used to obtain the subduced cycle index for each subgroup $\mathbf{C}_{n_j}$:

$$SCI(\mathbf{C}_{n_j};\, s_d) = \prod_{i=1}^{s} \left(Z(\Phi_i^{\downarrow \mathbf{C}_{n_j}};\, s_d) \right)^{a_i} = \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}. \tag{9}$$

By using the *SCI* (Eq. 9), the cycle index for counting isomers (as achiral isomers and enantiomeric pairs) is obtained by means of Eq. 40. It follows that

$$\begin{aligned} CI(\mathbf{G};\, s_d) &= \sum_{j=1}^{s} N_j SCI(\mathbf{C}_{n_j};\, s_d) = \sum_{j=1}^{s} N_j \prod_{i=1}^{s} \left(Z(\Phi_i^{\downarrow \mathbf{C}_{n_j}};\, s_d) \right)^{a_i} \\ &= \sum_{j=1}^{s} N_j \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}. \end{aligned} \tag{10}$$

Suppose that η_i of ligands X_i ($i = 1, 2, \cdots, \nu$) are selected from a set of ligands represented by

$$\mathbf{X} = \{X_1, X_2, \cdots, X_\nu\}, \tag{11}$$

where we have a partition:

$$[\eta] = \eta_1 + \eta_2 + \cdots + \eta_\nu = n. \tag{12}$$

They are placed on the positions of the skeleton to give isomers with the formula,

$$W_\eta = \prod_{\ell=1}^{\nu} X_\ell^{\eta_\ell}. \tag{13}$$

The number (F_η) of isomers with the formula W_η (Eq. 13) is enumerated by the following theorem.

Theorem 2. *The number (F_η) of isomers with W_η is calculated by a generating function,*

$$\sum_{[\eta]} F_\eta W_\eta = CI(\mathbf{G};\, s_d), \tag{14}$$

where the cycle index (Eq. 10) in the right-hand side is substituted by ligand inventories,

$$s_d = \sum_{\ell=1}^{\nu} X_\ell^d. \tag{15}$$

Example 4. Let us consider the adamantane skeleton **1** (Chart 1), where four hydrogens (H^a) on the bridgehead positions and twelve hydrogens (H^b) on the bridge positions are replaced by one kind of halogen atoms (X).

The fixed-point vector (FPV) for the 16 positions is obtained to be (16, 0, 4, 1, 0) by inspection. The FPV is multiplied by the inverse of the **Q**-conjugacy character table of $\mathbf{T}_d$:

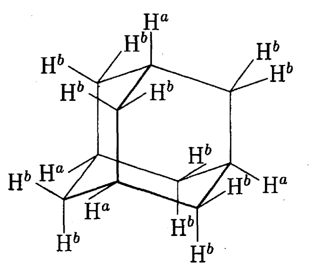

Chart 1. Skeleton **1**.

$$(16,\ 0,\ 4,\ 1,\ 0) \begin{pmatrix} \frac{1}{24} & \frac{1}{24} & \frac{1}{12} & \frac{1}{8} & \frac{1}{8} \\ \frac{1}{8} & \frac{1}{8} & \frac{1}{4} & -\frac{1}{8} & -\frac{1}{8} \\ \frac{1}{4} & -\frac{1}{4} & 0 & -\frac{1}{4} & \frac{1}{4} \\ \frac{1}{3} & \frac{1}{3} & -\frac{1}{3} & 0 & 0 \\ \frac{1}{4} & -\frac{1}{4} & 0 & \frac{1}{4} & -\frac{1}{4} \end{pmatrix} = (2,\ 0,\ 1,\ 1,\ 3) \tag{16}$$

The row vector in the right-hand side of Eq. 16 represents the multiplicities of **Q**-conjugacy represenations. It follows that **P** is reduced to give

$$\mathbf{P} = 2A_1 + E + T_1 + 3T_2. \tag{17}$$

By using the multiplicities (Eq. 16) and the characteristic monomials listed in Table 4, we obtain *SCI*s (Eq. 9) for the present example. Thereby, we obtain the *CI* by using the coefficients N_j collecting in the bottom part of Table 4.

$$\begin{aligned} f &= CI(\mathbf{T}_d;\, s_d) \\ &= \frac{1}{24}(s_1)^2(s_1^2)(s_1^3)(s_1^3)^3 + \frac{1}{8}(s_1)^2(s_1^2)(s_1^{-1}s_2^2)(s_1^{-1}s_2^2)^3 \\ &\quad + \frac{1}{4}(s_1^2)(s_2)(s_1^{-1}s_2^2)(s_1 s_2)^3 + \frac{1}{3}(s_1)^2(s_1^{-1}s_3)(s_3)(s_3)^3 \\ &\quad + \frac{1}{4}(s_1)^2(s_2)(s_1 s_2^{-1} s_4)(s_1^{-1}s_4)^3 \\ &= \frac{1}{24}s_1^{16} + \frac{1}{8}s_2^8 + \frac{1}{4}s_1^4 s_2^6 + \frac{1}{3}s_1 s_3^5 + \frac{1}{4}s_4^4. \end{aligned} \tag{18}$$

This *CI* is identical with Eq. 2 of Ref. 40, which has been obtained by means of the *USCI* approach. The ligand inventory for this case is represented by

$$s_d = 1 + x^d. \tag{19}$$

After Eq. 19 is introduced into Eq. 18, the resulting polynomial is expanded to give a generating function:

$$\begin{aligned} f &= (1 + x^{16}) + 2(x + x^{15}) + 9(x^2 + x^{14}) + 32(x^3 + x^{13}) \\ &\quad + 95(x^4 + x^{12}) + 203(x^5 + x^{11}) + 373(x^6 + x^{10}) \\ &\quad + 515(x^7 + x^9) + 584x^8. \end{aligned} \tag{20}$$

For illustrating the results of Eq. 20, Fig. 1 depicts two monosubstituted derivatives, the number of which appears as the coefficient of the term x in the right-hand side of Eq. 20. Both of these isomers are achiral.

Disubstituted isomers are chiral or achiral. Figure 2 depicts three enantiomeric pairs of disubstituted derivatives, since they are chiral isomers. Each rwo of Fig. 2 involves the two antipodes of an enantiomeric pair. On the other hand, Fig. 2 depicts six achiral disubstituted derivatives. The sum of 3 and 6 is equal to 9, which is equal to the coefficient of the term x^2 in the right-hand side of Eq. 20.

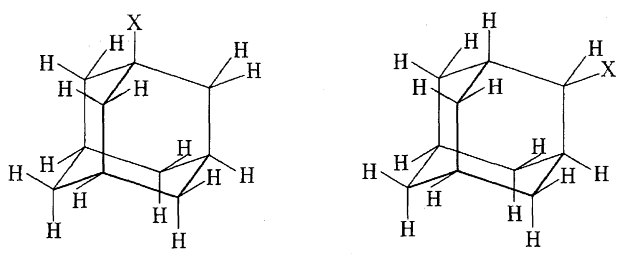

Fig. 1. Two monosubstituted derivatives.

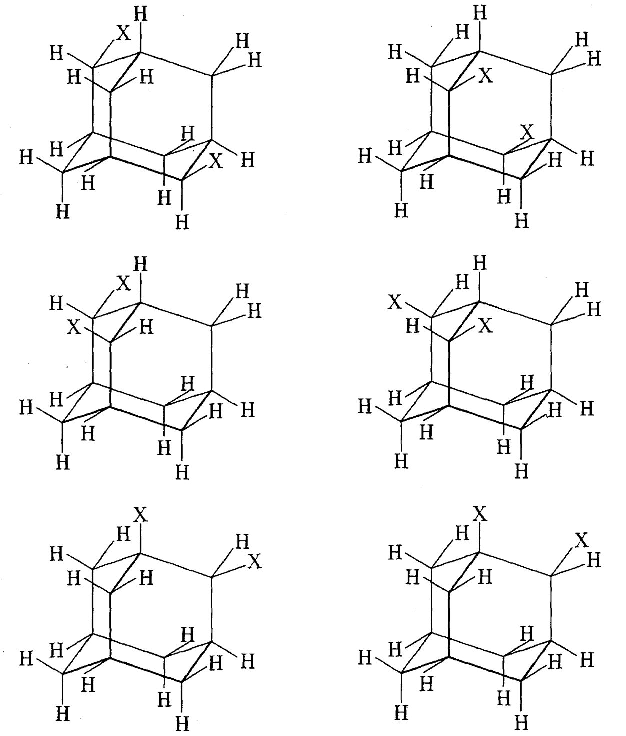

Fig. 2. Three enantiomeric pairs of disubstituted derivatives.

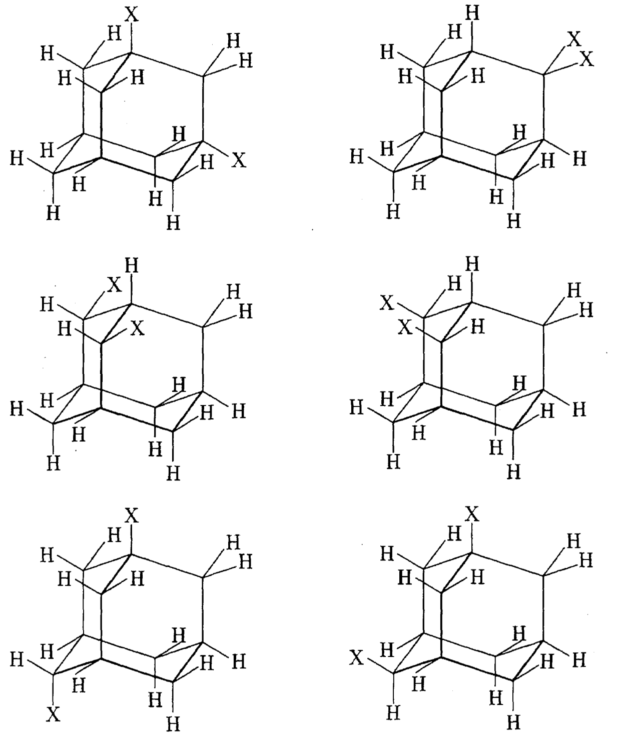

Fig. 3. Six achiral disubstituted derivatives.

2.2 Enumeration of Achiral Isomers and Chiral Isomers. Let us consider the two antipodes of an enantiomeric pair are both counted as distinct isomers. Thereby, we obtain the total number of achiral isomers and chiral isomers (Fig. 3). In other words, an isomer described in the present subsection corresponds to an equivalence class with respect to all of the operations of $\mathbf{G}^{(m)}$. Hence, the cycle index for counting such isomers (achiral isomers and chiral isomers) is obtained on the basis of a $\mathbf{G}^{(m)}$-skeleton.

In the light of Theorem 1, the multiplicities appearing in Eq. 8 can be used to obtain the *SCI* for this case. Thus, the use of Eq. 6 gives the subduced cycle index for each subgroup $\mathbf{C}_{n_{j'}}$:

$$SCI^{(m)}(\mathbf{C}_{n_{j'}};\, s_d) = \prod_{i=1}^{s}\left(Z(\Gamma_i^{\downarrow \mathbf{C}_{n_{j'}}};\, s_d)\right)^{a_i} = \prod_{i=1}^{s}\prod_{d|n_j} s_d^{a_i \nu_{id}}. \tag{21}$$

Note that the subscript i is originally concerned with the group $\mathbf{G}$ but is also applied to the group $\mathbf{G}^{(m)}$ in terms of Theorem 1. Thereby, we have the cycle index for counting isomers (as achiral isomers and chiral isomers) as follows.

$$\begin{aligned} CI^{(m)}(\mathbf{G}^{(m)};\, s_d) &= \sum_{j'} N_{j'}\, SCI^{(m)}(\mathbf{C}_{n_{j'}};\, s_d) \\ &= \sum_{j'} N_{j'} \prod_{i=1}^{s}\prod_{d|n_{j'}} s_d^{a_i \nu_{id}}, \end{aligned} \tag{22}$$

where j' runs to cover all of the cyclic subgroups of $\mathbf{G}^{(m)}$. In terms of Theorem 1 and Corollary 1, the numbering index (j') in Eq. 22 can be displaced by the numbering index (j). Hence, Eq. 22 is converted into

$$CI^{(m)}(\mathbf{G};\, s_d) = \sum_{j=1}^{s} N_j^{(m)} \prod_{i=1}^{s}\prod_{d|n_j} s_d^{a_i \nu_{id}}, \tag{23}$$

where we place $N_j^{(m)} = N_{j'}$ for chiral subgroups and $N_j^{(m)} = 0$ for achiral subgroups.

The number ($F_\eta^{(m)}$) of achiral isomers and chiral isomers with the formula (Eq. 13) is enumerated by the following theorem.

Theorem 3. *The number ($F_\eta^{(m)}$) of achiral isomers and chiral isomers with the weight W_η is calculated by a generating function,*

$$\sum_{[\eta]} F_\eta^{(m)} W_\eta = CI^{(m)}(\mathbf{G};\, s_d), \tag{24}$$

where the cycle index (Eq. 23) in the right-hand side is substituted by ligand inventories represented by Eq. 15.

Example 5. Let us consider the adamantane skeleton **1** as a continuation of Example 4. By using the multiplicities (Eq. 16) and the characteristic monomials listed in Table 4, we obtain the same *SCI*s (Eq. 9) as described in Example 4. Thereby, we obtain the *CI* by using the coefficients $N_j^{(m)}$ collected in the bottom part of Table 4.

$$\begin{aligned} f^{(m)} &= CI^{(m)}(\mathbf{T}_d;\, s_d) \\ &= \frac{1}{12}(s_1)^2(s_1^2)(s_1^3)(s_1^3)^3 + \frac{1}{4}(s_1)^2(s_1^2)(s_1^{-1}s_2^2)(s_1^{-1}s_2^2)^3 \\ &\quad + \frac{2}{3}(s_1)^2(s_1^{-1}s_3)(s_3)(s_3)^3 \\ &= \frac{1}{12}s_1^{16} + \frac{1}{4}s_2^8 + \frac{2}{3}s_1 s_3^5. \end{aligned} \tag{25}$$

The ligand inventory for this case is represented by Eq. 19, which is introduced into Eq. 25. The resulting polynomial is expanded to give a generating function:

$$f^{(m)} = (1+x^{16}) + 2(x+x^{15}) + 12(x^2+x^{14}) + 50(x^3+x^{13}) +162(x^4+x^{12}) + 364(x^5+x^{11}) + 688(x^6+x^{10}) +960(x^7+x^9) + 1090x^8. \quad (26)$$

Figure 1 involving two monosubstituted derivatives also illustrates the results of Eq. 26, since both of these isomers are achiral. The number of these appears as the coefficient of the term x in the right-hand side of Eq. 26.

Figure 2 is regarded to contain six chiral isomers from the present point of view, while Example 4 has regarded them as three enantiomeric pairs. On the other hand, Fig. 2 depicts six achiral disubstituted derivatives. The sum of 6 and 6 is equal to 12, which is equal to the coefficient of the term x^2 in the right-hand side of Eq. 26.

2.3 Enumeration of Enantiomeric Pairs. The cycle index for counting enantiomeric pairs is represented by $CI^{(m)}(\mathbf{G};\ s_d) - CI(\mathbf{G};\ s_d)$. Hence, Eqs. 10 and 23 give

$$\begin{aligned} CI^{(e)}(\mathbf{G};\ s_d) &= CI^{(m)}(\mathbf{G};\ s_d) - CI(\mathbf{G};\ s_d) \\ &= \sum_{j=1}^{s} N_j^{(m)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}} - \sum_{j=1}^{s} N_j \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}} \\ &= \sum_{j=1}^{s} N_j^{(e)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}, \end{aligned} \quad (27)$$

where we place $N_j^{(e)} = N_j^{(m)} - N_j$.

The number ($F_\eta^{(e)}$) of enantiomeric pairs with the formula (Eq. 13) is enumerated by the following theorem.

Theorem 4. *The number ($F_\eta^{(e)}$) of enantiomeric pairs with the weight W_η is calculated by a generating function,*

$$\sum_{[\eta]} F_\eta^{(e)} W_\eta = CI^{(e)}(\mathbf{G};\ s_d), \quad (28)$$

where the cycle index (Eq. 27) in the right-hand side is substituted by ligand inventories represented by Eq. 15.

Example 6. Let us consider the adamantane skeleton **1** as a continuation of Examples 4 and 5. The multiplicities (Eq. 16) and the characteristic monomials listed in Table 4 give the same *SCI*s (Eq. 9) as described in Example 4. Thereby, we obtain the *CI* by using the coefficients $N_j^{(e)}$ collected in the bottom part of Table 4.

$$\begin{aligned} f^{(e)} &= CI^{(e)}(\mathbf{T}_d;\ s_d) \\ &= \frac{1}{24}(s_1)^2(s_1^2)(s_1^3)(s_1^3)^3 + \frac{1}{8}(s_1)^2(s_1^2)(s_1^{-1}s_2^2)(s_1^{-1}s_2^2)^3 \\ &\quad -\frac{1}{4}(s_1^2)(s_2)(s_1^{-1}s_2^2)(s_1s_2)^3 + \frac{1}{3}(s_1)^2(s_1^{-1}s_3)(s_3)(s_3)^3 \\ &\quad -\frac{1}{4}(s_1)^2(s_2)(s_1s_2^{-1}s_4)(s_1^{-1}s_4)^3 \\ &= \frac{1}{24}s_1^{16} + \frac{1}{8}s_2^8 - \frac{1}{4}s_1^4s_2^6 + \frac{1}{3}s_1s_3^5 - \frac{1}{4}s_4^4. \end{aligned} \quad (29)$$

After the ligand inventory (Eq. 19) is introduced into Eq. 29, the resulting polynomial is expanded to give a generating function:

$$f^{(e)} = 3(x^2+x^{14}) + 18(x^3+x^{13}) + 67(x^4+x^{12}) +161(x^5+x^{11}) + 315(x^6+x^{10}) +445(x^7+x^9) + 506x^8. \quad (30)$$

Each of the two monosubstituted derivatives depicted in Fig. 1 is achiral and by no means enantiomeric pairs. This is in accord with the disappearance of the term x in the right-hand side of Eq. 30.

The three enantiomeric pairs depicted in Fig. 2 correspond to the term $3x^2$ in the right-hand side of Eq. 30. On the other hand, the six disubstituted derivatives depicted in Fig. 3 are achiral so as to be disregarded in the present enumeration.

2.4 Enumeration of Achiral Isomers. The cycle index for counting achiral isomers is represented by $2CI(\mathbf{G};\ s_d) - CI^{(m)}(\mathbf{G};\ s_d)$. Hence, Eqs. 10 and 23 give

$$\begin{aligned} CI^{(a)}(\mathbf{G};\ s_d) &= 2CI(\mathbf{G};\ s_d) - CI^{(m)}(\mathbf{G};\ s_d) \\ &= 2\sum_{j=1}^{s} N_j \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}} - \sum_{j=1}^{s} N_j^{(m)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}} \\ &= \sum_{j=1}^{s} N_j^{(a)} \prod_{i=1}^{s} \prod^{d|n_j} s_d^{a_i \nu_{id}}, \end{aligned} \quad (31)$$

where we place $N_j^{(a)} = 2N_j - N_j^{(m)}$.

The number ($F_\eta^{(a)}$) of achiral isomers with the formula (Eq. 13) is enumerated by the following theorem.

Theorem 5. *The number ($F_\eta^{(a)}$) of achiral isomers with the weight W_η is calculated by a generating function,*

$$\sum_{[\eta]} F_\eta^{(a)} W_\eta = CI^{(a)}(\mathbf{G};\ s_d), \quad (32)$$

where the cycle index (Eq. 31) in the right-hand side is substituted by ligand inventories represented by Eq. 15.

Example 7. Let us consider the adamantane skeleton **1** as a continuation of Examples 4, 5 and 6. The same *SCI*s (Eq. 9) as described in Example 4 along with the coefficients $N_j^{(a)}$ collected in the bottom part of Table 4 are used to give the *CI* represented by

$$\begin{aligned} f^{(a)} &= CI^{(a)}(\mathbf{T}_d;\ s_d) \\ &= \frac{1}{2}(s_1^2)(s_2)(s_1^{-1}s_2^2)(s_1s_2)^3 + \frac{1}{2}(s_1)^2(s_2)(s_1s_2^{-1}s_4)(s_1^{-1}s_4)^3 \\ &= \frac{1}{2}s_1^4s_2^6 + \frac{1}{2}s_4^4 \end{aligned} \quad (33)$$

After the ligand inventory (Eq. 19) is introduced into Eq. 33, the resulting polynomial is expanded to give a generating function:

$$f^{(a)} = (1+x^{16}) + 2(x+x^{15}) + 6(x^2+x^{14}) + 14(x^3+x^{13}) + 28(x^4+x^{12}) +42(x^5+x^{11}) + 58(x^6+x^{10}) + 70(x^7+x^9) + 78x^8. \quad (34)$$

The two monosubstituted derivatives depicted in Fig. 1 are achiral so as to illustrate the coefficient 2 of the term x in the right-hand side of Eq. 34.

The three enantiomeric pairs (or six chiral isomers) depicted in Fig. 2 are disregarded in the present enumeration. On the other hand, the six disubstituted derivatives depicted in Fig. 3 correspond to the term $6x^2$, since they are achiral.

3 Conclusion

The characteristic monomial table of an achiral group is proved to contain the characteristic monomial table of the maximum chiral subgroup. This means that the same set of characteristic monomials can be used for combinatorial enumeration of several types: (1) achiral isomers and enantiomeric pairs, (2) achiral isomers and chiral isomers, (3) enantiomeric pairs, and (4) achiral isomers, where the coefficients appearing in cycle indices for the respective cases are calculated by means of group-theoretical methods in advance.

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Appendix

This appendix is devoted to give the proofs of Theorem 1 and Corollary 1. The induced representation $\Gamma_i^{\uparrow \mathbf{G}}$ represented by Eqs. 2 and 3 is divided into two cases as follows.

Case 1: When Γ_i^{σ} is not identical with Γ_i, the character $\gamma_i^{\uparrow \mathbf{G}}$ corresponding to $\Gamma_i^{\uparrow \mathbf{G}}$ satisfies

$$\langle \gamma_i^{\uparrow \mathbf{G}}, \gamma_i^{\uparrow \mathbf{G}} \rangle = \frac{1}{|\mathbf{G}|} \sum_{x \in \mathbf{G}} (\gamma_i(x) + \gamma_i^{\sigma}(x))^2 = \sum_{x \in \mathbf{G}^{(m)}} (\gamma_i(x)^2 + \gamma_i^{\sigma}(x)^2)$$
$$= \frac{1}{|\mathbf{G}|} \times (|\mathbf{G}^{(m)}| + |\mathbf{G}^{(m)}|) = 1,$$

where $\gamma_i(x)$ and $\gamma_i^{\sigma}(x)$ represent the irreducible characters of $\mathbf{G}^{(m)}$. Hence, the induced representation $\Gamma_i^{\uparrow \mathbf{G}}$ an irreducible representation of $\mathbf{G}$. The irreducible representation $\Gamma_i^{\uparrow \mathbf{G}}$ is restricted into $\mathbf{G}^{(m)}$ to give

$$(\Gamma_i^{\uparrow \mathbf{G}})^{\downarrow \mathbf{G}^{(m)}} = \Gamma_i + \Gamma_i^{\sigma}. \tag{35}$$

Case 2: When Γ_i^{σ} is identical with Γ_i, the similarity transformation of the induced representation $\Gamma_i^{\uparrow \mathbf{G}}$ gives an equivalent representation $\Gamma_i^{\uparrow \mathbf{G}'}$ represented by

$$\Gamma_i^{\uparrow \mathbf{G}'}(x) = \begin{pmatrix} \Gamma_i(x) & 0 \\ 0 & \Gamma_i(x) \end{pmatrix} \tag{36a}$$

$$\Gamma_i^{\uparrow \mathbf{G}'}(x\sigma) = \begin{pmatrix} \Gamma_i(x) & 0 \\ 0 & -\Gamma_i(x) \end{pmatrix}, \tag{36b}$$

which is reduced to two representations of $\mathbf{G}$:

$$\Gamma_i^{\uparrow \mathbf{G}} = \Phi_{ig} + \Phi_{iu}. \tag{37}$$

One of them is a totally symmetric irreducible representation Φ_{ig} represented by

$$\Phi_{ig}(x) = \Gamma_i(x), \tag{38a}$$

$$\Phi_{ig}(x\sigma) = \Gamma_i(x). \tag{38b}$$

The other is an antisymmetric irreducible representation Φ_{iu} represented by

$$\Phi_{iu}(x) = \Gamma_i(x), \tag{39a}$$

$$\Phi_{iu}(x\sigma) = -\Gamma_i(x). \tag{39b}$$

They are obviously irreducible representations of $\mathbf{G}$. The irreducible representations are restricted into $\mathbf{G}^{(m)}$ to give

$$\Phi_{ig}^{\downarrow \mathbf{G}^{(m)}} = \Phi_{iu}^{\downarrow \mathbf{G}^{(m)}} = \Gamma_i. \tag{40}$$

We here examine the behavior of an irreducible representation Γ_i of $\mathbf{G}^{(m)}$ during induction into $\mathbf{G}$, where we pay attention to the maturity of the irreducible representation.

1. When the irreducible representation Γ_i is a matured representation (a $\mathbf{Q}$-conjugacy representation) of $\mathbf{G}^{(m)}$, there appears Case 2 only. Hence, Eq. 40 reveals that two irreducible representations Φ_{ig} and Φ_{iu}, which are both matured represenations ($\mathbf{Q}$-conjugacy representations), are restricted into the same Γ_i.

2. When the irreducible representation Γ_i is an unmatured representation of $\mathbf{G}^{(m)}$, there appear both Cases 1 and 2.

(a) Case 1 contains further two cases.

i. Induction of an unmatured representation into an unmatured representation: Suppose that the set $\{\Gamma_i, \Gamma_{i'}, \cdots, \Gamma_i^{\sigma}, \Gamma_{i'}^{\sigma}, \cdots\}$ constructs a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$. Then, each pair selected from the set (i.e., $\{\Gamma_i, \Gamma_i^{\sigma}\}$, $\{\Gamma_{i'}, \Gamma_{i'}^{\sigma}\}$, or $\cdots$) gives an induced representation of Case 1. This operation is conducted over every pair of the set to generate a set of irreducible representations ($\{\Gamma_i^{\uparrow \mathbf{G}}, \Gamma_{i'}^{\uparrow \mathbf{G}}$, or $\cdots\}$). Although each representation of this set is unmatured, the set totally constructs a matured representation ($\mathbf{Q}$-conjugacy representation) of $\mathbf{G}$.

When the $\mathbf{Q}$-conjugacy representation of $\mathbf{G}$ is restricted into $\mathbf{G}^{(m)}$, it produces the original set of irreducible representations, $\{\Gamma_i, \Gamma_{i'}, \cdots; \Gamma_i^{\sigma}, \Gamma_{i'}^{\sigma}, \cdots\}$, which in turn constructs a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$.

ii. Induction of an unmatured representation into a matured representation: This is a special case of the preceding case. Suppose that the set $\{\Gamma_i, \Gamma_i^{\sigma}\}$ constructs a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$. Then, the pair of Γ_i and Γ_i^{σ} generates an induced representation of Case 1, i.e. $\Gamma_i^{\uparrow \mathbf{G}}$, which is a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}$.

When the $\mathbf{Q}$-conjugacy representation of $\mathbf{G}$ is restricted into $\mathbf{G}^{(m)}$, it regenerates the original set of irreducible representations, $\{\Gamma_i, \Gamma_i^{\sigma}\}$, which constructs a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$.

(b) On the other hand, Case 2 contains the induction of an unmatured representation into an unmatured representation. Suppose that the set $\{\Gamma_i, \Gamma_{i'}, \cdots\}$, which constructs a $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$, is identical with the set $\{\Gamma_j^{\sigma}, \Gamma_{i'}^{\sigma} \cdots\}$. Then the set generates the following pairs of irreducible representations of $\mathbf{G}$ by means of Eq. 37:

$$\left\{ \begin{array}{l} \Phi_{ig} \\ \Phi_{iu} \end{array} \right. \left\{ \begin{array}{l} \Phi_{i'g} \\ \Phi_{i'u} \end{array} \right. \cdots \tag{41}$$

The collection of the tops and the bottoms of every pairs gives two sets of irreducible representations, $\{\Phi_{ig}, \Phi_{i'g}, \cdots\}$ and $\{\Phi_{iu}, \Phi_{i'u}, \cdots\}$. These sets respectively construct two $\mathbf{Q}$-conjugacy representations of $\mathbf{G}$.

When these $\mathbf{Q}$-conjugacy representations are restricted into $\mathbf{G}^{(m)}$, they produce the same set of irreducible representations, $\{\Gamma_i, \Gamma_{i'}, \cdots\}$, which obviously constructs the original $\mathbf{Q}$-conjugacy representation of $\mathbf{G}^{(m)}$.

The maturity of irreducible representations is closely related to the behavior of $\mathbf{Q}$-conjugacy representations. Hence, the preceding examination of repspective cases can be summarized into Theorem 1.

Since a set of characteristic monomials is assigned to each $\mathbf{Q}$-conjugacy representation, Theorem 1 gives Corollary 1.

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