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The USCI approach and elementary superposition for combinatorial enumeration

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Summary. The elementary superposition theorems are presented for enumerating chemical compounds that contain achiral and chiral ligands. Subduced cycle indices (SCI-CF), partial cycle indices (PCI-CF), and cycle indices (CI-CF) with chirality fittingness are defined by starting from unit subduced cycle indices with chirality fittingness (USCI-CF). All of these indices afford generating functions that are proved to be applicable to combinatorial enumeration. In addition, the concept of elementary superposition with and without chirality fittingness is proposed to provide the elementary superposition theorems. These theorems provide us with a new methodology of enumerating compounds, in which the numbers of isomers are obtained without relying on generating functions and are itemized with respect to molecular formulas (weights) and symmetries. The $\circledast$ operation is defined on the basis of the elementary superposition. Thereby, we derive superposition theorems concerning the PCI-CFs and the CI-CFs. These are applicable to combinatorial enumeration.

Key words: Unit subduced cycle index – Partial cycle index – Cycle index – Chirality fittingness – Elementary superposition

1. Introduction

Enumeration of chemical compounds has been accomplished by various methods [1]. Thus, according to enumeration problems to be solved, we can employ the Pólya–Redfield theorem [2–4] the Read–Redfield superposition theorem [4–6], methods based on double cosets [7–9], and methods using tables of marks [10–12]. We have recently reported an alternative method based on unit subduced cycle indices (the USCI approach) [13–15].

In these methods, chemical compounds are recognized as a kind of graphs, where their atoms and bonds correspond to vertices and edges in graphs. This fact implies that the atoms or vertices are regarded as being structureless. In other words, effects of (roto)reflection operations on the atoms are unnecessary to be considered, because the mirror image of each atom is identical with the atom itself.

On the other hand, chemical compounds are alternatively considered to be composed of ligands and bonds. According to this formulation, we should take account of such effects as chirality/achirality of ligands [16, 17]. A pioneering work has appeared to treat such chirality and achirality of ligands [12]. We ourselves have extended the USCI approach to be applicable to this type of enumeration [18], where we introduced the concept of chirality fittingness [19] and defined unit subduced cycle indices with chirality fittingness (USCI-CFs) in place of simple USCIs.

The original version of the USCI approach has been based on generating functions. Without using such generating functions, we have reported an alternative method combining USCIs and the superposition concept [20]. However, the strict proof of the latter treatment and the extension to use USCI-CFs have not been reported. These issues are the objects of the present paper.

2. Indices with chirality fittingness

The USCI approach has defined subduced cycle indices (SCIs) [14, 21–24], partial cycle indices (PCIs) [25], and cycle indices (CIs) [15] and utilized them for enumerating various compounds. We here introduce the corresponding indices with chirality fittingness, since we have discussed subduced cycle indices with chirality fittingness (SCI-CFs) only [18].

Consider a parent molecule of $\boldsymbol{G}$ symmetry that contains $|\Delta|$ positions (sites), which are regarded as constructing a domain (Δ) and can be replaced by an appropriate set of ligands (or atoms). In general, the set of ligands restricts the original $\boldsymbol{G}$ symmetry to produce a derivative of $\boldsymbol{G}_j$ symmetry. For a mathematical context, we use the term *configuration* in place of the terms *compound* or *derivative*.

The positions are partitioned into several orbits, which are subject to a sum of coset representations (CRs) [14]:

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

where the $\boldsymbol{G}_i$ is a subgroup of $\boldsymbol{G}$; s is the number of representatives of conjugate subgroups of $\boldsymbol{G}$; and the α_i is the multiplication of the $\boldsymbol{G}(/\boldsymbol{G}_i)$ CR. Let $\boldsymbol{G}_j$ be a subgroup of $\boldsymbol{G}$. If the set of ligands restricts the original $\boldsymbol{G}$ symmetry to produce a derivative of $\boldsymbol{G}_j$ symmetry, we have a subduction represented by:

$$\sum_{i=1}^{s} \alpha_i G(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j = \sum_{i=1}^{s} \alpha_i \sum_{k=1}^{v_j} \beta_k^{(ij)} \boldsymbol{G}_j(/\boldsymbol{G}_k^{(j)}), \tag{2}$$

where the $\boldsymbol{G}_k^{(j)}$ is a subgroup of $\boldsymbol{G}_j$; v_j is the number of representatives of conjugate subgroups of $\boldsymbol{G}_j$; and the $\beta_k^{(ij)}$ is the multiplicity of the $\boldsymbol{G}_j(/\boldsymbol{G}_k^{(j)})$ CR. The CRs are classified into achiral, neutral, and prochiral parts, which correspond to homospheric, hemispheric and enantiospheric orbits [19]. The nature of having such attributes is referred to as *chirality fittingness*, since it determines how the orbits accommodate achiral and/or chiral ligands [26]. In the process of the subduction, the Δ domain is divided into $\sum_{i=1}^{s} \alpha_i$ orbits ($\Delta_{i\alpha}$), each of which is subdivided into $\sum_{k=1}^{v_j} \beta_k^{(ij)}$ suborbits ($\Delta_{k\beta}^{(i\alpha)}$). In order to make notations precise, we use the following formal expression containing achiral, neutral, and prochiral parts:

$$\boldsymbol{G}_j(/\boldsymbol{G}_k^{(j)}) = \chi_{ak}^{(j)} \boldsymbol{G}_j^{(a)}(/\boldsymbol{G}_k^{(j)}) + \chi_{bk}^{(j)} \boldsymbol{G}_j^{(b)}(/\boldsymbol{G}_k^{(j)}) + \chi_{ck}^{(j)} \boldsymbol{G}_j^{(c)}(/\boldsymbol{G}_k^{(j)}), \tag{3}$$

where $\chi^{(j)}_{ak}$, $\chi^{(j)}_{bk}$, and $\chi^{(j)}_{ck}$ are equal to 0 or 1 and satisfy the equation:

$$\chi^{(j)}_{ak} + \chi^{(j)}_{bk} + \chi^{(j)}_{ck} = 1. \tag{4}$$

The superscripts and subscripts (a, b, and c) denote achiral, neutral, and prochiral parts. The right-hand side of Eq. (3) indicates that only one of the three parts is effective. In the light of this definition, each subduction appearing in the right-hand side of Eq. (2) is represented by:

$$\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j = \sum_{k=1}^{v_j} [\chi^{(j)}_{ak}\beta^{(ij)}_k \boldsymbol{G}^{(a)}_j(/\boldsymbol{G}^{(j)}_k) + \chi^{(j)}_{bk}\beta^{(ij)}_k \boldsymbol{G}^{(b)}_j(/\boldsymbol{G}^{(j)}_k) + \chi^{(j)}_{ck}\beta^{(ij)}_k \boldsymbol{G}^{(c)}_j(/\boldsymbol{G}^{(j)}_k)] \tag{5}$$

for $i = 1, 2, \ldots, s$ and $j = 1, 2, \ldots, s$. The suborbits created by the subduction (Eq. (2)) are classified into three categories, i.e.:

$$\begin{cases} \Delta^{(i\alpha)}_{k\beta a} & \text{that is subject to} \quad \boldsymbol{G}^{(a)}_j(/\boldsymbol{G}^{(j)}_k) \quad \text{(achiral part)} \\ \Delta^{(i\alpha)}_{k\beta b} & \text{that is subject to} \quad \boldsymbol{G}^{(b)}_j(/\boldsymbol{G}^{(j)}_k) \quad \text{(neutral part)} \\ \Delta^{(i\alpha)}_{k\beta c} & \text{that is subject to} \quad \boldsymbol{G}^{(c)}_j(/\boldsymbol{G}^{(j)}_k) \quad \text{(prochiral part)} \end{cases},$$

where the additional subscripts (a, b, and c) designate the assignment of the respective suborbits. In the light of this notation, we define a unit subduced cycle index with chirality fittingness (USCI-CF) [18] and related indices by the following formulas.

Definition 1 (USCI-CF, SCI-CF, PCI-CF, and CI-CF)

(1) A unit subduced cycle index with chirality fittingness (USCI-CF) is defined as:

$$ZC(\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j; a_{d_{jk}}, b_{d_{jk}}, c_{d_{jk}}) = \prod_{k=1}^{v_j} ((a_{d_{jk}})^{\chi^{(j)}_{ak}\beta^{(ij)}_k}(b_{d_{jk}})^{\chi^{(j)}_{bk}\beta^{(ij)}_k}(c_{d_{jk}})^{\chi^{(j)}_{ck}\beta^{(ij)}_k}) \tag{6}$$

for $i = 1, 2, \ldots, s$ and $j = 1, 2, \ldots, s$, where the symbol d_{jk} denotes the length of each suborbit:

$$d_{jk} = |\boldsymbol{G}_j|/|\boldsymbol{G}^{(j)}_k| \quad (k = 1, 2, \ldots, v_j), \tag{7}$$

and the variable $a_{d_{jk}}$, $b_{d_{jk}}$, and $c_{d_{jk}}$ are associated with the chirality fittingness.

(2) A subduced cyclic index with chirality fittingness (SCI-CF) is defined as follows on the basis of USCIs (Eq. (6)):

$$\begin{aligned} &SC(\boldsymbol{G}_j; a^{(i\alpha)}_{d_{jk}}, b^{(i\alpha)}_{d_{jk}}, c^{(i\alpha)}_{d_{jk}}) \\ &= \prod_{i=1}^{s} \prod_{\substack{\alpha=1 \\ \alpha_i \neq 0}}^{\alpha_i} ZC(\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j; a^{(i\alpha)}_{d_{jk}}, b^{(i\alpha)}_{d_{jk}}, c^{(i\alpha)}_{d_{jk}}) \\ &= \prod_{i=1}^{s} \prod_{\substack{\alpha=1 \\ \alpha_i \neq 0}}^{\alpha_i} \prod_{k=1}^{v_j} [(a^{(i\alpha)}_{d_{jk}})^{\chi^{(j)}_{ak}\beta^{(ij)}_k}(b^{(i\alpha)}_{d_{jk}})^{\chi^{(j)}_{bk}\beta^{(ij)}_k}(c^{(i\alpha)}_{d_{jk}})^{\chi^{(j)}_{ck}\beta^{(ij)}_k}] \quad \text{for } j = 1, 2, \ldots, s, \end{aligned} \tag{8}$$

where the superscript ($i\alpha$) represents the dependence upon the $\Delta_{i\alpha}$ orbit.

(3) A partial cycle index with chirality fittingness (PCI-CF) for $\boldsymbol{G}_i$ group is represented by

$$PC(\boldsymbol{G}_i; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}) = \sum_{j=1}^{s} \bar{m}_{ji} SC(\boldsymbol{G}_j; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}) \tag{9}$$

for $i = 1, 2, \ldots, s$, where the superscript $(i\alpha)$ represents the dependence upon the $\Delta_{i\alpha}$ orbit; and the symbol $\bar{m}_{ji}$ denotes the ji-element of the inverse of the mark table of $\boldsymbol{G}$ group.

(4) A cycle index with chirality fittingness (CI-CF) for $\boldsymbol{G}$ group is represented by

$$CC(\boldsymbol{G}; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}) = \sum_{j=1}^{s} \left(\left(\sum_{i=1}^{s} \bar{m}_{ji} \right) SC(\boldsymbol{G}_j; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}) \right). \tag{10}$$

(4′) Obviously, an alternative definition of the CI-CF is obtained in terms of the PCI-CF.

$$CC(\boldsymbol{G}; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}) = \sum_{i=1}^{s} PC(\boldsymbol{G}_i; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}). \tag{11}$$

The variables in the notations of these indices may be abbreviated if this abbreviation affords no confusion. Each of the SCI-CFs indicates the *site partition* produced by the restriction to the $\boldsymbol{G}_j$ symmetry. It should be noted that USCI-CFs can be precalculated by means of subduction of coset representations. Table 1 is the USCI-CF table for D_{2d} group.

Suppose that the set of ligands:

$$\theta_l X_l \ (l = 1, 2, \ldots, m), \quad \eta_l Q_l \quad \text{and} \quad \hat{\eta}_l \hat{Q}_l \ (l = 1, 2, \ldots, n) \tag{12}$$

is selected from the codomain:

$$\boldsymbol{X} = \{X_1, X_2, \ldots, X_m; Q_1, Q_2, \ldots, Q_n; \hat{Q}_1, \hat{Q}_2, \ldots, \hat{Q}_n\}, \tag{13}$$

where m and n represent non-negative integers ($m + n \neq 0$); X_l denotes an achiral ligand; and Q_l and $\hat{Q}_l$ are chiral ligands that construct an enantiomorphic pair [27]. The set of ligands occupies the $|\Delta|$ positions of the Δ domain to afford a configuration, where it satisfies the *ligand partition*:

$$[\theta] : \sum_{l=1}^{m} \theta_l + \sum_{l=1}^{n} \eta_l + \sum_{l=1}^{n} \hat{\eta}_l = |\Delta|. \tag{14}$$

Table 1. Unit subduced cycle indices with chirality fittingness for D_{2d}

	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_2'$	$\downarrow C_s$	$\downarrow S_4$	$\downarrow C_{2v}$	$\downarrow D_2$	$\downarrow D_{2d}$
$D_{2d}(/C_1)$	b_1^8	b_2^4	b_2^4	c_2^4	c_4^2	c_4^2	b_4^2	c_8
$D_{2d}(/C_2)$	b_1^4	b_1^4	b_2^2	c_2^2	c_2^2	c_2^2	b_2^2	c_4
$D_{2d}(/C_2')$	b_1^4	b_2^2	$b_1^2 b_2$	c_2^2	c_4	c_4	b_2^2	c_4
$D_{2d}(/C_s)$	b_1^4	b_2^2	b_2^2	$a_1^2 c_2$	c_4	a_2^2	b_4	a_4
$D_{2d}(/S_4)$	b_1^2	b_1^2	b_2	c_2	a_1^2	c_2	b_2	a_2
$D_{2d}(/C_{2v})$	b_1^2	b_1^2	b_2	a_1^2	c_2	a_1^2	b_2	a_2
$D_{2d}(/D_2)$	b_1^2	b_1^2	b_1^2	c_2	c_2	c_2	b_1^2	c_2
$D_{2d}(/D_{2d})$	b_1	b_1	b_1	a_1	a_1	a_1	b_1	a_1
$\sum_{i=1}^{s} \bar{m}_{ji}$	1/8	1/8	1/4	1/4	1/4	0	0	0

As a result, the weight (molecular formula) of the resulting configuration is expressed by:

$$W_\theta = \prod_{l=1}^{m} w_{i\alpha}(X_l)^{\theta_l} \prod_{l=1}^{n} w_{i\alpha}(Q_l)^{\eta_l} \prod_{l=1}^{n} w_{i\alpha}(\hat{Q}_l)^{\hat{\eta}_l}, \tag{15}$$

where the symbols $w_{i\alpha}(X_l)$, $w_{i\alpha}(Q_l)$, and $w_{i\alpha}(\hat{Q}_l)$ represent the weights for the cases in which the ligands are associated with the $\Delta_{i\alpha}$ orbit. Let $\varrho_{\theta j}$ be the number of such configurations as having the W_θ weight and the $\boldsymbol{G}_j$ symmetry. We refer to these configurations as $(W_\theta, \boldsymbol{G}_j)$-configurations or as $([\theta], \boldsymbol{G}_j)$-configurations, because the W_θ weight corresponds to the $[\theta]$ partition by virtue of Eqs. (14) and (15). The $\varrho_{\theta j}$ value is calculated by the following lemma.

Lemma 1 [Lemma 2 of [18]]
The $\varrho_{\theta j}$'s are given by the following generating functions:

$$\sum_{[\theta]} \varrho_{\theta j} W_\theta = SC(\boldsymbol{G}_j; a^{(i\alpha)}_{d_{jk}}, b^{(i\alpha)}_{d_{jk}}, c^{(i\alpha)}_{d_{jk}}) \quad (j = 1, 2, \dots, s), \tag{16}$$

wherein the right-hand side is substituted by the ligand inventories:

$$a^{(i\alpha)}_{d_{jk}} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}}, \tag{17}$$

$$b^{(i\alpha)}_{d_{jk}} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(Q_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(\hat{Q}_l)^{d_{jk}}, \tag{18}$$

$$c^{(i\alpha)}_{d_{jk}} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + 2\sum_{l=1}^{n} (w_{i\alpha}(Q_l) w_{i\alpha}(\hat{Q}_l))^{d_{jk}/2}. \tag{19}$$

Let $B_{\theta i}$ be the number of non-equivalent $(W_\theta, \boldsymbol{G}_i)$-configurations. It is calculated by the following theorem.

Theorem 1 [Theorem 4 of [18]]
The numbers $(B_{\theta i})$ of non-equivalent $(W_\theta, \boldsymbol{G}_i)$-configurations are obtained by solving the equations:

$$B_{\theta i} = \sum_{j=1}^{s} \varrho_{\theta j} \bar{m}_{ji} \quad (i = 1, 2, \dots, s), \tag{20}$$

where the symbol $\bar{m}_{ji}$ denotes the ji-element appearing in the inverse of the mark table for $\boldsymbol{G}$ group.

Chemically speaking, every non-equivalent $(W_\theta, \boldsymbol{G}_i)$-configuration (or $([\theta], \boldsymbol{G}_j)$-configuration) corresponds to an isomer with the W_θ weight and the $\boldsymbol{G}_j$-symmetry. Hence, we refer to the isomer as a $(W_\theta, \boldsymbol{G}_j)$-isomer or as a $([\theta], \boldsymbol{G}_j)$-isomer. It should be noted that the $\varrho_{\theta j}$ values for a pair of enantiomers $(\eta_l \neq \hat{\eta}_l)$ should be added before applied to Theorem 1. Table 2 is the inverse for D_{2d} group, which is cited from the previous paper [20].

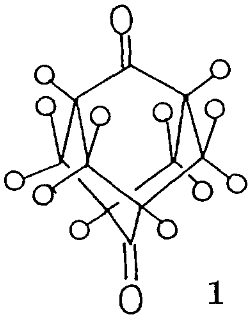
A simple example of Theorem 1 has been reported in the previous paper [18]. We here examine a more complicated case in order to employ this example as a standard case for verifying propositions described below.

Example 1. Consider that the twelve positions of adamantane-2,6-dione (**1**) of D_{2d} symmetry are replaced by a set of ligands selected from the codomain, $\{X, Y, Q, \hat{Q}\}$.

Table 2. The inverse of the mark table for D_{2d} point group

	D_{2d} $(/C_1)$	D_{2d} $(/C_2)$	D_{2d} $(/C'_2)$	D_{2d} $(/C_s)$	D_{2d} $(/S_4)$	D_{2d} $(/C_{2v})$	D_{2d} $(/D_2)$	D_{2d} $(/D_{2d})$	sum[a]
C_1	1/8	0	0	0	0	0	0	0	1/8
C_2	−1/8	1/4	0	0	0	0	0	0	1/8
C'_2	−1/4	0	1/2	0	0	0	0	0	1/4
C_s	−1/4	0	0	1/2	0	0	0	0	1/4
S_4	0	−1/4	0	0	1/2	0	0	0	1/4
C_{2v}	1/4	−1/4	0	−1/2	0	1/2	0	0	0
D_2	1/4	−1/4	−1/2	0	0	0	1/2	0	0
D_{2d}	0	1/2	0	0	−1/2	−1/2	−1/2	1	0

[a] sum $= \sum_{i=1}^{s} \bar{m}_{ji}$



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The twelve positions are partitioned into two orbits, *i.e.*, the eight bridge positions subject to $D_{2d}(/C_1)$ and the four bridgehead positions subject to $D_{2d}(/C_s)$. In terms of Def. 1 (2), we have the SCIs for this case:

$$(b_1^8)(b_1^4) = b_1^{12} = (x + y + q + \hat{q})^{12} \quad \text{for } C_1, \tag{21}$$

$$(b_2^4)(b_2^2) = b_2^6 = (x^2 + y^2 + q^2 + \hat{q}^2)^6 \quad \text{for } C_2, \tag{22}$$

$$(b_2^4)(b_2^2) = b_2^6 = (x^2 + y^2 + q^2 + \hat{q}^2)^6 \quad \text{for } C'_2, \tag{23}$$

$$(c_2^4)(a_1^2 c_2) = a_1^2 c_2^5 = (x + y)^2(x^2 + y^2 + 2q\hat{q})^5 \quad \text{for } C_s, \tag{24}$$

$$(c_4^2)(c_4) = c_4^3 = (x^4 + y^4 + 2q^2\hat{q}^2)^3 \quad \text{for } S_4, \tag{25}$$

$$(c_4^2)(a_2^2) = a_2^2 c_4^2 = (x^2 + y^2)^2(x^2 + y^2 + 2q\hat{q})^2 \quad \text{for } C_{2v}, \tag{26}$$

$$(b_4^2)(b_4) = b_4^3 = (x^4 + y^4 + q^4 + \hat{q}^4)^3 \quad \text{for } D_2, \tag{27}$$

and

$$(c_8)(a_4) = a_4 c_8 = (x^4 + y^4)(x^8 + y^8 + 2q^4\hat{q}^4) \quad \text{for } D_{2d}. \tag{28}$$

The first pair of parentheses in the left-hand side of each SCI consists of the USCI for the $D_{2d}(/C_1)$ orbit and the second contains the one for the $D_{2d}(/C_s)$ orbit. All of these USCIs are selected from the USCI-CF table for D_{2d} group (Table 1). Generating functions (the right-hand sides) are obtained by introducing the following ligand inventories into the SCIs.

$$a_d = x^d + y^d, \tag{29}$$

$$b_d = x^d + y^d + q^d + \hat{q}^d, \tag{30}$$

and

$$c_d = x^d + y^d + 2(q\hat{q})^{d/2}. \tag{31}$$

Expansion of these generating functions affords the $\varrho_{\theta j}$ values as the coefficients of W_θ terms, several of which are collected in Table 3. We regard Table 3 as a matrix and multiply this by the inverse matrix (Table 2). As the result, we have Table 4. When we have $W_\theta = x^8 y^0 q^2 \hat{q}^2$ and so forth, we denote $[\theta] = [8, 0; 2; 2]$ and so forth.

Figure 1 depicts three ([8, 0; 2; 2], S_4)-isomers and two ([8, 0; 2; 2], C_{2v})-isomers, where each X atom is expressed by the symbol ○. All of these isomers are classified into so-called *meso*-compounds. The numbers of these isomers appear in the [8, 0; 2; 2]-row of Table 4. □

By starting from Theorem 1, we have:

$$\sum_{[\theta]} B_{\theta i} W_\theta = \sum_{[\theta]} \left(\sum_{j=1}^{s} \varrho_{\theta j} \bar{m}_{ji} \right) W_\theta = \sum_{j=1}^{s} \bar{m}_{ji} \left(\sum_{[\theta]} \varrho_{\theta j} W_\theta \right). \tag{32}$$

Since the last summation of the right-hand side has been evaluated by Lemma 1, we summarize this derivation as follows by means of the PCI-CF defined in Def. 1 (3).

Theorem 2 (Enumeration by PCI-CF)
The $B_{\theta i}$ values are obtained as the coefficients appearing in generating functions:

$$\sum_{[\theta]} B_{\theta i} W_\theta = PC(\mathbf{G}_i; a^{(i\alpha)}_{d_{jk}}, b^{(i\alpha)}_{d_{jk}}, c^{(i\alpha)}_{d_{jk}}) \quad (i = 1, 2, \ldots, s), \tag{33}$$

Table 3. Several examples of the $\varrho_{\theta j}$ values

Power of				Symmetry of derivatives							
x	y	q	$\hat{q}$	C_1	C_2	C_2'	C_s	S_4	C_{2v}	D_2	D_{2d}
12	0	0	0	1	1	1	1	1	1	1	1
11	1	0	0	12	0	0	2	0	0	0	0
10	2	0	0	66	6	6	6	0	2	0	0
9	3	0	0	220	0	0	10	0	0	0	0
8	4	0	0	495	15	15	15	3	3	3	1
7	5	0	0	792	0	0	20	0	0	0	0
6	6	0	0	924	20	20	20	0	4	0	0
8	0	2	2	2970	30	30	40	6	4	0	0
7	1	2	2	23760	0	0	80	0	0	0	0
6	2	2	2	83160	120	120	160	0	8	0	0
5	3	2	2	166320	0	0	240	0	0	0	0
4	4	2	2	207900	180	180	240	12	8	0	0
4	0	4	4	34650	90	90	80	12	4	6	2
3	1	4	4	138600	0	0	160	0	0	0	0
2	2	4	4	207900	180	180	160	0	8	0	0

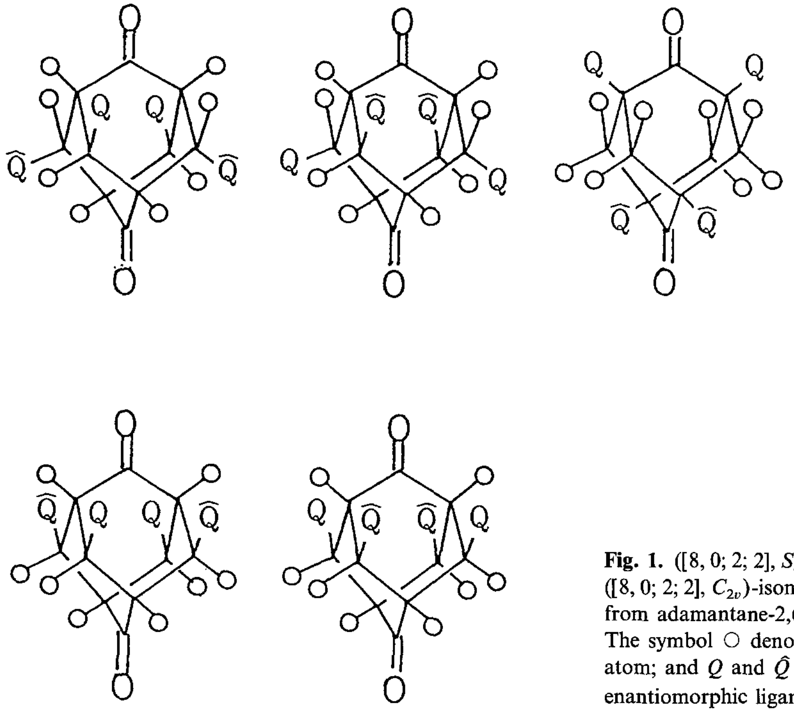

Fig. 1. ([8, 0; 2; 2], S_4)- and ([8, 0; 2; 2], C_{2v})-isomers derived from adamantane-2,6-dione (**1**). The symbol ○ denotes an X atom; and Q and $\hat{Q}$ are a pair of enantiomorphic ligands

Table 4. The numbers of (W_θ, G_j)-isomers

Power of				Symmetry of derivatives								Total
x	y	q	$\hat{q}$	C_1	C_2	C_2'	C_s	S_4	C_{2v}	D_2	D_{2d}	number
12	0	0	0	0	0	0	0	0	0	0	1	1
11	1	0	0	1	0	0	1	0	0	0	0	2
10	2	0	0	5	1	3	2	0	1	0	0	12
9	3	0	0	25	0	0	5	0	0	0	0	30
8	4	0	0	54	2	6	6	1	1	1	1	72
7	5	0	0	94	0	0	10	0	0	0	0	104
6	6	0	0	104	4	10	8	0	2	0	0	128
8	0	2	2	351	5	15	18	3	2	0	0	394
7	1	2	2	2950	0	0	40	0	0	0	0	2990
6	2	2	2	10312	28	60	76	0	4	0	0	10480
5	3	2	2	20730	0	0	120	0	0	0	0	20850
4	4	2	2	25862	40	90	116	6	4	0	0	26118
4	0	4	4	4280	18	42	38	5	1	2	2	4388
3	1	4	4	17285	0	0	80	0	0	0	0	17365
2	2	4	4	25882	43	90	76	0	4	0	0	26095

where each variable is substituted by:

$$a_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}}, \tag{34}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(Q_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(\hat{Q}_l)^{d_{jk}}, \tag{35}$$

$$c_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + 2\sum_{l=1}^{n} (w_{i\alpha}(Q_l)w_{i\alpha}(\hat{Q}_l))^{d_{jk}/2}. \tag{36}$$

This theorem is a generating-function version of Lemma 1 and Theorem 1.

Example 2. By means of Def. 1 (3), we calculate PCI-CFs for the same case as Example 1. The following PCI-CFs are easily obtained from the SCI-CFs described in Eqs. (21–28) and Table 2.

$$PC(C_1) = \tfrac{1}{8}b_1^{12} - \tfrac{3}{8}b_2^6 - \tfrac{1}{4}a_1^2c_2^5 + \tfrac{1}{4}a_2^2c_4^2 + \tfrac{1}{4}b_4^3 \tag{37}$$

$$PC(C_2) = \tfrac{1}{4}b_2^6 - \tfrac{1}{4}c_4^3 - \tfrac{1}{4}a_2^2c_4^2 - \tfrac{1}{4}b_4^3 + \tfrac{1}{2}a_4c_8 \tag{38}$$

$$PC(C_2') = \tfrac{1}{2}b_2^6 - \tfrac{1}{2}b_4^3 \tag{39}$$

$$PC(C_s) = \tfrac{1}{2}a_1^2c_2^5 - \tfrac{1}{2}a_2^2c_4^2 \tag{40}$$

$$PC(S_4) = \tfrac{1}{2}c_4^3 - \tfrac{1}{2}a_4c_8 \tag{41}$$

$$PC(C_{2v}) = \tfrac{1}{2}a_2^2c_4^2 - \tfrac{1}{2}a_4c_8 \tag{42}$$

$$PC(D_2) = \tfrac{1}{2}b_4^3 - \tfrac{1}{2}a_4c_8 \tag{43}$$

$$PC(D_{2d}) = a_4c_8. \tag{44}$$

After introducing the ligand inventories (Eqs. (29–31)), we expand the resulting generating functions. For example, the numbers of C_{2v} isomers are obtained by means of Eq. (42).

$$\begin{aligned} G(x, y, q, \hat{q}) &= \tfrac{1}{2}(x^2+y^2)^2(x^4+y^4+2q^2\hat{q}^2) - \tfrac{1}{2}(x^4+y^4)(x^8+y^8+2q^4\hat{q}^4) \\ &= (x^{10}y^2+x^2y^{10}) + (x^8y^4+x^4y^8) + 2x^6y^6 + 2(x^8q^2\hat{q}^2+y^8q^2\hat{q}^2) \\ &\quad + 4(x^6y^2q^2\hat{q}^2+x^2y^6q^2\hat{q}^2) + 4x^4y^4q^2\hat{q}^2 \\ &\quad + (x^4q^4\hat{q}^4+y^4q^4\hat{q}^4) + 4x^2y^2q^4\hat{q}^4. \end{aligned} \tag{45}$$

Several coefficients in this equation have appeared in the C_{2v} column of Table 4. □

Let the symbol B_i be the number of non-equivalent configurations with $\mathbf{G}_i$ symmetry. Then, Theorem 1 also affords:

$$B_i = \sum_{[\theta]} B_{\theta i} = \sum_{[\theta]} \left(\sum_{j=1}^{s} \varrho_{\theta j}\bar{m}_{ji} \right) = \sum_{j=1}^{s} \bar{m}_{ji} \left(\sum_{[\theta]} \varrho_{\theta j} \right). \tag{46}$$

Let ϱ_j be defined by:

$$\varrho_j = \sum_{[\theta]} \varrho_{\theta j}. \tag{47}$$

Then, Eq. (46) creates a corollary:

Corollary 1
The number (B_i) is obtained by:

$$B_i = \sum_{j=1}^{s} \varrho_j \bar{m}_{ji} \quad (i = 1, 2, \ldots, s). \tag{48}$$

This corollary provides an alternative proof of Theorem 3 of [18].

Let B_θ be the number of non-equivalent configurations with the W_θ weight. Theorem 1 produces:

$$B_\theta = \sum_{i=1}^{s} B_{\theta i} = \sum_{i=1}^{s} \sum_{j=1}^{s} \varrho_{\theta j} \bar{m}_{ji} = \sum_{j=1}^{s} \left(\sum_{i=1}^{s} \bar{m}_{ji} \right) \varrho_{\theta j}. \tag{49}$$

Thus, we arrive at a corollary.

Corollary 2
The number (B_θ) is obtained by:

$$B_\theta = \sum_{j=1}^{s} \left(\sum_{i=1}^{s} \bar{m}_{ji} \right) \varrho_{\theta j}. \tag{50}$$

The inner sum of the right-hand side can be obtained by summing up the $\mathbf{G}_j$ row of the inverse of the mark table of $\mathbf{G}$. For instance, the value for each subgroup for D_{2d} is listed in the rightmost column of Table 2.

This corollary is further converted into:

$$\sum_{[\theta]} B_\theta W_\theta = \sum_{[\theta]} \sum_{j=1}^{s} \left(\sum_{i=1}^{s} \bar{m}_{ji} \right) \varrho_{\theta j} W_\theta = \sum_{j=1}^{s} \left(\sum_{i=1}^{s} \bar{m}_{ji} \right) \sum_{[\theta]} \varrho_{\theta j} W_\theta. \tag{51}$$

Since the last summation of the right-hand side has been evaluated by Lemma 1, we summarize this derivation as follows by means of the CI-CF defined in Def. 1 (4).

Theorem 3 (Enumeration by CI-CF)
The B_θ value is obtained by a generating function:

$$\sum_{[\theta]} B_\theta W_\theta = CC(\mathbf{G}_i; a_{d_{jk}}^{(i\alpha)}, b_{d_{jk}}^{(i\alpha)}, c_{d_{jk}}^{(i\alpha)}), \tag{52}$$

where each variable is substituted by:

$$a_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}}, \tag{53}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(Q_l)^{d_{jk}} + \sum_{l=1}^{n} w_{i\alpha}(\hat{Q}_l)^{d_{jk}}, \tag{54}$$

$$c_{d_{jk}}^{(i\alpha)} = \sum_{l=1}^{m} w_{i\alpha}(X_l)^{d_{jk}} + 2 \sum_{l=1}^{n} (w_{i\alpha}(Q_l) w_{i\alpha}(\hat{Q}_l))^{d_{jk}/2}. \tag{55}$$

Example 3. By means of Def. 1 (4), we calculate CI-CFs for the same case as Example 1. The following CI-CF is easily obtained from the SCI-CFs described in Eqs. (21–28) and the data listed in the rightmost column of Table 2 (or in the bottom of Table 1). Alternatively, the CI-CF can be obtained by summing up all of the PCI-CFs (Eqs. (37–44)) on the basis of Def. 1 (4′).

$$CC(D_{2d}) = \tfrac{1}{8} b_1^{12} + \tfrac{3}{8} b_2^{6} + \tfrac{1}{4} a_1^{2} c_2^{5} + \tfrac{1}{4} c_4^{3}. \tag{56}$$

After introducing the ligand inventories (Eqs. (29–31)), we expand the resulting generating function. Several coefficients in this equation have appeared in the rightmost column of Table 4. □

3. Elementary superposition with chirality fittingness

3.1. Extended cycle indices

For manipulating the chirality/achirality problem, we introduce two types of cycle indices (*extended cycle indices*), because chiral ligands behave in different ways according to environment [19]. If we take account of achiral ligands only, we can develop a simpler treatment as shown in Appendix A.

Consider n chiral ligands of the same kind (Q) and the same number of their enantiomorphic chiral ligands ($\hat{Q}$). If the set of ligands $Q^n\hat{Q}^n$ is placed in an achiral environment and if it conserves this achirality, two ligands with opposite chirality ($Q\hat{Q}$) behave pairwise. This fact can be verified by the *meso*-isomers depicted in Fig. 1. Hence, we shall consider a symmetric group of degree n (denoted as $\widetilde{\mathbb{S}}^{[n]}$), which acts on n sets of $Q\hat{Q}$. The cycle index of the group is represented by:

$$CI(\widetilde{\mathbb{S}}^{[n]}; c_{2d}) = \sum_{(\nu)} \frac{1}{\nu_1!2^{\nu_1}\nu_2!4^{\nu_2}\cdots\nu_l!(2l)^{\nu_l}\cdots\nu_n!(2n)^{\nu_n}} c_2^{\nu_1}c_4^{\nu_2}\cdots c_{2l}^{\nu_l}\cdots c_{2n}^{\nu_n}, \tag{57}$$

where the summation runs over the partition:

$$(\nu): \sum_{l=1}^{n} l\nu_l = n. \tag{58}$$

If the set of ligands $Q^n\hat{Q}^{\hat{n}}$ is placed in a chiral environment, the sets of Q^n and of $\hat{Q}^{\hat{n}}$ behave in distinct ways. Note that n may be equal to or different from $\hat{n}$. We consider a direct product $\mathbb{S}^{[n]} \times \mathbb{S}^{[\hat{n}]}$ that is concerned with the respective sets. It follows that we consider the corresponding cycle index:

$$\begin{aligned} CI(\mathbb{S}^{[n]} \otimes \mathbb{S}^{[\hat{n}]}; b_d) &= CI(\mathbb{S}^{[n]}; b_d) \times CI(\mathbb{S}^{[\hat{n}]}; b_d) \\ &= \left(\sum_{(\nu)} \frac{1}{\nu_1!1^{\nu_1}\nu_2!2^{\nu_2}\cdots\nu_n!n^{\nu_n}} b_1^{\nu_1}b_2^{\nu_2}\cdots b_n^{\nu_n}\right) \\ &\quad \times \left(\sum_{(\hat{\nu})} \frac{1}{\hat{\nu}_1!1^{\hat{\nu}_1}\hat{\nu}_2!2^{\hat{\nu}_2}\cdots\hat{\nu}_{\hat{n}}!\hat{n}^{\hat{\nu}_{\hat{n}}}} b_1^{\hat{\nu}_1}b_2^{\hat{\nu}_2}\cdots b_{\hat{n}}^{\hat{\nu}_{\hat{n}}}\right), \end{aligned} \tag{59}$$

where the summations run over the partitions:

$$(\nu): \sum_{l=1}^{n} l\nu_l = n \tag{60}$$

and

$$(\hat{\nu}): \sum_{l=1}^{\hat{n}} l\hat{\nu}_l = \hat{n}. \tag{61}$$

In general, let us consider a compound that contains achiral and chiral ligands selected from X (Eq. (13)). According to the ligand partition represented by Eq. (14), we define two distinct permutation groups.

$$\boldsymbol{H} = \boldsymbol{S}^{[\theta_1]} \otimes \boldsymbol{S}^{[\theta_2]} \otimes \cdots \otimes \boldsymbol{S}^{[\theta_m]} \otimes \widetilde{\mathbb{S}}^{\eta_1} \otimes \widetilde{\mathbb{S}}^{\eta_2} \otimes \cdots \otimes \widetilde{\mathbb{S}}^{\eta_n}, \tag{62}$$

for $\eta_l = \hat{\eta}_l$ ($l = 1, 2, \ldots, n$) and

$$\boldsymbol{H}' = S^{[\theta_1]} \otimes S^{[\theta_2]} \otimes \cdots \otimes S^{[\theta_m]} \otimes \$^{\eta_1} \otimes \$^{\hat{\eta}_1} \otimes \$^{\eta_2} \otimes \$^{\hat{\eta}_2} \otimes \cdots \otimes \$^{\eta_n} \otimes \$^{\hat{\eta}_n}, \tag{63}$$

for any ligand partition.

As a result, we have the definition of *extended cycle indices*:

$$\begin{aligned} CI(\boldsymbol{H}; s_d; c_d) = {} & CI(S^{[\theta_1]}; s_d) \times CI(S^{[\theta_2]}; s_d) \times \cdots \times CI(S^{[\theta_m]}; s_d) \\ & \times CI(\tilde{\$}^{\eta_1}; c_{2d}) \times CI(\tilde{\$}^{\eta_2}; c_{2d}) \times \cdots \times CI(\tilde{\$}^{\eta_n}; c_{2d}), \end{aligned} \tag{64}$$

and

$$\begin{aligned} CI(\boldsymbol{H}'; s_d, b_d) = {} & CI(S^{[\theta_1]}; s_d) \times CI(S^{[\theta_2]}; s_d) \times \cdots \times CI(S^{[\theta_m]}; s_d) \\ & \times CI(\$^{\eta_1}; b_d) \times CI(\$^{\hat{\eta}_1}; b_d) \times CI(\$^{\eta_2}; b_d) \\ & \times CI(\$^{\hat{\eta}_2}; b_d) \times \cdots \times CI(\$^{\eta_n}; b_d) \times CI(\$^{\hat{\eta}_n}; b_d). \end{aligned} \tag{65}$$

We refer by the term *regular ligand partition* to a case in which $\eta_l = \hat{\eta}_l$ holds for $\forall l$. In this case, we have to employ $\boldsymbol{H}'$ or $\boldsymbol{H}$ according to $\boldsymbol{G}_j$. This corresponds to the fact that the regular ligand partition is compatible with an achiral $\boldsymbol{G}_j$ as well as with a chiral $\boldsymbol{G}_j$. On the other hand, a case in which $\eta_l \neq \hat{\eta}_l$ holds for $\exists l$ is called an *irregular ligand partition*. In this case, we have to use $\boldsymbol{H}'$, not to employ $\boldsymbol{H}$ because of Eq. (62). This means that the irregular ligand partition is compatible with a chiral $\boldsymbol{G}_j$ but is incapable of being associated with an achiral $\boldsymbol{G}_j$. For simplicity's sake, we sum up these facts by defining $\tilde{\boldsymbol{H}}$:

- For a regular ligand partition:

$$\tilde{\boldsymbol{H}} = \begin{cases} \boldsymbol{H} & \text{for an achiral } \boldsymbol{G}_j \\ \boldsymbol{H}' & \text{for a chiral } \boldsymbol{G}_j \end{cases} \tag{66}$$

- for an irregular ligand partition:

$$\tilde{\boldsymbol{H}} = \begin{cases} \text{none} & \text{for an achiral } \boldsymbol{G}_j \\ \boldsymbol{H}' & \text{for a chiral } \boldsymbol{G}_j \end{cases}. \tag{67}$$

In addition, we define two cases:

- For a regular ligand partition:

$$CI(\tilde{\boldsymbol{H}}; s_d, b_d, c_d) = \begin{cases} CI(\boldsymbol{H}; s_d, c_d) & \text{for an achiral } \boldsymbol{G}_j \\ CI(\boldsymbol{H}'; s_d, b_d) & \text{for a chiral } \boldsymbol{G}_j \end{cases} \tag{68}$$

- for an irregular ligand partition:

$$CI(\tilde{\boldsymbol{H}}; s_d, b_d, c_d) = \begin{cases} 0 & \text{for an achiral } \boldsymbol{G}_j \\ CI(\boldsymbol{H}'; s_d, b_d) & \text{for a chiral } \boldsymbol{G}_j \end{cases}. \tag{69}$$

3.2. The ⊛ operation

In order to simplify our discussions, we introduce a new operation (⊛) between two polynomials. Let A be a polynomial that is associated with a set of site partitions, i.e.:

$$A = \sum_{(\mu(A))} N_{(\mu(A))} a_1^{\mu_1} a_2^{\mu_2} \cdots a_p^{\mu_p} b_1^{\nu_1} b_2^{\nu_2} \cdots b_p^{\nu_p} c_1^{\phi_1} c_2^{\phi_2} \cdots c_p^{\phi_p}, \tag{70}$$

where the ϕ_l is equal to 0 if l is odd; and the powers run over the site partitions represented by:

$$(\mu(A)) : (\mu_1 + \nu_1 + \phi_1) + (\mu_2 + \nu_2 + \phi_2) + \cdots + (\mu_p + \nu_p + \phi_p) = p \quad (p = |\Delta|). \tag{71}$$

Let B be a polynomial that is associated with a set of ligand partitions, i.e.:

$$B = \sum_{(\mu(B))} N_{(\mu(B))} s_1^{\mu'_1} s_2^{\mu'_2} \cdots s_p^{\mu'_p} b_1^{\nu'_1} b_2^{\nu'_2} \cdots b_p^{\nu'_p} c_1^{\phi'_1} c_2^{\phi'_2} \cdots c_p^{\phi'_p}, \tag{72}$$

where the ϕ'_l is equal to 0 if l is odd; and the powers run over the ligand partitions represented by:

$$(\mu(B)) : (\mu'_1 + \nu'_1 + \phi'_1) + (\mu'_2 + \nu'_2 + \phi'_2) + \cdots + (\mu'_p + \nu'_p + \phi'_p) = p \quad (p = |\Delta|). \tag{73}$$

A monomial contained in the polynomial B is defined as being compatible with a monomial contained in the polynomial A if we have:

$$\mu_l + \nu_l + \phi_l = \mu'_l + \nu'_l + \phi'_l \quad \text{and} \quad \phi_l \geqslant \phi'_l \quad \text{for all } l. \tag{74}$$

We denote this condition by the symbol $(\mu(A)) = (\mu(B))$. By omitting incompatible monomials, we define the $\circledast$ operation by:

$$B \circledast A = \sum_{(\mu(A)) = (\mu(B))} N_{(\mu(A))} N_{(\mu(B))} \prod_{l=1}^{p} (\mu_l ! l^{\mu_l} \nu_l ! l^{\nu_l} \phi_l ! l^{\phi_l}) \prod_{l=1}^{p} a_l^{\mu_l} b_l^{\mu_l} c_l^{\phi_l}. \tag{75}$$

In addition, we define:

$$N\{B \circledast A\} = \sum_{(\mu(A)) = (\mu(B))} N_{(\mu(A))} N_{(\mu(B))} \prod_{l=1}^{p} (\mu_l ! l^{\mu_l} \nu_l ! l^{\nu_l} \phi_l ! l^{\phi_l}). \tag{76}$$

Consider t ligand partitions, to which we assign polynomials B_t. Then, we have:

$$\begin{aligned} \left(\circledast \prod_{\epsilon=1}^{t} B_\epsilon \right) \circledast A &\overset{\text{def}}{=} (B_t \circledast (B_{t-1} \circledast (\cdots \circledast (B_2 \circledast (B_1 \circledast A))))) \\ &= \sum_{(\mu(A)) = (\mu(B_\epsilon))} \left(N_{(\mu(A))} \prod_{\epsilon=1}^{t} N_{(\mu(B_\epsilon))} \right) \\ &\quad \times \left(\prod_{l=1}^{p} \mu_l ! l^{\mu_l} \nu_l ! l^{\nu_l} \phi_l ! l^{\phi_l} \right)^{\epsilon} \prod_{l=1}^{p} a_l^{\mu_l} b_l^{\nu_l} c_l^{\phi_l}. \end{aligned} \tag{77}$$

Thereby, we define:

$$N\left\{ \left(\circledast \prod_{\epsilon=1}^{t} B_\epsilon \right) \circledast A \right\} \overset{\text{def}}{=} \sum_{(\mu(A)) = (\mu(B_\epsilon))} \left(N_{(\mu(A))} \prod_{\epsilon=1}^{t} N_{(\mu(B_\epsilon))} \right) \left(\prod_{l=1}^{p} \mu_l ! l^{\mu_l} \nu_l ! l^{\nu_l} \phi_l ! l^{\phi_l} \right)^{\epsilon}. \tag{78}$$

3.3. Chiral site partition

Let us consider a case in which a chiral group $\boldsymbol{G}_j$ affords a chiral site partition $((\mu))$. This situation allows an irregular ligand partition as well as a regular ligand partition. For both of the ligand partitions, we should consider $\boldsymbol{H}'$.

Suppose that an irregular ligand partition $[\theta]$ (Eq. (14) and $\eta_l \neq \hat{\eta}_l$ for $\exists l$) is associated with the $\boldsymbol{H}'$. For evaluating $\varrho_{\theta j}$, we consider the site partition (ν) corresponding to the SCI-CF (Def. 1 (2)), which is rewritten as being:

$$S(\boldsymbol{G}_j; b_{d_{jk}}) = b_1^{\nu_1} b_2^{\nu_2} \cdots b_m^{\nu_m}, \tag{79}$$

where

$$(\nu) : \sum_{l=1}^{m} l\nu_l = m \ (=|\Delta|). \tag{80}$$

The discussion in Appendix A holds for this case if $\boldsymbol{H}^0$ is replaced by $\boldsymbol{H}'$. Hence, we obtain:

$$\varrho_{\theta j} = \frac{N_{(\nu)}}{|\boldsymbol{H}'|} \nu_1 ! 1^{\nu_1} \nu_2 ! 2^{\nu_2} \cdots \nu_m ! m^{\nu_m}. \tag{81}$$

When we apply the $\circledast$ operation to this case, we obtain:

$$N\{CI(\boldsymbol{H}') \circledast SC(\boldsymbol{G}_j)\} = \frac{N_{(\nu)}}{|\boldsymbol{H}'|} \nu_1 ! 1^{\nu_1} \nu_2 ! 2^{\nu_2} \cdots \nu_m ! m^{\nu_m}. \tag{82}$$

Comparison between Eq. (81) and Eq. (82) affords the following lemma. The present discussion is also true for a regular ligand partition applied to the chiral $\boldsymbol{G}_j$.

Lemma 2 (Elementary superposition for a chiral site partition)
Let $\boldsymbol{G}_j$ be a chiral subgroup of $\boldsymbol{G}$. Let $[\theta]$ be an irregular or a regular ligand partition. Then, the $\varrho_{\theta j}$ value is obtained by:

$$\varrho_{\theta j} = N\{CI(\boldsymbol{H}') \circledast SC(\boldsymbol{G}_j)\} \quad (j = 1, 2, \ldots, s). \tag{83}$$

It should be noted that the operand of the right-hand side of Eq. (83) is a monomial, the concrete form of which is represented by Eq. (81). The term “elementary superposition” comes from this feature. If the $\varrho_{\theta j}$ values obtained by this theorem are introduced into Theorem 1, we can obtain the numbers of non-equivalent configurations.

3.4. Prochiral site partition

Let us consider a case in which an achiral group $\boldsymbol{G}_j$ affords a prochiral site partition $((\mu))$. This situation requires a regular ligand partition $[\theta]$ (Eq. (14)) which is associated with the $\boldsymbol{H}$. For evaluating $\varrho_{\theta j}$, we consider the site partition (μ) corresponding to the SCI-CF (Def. 1 (2)), which is rewritten as being:

$$SC(\boldsymbol{G}_j; s_{d_{jk}}) = a_1^{\mu_1} a_2^{\mu_2} \cdots a_m^{\mu_m} c_1^{\phi_1} c_2^{\phi_2} \cdots c_m^{\phi_m} \tag{84}$$

where

$$(\mu) : \sum_{l=1}^{m} l(\mu_l + \phi_l) = m \ (=|\Delta|). \tag{85}$$

Note that c_l is equal to 0 if l is odd. Obviously, the SCI-CF is a monomial. Let us examine configurations with the site partition (μ) (Eq. (85)). Suppose that the configurations are fixed on the operations (permutations) of $\boldsymbol{H}$. Then, the value $\varrho_{\theta j}$ is the number of orbits of configurations generated by the action of $\boldsymbol{H}$. We obtain the following equation by means of the Cauchy–Frobenius lemma (so-called Burnside's lemma) [28].

$$\varrho_{\theta j} = \frac{1}{|\boldsymbol{H}|} \sum_{h \in \boldsymbol{H}} n_{(h)}, \tag{86}$$

where $n_{(h)}$ denotes the number of configurations that are fixed by $\boldsymbol{H}$.

If h ($\in \boldsymbol{H}$) fixes one of the configurations having the site partition $((\mu))$, it must possess the same cycle structure as Eq. (85). The same discussion as the previous section holds for the achiral part represented by a of Eq. (84). Thereby, we obtain:

$$\mu_1!1^{\mu_1}\mu_2!2^{\mu_2} \cdots \mu_m!m^{\mu_m} \tag{87}$$

configurations that are fixed by h.

For the prochiral part represented by c of Eq. (84), we should take account of pairwise behavior described above. A suborbit of length l in the configuration has $l/2$ chiral ligands of the same kind and the same number of the enantiomorphic ligands, affording $l/2$ enantiotopic pairs of ligands [29]. If the pairs are permuted cyclically, they afford an equivalent configuration that is also fixed by h; there are $l/2$ different ways for each suborbit of length l and $(l/2)^{\phi_l}$ ways in all. Moreover, there exist two *meso* isomers for each permutation; hence we have 2^{ϕ_l}. We are able to alter the order of the suborbits of length l in $\mu_l!$ ways. For each l, we obtain:

$$(l/2)^{\phi_l}2^{\phi_l}\phi_l! = \phi_l!l^{\phi_l}.$$

When l runs from 1 to m, we have:

$$\phi_1!1^{\phi_1}\phi_2!2^{\phi_2} \cdots \phi_m!m^{\phi_m} \tag{88}$$

configurations that are fixed by h. Equations (87) and (88) hold for any operation (permutation) that has the same cycle structure as h. The number of such operations is denoted by the symbol $N_{(\mu)}$. Thereby, Eq. (86) is converted into:

$$\varrho_{\theta j} = \frac{N_{(\mu)}}{|\boldsymbol{H}|} \mu_1!1^{\mu_1}\mu_2!2^{\mu_2} \cdots \mu_m!m^{\mu_m}\phi_1!1^{\phi_1}\phi_2!2^{\phi_2} \cdots \mu_m!m^{\phi_m} \tag{89}$$

We apply the $\circledast$ operation to this case:

$$N\{CI(\boldsymbol{H}) \circledast SC(\boldsymbol{G}_j)\} = \frac{N_{(\mu)}}{|\boldsymbol{H}|} \mu_1!1^{\mu_1}\mu_2!2^{\mu_2} \cdots \mu_m!m^{\mu_m}\phi_1!1^{\phi_1}\phi_2!2^{\phi_2} \cdots \mu_m!m^{\phi_m} \tag{90}$$

For simplicity's sake, the operands of cycle indices are abbreviated. Comparison between Eq. (89) and Eq. (90) affords the following lemma.

Lemma 3 (Elementary superposition for a prochiral site partition)
Let $\boldsymbol{G}_j$ be an achiral subgroup of $\boldsymbol{G}$. Let $[\theta]$ be a regular ligand partition. The $\varrho_{\theta j}$ value is obtained by:

$$\varrho_{\theta j} = N\{CI(\boldsymbol{H}) \circledast SC(\boldsymbol{G}_j)\} \quad (j = 1, 2, \ldots, s). \tag{91}$$

Note again that the $CI(\boldsymbol{H}) \circledast SC(\boldsymbol{G}_j)$ in Eq. (91) is a monomial. If the $\varrho_{\theta j}$ values obtained by this theorem are introduced into Theorem 1, we can obtain the numbers of non-equivalent configurations.

Example 4. For illustrating Lemmas 2 and 3, we reexamine the case of Example 1. Let us consider a regular ligand partition, $[\theta] = [4, 4; 2, 2]$, which is concerned with isomers having $X^4Y^4Q^2\hat{Q}^2$. For this purpose, we consider:

$$\boldsymbol{H} = S^{[4]} \otimes S^{[4]} \otimes \tilde{\$}^{[2]}$$

and

$$\boldsymbol{H}' = S^{[4]} \otimes S^{[4]} \otimes \$^{[2]} \otimes \$^{[2]}.$$

The corresponding extended cycle indices are calculated as:

$$\begin{aligned} CI(\boldsymbol{H}) &= [\tfrac{1}{24}(6s_4 + 8s_1s_3 + 3s_2^2 + 6s_1^2s_2 + s_1^4)]^2 \times \tfrac{1}{2}(c_2^2 + c_4) \\ &= \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times (s_1^8c_2^2 + 36s_4^2c_4 + 36s_2^2s_4c_4 + \cdots) \end{aligned} \tag{92}$$

$$\begin{aligned} CI(\boldsymbol{H}') &= [\tfrac{1}{24}(6s_4 + 8s_1s_3 + 3s_2^2 + 6s_1^2s_2 + s_1^4)]^2 \times [\tfrac{1}{2}(b_1^2 + b_2)]^2 \\ &= \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times \tfrac{1}{2} \times (s_1^8b_1^4 + 9s_2^4b_2^2 + 36s_1^2s_2^3b_1^2 + 36s_4^2b_2^2 + 36s_2^2s_4b_2^2 \cdots). \end{aligned} \tag{93}$$

The condition described in Eq. (74) allows us to convert a variable s into any of a, b, and c so long as the subscript of the variable is conserved. This allowance corresponds to the fact that achiral ligands are capable of occupying any kinds of orbits. For C_1, we select $s_1^8b_1^4$ from $CI(\boldsymbol{H}')$ (Eq. (93)) as being compatible with the SCI (b_1^{12}) of C_1. It follows that:

$$\varrho_{\theta C_1} = \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times \tfrac{1}{2} \times 1^{12}12! = 207900. \tag{94}$$

For C_2 and C_2', the term $9s_2^4b_2^2$ of $CI(\boldsymbol{H}')$ (Eq. (93)) is compatible with the SCI (b_2^6). Thereby, we have:

$$\varrho_{\theta C_2} = \varrho_{\theta C_2'} = \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times \tfrac{1}{2} \times 9 \times 2^6 6! = 180. \tag{95}$$

For C_s, we select $36s_1^2s_2^3c_2^2$ from $CI(\boldsymbol{H})$ (Eq. (92)) as being compatible with the SCI $(a_1^2c_2^5)$ of C_s. We obtain:

$$\varrho_{\theta C_s} = \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 1^2 2! 2^5 5! = 240. \tag{96}$$

For S_4, the term $36s_4^2c_4$ of $CI(\boldsymbol{H})$ (Eq. (92)) is compatible with the SCI (c_4^3) of S_4. Hence, we have:

$$\varrho_{\theta S_4} = \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 4^3 3! = 12. \tag{97}$$

For C_{2v}, the term $36s_2^2s_4c_4$ appearing in $CI(\boldsymbol{H})$ (Eq. (92)) is compatible with the SCI $(a_2^2c_4^2)$ of C_{2v}. Hence, we have:

$$\varrho_{\theta C_{2v}} = \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 2^2 2! 4^2 2! = 8. \tag{98}$$

Since the SCIs for D_2 and D_{2d} do not agree with any of the terms appearing in $\boldsymbol{H}$ or $\boldsymbol{H}'$, both $\varrho_{\theta D_2}$ and $\varrho_{\theta D_{2d}}$ are equal to 0. These values are collected to form a row vector:

$$(207900 \quad 180 \quad 180 \quad 240 \quad 12 \quad 8 \quad 0 \quad 0),$$

which is equal to the $x^4y^4q^2\hat{q}^2$ row of Table 3. The multiplication of the row vector by the inverse (Table 2) affords:

$$(25862 \quad 40 \quad 90 \quad 116 \quad 6 \quad 4 \quad 0 \quad 0),$$

which is equal to the $x^4y^4q^2\hat{q}^2$ row of Table 4. □

Lemmas 2 and 3 provide the number of non-equivalent configurations when the $\varrho_{\theta j}$'s obtained are introduced into Theorem 1. For further derivation, we integrate Lemmas 2 and 3 into the following theorem by using $\tilde{\boldsymbol{H}}$ described above (Eqs. (66) and (67)).

Theorem 4 (Elementary superposition with chirality fittingness)
The $\varrho_{\theta j}$ value is obtained by:

$$\varrho_{\theta j} = N\{CI(\tilde{\boldsymbol{H}}) \circledast SC(\boldsymbol{G}_j)\} \quad (j = 1, 2, \ldots, s). \tag{99}$$

4. Partial superposition and superposition with chirality fittingness

We formally apply the $\circledast$ operation to the PCI-CF (Def. 1 (3)). It follows that:

$$N\{CI(\tilde{\boldsymbol{H}}) \circledast PC(\boldsymbol{G}_i)\}$$

$$= N\left\{CI(\tilde{\boldsymbol{H}}) \circledast \sum_{j=1}^{s} \bar{m}_{ji} SC(\boldsymbol{G}_j)\right\} \tag{100}$$

$$= \sum_{j=1}^{s} \bar{m}_{ji} N\{CI(\tilde{\boldsymbol{H}}) \circledast SC(\boldsymbol{G}_j)\} \tag{101}$$

$$= \sum_{j=1}^{s} \bar{m}_{ji} \varrho_{\theta j} = B_{\theta i}, \tag{102}$$

where we use Theorem 4 for the $\varrho_{\theta j}$ values; and Theorem 1 for the $B_{\theta i}$ values. Hence, we end up with the following theorem.

Theorem 5 (Partial superposition with chirality fittingness)
The number ($B_{\theta i}$) of non-equivalent configurations with W_θ and $\boldsymbol{G}_i$ is obtained by:

$$B_{\theta i} = N\{CI(\tilde{\boldsymbol{H}}) \circledast PC(\boldsymbol{G}_i)\} \quad (i = 1, 2, \ldots, s). \tag{103}$$

Example 5. For illustrating Theorem 5, we reexamine the case of Example 1. This is a continuation of Example 4. Thus, we use $\boldsymbol{H}$ and $\boldsymbol{H}'$ and their extended cycle indices (Eqs. (92) and (93)). For example, we calculate $B_{\theta C_s}$. We have obtained $PC(C_s)$ (Eq. (40)) in Example 2. Thereby, Theorem 5 holds for this case affording:

$$\begin{aligned} B_{\theta C_s} &= \tfrac{1}{2} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 1^2 2! 2^5 5! - \tfrac{1}{2} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 2^2 2! 4^2 2! \\ &= \tfrac{1}{2}(240 - 8) = 116. \end{aligned}$$

This is equal to the value in the intersection between the $x^4 y^4 q^2 \hat{q}^2$ row and the C_s column of Table 4. Obviously, the process of this calculation contains $\varrho_{\theta C_s}$ and $\varrho_{\theta C_{2v}}$; thus, it corresponds to a portion of the matrix multiplication described in Example 4. □

By starting from the CI-CF (Def. 1 (4′)), we have:

$$N\{CI(\tilde{\boldsymbol{H}}) \circledast CC(\boldsymbol{G})\}$$

$$= N\left\{CI(\tilde{\boldsymbol{H}}) \circledast \sum_{i=1}^{s} PC(\boldsymbol{G}_i)\right\} \tag{104}$$

$$= \sum_{i=1}^{s} N\{CI(\tilde{\boldsymbol{H}}) \circledast PC(\boldsymbol{G}_i)\} \tag{105}$$

$$= \sum_{i=1}^{s} B_{\theta i} = B_\theta, \tag{106}$$

where we use Theorem 5. Hence, we arrive at the following theorem.

Theorem 6 (Superposition with chirality fittingness)
The number (B_θ) of non-equivalent configurations with W_θ is obtained by:

$$B_\theta = N\{CI(\tilde{\boldsymbol{H}}) \circledast CC(\boldsymbol{G})\}. \tag{107}$$

Example 6. We again examine the case of Example 1. This is a continuation of Example 4. Thus, we use the $\boldsymbol{H}$ and $\boldsymbol{H}'$ and their extended cycle indices (Eqs. (92) and (93)). In this example, we calculate B_θ. We have obtained $CC(\boldsymbol{D}_{2d})$ (Eq. (56)) in Example 3. Thereby, Theorem 6 holds for this case as follows.

$$\begin{aligned}B_\theta &= \tfrac{1}{8} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times \tfrac{1}{2} \times 1^{12}12! + \tfrac{3}{8} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times \tfrac{1}{2} \times 9 \times 2^6 6!\\ &\quad + \tfrac{1}{4} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 1^2 2! 2^5 5! + \tfrac{1}{4} \times \tfrac{1}{24} \times \tfrac{1}{24} \times \tfrac{1}{2} \times 36 \times 4^3 3!\\ &= \tfrac{1}{8} \times 207900 + \tfrac{3}{8} \times 180 + \tfrac{1}{4} \times 240 + \tfrac{1}{4} \times 12 = 26118.\end{aligned}$$

This is equal to the value that appears in the rightmost side of the $x^4y^4q^2\hat{q}^2$ row of Table 4. It should be noted that the value is also obtained by:

$$B_\theta = \tfrac{1}{8}\varrho_{\theta C_1} + \tfrac{1}{8}\varrho_{\theta C_2} + \tfrac{1}{4}\varrho_{\theta C'_2} + \tfrac{1}{4}\varrho_{\theta C_s} + \tfrac{1}{4}\varrho_{\theta S_4},$$

in which each term is adopted from Example 4. The last equation is a direct application of Corollary 2. □

5. Multicomponent elementary superposition with chirality fittingness

In this section, we extend the theorems described in the preceding section. Let us consider permutation groups $\boldsymbol{H}'_\epsilon$ ($\epsilon = 1, 2, \ldots, t$) that are associated with appropriate ligand partitions $[\theta^{(\epsilon)}]$, as discussed for $\boldsymbol{H}'$ (Lemma 2). Lemma 2 also holds for each of the groups ($\boldsymbol{H}'_\epsilon$). It follows that:

$$\varrho^{(\epsilon)}_{\theta j} = N\{CI(\boldsymbol{H}'_\epsilon) \circledast SC(\boldsymbol{G}_j)\}, \tag{108}$$

where $\varrho^{(\epsilon)}_{\theta j}$ denotes the number of fixed configurations on the effect of $\boldsymbol{H}'_\epsilon$. When ϵ runs over 1 from t, the t events are capable of taking place independently. The equations described for $\boldsymbol{H}^0_\epsilon$ (Eq. (132)) also hold for this case if $\boldsymbol{H}'_\epsilon$ is used in place of $\boldsymbol{H}^0_\epsilon$. Hence, we have the following extension of Lemma 2.

Lemma 4 (Multicomponent elementary superposition for a chiral site partition)
Let $\boldsymbol{G}_j$ be a chiral subgroup of $\boldsymbol{G}$. Let $[\theta]$ be an irregular or a regular ligand partition. The $\varrho_{\theta j}$ values are represented by:

$$\varrho_{\theta j} = \prod_{\epsilon=1}^{t} \varrho^{(\epsilon)}_{\theta j} = N\left\{\left(\circledast \prod_{\epsilon=1}^{t} CI(\boldsymbol{H}'_\epsilon)\right) \circledast SC(\boldsymbol{G}_j)\right\} \quad (j = 1, 2, \ldots, s), \tag{109}$$

where $\varrho^{(\epsilon)}_{\theta j}$ denote the number of fixed configurations on the effect of $\boldsymbol{H}'_\epsilon$ ($\epsilon = 1, 2, \ldots, t$).

Let us consider permutation groups $\boldsymbol{H}_\epsilon$ ($\epsilon = 1, 2, \ldots, t$) that are associated with an appropriate ligand partition ($[\theta^{(\epsilon)}]$), as discussed for $\boldsymbol{H}$ (Lemma 3). Lemma 3 is true for the $\boldsymbol{H}_\epsilon$. Hence, we have the following extension of Lemma 3.

Lemma 5 (Multicomponent elementary superposition for an achiral site partition)

Let $\boldsymbol{G}_j$ be an achiral subgroup of $\boldsymbol{G}$. This requires a regular ligand partition $[\theta]$. In this case, the $\varrho_{\theta j}$ values are represented by:

$$\varrho_{\theta j} = \prod_{\epsilon=1}^{t} \varrho_{\theta j}^{(\epsilon)} = N\left\{\left({}^{\circledast}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon)\right) \circledast SC(\boldsymbol{G}_j)\right\} \quad (j = 1, 2, \ldots, s), \tag{110}$$

where $\varrho_{\theta j}^{(\epsilon)}$ denote the number of fixed configurations on the effect of $\boldsymbol{H}_\epsilon$ $(\epsilon = 1, 2, \ldots, t)$.

The equation in the braces of Eq. (110) is a monomial. Lemmas 4 and 5 are summarized to a theorem.

Theorem 7 (Multicomponent elementary superposition with chirality fittingness)
The $\varrho_{\theta j}$ values are represented by:

$$\varrho_{\theta j} = N\left\{\left({}^{\circledast}\prod_{\epsilon=1}^{t} CI(\tilde{\boldsymbol{H}}_\epsilon)\right) \circledast SC(\boldsymbol{G}_j)\right\} \quad (j = 1, 2, \ldots, s). \tag{111}$$

The $\varrho_{\theta j}$ values obtained by Theorem 7 (equivalently by Lemmas 4 and 5) are introduced into Theorem 1 to afford the number of $(W_\theta, \boldsymbol{G}_i)$-isomers. They are also applicable to Corollary 1 and Corollary 2.

When we formally construct the $\circledast$ product concerning the PCI-CF (Def. 1 (3)), we have the following theorem.

Theorem 8 (Multicomponent partial superposition with chirality fittingness)
The number $B_{\theta i}$ of non-equivalent $(W_\theta, \boldsymbol{G}_i)$-configurations is represented by:

$$\begin{aligned} B_{\theta i} &= \sum_{j=1}^{s} \varrho_{\theta j} \bar{m}_{ji} \\ &= N\left\{\left({}^{\circledast}\prod_{\epsilon=1}^{t} CI(\tilde{\boldsymbol{H}}_\epsilon)\right) \circledast PC(\boldsymbol{G}_i)\right\} \quad (i = 1, 2, \ldots, s). \end{aligned} \tag{112}$$

Let us next construct the $\circledast$ product concerning the CI-CF. Then we have the following theorem.

Theorem 9 (Multicomponent superposition with chirality fittingness)
The number B_θ of non-equivalent W_θ-configurations is represented by:

$$\begin{aligned} B_\theta &= \sum_{i=1}^{s} B_{\theta i} \\ &= N\left\{\left({}^{\circledast}\prod_{\epsilon=1}^{t} CI(\tilde{\boldsymbol{H}}_\epsilon)\right) \circledast CC(\boldsymbol{G})\right\}. \end{aligned} \tag{113}$$

Example 7. For illustrating these theorems, we examine a hypothetical two-step conversion depicted in Fig. 2.

We consider the four hydroxylmethyl groups (X) of the compound (**2**), which are subject to $D_{2d}(/C_s)$. The first step is the oxidation of two of the four hydroxymethyl groups. The oxidation produces several compounds (**3**) having two carboxyl (Y) and two hydroxylmethyl groups. The second step contains the reaction of the product with a chiral *tert*-alkyl alcohol (Q-OH or $\hat{Q}$-OH) to produce derivatives (**4**) having ester and/or ether groups. Among them, let us obtain the number of possible derivatives having one ester group and one ether group.

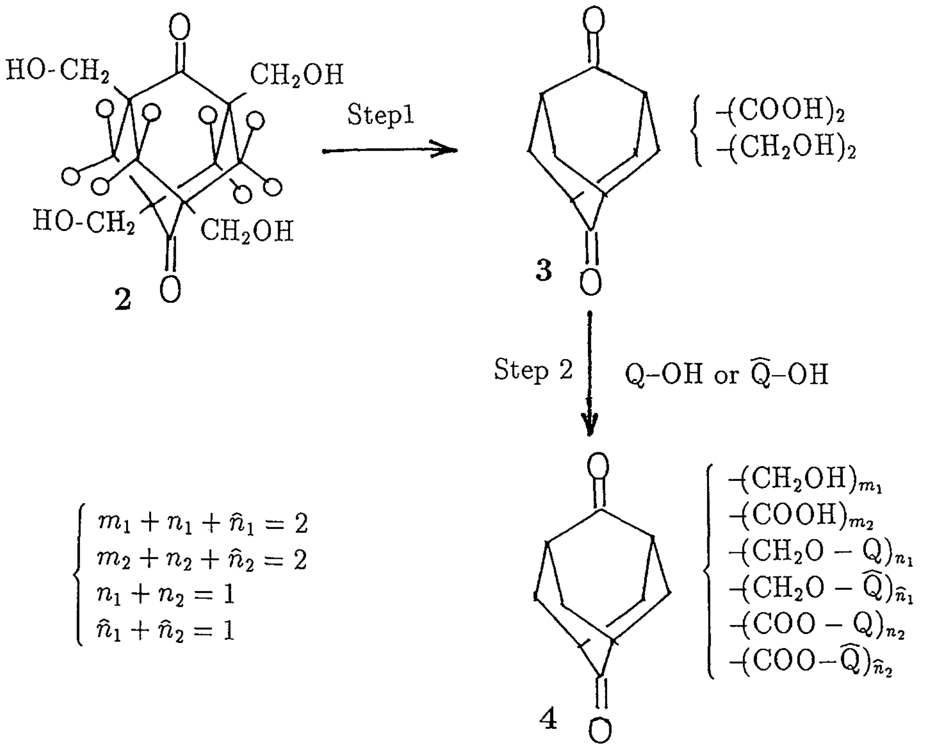

Fig. 2. Two-step conversion for illustrating the superposition

For the first step, we consider the ligand partition $[\theta] = [2, 2; 0; 0]$. Then, we have:

$$CI(\boldsymbol{H}_1) = CI(S^{[2]} \otimes S^{[2]}) = (\tfrac{1}{2}(s_1^2 + s_2))^2 = \tfrac{1}{4}(s_1^4 + 2s_1^2 s_2 + s_2^2)$$
$$CI(\boldsymbol{H}_1') = CI(\$^{[2]} \otimes \$^{[2]}) = (\tfrac{1}{2}(s_1^2 + s_2))^2 = \tfrac{1}{4}(s_1^4 + 2s_1^2 b_2 + s_2^2).$$

For the second step, we consider the ligand partition $[\theta'] = [2; 1; 1]$. This treatment is based on the presumption that one Q and one $\hat{Q}$ occupy two of the reaction positions without taking account of the first step, i.e., whether these are carboxyl or hydroxymethyl groups. The remaining two positions are not occupied in this step. Hence, we have:

$$CI(\boldsymbol{H}_2) = CI(S^{[2]} \otimes \widetilde{\$}^{[1]}) = \tfrac{1}{2}(s_1^2 + s_2)c_2 = \tfrac{1}{2}(s_1^2 c_2 + s_2 c_2)$$
$$CI(\boldsymbol{H}_2') = CI(S^{[2]} \otimes \$^{[1]} \otimes \$^{[1]}) = \tfrac{1}{2}(b_1^2 + b_2)b_1^2 = \tfrac{1}{2}(s_1^2 b_1^2 + s_2 b_1^2)$$

Consider the superposition of $[\theta]$ and $[\theta']$ onto the site partitions produced from the $D_{2d}(/C_s)$ orbit. Hence, Theorem 7 (equivalently Lemmas 4 and 5) affords:

$$\varrho_{[\theta\theta']C_1} = N\{(CI(\boldsymbol{H}_1') \circledast (CI(\boldsymbol{H}_2') \circledast b_1^4))\} = \tfrac{1}{4} \times \tfrac{1}{2} \times (1^4 4!)^2 = 72$$
$$\varrho_{[\theta\theta']C_2} = N\{(CI(\boldsymbol{H}_1') \circledast (CI(\boldsymbol{H}_2') \circledast b_2^2))\} = 0$$
$$\varrho_{[\theta\theta']C_2'} = N\{(CI(\boldsymbol{H}_1') \circledast (CI(\boldsymbol{H}_2') \circledast b_2^2))\} = 0$$
$$\varrho_{[\theta\theta']C_s} = N\{(CI(\boldsymbol{H}_1) \circledast (CI(\boldsymbol{H}_2) \circledast a_1^2 c_2))\} = \tfrac{1}{4} \times 2 \times \tfrac{1}{2} \times (1^2 2! 2^1 1!)^2 = 4$$

$$\varrho_{[\theta\theta']S_4} = N\{(CI(\boldsymbol{H}_1) \circledast (CI(\boldsymbol{H}_2) \circledast c_4))\} = 0$$

$$\varrho_{[\theta\theta']C_{2v}} = N\{(CI(\boldsymbol{H}_1) \circledast (CI(\boldsymbol{H}_2) \circledast a_2^2))\} = 0$$

$$\varrho_{[\theta\theta']D_2} = N\{(CI(\boldsymbol{H}'_1) \circledast (CI(\boldsymbol{H}'_2) \circledast b_4))\} = 0$$

and

$$\varrho_{[\theta\theta']D_{2d}} = N\{(CI(\boldsymbol{H}_1) \circledast (CI(\boldsymbol{H}_2) \circledast a_4))\} = 0$$

where the SCI-CFs are adopted from the $D_{2d}(/C_s)$ row of Table 1. Using Theorem 1, we obtain:

$$(72\ 0\ 0\ 4\ 0\ 0\ 0\ 0)M^{-1} = (8\ 0\ 0\ 2\ 0\ 0\ 0\ 0), \tag{114}$$

where M^{-1} is the matrix form of Table 2. Therefore, we have eight C_1- and two C_s-derivatives in this enumeration. On the basis of these results, we can easily verify Theorems 8 and 9.

Alternatively, the same result is obtained as follows. The two-step reaction produces three types of derivatives, i.e., $X^2Q_Y\hat{Q}_Y$ (*meso*), $Y^2Q_X\hat{Q}_X$ (*meso*), and $XYQ_X\hat{Q}_Y$ (*enantiomeric*), where $X = CH_2OH$, $Y = COOH$, $Q_X = CH_2OQ$, $\hat{Q}_X = CH_2O\hat{Q}$, $Q_Y = COOQ$, and $\hat{Q}_Y = COO\hat{Q}$. By applying Lemma 1 and Theorem 1 to the respective cases [30], we can obtain:

$$(1\ 0\ 0\ 1\ 0\ 0\ 0\ 0) \quad \text{for } X^2Q_Y\hat{Q}_Y,$$

$$(1\ 0\ 0\ 1\ 0\ 0\ 0\ 0) \quad \text{for } Y^2Q_X\hat{Q}_X,$$

and

$$(6\ 0\ 0\ 0\ 0\ 0\ 0\ 0) \quad \text{for } XYQ_X\hat{Q}_Y.$$

When we sum up these row vectors, we obtain the same vector as Eq. (114). □

6. Conclusion

Two methodologies based on unit subduced cycle indices (USCI) are discussed for enumerating chemical compounds or other objects. We take account of chirality fittingness in order to treat such objects that contain achiral and chiral ligands. First, we define subduced cycle indices (SCI), partial cycle indices (PCI) and cycle indices (CI) by starting from the USCIs, all of which are accompanied with chirality fittingness. These indices provide generating functions which are applied to solve enumeration problems. Second, we introduce the concept of elementary superposition, which is also versatile to combinatorial enumeration. On the basis of this concept, we give an alternative proof and an extension of the Read–Redfield superposition theorem.

Appendix A

Elementary superposition without chirality fittingness

This appendix is devoted to deriving the elementary superposition theorem, in which no chiral ligands are taken into consideration. We have already proved this theorem by starting from the Read–Redfield superposition theorem [20].

However, we are able to prove the elementary superposition theorem directly, from which the Read–Redfield superposition theorem is derived backward. Any group described here is a group of finite order unless otherwise stated.

To begin with, we shall quote the cycle index of the symmetric group of order n, which is here denoted as $\boldsymbol{S}^{[n]}$ [2].

$$CI(\boldsymbol{S}^{[n]}; s_d) = \sum_{(v)} \frac{1}{v_1!1^{v_1}v_2!2^{v_2} \cdots v_n!n^{v_n}} s_1^{v_1}s_2^{v_2} \cdots s_n^{v_n}, \tag{115}$$

where the summation runs over all partitions (v):

$$(v) : \sum_{l}^{n} lv_l = n. \tag{116}$$

We consider the ligand partition represented by Eq. (14), in which we take only achiral ligands into consideration. Then, we introduce the direct product:

$$\boldsymbol{H}^0 = \boldsymbol{S}^{[\theta_1]} \otimes \boldsymbol{S}^{[\theta_2]} \otimes \cdots \otimes \boldsymbol{S}^{[\theta_m]}. \tag{117}$$

The cycle index of $\boldsymbol{H}^0$ is represented by the equation [2]:

$$CI(\boldsymbol{H}^0; s_d) = CI(\boldsymbol{S}^{[\theta_1]}; s_d) \times CI(\boldsymbol{S}^{[\theta_2]}; s_d) \times \cdots \times CI(\boldsymbol{S}^{[\theta_m]}; s_d) \tag{118}$$

$$= \frac{1}{|\boldsymbol{H}^0|} \sum_{(\mu')} N_{(\mu')} s_1^{\mu'_1} s_2^{\mu'_2} \cdots s_m^{\mu'_m}, \tag{119}$$

where the partition represented by the cycle structure (μ') runs over:

$$(\mu') : \sum_{l=1}^{m} l\mu'_l = m \ (= |\Delta|), \tag{120}$$

and where the symbol $N_{(\mu')}$ denotes the number of permutations having the cycle structure (μ'). Note that the cycle structure $((\mu'))$ is associated with the ligand partition $[\theta]$.

For evaluating $\varrho_{\theta j}$, we consider SCIs derived by substituting s for the variables (a, b, and c) of the SCI-CFs (Def. 1 (2)) [14]. We rewrite the SCIs to be:

$$S(\boldsymbol{G}_j; s_{d_{jk}}) = s_1^{\mu_1} s_2^{\mu_2} \cdots s_m^{\mu_m} \quad (j = 1, 2, \ldots, s), \tag{121}$$

where the partition is determined to be a specific set of integers of the equation:

$$(\mu) : \sum_{l=1}^{m} l_{\mu_l} = m \ (= |\Delta|). \tag{122}$$

Note that the SCI (Eq. (121)) is a monomial having the partition $((\mu))$ that is specified by the subduction to $\boldsymbol{G}_j$.

Let us now consider a set $(\boldsymbol{F})$ of configurations in which the m positions of the site partition $((\mu))$ accommodate the set of ligands $(X^{\theta_1}X^{\theta_2} \cdots X^{\theta_m})$. Each of the configurations may belong to $\boldsymbol{G}_j$ or to a supergroup of $\boldsymbol{G}_j$. When we apply the permutations of the $\boldsymbol{H}^0$ to one of these configurations, we obtain equivalent configurations. This means that the $\boldsymbol{F}$ is partitioned by the action of $\boldsymbol{H}^0$ into several equivalence classes (i.e., orbits) and that the value $\varrho_{\theta j}$ can be regarded as the number of the orbits. Therefore, we obtain the following equation by means of the Cauchy–Frobenius lemma (so-called Burnside's lemma) [28].

$$\varrho_{\theta j} = \frac{1}{|\boldsymbol{H}^0|} \sum_{h \in \boldsymbol{H}^0} n_{(h)}, \tag{123}$$

where $n_{(h)}$ denotes the number of configurations that are fixed by $h \in \boldsymbol{H}^0$.

If a permutation h ($\in \boldsymbol{H}^0$) fixes the configuration having the site partition $((\mu))$, it must possess the same cycle structure as Eq. (122), i.e., $(\mu') = (\mu)$. A suborbit of length l in the configuration has l ligands of the same kind. The suborbit is fixed by an l-cycle contained in the permutation (h). If the ligands in the suborbit are permuted cyclically, the resulting configuration is also fixed on the action of h; there are l different ways for each suborbit of length l and l^{μ_l} ways in all. Moreover, we are able to alter the order of the suborbits of length l in $\mu_l!$ ways. When l runs from 1 to m, we have:

$$\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m} \quad (= n_{(h)}) \tag{124}$$

configurations that are fixed by h. This result holds for such a permutation that has the same cycle structure as h. The number of such operations is denoted by the symbol $N_{(\mu)}$. Thereby, Eq. (123) is converted into:

$$\varrho_{\theta j} = \frac{N_{(\mu)}}{|\boldsymbol{H}^0|}\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m}. \tag{125}$$

If we apply the $*$ operation [5, 4] to this case, we obtain:

$$CI(\boldsymbol{H}^0; s_d) * S(\boldsymbol{G}_j; s_{d_{jk}}) = \frac{N_{(\mu)}}{|\boldsymbol{H}^0|}(\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m})s_1^{\mu_1}s_2^{\mu_2}\cdots s_m^{\mu_m}. \tag{126}$$

Let the symbol $N\{\cdots\}$ denote the sum of the coefficients of the polynomial in the braces. We employ this symbol, although Eq. (126) comprises a monomial. It follows that:

$$N\{CI(\boldsymbol{H}^0; s_d) * S(\boldsymbol{G}_j; s_{d_{jk}})\} = \frac{N_{(\mu)}}{|\boldsymbol{H}^0|}(\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m}). \tag{127}$$

Comparison between Eq. (125) and Eq. (127) affords the following theorem.

Theorem 10 (Elementary superposition)
The $\varrho_{\theta j}$ value is obtained by:

$$\varrho_{\theta j} = \frac{N_{(\mu)}}{|\boldsymbol{H}^0|}\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m}. \tag{128}$$

$$= N\{CI(\boldsymbol{H}^0; s_d) * S(\boldsymbol{G}_j; s_{d_{jk}})\} \quad (j = 1, 2, \ldots, s). \tag{129}$$

If the $\varrho_{\theta j}$ values obtained by this theorem are introduced into Theorem 1, we can obtain the numbers of non-equivalent configurations, which are itemized with respect to the weight W_θ as well as to the symmetry $\boldsymbol{G}_j$.

This theorem is a special case of Theorem 4. Note that the $\circledast$ operation involves $*$ operation as a special case.

Let us consider $\boldsymbol{H}^0_\epsilon$ ($\epsilon = 1, 2, \ldots, t$) that are associated with an appropriate ligand partition $[\theta^{(\epsilon)}]$, as discussed for $\boldsymbol{H}^0$. Theorem 10 is true for the $\boldsymbol{H}^0_\epsilon$. It follows that:

$$\varrho^{(\epsilon)}_{\theta j} = N\{CI(\boldsymbol{H}^0_\epsilon; s_d) * S(\boldsymbol{G}_j; s_{d_{jk}})\}, \tag{130}$$

where $\varrho^{(\epsilon)}_{\theta j}$ denote the number of fixed configurations on the effect of $\boldsymbol{H}^0_\epsilon$. Then, we construct the product represented by:

$$\begin{aligned}\varrho_{\theta j} &= \prod_{\epsilon=1}^{t} \varrho_{\theta j}^{(\epsilon)} \\ &= \prod_{\epsilon=1}^{t} N\{CI(\boldsymbol{H}_\epsilon^0; s_d) * S(\boldsymbol{G}_j; s_{d_{jk}})\} \\ &= \left(\prod_{\epsilon=1}^{t} \frac{N_{(\mu)}^{(\epsilon)}}{|\boldsymbol{H}_\epsilon^0|}\right)(\mu_1!1^{\mu_1}\mu_2!2^{\mu_2}\cdots\mu_m!m^{\mu_m})^{\epsilon} \qquad (131) \\ &= N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * S(\boldsymbol{G}_j; s_{d_{jk}})\right\}, \qquad (132)\end{aligned}$$

where the last equality symbol comes from the definition of the $*$ operation [5]. The symbol $N_{(\mu)}^{(\epsilon)}$ denotes the number of permutations corresponding to the single $N_{(\mu)}$ in Eq. (125). The product symbol with an asterisk represents a multiplication concerning the $*$ operation. Hence, we have the following extension of Theorem 10.

Theorem 11 (Multicomponent elementary superposition)
The $\varrho_{\theta j}$ values are represented by:

$$\varrho_{\theta j} = N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * S(\boldsymbol{G}_j; s_{d_{jk}})\right\} \quad (j = 1, 2, \ldots, s). \tag{133}$$

Since the equation in the braces of Eq. (129) (and Eq. (133)) is a monomial, it indicates an essential nature of the superposition theorem. Accordingly, we refer to this theorem as the *elementary superposition*.

We formally apply the $*$ operation to a partial subduced cycle index without chirality fittingness (PCI), which is derived by substituting s for a, b, and c in the PCI-CF (Def. 1 (3)) and denoted by $P(\boldsymbol{G}_i; s_{d_{jk}})$. As a result, we have:

$$\begin{aligned}&N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * P(\boldsymbol{G}_i; s_{d_{jk}})\right\} \\ &= N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * \sum_{j=1}^{s} \bar{m}_{ji} S(\boldsymbol{G}_j; s_{d_{jk}})\right\} \\ &= N\left\{\sum_{j=1}^{s} \bar{m}_{ji}\left(\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * S(\boldsymbol{G}_j; s_{d_{jk}})\right)\right\} \\ &= \sum_{j=1}^{s} \bar{m}_{ji} N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * S(\boldsymbol{G}_j; s_{d_{jk}})\right\}. \qquad (134)\end{aligned}$$

Comparison between Eq. (133) and Eq. (134) affords the following theorem.

Theorem 12 (Multicomponent partial superposition)
The number $B_{\theta i}$ of non-equivalent $(W_\theta, \boldsymbol{G}_i)$-configurations is represented by:

$$\begin{aligned}B_{\theta i} &= \sum_{j=1}^{s} \varrho_{\theta j} \bar{m}_{ji} \\ &= N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * P(\boldsymbol{G}_i; s_{d_{jk}})\right\} \quad (i = 1, 2, \ldots, s). \qquad (135)\end{aligned}$$

It should be noted that, if $\boldsymbol{G}_i$ is a chiral group, the values of each enantiomeric pair should be added to obtain a correct value. This note will be effective throughout the present report.

Let us next construct the $*$ operation concerning the CI, which is derived by substituting s for a, b, and c in the CI-CF (Def. 1 (4′)) and denoted by $CI(\boldsymbol{G}_i; s_{d_{jk}})$ [15]. Hence, we have:

$$\begin{aligned}
&N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * CI(\boldsymbol{G}; s_{d_{jk}})\right\} \\
&= N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * \sum_{i=1}^{s} P(\boldsymbol{G}_i; s_{d_{jk}})\right\} \\
&= N\left\{\sum_{i=1}^{s}\left(\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * P(\boldsymbol{G}_i; s_{d_{jk}})\right)\right\} \\
&= \sum_{i=1}^{s} N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * P(\boldsymbol{G}_i; s_{d_{jk}})\right\}.
\end{aligned} \tag{136}$$

Comparison between Eq. (136) and Theorem 12 affords the following theorem.

Theorem 13 (Multicomponent superposition)
The number B_θ of non-equivalent W_θ-configurations is represneted by:

$$\begin{aligned}
B_\theta &= \sum_{i=1}^{s} B_{\theta i} \\
&= N\left\{\left({}^{*}\prod_{\epsilon=1}^{t} CI(\boldsymbol{H}_\epsilon^0; s_d)\right) * CI(\boldsymbol{G}; s_{d_{jk}})\right\}.
\end{aligned} \tag{137}$$

This theorem is equivalent to the Read–Redfield superposition theorem. Further derivation starting from Theorem 10 and applications are described elsewhere [20, 25].

It is worthwhile comparing the present results with the Read–Redfield superposition theorem. In Theorem 13, the treatment of a point group $\boldsymbol{G}$ is distinct from that of a permutation group $\boldsymbol{H}_\epsilon^0$. However, such discrimination is unnecessary to be considered, if $\boldsymbol{G}$ is a permutation group. Obviously, the present derivation also holds for such a case. In this meaning, Theorem 13 is equivalent to the Read–Redfield Theorem. It should be emphasized that the present theorem is based on the concept of elementary superposition, which enables us to obtain more detailed results that are itemized with respect weights and symmetries.

On the other hand, Theorem 9 is somewhat different, since it manipulates chiral ligands as well as achiral ones. Does this theorem hold for the case in which $\boldsymbol{G}$ is a permutation group? This problem is open to further investigation.

References and notes

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13. The USCI is the acronym of unit subduced cycle index. See [14]
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16. An abstract ligand that has chirality or achirality has been formulated as a proligand. See [17]
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26. When $\boldsymbol{G}_j$ and $\boldsymbol{G}_k^{(j)}$ are both achiral, the $\boldsymbol{G}_j(/\boldsymbol{G}_k^{(j)})$ *CR* is an achiral part and the corresponding orbit is homospheric. The *CR* in which $\boldsymbol{G}_j$ is achiral and $\boldsymbol{G}_k^{(j)}$ is chiral is referred to as a prochiral part; this is associated with an enantiospheric orbit. When both $\boldsymbol{G}_j$ and $\boldsymbol{G}_k^{(j)}$ are chiral, the $\boldsymbol{G}_j(/\boldsymbol{G}_k^{(j)})$ *CR* is a neutral part; the *CR* corresponds to a hemispheric orbit. See [19]
27. We use the term enantiomorphic to designate the relationship between a ligand in isolation and its mirror image. This terminology corresponds to the term enantiomeric for compounds
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29. For the term enantiotopic, see ref. [31]
30. This enumeration is mathematically equivalent to an enumeration reported for an allene skeleton [17]. The C_s isomers of $X^2Q_Y\hat{Q}_Y$- or $Y^2Q_X\hat{Q}_X$-type of the present paper correspond to the compound (52) appearing in Table 5 of [17]. The compound (68) of [17] correlates to the C_1 isomer of the same type. The compounds (86 to 91) of [17] correspond to the six C_s isomers of the present $XYQ_X\hat{Q}_Y$-type
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