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Enumeration of non-rigid molecules by means of unit subduced cycle indices

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Summary. Unit subduced cycle indices (USCIs) are applied to the enumeration of isomers derived from a non-rigid parent molecule, the non-rigidity of which stems from bond-rotations. The parent is divided into a rigid skeleton of $\boldsymbol{G}$-symmetry and mobile moieties of $\boldsymbol{H}$-symmetries, where each mobile moiety is linked to a root that is a terminal vertex of the skeleton. In the first step, isomeric mobile moieties are enumerated with respect to the $\boldsymbol{H}$-symmetry in terms of USCIs for $\boldsymbol{H}$. Second, the mobile moieties counted are regarded as substituents on the vertices of the rigid skeleton. This formulation allows us to enumerate mobile isomers by means of USCIs for the $\boldsymbol{G}$-symmetry.

Key words: Enumeration – Non-rigid isomers – Unit subduced cycle index – Subduced cycle index – Table of marks

1. Introduction

Isomer enumeration has been extensively studied using the Pólya–Redfield theory [1, 2]. Comprehensive reviews have appeared to show the usefulness of this theory [3–6]. Recently, this theory has been applied to the enumeration of organic reactions [7]. Double coset algebra has also been applied to isomer enumeration [8]. These enumerations deal with molecular formulas of isomers and take no account of their spatial symmetries.

More recently, isomer enumerations taking into account molecular formulas and spatial symmetries have been discussed using tables of marks [9, 10] and combining double cosets and framework groups [11]. A method using unit subduced cycle indices has been reported to solve this type of enumerations [12].

Systematic enumeration of non-rigid molecules has been presented in terms of "coronas" by Pólya [1]. This concept is essentially equivalent to wreath products. A generalized wreath product method has been proposed for the enumeration of stereo and positional isomers [13]. Non-rigid cyclohexane isomers have been counted [14]. However, these enumerations of non-rigid isomers have not taken into consideration the spatial symmetries of the isomers counted. We will report here the systematic enumeration of non-rigid isomers with respect not only to their molecular formulas but also to their symmetries. This manipulation reveals some advantages of the method that uses unit subduced cycle indices. In the present paper, the term "non-rigid" is used in the limited sense of rotations about bonds, although a conventional usage of this term involves torsions as well as rotations [15].

2. Orbits for non-rigid molecules

When a molecule is considered to be a three-dimensional (3D) object, its ligands are classified into several equivalence classes. These equivalence classes are called *orbits* in the terminology of permutation-group theory [16, 17]. Each of the orbits corresponds to a coset representation (CR) $G(/G_i)$ in one-one fashion, where G is a (point) group characterizing the symmetry of the molecule and G_i is a subgroup of G [12]. The assignment of the CR ($G(/G_i)$) to each orbit is accomplished using a table of marks for G-symmetry [18]. For a non-rigid molecule the assignment should be modified from the viewpoint of wreath products [1] and generalized wreath products [5].

For simplicity of discussion, we take account of bond-rotation non-rigidity only. We may then consider a non-rigid molecule to consist of a rigid skeleton and mobile moieties. The non-rigid skeleton is defined as a 3D-object that is invariant to any rotation about the bonds contained in the skeleton. The mobile moiety is defined a 3D-object that contains terminal atoms and that is itself invariant to any rotation about the bonds contained in the moiety. Each of the moieties is attached to the rigid skeleton through a root that is a central atom of the moiety as well as a terminal vertex of the rigid skeleton. For example, Fig. 1 illustrates 2,2-dimethylpropane (Fig. 1a), in which the five carbons construct a rigid skeleton (Fig. 1b) and each set of three hydrogens and a central carbon (Fig. 1c) constitute a mobile moiety. We consider such terminal hydrogens to be substitution positions.

The four roots of the rigid skeleton (Fig. 1b) construct an orbit which is subject to a CR $T_d(/C_{3v})$ [12]. The three vertices of the mobile moiety (Fig. 1c) belong to an orbit governed by a CR $C_{3v}(/C_s)$. Hence, the non-rigid molecule (Fig. 1a) is represented by $T_d(/C_{3v})[C_{3v}(/C_s)]$. We refer to this as the *extended wreath product* (EWP) notation in the present paper, since each CR is a permutation representation and such a combination can be regarded as a kind of wreath product. Since the length of the $G(/G_i)$ orbit is represented by $|G|/|G_i|$, the number of vertices to be considered is represented by $(|T_d|/|C_{3v}|) \times (|C_{3v}|/|C_s|) = (24/6) \times (6/2) = 12$.

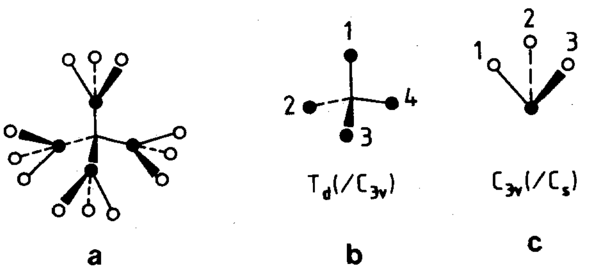


Fig. 1. A $T_d(/C_{3v})[C_{3v}(/C_s)]$ molecule. ●, roots; ○, vertices

3. Mobile moieties

3.1. Unit subduced cycle indices for mobile moieties

Although the mathematical background is essentially the same as described in the previous paper [12], we shall define unit subduced cycle indices (USCIs) for a given mobile moiety. If the moiety consists of several atoms whose symmetrical properties are characterized by a permutation representation ($\boldsymbol{P}_{\boldsymbol{H}}$), we can reduce $\boldsymbol{P}_{\boldsymbol{H}}$ into the sum of coset representations in terms of

$$\boldsymbol{P}_{\boldsymbol{H}} = \sum_{p=1}^{C_H} \gamma_p \boldsymbol{H}(/\boldsymbol{H}_p), \tag{1}$$

where $\boldsymbol{H}$ is a (point) group for describing the symmetry of this moiety, the symbol $\boldsymbol{H}_p$ ($p = 1, 2, \ldots, C_H$) denotes a representative of conjugate subgroups and γ_p represents the multiplicity of the coset representation $\boldsymbol{H}(/\boldsymbol{H}_p)$. The multiplicity γ_p can be algebraically obtained [12].

The permutation representation $\boldsymbol{P}_{\boldsymbol{H}}$ acts on a set of all substitution positions in the moiety, which is considered as a domain,

$$\Psi = \{\psi_1, \psi_1, \ldots, \psi_{|\Psi|}\}. \tag{2}$$

Equation (1) provides a partition of Ψ into several sets of equivalent positions.

If we subduce the CR $\boldsymbol{H}(/\boldsymbol{H}_p)$ by the $\boldsymbol{H}_q$ subgroup of $\boldsymbol{H}$, we can obtain the subduced representation (SR), $\boldsymbol{H}(/\boldsymbol{H}_p) \downarrow \boldsymbol{H}_q$. This SR reduces to a sum of coset representations

$$\boldsymbol{H}(/\boldsymbol{H}_p) \downarrow \boldsymbol{H}_q = \sum_{r=1}^{v_q} \delta_{pqr} \boldsymbol{H}_q(/\boldsymbol{H}_{qr}), \tag{3}$$

where the symbol $\boldsymbol{H}_{qr}$ ($r = 1, 2, \ldots, v_q$) denotes a representative of conjugate subgroups of $\boldsymbol{H}_q$; and the non-negative integer δ_{pqr} represents the multiplicity of the CR $\boldsymbol{H}_q(/\boldsymbol{H}_{qr})$. The multiplicity can be algebraically obtained by means of the inverse of a mark table [12]. The SR, $\boldsymbol{H}(/\boldsymbol{H}_p) \downarrow \boldsymbol{H}_q$, is determined by $\boldsymbol{H}$, $\boldsymbol{H}_p$, and $\boldsymbol{H}_q$; this means that the multiplicity δ_{pqr} can be predetermined as an integer constant. Since the length of the $\boldsymbol{H}_q(/\boldsymbol{H}_{qr})$ orbit is represented by

$$d_{qr} = |\boldsymbol{H}_q|/|\boldsymbol{H}_{qr}|, \tag{4}$$

we can define a unit subduced cycle index (USCI) corresponding to Eq. (1) as

$$Z(\boldsymbol{H}(/\boldsymbol{H}_p) \downarrow \boldsymbol{H}_q; t_{d_{qr}}) = \prod_{r=1}^{v_q} (t_{d_{qr}})^{\delta_{pqr}} \tag{5}$$

for $p = 1, 2, \ldots, C_H$ and $q = 1, 2, \ldots, C_H$, where the t-variables are dummy symbols. The method of calculating USCIs was reported elsewhere [12]. It is convenient to predetermine such USCIs in the form of a table of USCIs for every point group. For example, Tables 1 and 2 list USCIs for $\boldsymbol{C}_{3v}$ and $\boldsymbol{T}_d$ groups. Note that these tables contain s-variables in place of t-variables, since the variables are just dummy symbols.

Table 1. USCIs for C_{3v} point group

	Unit subduced cycle index[a]			
	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_3$	$\downarrow C_{3v}$
$C_{3v}(/C_1)$	$s_1^6\,(b_1^6)$	$s_2^3\,(c_2^3)$	$s_3^2\,(b_3^2)$	$s_6\,(c_6)$
$C_{3v}(/C_s)$	$s_1^3\,(b_1^3)$	$s_1 s_2\,(a_1 c_2)$	$s_3\,(b_3)$	$s_3\,(a_3)$
$C_{3v}(/C_3)$	$s_1^2\,(b_1^2)$	$s_2\,(c_2)$	$s_1^2\,(b_1^2)$	$s_2\,(c_2)$
$C_{3v}(/C_{3v})$	$s_1\,(b_1)$	$s_1\,(a_1)$	$s_1\,(b_1)$	$s_1\,(a_1)$

[a] A variable in parentheses is a USCI with chirality fittingness

The multiplication of USCIs (Eq. (5)) over all of the orbits obtained by Eq. (1) produces a subduced cycle index (SCI) for each subgroup ($\boldsymbol{H}_q$) as follows:

$$ZI(\boldsymbol{H}_q; t_{d_{qr}}) = \prod_{p=1}^{C_H} [Z(\boldsymbol{H}(/\boldsymbol{H}_p) \downarrow \boldsymbol{H}_q; t_{d_{qr}})]^{\gamma_p}$$

$$= \prod_{p=1}^{C_H} \left[\prod_{r=1}^{v_p} (t_{d_{qr}})^{\delta_{pqr}} \right]^{\gamma_p} = \prod_{r=1}^{v_p} (t_{d_{qr}})^{\sum_{p=1}^{C_H} \gamma_p \delta_{pqr}} \qquad (6)$$

for $q = 1, 2, \ldots, C_H$ [12]. The concrete SCI can be obtained from a table of USCIs such as Tables 1 and 2.

Table 2. USCIs for T_d point group

	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$T_d(/C_1)$	s_1^{24} (b_1^{24})	s_2^{12} (b_2^{12})	s_2^{12} (c_2^{12})	s_3^8 (b_3^8)	s_4^6 (c_4^6)	s_4^6 (b_4^6)	s_4^6 (c_4^6)	s_6^4 (c_4^6)	s_8^3 (c_8^3)	s_{12}^2 (b_{12}^2)	s_{24} (c_{24})
$T_d(/C_2)$	s_1^{12} (b_1^{12})	$s_1^4 s_2^4$ $(b_1^4 b_2^4)$	s_2^6 (c_2^6)	s_3^4 (b_3^4)	$s_2^2 s_4^2$ $(c_2^2 c_4^2)$	s_2^6 (b_2^6)	$s_2^2 s_4^2$ $(c_2^2 c_4^2)$	s_6^2 (c_6^2)	s_4^3 (c_4^3)	s_6^2 (b_6^2)	s_{12} (c_{12})
$T_d(/C_s)$	s_1^{12} (b_1^{12})	s_2^6 (b_2^6)	$s_1^2 s_2^5$ $(a_1^2 c_2^5)$	s_3^4 (b_3^4)	s_4^3 (c_4^3)	s_4^3 (b_4^3)	$s_2^2 s_4^2$ $(a_2^2 c_4^2)$	$s_3^2 s_6$ $(a_3^2 c_6)$	$s_4 s_8$ $(a_4 c_8)$	s_{12} (b_{12})	s_{12} (a_{12})
$T_d(/C_3)$	s_1^8 (b_1^8)	s_2^4 (b_2^4)	s_2^4 (c_2^4)	$s_1^2 s_3^2$ $(b_1^2 b_3^2)$	s_4^2 (c_4^2)	s_4^2 (b_4^2)	s_4^2 (c_4^2)	$s_2 s_6$ $(c_2 c_6)$	s_8 (c_8)	s_4^2 (b_4^2)	s_8 (c_8)
$T_d(/S_4)$	s_1^6 (b_1^6)	$s_1^2 s_2^2$ $(b_1^2 b_2^2)$	s_2^3 (c_2^3)	s_2^3 (b_3^2)	$s_1^2 s_4$ $(a_1^2 c_4)$	s_2^3 (b_2^3)	$s_2 s_4$ $(c_2 c_4)$	s_6 (c_6)	$s_2 s_4$ $(a_2 c_4)$	s_6 (b_6)	s_6 (a_6)
$T_d(/D_2)$	s_1^6 (b_1^6)	s_1^6 (b_1^6)	s_2^3 (c_2^3)	s_3^2 (b_3^2)	s_2^3 (c_2^3)	s_1^6 (b_1^6)	s_2^3 (c_2^3)	s_6 (c_6)	s_2^3 (c_2^3)	s_3^2 (b_3^2)	s_6 (c_6)
$T_d(/C_{2v})$	s_1^6 (b_1^6)	$s_1^2 s_2^2$ $(b_1^2 b_2^2)$	$s_1^2 s_2^2$ $(a_1^2 c_2^2)$	s_3^2 (b_3^2)	$s_2 s_4$ $(c_2 c_4)$	s_2^3 (b_2^3)	$s_1^2 s_4$ $(a_1^2 c_4)$	s_3^2 (a_3^2)	$s_2 s_4$ $(a_2 c_4)$	s_6 (b_6)	s_6 (a_6)
$T_d(/C_{3v})$	s_1^4 (b_1^4)	s_2^2 (b_2^2)	$s_1^2 s_2$ $(a_1^2 c_2)$	$s_1 s_3$ $(b_1 b_3)$	s_4 (c_4)	s_4 (b_4)	s_2^2 (a_2^2)	$s_1 s_3$ $(a_1 a_3)$	s_4 (a_4)	s_4 (b_4)	s_4 (a_4)
$T_d(/D_{2d})$	s_1^3 (b_1^3)	s_1^3 (b_1^3)	$s_1 s_2$ $(a_1 c_2)$	s_3 (b_3)	$s_1 s_2$ $(a_1 c_2)$	s_1^3 (b_1^3)	$s_1 s_2$ $(a_1 c_2)$	s_3 (a_3)	$s_1 s_2$ $(a_1 c_2)$	s_3 (b_3)	s_3 (a_3)
$T_d(/T)$	s_1^2 (b_1^2)	s_1^2 (b_1^2)	s_2 (c_2)	s_1^2 (b_1^2)	s_2 (a_2)	s_1^2 (b_1^2)	s_2 (c_2)	s_2 (c_2)	s_2 (c_2)	s_1^2 (b_1^2)	s_2 (c_2)
$T_d(/T_d)$	s_1 (b_1)	s_1 (b_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)	s_1 (a_1)	s_1 (a_1)	s_1 (b_1)	s_1 (a_1)
$\sum_i \bar{m}_{ji}$	1/24	1/8	1/4	1/3	1/4	0	0	0	0	0	0

3.2. Enumeration of mobile moieties

This process is essentially equivalent to that for rigid molecules [12]. Suppose that a set of substituents are selected from the codomain,

$$X = \{x_1, x_2, \ldots, x_{|X|}\}. \tag{7}$$

If we select $|\Psi|$ of substituents from X and put them onto the positions of Ψ, such a function,

$$y : \Psi \rightarrow X, \tag{8}$$

is an expression of the resulting configuration. Since the domain Ψ is divided into orbits, $\Psi_{p\gamma}$ ($p = 1, 2, \ldots, C_H$, $\gamma = 1, 2, \ldots, \gamma_p$), in terms of Eq. (1), we can describe the function y in detail. If $n_{p\gamma r}^{(y)}$ of x_r's ($r = 1, 2, \ldots, |X|$) occupy the orbit ($\Psi_{p\gamma}$), the weight (molecular formula) of this function (configuration) is represented by

$$w_\xi(y) = \prod_{p=1}^{C_H} \prod_{\gamma=1}^{\gamma_p} \prod_{r=1}^{|X|} x_r^{n_{p\gamma r}^{(y)}}, \tag{9}$$

where $n_{p\gamma r}^{(y)}$ is greater than 0 if $\Psi_{p\gamma}$ contains x_r; otherwise, it is equal to 0. Obviously, the following equation holds for this case:

$$\prod_{p=1}^{C_H} \prod_{\gamma=1}^{\gamma_p} \prod_{r=1}^{|X|} n_{p\gamma r}^{(y)} = |\Psi|. \tag{10}$$

Let $\varrho_{\xi q}$ be the number of such isomeric moieties ($y_{\xi q}$) with the weight w_ξ that are invariant (or fixed) under the operation of $\boldsymbol{H}_q$. Then, $\varrho_{\xi q}$ is obtained by means of generating functions [12], i.e.,

Lemma 1.

$$\sum_{\xi} \varrho_{\xi q} w_\xi = ZI(\boldsymbol{H}_q; t_{d_{qr}}) \tag{11}$$

for $q = 1, 2, \ldots, C_H$, *in which every term of the right-hand side is substituted by*

$$t_{d_{qr}} = \sum_{r=1}^{|X|} x_r^{d_{qr}}. \tag{12}$$

This generating function (Eq. (12)) is here called a moiety-figure inventory. The number $\varrho_{\xi q}$ contains multiple counting because of conjugate subgroups. Hence, the net number of mobile moieties ($B_{\xi p}$) is obtained by

Theorem 1 (enumeration of mobile moieties).

$$\varrho_{\xi q} = \sum_{p=1}^{C_H} B_{\xi p} m_{pq} \tag{13}$$

for $q = 1, 2, \ldots, C_H$, *where* $B_{\xi p}$ *is the number of* $\boldsymbol{H}_p$, w_ξ*-moieties,* m_{pq} *is an* pq*-element of the mark table of* ***H*****-group.**

The proof of Theorem 1 is essentially equivalent to that described for the enumeration of rigid molecules [12].

When $\bar{m}_{qp}$ is an element of the inverse of the mark table, Eq. (13) is converted into

$$B_{\xi p} = \sum_{q=1}^{C_H} \varrho_{\xi q} \bar{m}_{qp}. \tag{14}$$

This result is alternatively expressed in the form of a matrix, i.e.,

$$(B_{\xi p}) = \begin{array}{c} \\ w_1 \\ w_2 \\ \vdots \\ w_{|\xi|} \end{array} \begin{array}{c} \begin{array}{cccc} \boldsymbol{H}_1 & \boldsymbol{H}_2 & \cdots & \boldsymbol{H}_{C_H} \end{array} \\ \begin{pmatrix} B_{11} & B_{12} & \cdots & B_{1C_H} \\ B_{21} & B_{22} & \cdots & B_{2C_H} \\ \vdots & \vdots & & \vdots \\ B_{|\xi|1} & B_{|\xi|2} & \cdots & B_{|\xi|C_H} \end{pmatrix} \end{array}, \tag{15}$$

where $|\xi|$ denotes the number of monomials generated. Each element $(B_{\xi p})$ indicates the number of isomeric moieties, $y_{\xi p}$ ($\xi = 1, 2, \ldots, |\xi|$ and $p = 1, 2, \ldots, C_H$). In this enumeration, if $\boldsymbol{H}_p$ is proper, every pair of antipodes is counted once. This fact should be taken into consideration in the next step of enumeration. The following example illustrates the enumeration of mobile moieties.

Example 1 (A $\boldsymbol{C}_{3v}(/\boldsymbol{C}_s)$ mobile moiety (Fig. 1c)). Suppose that the three positions (○) of Fig. 1c are occupied by either X or Y. Then, the given codomain is $\boldsymbol{X} = \{X, Y\}$. If we number the positions sequentially, we obtain a domain which is expressed by $\Psi = \{1, 2, 3\}$. This domain is subject to $\boldsymbol{C}_{3v}(/\boldsymbol{C}_s)$. We construct the SCIs for this case, using the $\boldsymbol{C}_{3v}(/\boldsymbol{C}_s)$ row of Table 1. We introduce a moiety-figure inventory, $s_d = X^d + Y^d$, into these SCIs to produce generating functions for $\varrho_{\xi q}$, i.e.,

$$s_1^3 = (X + Y)^3 \quad \text{for } \boldsymbol{C}_1, \tag{16}$$

$$s_1 s_2 = (X + Y)(X^2 + Y^2) \quad \text{for } \boldsymbol{C}_s, \tag{17}$$

$$s_3 = X^3 + Y^3 \quad \text{for } \boldsymbol{C}_3, \tag{18}$$

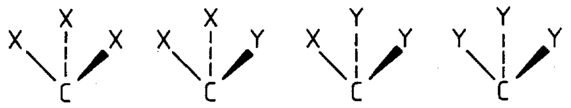
and

$$s_3 = X^3 + Y^3 \quad \text{for } \boldsymbol{C}_{3v}. \tag{19}$$

The expansion of these equations affords a matrix $(\varrho_{\xi q})$, which is in turn multiplied by the inverse of a mark table of $\boldsymbol{C}_{3v}$, i.e.,

$$\begin{array}{c} \\ X^3 \\ X^2Y \\ XY^2 \\ Y^3 \\ \\ \end{array} \begin{array}{c} \begin{array}{cccc} \boldsymbol{C}_1 & \boldsymbol{C}_s & \boldsymbol{C}_3 & \boldsymbol{C}_{3v} \end{array} \\ \begin{pmatrix} 1 & 1 & 1 & 1 \\ 3 & 1 & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix} \\ (\varrho_{\xi q}) \end{array} \begin{array}{c} \\ \begin{pmatrix} \frac{1}{6} & 0 & 0 & 0 \\ -\frac{1}{2} & 1 & 0 & 0 \\ \frac{1}{6} & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -1 & -\frac{1}{2} & 1 \end{pmatrix} \\ \textit{the inverse} \end{array} = \begin{array}{c} \begin{array}{cccc} \boldsymbol{C}_1 & \boldsymbol{C}_s & \boldsymbol{C}_3 & \boldsymbol{C}_{3v} \end{array} \\ \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\ (B_{\xi p}) \end{array}. \tag{20}$$

The resulting matrix affords the numbers of respective moieties, which are depicted in Fig. 2. All of the mobile moieties collected in Fig. 2 are achiral.



Weight (w_{ξ})	X^3	X^2Y	XY^2	Y^3
Weight ($y_{\xi p}$)	y_{14}	y_{22}	y_{32}	y_{44}
Symmetry	C_{3v}	C_s	C_s	C_{3v}
Orbit	$C_{3v}(/C_s)$	$C_s(/C_1)$ $C_s(/C_s)$	$C_s(/C_1)$ $C_s(/C_s)$	$C_{3v}(/C_s)$

Fig. 2. Mobile moieties based on a $C_{3v}(/C_s)$ orbit

4. Non-rigid molecules

4.1. Unit subduced cycle indices with chirality fittingness for a non-rigid molecule

Suppose that the rigid skeleton of a non-rigid molecule of $\boldsymbol{G}$-symmetry has $|\Phi|$ substitution positions, which construct a domain,

$$\Phi = \{\phi_1, \phi_2, \ldots, \phi_{|\Phi|}\}. \tag{21}$$

When this domain is permuted by a permutation representation $\boldsymbol{P}_G$, this can be reduced into the sum of CRs, i.e.,

$$\boldsymbol{P}_G = \sum_{i=1}^{C_G} \alpha_i \boldsymbol{G}(/\boldsymbol{G}_i), \tag{22}$$

wherein α_i is the multiplicity of the CR, $\boldsymbol{G}(/\boldsymbol{G}_i)$. This equation divides the domain (Φ) into several orbits,

$$\Phi_{i\alpha} \quad (i = 1, 2, \ldots, C_H; \alpha = 1, 2, \ldots, \alpha_i), \tag{23}$$

each of which is subject to the αth CR, $\boldsymbol{G}(/\boldsymbol{G}_i)$.

In terms of the subduction of the CR represented by

$$\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j = \sum_{k=1}^{u_j} \beta_{ijk} \boldsymbol{G}_j(/\boldsymbol{G}_{jk}), \tag{24}$$

we define a USCI with chirality fittingness for this case as

$$Z(\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j; \$_{d_{jk}}) = \prod_{k=1}^{u_j} (\$_{d_{jk}})^{\beta_{ijk}}, \tag{25}$$

for $i = 1, 2, \ldots, C_G$ and $j = 1, 2, \ldots, C_G$, where

$$d_{jk} = |\boldsymbol{G}_j|/|\boldsymbol{G}_{jk}|. \tag{26}$$

The dummy variable $\$$ is replaced by the variable (a) for the case where both $\boldsymbol{G}_j$ and $\boldsymbol{G}_{jk}$ are improper; by the variable (b) for the case where both $\boldsymbol{G}_j$ and $\boldsymbol{G}_{jk}$ are proper; or by the variable (c) for the case where $\boldsymbol{G}_j$ is improper and $\boldsymbol{G}_{jk}$ is proper [19]. Even if two or more orbits are governed by the same CR, they can take different kinds of mobile moieties as substituents. Hence, the dummy variable should be dependent upon the respective orbit. This is designated by the symbol $\$_{d_{ijk}}^{(i\alpha)}$, in which the superscript $(i\alpha)$ indicates the dependence upon the αth $\boldsymbol{G}(/\boldsymbol{G}_i)$ orbit, i.e., $\Phi_{i\alpha}$. In this case [12, 20], the corresponding subduced cycle index (SCI) is expressed by

$$\begin{aligned} ZI(\boldsymbol{G}_j; \$_{d_{qr}}^{(i\alpha)}) &= \prod_{\substack{i=1 \\ (\alpha_i \neq 0)}}^{C_G} \prod_{\alpha=1}^{\alpha_i} Z(\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j; \$_{d_{qr}}^{(i\alpha)}) \\ &= \prod_{\substack{i=1 \\ (\alpha_i \neq 0)}}^{C_G} \prod_{\alpha=1}^{\alpha_i} \left[\prod_{k=1}^{u_i} (\$_{d_{qr}}^{(i\alpha)})^{\beta_{ijk}} \right] \quad (j = 1, 2, \ldots, C_G). \end{aligned} \tag{27}$$

4.2. *Enumeration of non-rigid isomers*

A non-rigid compound is regarded as a derivative of a $\boldsymbol{G}$ rigid skeleton, in which the αth $\boldsymbol{G}(/\boldsymbol{G}_i)$ orbit ($\Phi_{i\alpha}$) is substituted by $\boldsymbol{H}_p^{(i\alpha)}$ moieties, as is shown in Fig. 3. The mobile moieties are enumerated by Theorem 2 with respect to every $\Phi_{i\alpha}$. Hence, all of the participants in Theorem 2 are dependent upon the orbit ($\Phi_{i\alpha}$). These dependences are denoted by such a superscript $(i\alpha)$ as appears in $\boldsymbol{H}_p^{(i\alpha)}$, etc.

Suppose that appropriate moieties are selected as substituents from a set of mobile moieties enumerated in the preceding section. In general, mobile moieties are either achiral or chiral depending on $\boldsymbol{H}_p^{(i\alpha)}$. We thus consider a set of $|\xi| \times C_{\boldsymbol{H}^{(i\alpha)}}$ moieties represented by

$$\boldsymbol{Y}_1^{(i\alpha)} = \begin{array}{c} \\ w_1 \\ w_2 \\ \vdots \\ w_{|\xi|} \end{array} \begin{array}{c} \begin{array}{cccc} \boldsymbol{H}_1^{(i\alpha)} & \boldsymbol{H}_2^{(i\alpha)} & \cdots & \boldsymbol{H}_{C_{\boldsymbol{H}^{(i\alpha)}}}^{(i\alpha)} \end{array} \\ \begin{pmatrix} y_{11}^{(i\alpha)} & y_{12}^{(i\alpha)} & \cdots & y_{1C_{\boldsymbol{H}^{(i\alpha)}}}^{(i\alpha)} \\ y_{21}^{(i\alpha)} & y_{22}^{(i\alpha)} & \cdots & y_{2C_{\boldsymbol{H}^{(i\alpha)}}}^{(i\alpha)} \\ \vdots & \vdots & & \vdots \\ y_{|\xi|1}^{(i\alpha)} & y_{|\xi|2}^{(i\alpha)} & \cdots & y_{|\xi|C_{\boldsymbol{H}^{(i\alpha)}}}^{i\alpha} \end{pmatrix} \end{array} . \tag{28}$$

Note that we select a representative ($y_{\xi p}^{(i\alpha)}$) from each set of w_ξ, $\boldsymbol{H}_p^{(i\alpha)}$-moieties, since these are presumed to have the same weight. The number of such w_ξ, $\boldsymbol{H}_p^{(i\alpha)}$-moieties has been given by Eqs. (14) and (15). Since there are the

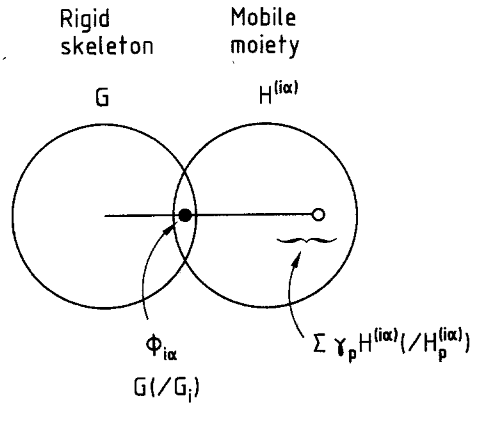


Fig. 3. Schematic representation of a non-rigid compound

corresponding antipodes for the respective isomeric moieties, we should consider another set of mobile moieties, i.e.,

$$\tilde{\boldsymbol{Y}}_{1}^{(i\alpha)} = \begin{array}{c} \\ w_1 \\ w_2 \\ \vdots \\ w_{|\xi|} \end{array} \begin{array}{c} \begin{array}{cccc} \boldsymbol{H}_{1}^{(i\alpha)} & \boldsymbol{H}_{2}^{(i\alpha)} & \cdots & \boldsymbol{H}_{C_{\boldsymbol{H}}(i\alpha)}^{(i\alpha)} \end{array} \\ \begin{pmatrix} \tilde{y}_{11}^{(i\alpha)} & \tilde{y}_{12}^{(i\alpha)} & \cdots & \tilde{y}_{1C_{\boldsymbol{H}}(i\alpha)}^{(i\alpha)} \\ \tilde{y}_{21}^{(i\alpha)} & \tilde{y}_{22}^{(i\alpha)} & \cdots & \tilde{y}_{2C_{\boldsymbol{H}}(i\alpha)}^{(i\alpha)} \\ \vdots & \vdots & & \vdots \\ \tilde{y}_{|\xi|1}^{(i\alpha)} & \tilde{y}_{|\xi|2}^{(i\alpha)} & \cdots & \tilde{y}_{|\xi|C_{\boldsymbol{H}}(i\alpha)}^{(i\alpha)} \end{pmatrix} \end{array}, \tag{29}$$

where each $\tilde{y}_{\xi p}^{(i\alpha)}$ is the antipode of $y_{\xi p}^{(i\alpha)}$. If $\tilde{y}_{\xi p}^{(i\alpha)} = y_{\xi p}^{(i\alpha)}$, this represents an archiral moiety. Hence, we construct an effective set of mobile moieties as follows:

$$\boldsymbol{Y}^{(i\alpha)} = \boldsymbol{Y}_{1}^{(i\alpha)} \cup \tilde{\boldsymbol{Y}}_{1}^{(i\alpha)}. \tag{30}$$

We then consider a function,

$$f : \Phi_{i\alpha} \to \boldsymbol{Y}^{(i\alpha)} \tag{31}$$

for $i = 1, 2, \ldots, C_G$ and $\alpha = 1, 2, \ldots, \alpha_i$. This function corresponds to a non-rigid derivative. If, in this function, an orbit $\Phi_{i\alpha}$ contains $n_{\xi p(f)}^{(i\alpha)}$ of $y_{\xi p}^{(i\alpha)}$ and $\tilde{n}_{\xi p(f)}^{(i\alpha)}$ of $\tilde{y}_{\xi p}^{(i\alpha)}$, the weight (W_θ) of the function (f) is represented by

$$W_\theta(f) = \prod_{\substack{i=1 \\ (\alpha_i \neq 0)}}^{C_G} \prod_{\alpha}^{\alpha_i} \left[\prod_{p=1}^{C_{\boldsymbol{H}}(i\alpha)} \prod_{\xi} (y_{\xi p}^{(i\alpha)})^{n_{\xi p(f)}^{(i\alpha)}} \prod_{p=1}^{C_{\boldsymbol{H}}(i\alpha)} \prod_{\xi} (\tilde{y}_{i}^{(}\alpha)\xi p)^{\tilde{n}_{\xi p(f)}^{(i\alpha)}} \right], \tag{32}$$

where

$$n_{\xi p(f)}^{(i\alpha)} > 0, \quad \text{if } \Phi_{i\alpha} \text{ contains } y_{\xi p}^{(i\alpha)}; \text{ otherwise} = 0$$

and

$$\tilde{n}_{\xi p(f)}^{(i\alpha)} > 0, \quad \text{if } \Phi_{i\alpha} \text{ contains } \tilde{y}_{\xi p}^{(i\alpha)}; \text{ otherwise} = 0.$$

The subscript (θ) is a descriptor for differentiating the weights.

The following lemma can be obtained by a slight modification of the method described elsewhere [20].

Lemma 2. *Let σ_{θ_j} be the number of derivatives with the weight (W_θ) that are invariant (or fixed) on the operation of $\boldsymbol{G}_j$. We can estimate $\sigma_{\theta j}$ in terms of generating functions,*

$$\sum_{\theta} \sigma_{\theta j} W_\theta = ZI(\boldsymbol{G}_j; \$_{d_{jk}}^{(i\alpha)}) \tag{33}$$

for $j = 1, 2, \ldots, C_G$, in which every variable of the right-hand side is substituted by figure inventories,

$$a_{d_{jk}}^{(i\alpha)} = \sum_{\substack{p=1 \\ \text{improper}}}^{C_{\boldsymbol{H}}(i\alpha)} \sum_{\xi} B_{\xi p}^{(i\alpha)} (y_{\xi p}^{(i\alpha)})^{d_{jk}} \quad \text{for } \$ = a, \tag{34}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_{\substack{p=1 \\ \text{improper}}}^{C_{\boldsymbol{H}}(i\alpha)} \sum_{\xi} B_{\xi p}^{(i\alpha)} (y_{\xi p}^{(i\alpha)})^{d_{jk}} + \sum_{\substack{p=1 \\ \text{proper}}}^{C_{\boldsymbol{H}}(i\alpha)} \sum_{\xi} B_{\xi p}^{(i\alpha)} (y_{\xi p}^{(i\alpha)})^{d_{jk}}$$

$$+ \sum_{\substack{p=1 \\ \text{proper}}}^{C_{\boldsymbol{H}}(i\alpha)} \sum_{\xi} B_{\xi p}^{(i\alpha)} (\tilde{y}_{\xi p}^{(i\alpha)})^{d_{jk}} \quad \text{for } \$ = b, \tag{35}$$

$$c_{d_{jk}}^{(i\alpha)} = \underbrace{\sum_{p=1}^{C_{\boldsymbol{H}(i\alpha)}}}_{\text{improper}} \sum_{\xi} B_{\xi p}^{(i\alpha)} (y_{\xi p}^{(i\alpha)})^{d_{jk}} + 2 \underbrace{\sum_{p=1}^{C_{\boldsymbol{H}(i\alpha)}}}_{\text{proper}} \sum_{\xi} B_{\xi p}^{(i\alpha)} (y_{\xi p}^{(i\alpha)} \tilde{y}_{\xi p}^{(i\alpha)})^{d_{jk}/2} \quad \text{for } \$ = c. \tag{36}$$

The summation over p is restricted within either improper or proper point groups according to the indication shown below the symbol. When all $y_{\xi p}^{(i\alpha)}$'s in $W_\theta(f)$ are replaced by $\tilde{y}_{\xi p}^{(i\alpha)}$'s and vice versa, the $W_\theta(f)$ is presumed to convert into $\tilde{W}_\theta(f)$. Since the resulting molecule is antipodal to the original one, we should sum up the coefficients of $W_\theta(f)$ and $\tilde{W}_\theta(f)$ in order to produce $\sigma_{\theta j}$. Note that the present enumeration is concerned with every pair of antipodes.

Now we arrive at

Theorem 2 (enumeration of $W_\theta, \boldsymbol{G}_i$-isomers). *Let $A_{\theta i}$ be the number of $W_\theta, \boldsymbol{G}_i$-isomers. This is calculated by using $\sigma_{\theta j}$ (Lemma 2) by means of*

$$\sigma_{\theta j} = \sum_{i=1}^{C_{\boldsymbol{G}}} A_{\theta i} M_{ij} \quad \textit{for } j = 1, 2, \ldots, C_{\boldsymbol{G}}, \tag{37}$$

or inversely,

$$A_{\theta i} = \sum_{j=1}^{C_{\boldsymbol{G}}} \sigma_{\theta i} \bar{M}_{ji} \quad \textit{for } i = 1, 2, \ldots, C_{\boldsymbol{G}}, \tag{38}$$

*wherein M_{ij} is the ij-element of a mark table (M_{ij}) for the **G**-group and $(\bar{M}_{ji})$ denotes the inverse of the matrix (M_{ij}).*

For illustrating Lemma 2 and Theorem 2, we further examine the case of Example 1.

Example 2 (enumeration of isomers based on 1). We assign dummy variables y_{14}, y_{22}, y_{32} and y_{44} to the mobile moieties counted in Example 1 (Fig. 2). Since this case contains no chiral moieties, we are allowed to consider $\$$ to be s in Lemma 2. Thus, we obtain a figure inventory,

$$s_d = y_{14}^d + y_{22}^d + y_{32}^d + y_{44}^d. \tag{39}$$

by means of Eq. (20). Since the rigid skeleton (Fig. 1b) is subject to $\boldsymbol{T}_d(/\boldsymbol{C}_{3v})$, the $\boldsymbol{T}_d(/\boldsymbol{C}_{3v})$ row of Table 2 is selected to afford the following SCIs:

$$s_1^4 = (y_{14} + y_{22} + y_{32} + y_{44})^4 \quad \text{for } \boldsymbol{C}_1, \tag{40}$$

$$s_2^2 = (y_{14}^2 + y_{22}^2 + y_{32}^2 + y_{44}^2)^2 \quad \text{for } \boldsymbol{C}_2 \text{ and } \boldsymbol{C}_{2v}, \tag{41}$$

$$s_1^2 s_2 = (y_{14} + y_{22} + y_{32} + y_{44})^2 (y_{14}^2 + y_{22}^2 + y_{32}^2 + y_{44}^2) \quad \text{for } \boldsymbol{C}_s, \tag{42}$$

$$s_1 s_3 = (y_{14} + y_{22} + y_{32} + y_{44})(y_{14}^3 + y_{22}^3 + y_{32}^3 + y_{44}^3) \quad \text{for } \boldsymbol{C}_3 \text{ and } \boldsymbol{C}_{3v}, \tag{43}$$

and

$$s_4 = y_{14}^4 + y_{22}^4 + y_{32}^4 + y_{44}^4 \text{ for } \boldsymbol{S}_4,\ \boldsymbol{D}_2,\ \boldsymbol{D}_{2d},\ \boldsymbol{T}, \text{ and } \boldsymbol{T}_d, \tag{44}$$

according to Eqs. (27) and (33). These equations are expanded and the terms of the same powers are collected. In the present case, the terms are classified into 5 types, which are designated by the following *type index*, [4] for y_{14}^4, etc. (4 terms), [31] for $y_{14}^3 y_{22}$, etc. (12 terms), [22] for $y_{14}^2 y_{22}^2$, etc. (6 terms), [211] for $y_{14}^2 y_{22} y_{32}$, etc. (12 terms), and [1111] for $y_{14} y_{22} y_{32} y_{44}$ (1 term). The terms of the same type have equal coefficients to each other. Table 3 collects such coefficients.

Table 3 is considered to be a matrix, which is in turn multiplied by the inverse of the mark table (Table 4). The resulting matrix (Table 5) shows the number of

Table 3. Coefficients derived from generating functions

Index	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
[4]	1	1	1	1	1	1	1	1	1	1	1
[31]	4	0	2	1	0	0	0	1	0	0	0
[22]	6	2	2	0	0	0	2	0	0	0	0
[211]	12	0	2	0	0	0	0	0	0	0	0
[1111]	24	0	0	0	0	0	0	0	0	0	0

Table 4. The inverse of the mark table of T_d

	T_d $(/C_1)$	T_d $(/C_2)$	T_d $(/C_s)$	T_d $(/C_3)$	T_d $(/S_4)$	T_d $(/D_2)$	T_d $(/C_{2v})$	T_d $(/C_{3v})$	T_d $(/D_{2d})$	T_d $(/T)$	T_d $(/T_d)$
C_1	$\frac{1}{24}$	0	0	0	0	0	0	0	0	0	0
C_2	$-\frac{1}{8}$	$\frac{1}{4}$	0	0	0	0	0	0	0	0	0
C_s	$-\frac{1}{4}$	0	$\frac{1}{2}$	0	0	0	0	0	0	0	0
C_3	$-\frac{1}{6}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0	0
S_4	0	$-\frac{1}{4}$	0	0	$\frac{1}{2}$	0	0	0	0	0	0
D_2	$\frac{1}{12}$	$-\frac{1}{4}$	0	0	0	$\frac{1}{6}$	0	0	0	0	0
C_{2v}	$\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{2}$	0	0	0	$\frac{1}{2}$	0	0	0	0
C_{3v}	$\frac{1}{2}$	0	-1	$-\frac{1}{2}$	0	0	0	1	0	0	0
D_{2d}	0	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0	1	0	0
T	$\frac{1}{6}$	0	0	$-\frac{1}{2}$	0	$-\frac{1}{6}$	0	0	0	$\frac{1}{2}$	0
T_d	$-\frac{1}{2}$	0	1	$\frac{1}{2}$	0	$\frac{1}{2}$	0	-1	-1	$-\frac{1}{2}$	1

Table 5. Enumeration of isomers derived from 1

Index	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
[4]	0	0	0	0	0	0	0	0	0	0	1
[31]	0	0	0	0	0	0	0	1	0	0	0
[22]	0	0	0	0	0	0	1	0	0	0	0
[211]	0	0	1	0	0	0	0	0	0	0	0
[1111]	1	0	0	0	0	0	0	0	0	0	0

isomers of each type and each subsymmetry. Figure 4 depicts all 35 isomers ($35 = 4 + 12 + 6 + 12 + 1$), each of which is denoted by the type index and the point group of the respective rigid skeleton. In this case, the T_d, C_{3v}, C_{2v}, C_s, and C_1 symmetries of the rigid skeletons corresponds to the type indices, [4], [31], [22], [211], and [1111], respectively. It should be noted that the symmetries of such non-rigid molecules are designated by extended wreath product (EWP) symbols. For example, the two [4]-structures listed in Fig. 4 [21] are denoted as $T_d(/C_{3v})[C_{3v}(/C_s)]$ and $T_d(/C_{3v})[C_s(/C_1, /C_s)]$. If we assign each molecule to the point group of its conformation of the highest symmetry, the $T_d(/C_{3v})[C_{3v}(/C_s)]$ molecule would belong to T_d symmetry. On the other hand, the $T_d(/C_{3v})[C_s(/C_1, /C_s)]$ molecule has D_{2d} symmetry in its conformation of the highest symmetry.

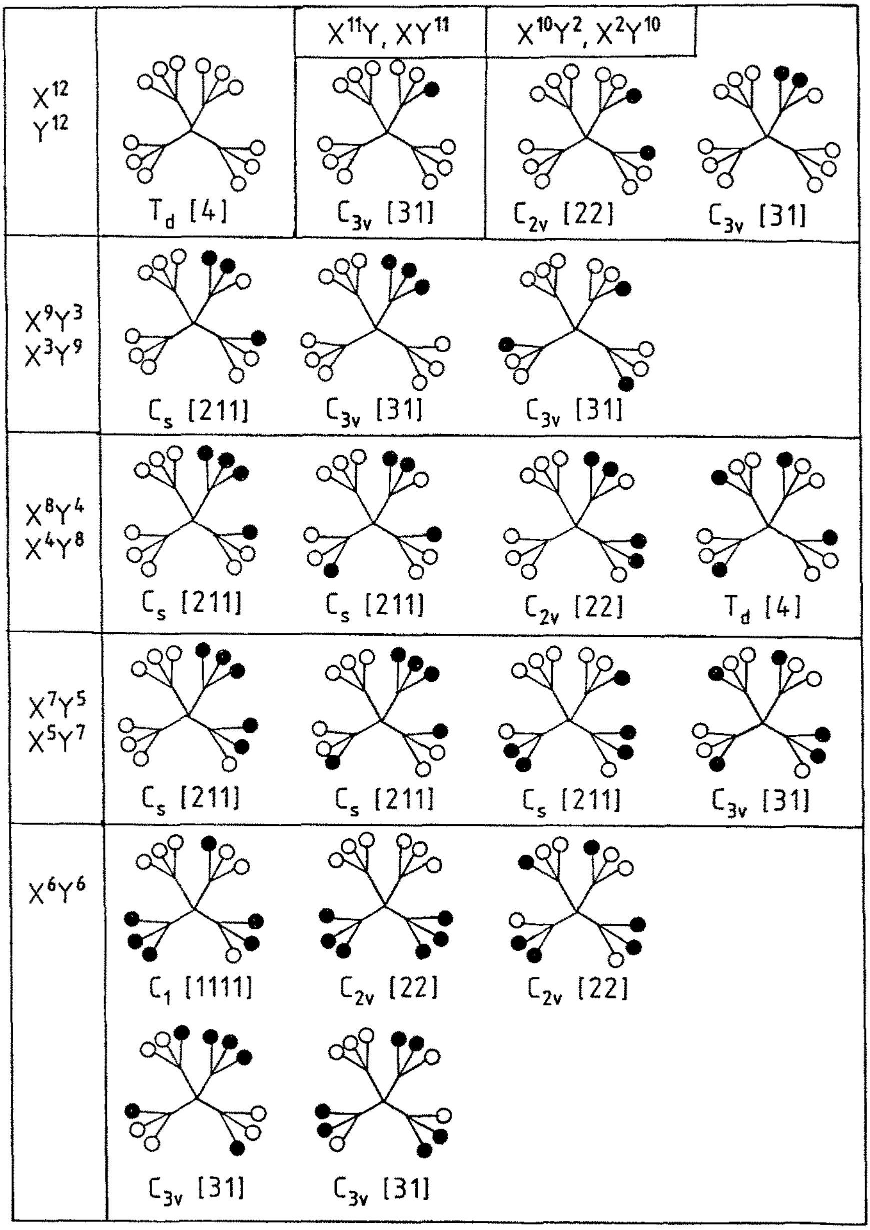


Fig. 4. Isomers derived from 1

If all $y_{\xi p}^{(i\alpha)}$'s and $\tilde{y}_{\xi p}^{(i\alpha)}$'s ($p = 1, 2, \ldots, C_{H^{(i\alpha)}}$) have the same weight ($w_{\xi}^{(i\alpha)}$), Lemma 2 is converted into a more convenient form:

Lemma 3 (modified enumeration). *The variables* ($a_{d_{jk}}^{(i\alpha)}$, $b_{d_{jk}}^{(i\alpha)}$, *and* $c_{d_{jk}}^{(i\alpha)}$) *can be rewritten for the present case*:

$$a_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \kappa_{\xi a} (w_{\xi}^{(i\alpha)})^{d_{jk}} \quad \textit{for } \$ = a, \tag{45}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \kappa_{\xi a}(w_{\xi}^{(i\alpha)})^{d_{jk}} + 2\sum_{\xi} \kappa_{\xi c}(w_{\xi}^{(i\alpha)})^{d_{jk}} \quad \textit{for } \$ = b, \tag{46}$$

and

$$c_{d_{jk}}^{(i\alpha)} = \sum_{\xi} \kappa_{\xi a}(w_{\xi}^{(i\alpha)})^{d_{jk}} + 2\sum_{\xi} \kappa_{\xi c}(w_{\xi}^{(i\alpha)})^{d_{jk}} \quad \textit{for } \$ = c, \tag{47}$$

where $\kappa_{\xi a}$ *and* $\kappa_{\xi c}$ *are represented by*

$$\kappa_{\xi a} = \underset{\text{improper}}{\underline{\sum_{p=1}^{C_{H^{(i\alpha)}}}}} B_{\xi p}^{(i\alpha)} \tag{48}$$

and

$$\kappa_{\xi c} = \underset{\text{proper}}{\underline{\sum_{p=1}^{C_{H^{(i\alpha)}}}}} B_{\xi p}^{(i\alpha)}. \tag{49}$$

For illustrating Lemma 3, we again treat the case of Examples 1 and 2 in detail.

Example 3 (enumeration based on 1). Since all of the mobile moieties counted in Example 1 are achiral, we can use the symbol (s) in place of $\$$. From the data of Eq. (20), we obtain $\kappa_{\xi a} = 1$ for all w_{ξ}. Hence, Lemma 3 yields a figure inventory,

$$s_d = X^{3d} + (X^2Y)^d + (XY^2)^d + Y^{3d} \tag{50}$$

for this case. This figure inventory is introduced into SCIs which are derived from the $\boldsymbol{T_d}(/\boldsymbol{C_{3v}})$ row of Table 2. Thereby, we obtain

$$s_1^4 = (X^3 + X^2Y + XY^2 + Y^3)^4 \quad \text{for } \boldsymbol{C}_1, \tag{51}$$

$$s_2^2 = (X^6 + X^4Y^2 + X^2Y^4 + Y^6)^2 \quad \text{for } \boldsymbol{C}_2 \text{ and } \boldsymbol{C}_{2v}, \tag{52}$$

$$s_1^2 s_2 = (X^3 + X^2Y + XY^2 + Y^3)^2(X^6 + X^4Y^2 + X^2Y^4 + Y^6) \quad \text{for } \boldsymbol{C}_s, \tag{53}$$

$$s_1 s_3 = (X^3 + X^2Y + XY^2 + Y^3)(X^9 + X^6Y^3 + X^3Y^6 + Y^9) \quad \text{for } \boldsymbol{C}_3 \text{ and } \boldsymbol{C}_{3v}, \tag{54}$$

and

$$s_4 = X^{12} + X^8Y^4 + X^4Y^8 + Y^{12} \quad \text{for } \boldsymbol{S}_4,\ \boldsymbol{D}_2,\ \boldsymbol{D}_{2d},\ \boldsymbol{T}, \text{ and } \boldsymbol{T}_d. \tag{55}$$

The expansion of these generating functions and the collection of the terms of the same power give such coefficients as listed in Table 6. This table as a matrix

Table 6. Coefficients derived from generating functions

	$\boldsymbol{C}_1$	$\boldsymbol{C}_2$	$\boldsymbol{C}_s$	$\boldsymbol{C}_3$	$\boldsymbol{S}_4$	$\boldsymbol{D}_2$	$\boldsymbol{C}_{2v}$	$\boldsymbol{C}_{3v}$	$\boldsymbol{D}_{2d}$	$\boldsymbol{T}$	$\boldsymbol{T}_d$
X^{12}, Y^{12}	1	1	1	1	1	1	1	1	1	1	1
$X^{11}Y, XY^{11}$	4	0	2	1	0	0	0	1	0	0	0
$X^{10}Y^2, X^2Y^{10}$	10	2	4	1	0	0	2	1	0	0	0
X^9Y^3, X^3Y^9	20	0	6	2	0	0	0	2	0	0	0
X^8Y^4, X^4Y^8	31	3	7	1	1	1	3	1	1	1	1
X^7Y^5, X^5Y^7	40	0	8	1	0	0	0	1	0	0	0
X^6Y^6	44	4	8	2	0	0	4	2	0	0	0

Table 7. Enumeration of isomers derived from 1

Term	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
X^{12}, Y^{12}	0	0	0	0	0	0	0	0	0	0	1
$X^{11}Y, XY^{11}$	0	0	0	0	0	0	0	1	0	0	0
$X^{10}Y^2, X^2Y^{10}$	0	0	0	0	0	0	1	1	0	0	0
X^9Y^3, X^3Y^9	0	0	1	0	0	0	0	2	0	0	0
X^8Y^4, X^4Y^8	0	0	3	0	0	0	0	1	0	0	0
X^7Y^5, X^5Y^7	0	0	3	0	0	0	0	1	0	0	0
X^6Y^6	1	0	0	0	0	0	2	2	0	0	0

is multiplied by the inverse (Table 4) to afford Table 7, in which the value at the intersection of each subsymmetry column and the term X^mY^n row indicates the number of the $C_5X_mY_n$-isomers with the subsymmetry.

Figure 4 also illustrates these results, which are designated by X^mY^n. Although Examples 2 and 3 contain no chiral mobile moieties, the present method can be applied to a general case that involves chiral as well as achiral moieties.

5. Conclusion

Unit subduced cycle indices (USCIs) introduced for enumerating isomers derived from a rigid skeleton [12] are proven to also be effective in counting non-rigid isomers, where the non-rigidity stems from rotations around bonds, after some modifications and extensions. Thus, a given non-rigid skeleton is divided into a rigid skeleton and mobile moieties. The latter moieties are considered attached to the vertices of the rigid skeleton. This formulation allows us to apply the USCIs to the mobile moieties and to the rigid skeleton for enumerating such non-rigid molecules.

References and notes

1. (a) Pólya G (1937) Acta Math 68:135
   (b) Pólya G, Read RC (1987) Combinatorial enumeration of groups, graphs, and chemical compounds. Springer, Berlin Heidelberg New York
2. (a) Redfield JH (1927) Am J Math 49:433
   (b) Read RC (1959) J London Math Soc 34:417
   (c) Read RC (1960) J London Math Soc 35:344
   (d) Davidson RA (1981) J Am Chem Soc 103:312
3. (a) Rouvray DH (1974) Chem Soc Rev 3:355
   (b) Rouvray DH (1975) Endeavour 34:28
4. Balaban AT (ed) (1976) Chemical application of graph theory. Academic Press, London
5. Balasubramanian K (1985) Chem Rev 85:599
6. Hansen RJ, Jurs PC (1988) J Chem Ed 65:661
7. (a) Fujita S (1986) J Chem Inf Comput Sci 26:212
   (b) Fujita s (1987) J Chem Inf Comput Sci 27:99
   (c) Fujita S (1988) Bull Chem Soc Jpn 61:4189
   (d) Fujita S (1989) Bull Chem Soc Jpn 62:662
   (e) Fujita S (1989) J Chem Inf Comput Sci 29:22

8. Ruch E, Hässelbarth W, Richter B (1970) Theor Chim Acta 19:288
9. Hässelbarth W (1985) Theor Chim Acta 67:339
10. Mead CA (1987) J Am Chem Soc 109:2130
11. Brocas J (1986) J Am Chem Soc 108:1135
12. (a) Fujita S (1989) Theor Chim Acta 76:247
    (b) Fujita S (1989) Bull Chem Soc Jpn 62:3771
    (c) Fujita S (1990) Bull Chem Soc Jpn 63:203
    (d) Fujita S (1990) Tetrahedron 46:365
13. Balasubramanian K (1979) Theor Chim Acta 51:37
14. (a) Leonard JE, Hammond GS, Simmons HE (1975) J Am Chem Soc 97:5052
    (b) Leonard JE (1977) J Phys Chem 81:2212
15. Balasubramanian K (1981) J Chem Phys 75:4752
16. Baumslag B, Chandler B (1968) Theory and problems of group theory. McGraw-Hill, New York
17. Armstrong MA (1988) Groups and symmetry. Springer, Berlin Heidelberg New York
18. Burnside W (1911) Theory of groups of finite order, 2nd edn. Cambridge University Press, Cambridge
19. This assignment is based on the chirality fittingness of an orbit governed by $G_j(/G_{jk})$. See Fujita S (1990) Bull Chem Soc Jpn 63:315; Fujita S (1990) J Am Chem Soc 112:3390
20. Fujita S: J Math Chem, in press
21. Each structure in Fig. 4 corresponds to a pair of molecules which are produced by interchanging open circles and solid ones