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The Use of Different Figure-Inventories in the Enumeration of Isomers Derived from Non-Rigid Parent Molecules

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Inevitable use of different figure-inventories is discussed in the enumeration of non-rigid isomers derived from 2,2-diphenyl-(**1**) and 2,2-dimethylpropane (**2**) by means of unit subduced cycle indices (USCIs). Such a parent non-rigid molecule is divided into a rigid skeleton and mobile moieties. Thus, the molecule (**1**) consists of a rigid skeleton of $\mathbf{C}_{2v}$ symmetry, a methyl moiety of $\mathbf{C}_{3v}$ symmetry and a phenyl moiety of $\mathbf{C}_{2v}$ symmetry. The molecule (**2**) contains a $\mathbf{T}_d$ rigid skeleton and a $\mathbf{C}_{3v}$ moiety. The USCIs are used in the first enumeration of mobile moieties as well as the subesequent enumeration based on a rigid skeleton. A general procedure for enumerating non-rigid isomers is discussed.

Enumeration of rigid molecules has long been studied by the Pólya-Redfield theory,[1,2] by a method based on double cosets[3], and by a method using tables of marks.[4] The relationship between them has been discussed.[3,5] Applications of these methods to various problems in chemistry have been developed, as reviewed for the former theory[6–9] and for the latter methods.[10] Recently, we have applied the Pólya–Redfield theory to enumeration of organic reactions,[11] in which we have used different figure-inventories according to the OMV (obligatory minimum valency) restriction of vertices.

Isomer enumerations that take spacial symmetry into account have recently been developed by using tables of marks,[12] by coupling double cosest and tables of marks,[13] and by combining double cosets and framework groups.[14] We have reported a method using unit subduced cycle indices (USCIs) for solving this type of enumerations,[15] where we have also taken account of the effect of different figure-inventories in order to meet the OMV restriction.

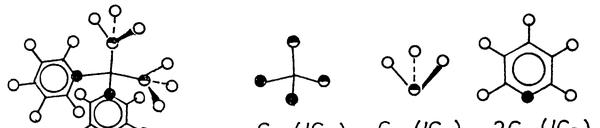
On the other hand, enumeration of non-rigid molecules has attracted less attention than that of rigid ones, probably because of its complicated nature. Pólya[1] has already mentioned the enumeration of non-rigid molecules in terms of "coronas", which are equivalent to wreath products. The counting of non-rigid cyclohexane isomers was discussed by introducing a ring-flip-rotation operator along with usual symmetry operations.[16] Isomers derived from a non-rigid ethane were enumerated by means of the concept of covering groups.[17] A generalized wreath product method was presented for enumerating stereo- and positional isomeres.[18]

We reported a mathematical foundation for the application of the USCIs to the systematic enumeration of non-rigid isomers.[19] This enumeration took account of spacial symmetries of isomers; however, it was restricted to the cases in which a single figure-inventory is taken into consideration. As a continuation of the work, the present paper will deal with a further extension of the USCI approach by using 2,2-diphenyl and 2,2-dimethylpropane as examples. In particular, we will discuss additional cases in which two or more figure-inventories should be used.

Results and Discussion

Rigid Skeleton and Mobile Moieties of a Non-Rigid Parent Molecule. In order to enumerate isomers, a non-rigid parent molecule is regarded as a three-dimensional object that has terminal substitution positions. These positions can be chemically classified into several equivalence classes. Although this classification should be discussed by using wreath products[1] and generalized wreath products,[8] we here adopt a more intuitive approach which is suitable for the application of USCIs. In the present paper, we take account of the non-rigidity that comes from bond rotations and not from tortions.[20]

A non-rigid moelcules is considered to be divided into a rigid skeleton and mobile moieties. For example, 2,2-diphenylpropane (**1**) is divided into three parts (**1a**, **1b**, and **1c**) as shown in Fig. 1. Note that free bond-rotations are considered to be allowed in this compound. The rigid skeleton (**1a**) of $\mathbf{C}_{2v}$ symmetry has four roots (● and ◓) to which the mobile moieties attach. The mobile moiety (**1b**) of $\mathbf{C}_{3v}$ symmetry consists of such a root (◓) and 3 substitution positions



1    $C_{2v}(/C_s)$ 1a $C_{3v}(/C_s)$ 1b $2C_{2v}(/C_s)$ $C_{2v}(/C_{2v})$ 1c

Fig. 1. A $\mathbf{C}_{2v}[(/\mathbf{C}_s)[\mathbf{C}_{3v}(/\mathbf{C}_s)],\ (/\mathbf{C}'_s)[\mathbf{C}_{2v}(2/\mathbf{C}_s,\mathbf{C}_{2v})]]$ molecule.

(○). The mobile moiety (**1c**) of $\mathbf{C}_{2v}$ symmetry contains the root (●) and 5 substitution positions (○). The other positions of these parts are not taken into consideration.

In the light of this formulation, the rigid skeleton (**1a**) is invariant on any chemical bond-rotations around the bonds contained in the skeleton. Moreover, the mobile moieties (**1b** and **1c**) are allowed to be regarded as rigid objects, since they are also invariant on any bond-rotations. Hence, the previously developed method[15] for enumerating rigid molecules are applicable to the present case. The roots (● and ◓) are thus considered to be substitution positions and divided into two equivalence classes, which are called *orbits* in terms of the terminology of permutation groups.[21,22] The 3 positions of **1b** and the 5 positions of **1c** are also divided into several orbits.

Each of the *orbits* corresponds to a coset representation (CR), $\mathbf{G}(/\mathbf{G}_i)$ in one-to-one fashion, where $\mathbf{G}$ is a (point) group for characterizing the symmetry of such a rigid skeleton or a mobile moiety and $\mathbf{G}_i$ is a subgroup of $\mathbf{G}$.[15] A table of marks for the $\mathbf{G}$-symmetry[23] is used for assigining an orbit to a $\mathrm{CR}(\mathbf{G}(/\mathbf{G}_i))$.

The four roots of the rigid skeleton (**1a**) construct two orbits that are subject to CRs, $\mathbf{C}_{2v}(/\mathbf{C}_s)$ and $\mathbf{C}_{2v}(/\mathbf{C}'_s)$, respectively. This fact can be formulated as

$$\mathbf{P}_{1a} = \mathbf{C}_{2v}(/\mathbf{C}_s) + \mathbf{C}_{2v}(/\mathbf{C}'_s). \tag{1}$$

The three substitution positions (○) of the mobile moiety (**1b**) belong to an orbit governed by a CR, $\mathbf{C}_{3v}(/\mathbf{C}_s)$.

The mobile moiety (**1c**) has five vertices to be considered (○). Since this unit belongs to $\mathbf{C}_{2v}$-symmetry, they are classified into three orbits that are subject to $\mathbf{C}_{2v}(/\mathbf{C}_s)$, $\mathbf{C}_{2v}(/\mathbf{C}_s)$, and $\mathbf{C}_{2v}(/\mathbf{C}_{2v})$. This assignment is algebraically represented by

$$\mathbf{P}_{1c} = 2\mathbf{C}_{2v}(/\mathbf{C}_s) + \mathbf{C}_{2v}(/\mathbf{C}_{2v}), \tag{2}$$

the determination of which can be accomplished by using the table of marks,[15] where $\mathbf{P}_{1c}$ is a permutation representation of the $\mathbf{C}_{2v}$ unit (**1c**). As a result, the non-rigid molecule (**1**) is represented by the symbol, $\mathbf{C}_{2v}[(/\mathbf{C}_s)[\mathbf{C}_{3v}(/\mathbf{C}_s)], (/\mathbf{C}'_s)[\mathbf{C}_{2v}(2/\mathbf{C}_s,\mathbf{C}_{2v})]]$, to which we refer as an *extended wreath product (EWP) notation* in the present paper.

Enumeration of Mobile Moieties. The formulation described in the previous section allows us to apply the method using unit subduced cycle indices (USCIs) (Appendix 1), since a mobile moiety can be considered to be rigid. Tables 1 and 2 list USCIs for $\mathbf{C}_{2v}$ and $\mathbf{C}_{3v}$. The table of USCIs for $\mathbf{T}_d$ group has been reported elsewhere.[15]

For the purpose of illustrating the enumeration of mobile moieties, let us work out a $\mathbf{C}_{2v}(/\mathbf{C}_s)$ mobile

Table 1. USCIs for $\mathbf{C}_{2v}$ Point Group

	Unit subduced cycle index[a)] for				
	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_2$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{C}'_s$	$\downarrow\mathbf{C}_{3v}$
$\mathbf{C}_{2v}(/\mathbf{C}_1)$	$s_1^4\ (b_1^4)$	$s_2^2\ (b_2^2)$	$s_2^2\ (c_2^2)$	$s_2^2\ (c_2^2)$	$s_4\ (c_4)$
$\mathbf{C}_{2v}(/\mathbf{C}_2)$	$s_1^2\ (b_1^2)$	$s_1^2\ (b_1^2)$	$s_2\ c_2$	$s_2\ (c_2)$	$s_2\ (c_2)$
$\mathbf{C}_{2v}(/\mathbf{C}_s)$	$s_1^2\ (b_1^2)$	$s_2\ (b_2)$	$s_1^2\ (a_1^2)$	$s_2\ (c_2)$	$s_2\ (a_2)$
$\mathbf{C}_{2v}(/\mathbf{C}'_s)$	$s_1^2\ (b_1^2)$	$s_2\ (b_2)$	$s_2\ (c_2)$	$s_1^2\ (a_1^2)$	$s_2\ (a_2)$
$\mathbf{C}_{2v}(/\mathbf{C}_{2v})$	$s_1\ (b_1)$	$s_1\ (b_1)$	$s_1\ (a_1)$	$s_1\ (a_1)$	$s_1\ (a_1)$

a) A variable in the parentheses is a USCI with chirality fittingness.

Table 2. USCIs for $\mathbf{C}_{3v}$ Point Group

	Unit subduced cycle index[a)] for			
	$\downarrow\mathbf{C}_1$	$\downarrow\mathbf{C}_s$	$\downarrow\mathbf{C}_3$	$\downarrow\mathbf{C}_{3v}$
$\mathbf{C}_{3v}(/\mathbf{C}_1)$	$s_1^6\ (b_1^6)$	$s_2^3\ (c_2^3)$	$s_3^2\ (b_3^2)$	$s_6\ (c_6)$
$\mathbf{C}_{3v}(/\mathbf{C}_s)$	$s_1^3\ (b_1^3)$	$s_1 s_2\ (a_1 c_2)$	$s_3\ (b_3)$	$s_3\ (a_3)$
$\mathbf{C}_{3v}(/\mathbf{C}_3)$	$s_1^2\ (b_1^2)$	$s_2\ (c_2)$	$s_1^2\ (b_1^2)$	$s_2\ (c_2)$
$\mathbf{C}_{3v}(/\mathbf{C}_{3v})$	$s_1\ (b_1)$	$s_1\ (a_1)$	$s_1\ (b_1)$	$s_1\ (a_1)$

a) A variable in the parentheses is a USCI with chirality fittingness.

moiety (**1c**). Suppose that the five positions of **1c** are occupied by either X or Y. Then, the codomain of the present case is $\mathbf{X}=\{\mathrm{X}, \mathrm{Y}\}$. The domain containing the five positions is designated by $\psi=\{1,2,3,4,5\}$, which is divided into three *orbits*,

$$\begin{aligned} \psi_1 &= \{1,2\} \text{ subject to } \mathbf{C}_{2v}(/\mathbf{C}_s), \\ \psi_2 &= \{3,4\} \text{ subject to } \mathbf{C}_{2v}(/\mathbf{C}_s), \text{ and} \\ \psi_3 &= \{5\} \text{ subject to } \mathbf{C}_{2v}(/\mathbf{C}_{2v}), \end{aligned}$$

according to Eq. 2. Lemma 1 (Appendix 1) affords the SCIs for this case, where these are obtained from the $\mathbf{C}_{2v}(/\mathbf{C}_s)$ (twice) and $\mathbf{C}_{2v}(/\mathbf{C}_{2v})$ rows of Table 1. Introduction of a figure inventory, $s_d=X^d+Y^d$, into these SCIs provides generating functions,

$$(s_1^2)^2 s_1 = (X + Y)^5 \text{ for } \mathbf{C}_1, \tag{3}$$

$$(s_2)^2 s_1 = (X + Y)(X^2 + Y^2)^2 \text{ for } \mathbf{C}_2, \tag{4}$$

$$(s_1^2)^2 s_1 = (X + Y)^5 \text{ for } \mathbf{C}_s, \tag{5}$$

$$(s_2)^2 s_1 = (X + Y)(X^2 + Y^2)^2 \text{ for } \mathbf{C}'_2, \tag{6}$$

and

$$(s_2)^2 s_1 = (X + Y)(X^2 + Y^2)^2 \text{ for } \mathbf{C}_{2v}. \tag{7}$$

Note that a single figure-inventory is used in this case, since all of the five positions are monovalent. These equations are expanded to give a matrix ($\rho_{\xi q}$) as the coefficients of respective terms. According to Lemma 2 (Appendix 1), this matrix is in turn multiplied by the inverse of the mark table of $\mathbf{C}_{2v}$. Thereby, we arrive at the following matrix expression,

$$
\begin{array}{c}
X^5 \\ X^4Y \\ X^3Y^2 \\ X^2Y^3 \\ XY^4 \\ Y^5
\end{array}
\begin{vmatrix}
1 & 1 & 1 & 1 & 1 \\
5 & 1 & 5 & 1 & 1 \\
10 & 2 & 10 & 2 & 2 \\
10 & 2 & 10 & 2 & 2 \\
5 & 1 & 5 & 1 & 1 \\
1 & 1 & 1 & 1 & 1
\end{vmatrix}
\begin{vmatrix}
\frac{1}{4} & 0 & 0 & 0 & 0 \\
-\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\
-\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\
-\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\
\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1
\end{vmatrix}
=
$$

$(\sigma_{\xi q})$ *the inverse*

$$
\begin{array}{c}
\\ X^5 \\ X^4Y \\ X^3Y^2 \\ X^2Y3 \\ XY^4 \\ Y^5
\end{array}
\begin{array}{ccccc}
\mathbf{C}_1 & \mathbf{C}_2 & \mathbf{C}_s & \mathbf{C'}_s & \mathbf{C}_{2v} \\
0 & 0 & 0 & 0 & 1 \\
0 & 0 & 2 & 0 & 1 \\
0 & 0 & 4 & 0 & 2 \\
0 & 0 & 4 & 0 & 2 \\
0 & 0 & 2 & 0 & 1 \\
0 & 0 & 0 & 0 & 1
\end{array}
\qquad (8)
$$

$(B_{\xi p})$

The resulting matrix affords the numbers of respective moieties, which are depicted in Fig. 2. The set of symbols (m of ● and n of ○) in Fig. 2 corresponds to X^mY^n and X^nY^m. All of the mobile moieties collected in Fig. 2 are achiral.

In a similar way, we enumerated mobile based on **1b**, where we used the table of USCIs for $\mathbf{C}_{3v}$ group. Since X and Y were taken as substituents, there appeared only achiral moieties. If we use three kinds of substituents, we have a chiral moiety in addition of achiral ones, as shown below.

Enumeration of Non-Rigid Isomers. A rigid skeleton such as **1a** has several orbits as a result of displacement by different sets of mobile moieties. This situation inevitably requires the use of different figure-inventories with respect to the respective *orbits*. In this case, the figure-inventories are determined by the preceding estimation of mobile moieties. Assignment of different figure-inventories to two or more *orbits* has been discussed in previous papers,[11] in which an OMV restriction controls the determination of figure-inventories. Although the two cases have different chemical meanings, they can be mathematically manipulated in the same line (Appendix 2), except that the present case uses figure-inventories calculated by preceding enumerations.

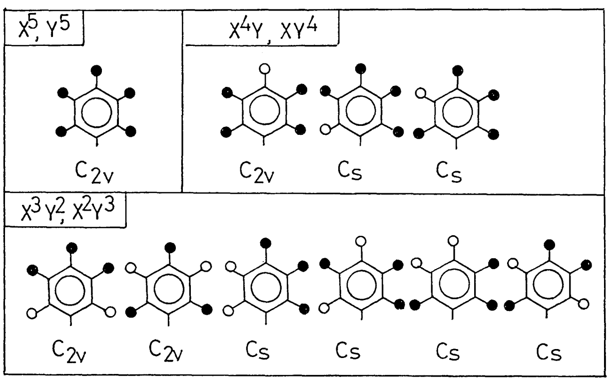


Fig. 2. Mobile moieties based on **1c**.

Let us examine the parent **1** with substituents selected from {X, Y}. Since this case produces no chiral mobile moieties, we can obtain the same result, whether we use Lemma 3 or Lemma 4 (Appendix 2). A figure inventory for **1c** is obtained in the light or Eq. 8, where the values in each row of the right-hand matrix are summed up to give the coefficient of the corresponding term. Thus, we have

$$
\kappa_{\xi a}
\begin{cases}
= 1 \text{ for } \omega_\xi = X^5 \text{ and } Y^5 \\
= 3 \text{ for } \omega_\xi = X^4Y \text{ and } XY^4 \\
= 6 \text{ for } \omega_\xi = X^3Y^2 \text{ and } X^2Y^3.
\end{cases}
\qquad (9)
$$

According to Lemma 4 (Appendix 2), we obtain the figure-inventory,

$$
s_d^{(2)} = X^{5d} + 3(X^4Y)^d + 6(X^3Y^2)^d + 6(X^2Y^3)^d + 3(XY^4)^d + Y^{5d} \qquad (10)
$$

for **1c**.

A figure inventory for **1b** can be obtained by a similar enummeration as described in the previous section. Alternatively, we can easily obtain the same result, because there are four patterns of substitutions (X^3, X^2Y, XY^2, and Y^3) on the basis of the basis of the mobile moiety (**1b**).

$$
s_d^{(1)} = X^{3d} + (X^2Y)^d + (XY^2)^d + Y^{3d} \qquad (11)
$$

for **1b**.

The four vertices of the rigid skeleton (**1a**) are divided into two categories which are subject to $\mathbf{C}_{2v}(/\mathbf{C}_s)$ and $\mathbf{C}_{2v}(/\mathbf{C}_s)$, as characterized by Eq. 2. Hence, the above figure-inventories are introduced into SCIs which are derived from the $\mathbf{C}_{2v}(/\mathbf{C}_s)$ and $\mathbf{C}_{2v}(/\mathbf{C'}_s)$ rows of Table 1 (Lemma of Appendix 2). Thereby, we obtain

$$
(s_1^2)^{(1)}(s_1^2)^{(2)} = (X^3 + X^2Y + XY^2 + Y^3)^2 \times (X^5 + 3X^4Y + 6X^3Y^2 + 6X^2Y^3 + 3XY^4 + Y^5)^2 \qquad (12)
$$

for $\mathbf{C}_1$,

$$
(s_2)^{(1)}(s_2)^{(2)} = (X^6 + X^4Y^2 + X^2Y^4 + Y^6) \times (X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10}) \qquad (13)
$$

for $\mathbf{C}_2$,

$$
(s_1^2)^{(1)}(s_2)^{(2)} = (X^3 + X^2Y + XY^2 + Y^3)^2 \times (X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10}) \qquad (14)
$$

for $\mathbf{C}_s$,

$$(s_2)^{(1)}(s_1^2)^{(2)} = (X^6 + X^4Y^2 + X^2Y^4 + Y^6) \times (X^5 + 3X^4Y + 6X^3Y^2 + 6X^2Y^3 + 3XY^4 + Y^5)^2 \quad (15)$$

for $\mathbf{C'}_s$, and

$$(s_2)^{(1)}(s_2)^{(2)} = (X^6 + X^4Y^2 + X^2Y^4 + Y^6) \times (X^{10} + 3X^8Y^2 + 6X^6Y^4 + 6X^4Y^6 + 3X^2Y^8 + Y^{10}) \quad (16)$$

for $\mathbf{C}_{2v}$,

in which superscripts (1) and (2) denote the $\mathbf{C}_{2v}(/\mathbf{C}_s)$ and $\mathbf{C}_{2v}(/\mathbf{C'}_s)$ *orbits*, respectively. Note that we apply the different figure-inventories to the respective *orbits*. Expansion of these generating functions and collection of the terms of the same power give a matrix involving the values of $\sigma_{\xi j}$. This matrix is multiplied by the inverse of the mark table of $\mathbf{C}_{2v}$, i.e.,

$$\begin{array}{c} \\ X^{16} \\ X^{15}Y \\ X^{14}Y^2 \\ X^{13}Y^3 \\ X^{12}Y^4 \\ X^{11}Y^5 \\ X^{10}Y^6 \\ X^9Y^7 \\ X^8Y^8 \end{array} \underbrace{\left(\begin{array}{ccccc} \mathbf{C}_1 & \mathbf{C}_2 & \mathbf{C}_s & \mathbf{C'}_s & \mathbf{C}_{2v} \\ 1 & 1 & 1 & 1 & 1 \\ 8 & 0 & 2 & 6 & 0 \\ 36 & 4 & 6 & 22 & 4 \\ 112 & 0 & 10 & 54 & 0 \\ 264 & 10 & 18 & 100 & 10 \\ 496 & 0 & 26 & 146 & 0 \\ 764 & 16 & 34 & 178 & 16 \\ 986 & 0 & 42 & 194 & 0 \\ 1070 & 18 & 42 & 198 & 18 \end{array}\right)}_{(\sigma_{\xi j})} \underbrace{\left(\begin{array}{ccccc} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{array}\right)}_{\textit{the inverse}} =$$

$$\begin{array}{c} \\ X^{16} \\ X^{15}Y \\ X^{14}Y^2 \\ X^{13}Y^3 \\ X^{12}Y^4 \\ X^{11}Y^5 \\ X^{10}Y^6 \\ X^9Y^7 \\ X^8Y^8 \end{array} \underbrace{\left(\begin{array}{ccccc} \mathbf{C}_1 & \mathbf{C}_2 & \mathbf{C}_s & \mathbf{C'}_s & \mathbf{C}_{2v} \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 3 & 0 \\ 3 & 0 & 1 & 9 & 4 \\ 12 & 0 & 5 & 27 & 0 \\ 39 & 0 & 4 & 45 & 10 \\ 81 & 0 & 13 & 73 & 0 \\ 142 & 0 & 9 & 81 & 16 \\ 187 & 0 & 21 & 97 & 0 \\ 212 & 0 & 12 & 90 & 18 \end{array}\right)}_{(A_{\xi p})} . \quad (17)$$

Since the X^mY^n and X^nY^m terms afford the same results, Eq. 17 lists the values of the X^mY^n term ($m \geq n$).

Figure 3 depicts 17 $X^{14}Y^2$-isomers having the subsymmetries of the $\mathbf{C}_{2v}$-symmetry, in which the symbol (O) denotes a Y-substitution and the remaining 14 positions are occupied by X. Thus, there emerge 3 $\mathbf{C}_1$ (asymmetric) molecules, one $\mathbf{C}_s$-molecule, 9 $\mathbf{C'}_s$ molecules and 4 $\mathbf{C}_{2v}$-molecules in accord with the data listed in the 3rd row of the rightmost matrix in Eq. 17. Note that these symmetries are concerned with the subduction of the rigid skeleton (**1a**). For a more detailed description, they should be denoted by EWP symbols.

Enumeration Involving Chiral Mobile Moieties. The enumeration described in the previous section involves achiral mobile moieties only, where we have used Lemma 4. On the other hand, we should use Lemma 3 in the case that involves chiral mobile moieties in addition to achiral ones. This section is devoted to giving a typical procedure for utilizing Lemma 3. Let us work out an enumeration based on 2,2-dimethylpropane (**2**), which involves a participation of a chiral mobile moiety. We consider 12 substituents selected from a domain, **X**={X, Y, Z} to occupy the 12 positions of 2,2-dimethypropane (**2**).

Step 1 is the decomposition of **2** into a rigid skeleton (**2a**) and a mobile moiety (**2b**) as shown in Fig. 4.

Step 2 is the classification of the vertices (substitution positions) of each mobile moiety (i.e., **2b** in this case) into orbits and the assignment of coset representations (CRs) to the orbits. This assignment has been described in the previous sections. Thus, the vertices

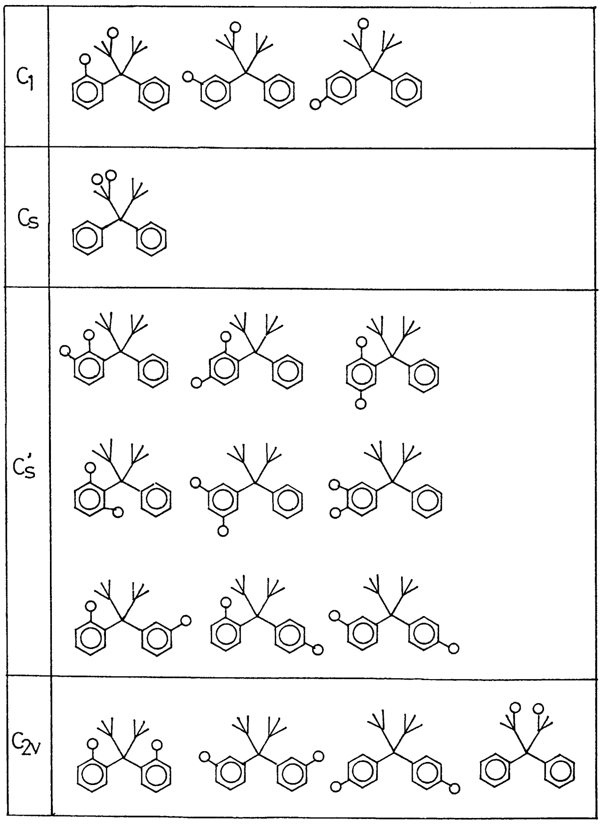


Fig. 3. $X^{14}Y^2$-isomers based on **1**.

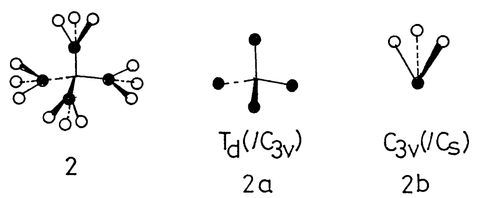


Fig. 4. Enumeration based on 2,2-dimethylpropane (**2**).

of **2b** are subject to $\mathbf{C}_{3v}(/\mathbf{C}_s)$.

In Step 3, we construct the SCIs for this case, using the $\mathbf{C}_{3v}(/\mathbf{C}_s)$ row of Table 2. When we introduce a moiety-figure inventory, $s_d = X^d + Y^d + Z^d$, into these SCIs, we have generating functions for $\rho_{\xi q}$, i,e.,

$$s_1^3 = (X + Y + Z)^3 \text{ for } \mathbf{C}_1, \tag{18}$$

$$s_1 s_2 = (X + Y + Z)(X^2 + Y^2 + Z^2) \text{ for } \mathbf{C}_s, \tag{19}$$

$$s_3 = X^3 + Y^3 + Z^3 \text{ for } \mathbf{C}_3, \tag{20}$$

and

$$s_3 = X^3 + Y^3 + Z^3 \text{ for } \mathbf{C}_{3v}. \tag{21}$$

There equations are expanded to afford a matrix $(\rho_{\xi q})$.

In Step 4, the matrix $(\rho_{\xi q})$ is multiplied by the inverse of the mark table of $\mathbf{C}_{3v}$, i.e.,

$$\begin{array}{c} \\ X^3 \\ X^2Y \\ XY^2 \\ Y^3 \\ X^2Z \\ XYZ \\ Y^2Z \\ XZ^2 \\ YZ^2 \\ Z^3 \end{array}
\begin{array}{c} \mathbf{C}_1\ \mathbf{C}_s\ \mathbf{C}_3\ \mathbf{C}_{3v} \\ \left(\begin{array}{cccc} 1 & 1 & 1 & 1 \\ 3 & 1 & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 \\ 3 & 1 & 0 & 0 \\ 6 & 0 & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 3 & 1 & 0 & 0 \\ 1 & 1 & 1 & 1 \end{array}\right) \\ (\rho_{\xi q}) \end{array}
\begin{array}{c} \left(\begin{array}{cccc} \frac{1}{6} & 0 & 0 & 0 \\ -\frac{1}{2} & 1 & 0 & 0 \\ -\frac{1}{6} & 0 & \frac{1}{2} & 0 \\ -\frac{1}{2} & -1 & -\frac{1}{2} & 1 \end{array}\right) \\ \textit{the inverse} \end{array} =$$

$$\begin{array}{c} \\ X^3 \\ X^2Y \\ XY^2 \\ Y^3 \\ X^2Z \\ XYZ \\ Y^2Z \\ XZ^2 \\ YZ^2 \\ Z^3 \end{array}
\begin{array}{c} \mathbf{C}_1\ \mathbf{C}_s\ \mathbf{C}_3\ \mathbf{C}_{3v} \\ \left(\begin{array}{cccc} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{array}\right) \\ (B_{\xi p}) \end{array} . \tag{22}$$

The matrix obtained indicates that there appear three types of mobile moieties shown in Fig. 5. Note that the XYZ-moiety is chiral.

Step 5 is the construction of figure inventories. Application of Lemma 3 to the data of Eq. 22 yields the following inventories:

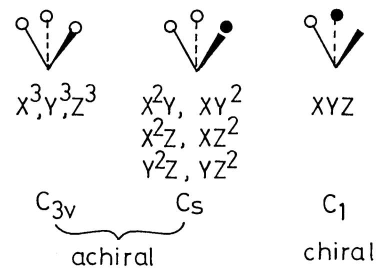


Fig. 5. Mobile moieties derived from **2b**.

$$\begin{aligned} a_d = {} & X^{3d} + (X^2Y)^d + (XY^2)^d + Y^{3d} \\ & + (X^2Z)^d + (Y^2Z)^d + (XZ^2)^d + (YZ^2)^d + ZX^{3d}, \end{aligned} \tag{23}$$

$$\begin{aligned} b_d = {} & X^{3d} + (X^2Y)^d + (XY^2)^d \\ & + Y^{3d} + (X^2Z)^d + (Y^2Z)^d \\ & + (XZ^2)^d + (YZ^2)^d + Z^{3d} + 2(XYZ)^d, \end{aligned} \tag{24}$$

and

$$\begin{aligned} c_d = {} & X^{3d} + (X^2Y)^d + (XY^2)^d \\ & + Y^{3d} + (X^2Z)^d + (Y^2Z)^d \\ & + (XZ^2)^d + (YZ^2)^d + Z^{3d} + 2(XYZ)^d. \end{aligned} \tag{25}$$

Step 6 is the construction of SCIs for a rigid skeleton (i.e., **2a** in this case). Since the four vertices (roots) are subject to $\mathbf{T}_d(/\mathbf{C}_{3v})$, we select the USCIs with chirality fittingness appearing in the $\mathbf{T}_d(/\mathbf{C}_{3v})$ row of a table of USCIs.[15] After introducing the above figure inventories into the SCIs, we obtain generating functions:

$$\begin{aligned} b_1^4 = {} & (X^3 + X^2Y + XY^2 + Y^3 \\ & + X^2Z + Y^2Z + XZ^2 + YZ^2 + Z^3 + 2XYZ)^4 \\ & \text{for } \mathbf{C}_1, \end{aligned} \tag{26}$$

$$\begin{aligned} b_2^2 = {} & (X^6 + X^4Y^2 + X^2Y^4 + Y^6 \\ & + X^4Z^2 + Y^4Z^2 + X^2Z^4 + Y^2Z^4 + Z^6 + 2X^2Y^2Z^2)^2 \\ & \text{for } \mathbf{C}_2, \end{aligned} \tag{27}$$

$$\begin{aligned} a_1^2 c_2 = {} & (X^3 + X^2Y + XY^2 + Y^3 \\ & + X^2Z + Y^2Z + XZ^2 + YZ^2 + Z^3)^2 \\ & \times (X^6 + X^4Y^2 + X^2Y^4 + Y^6 + X^4Z^2 + Y^4Z^2 \\ & + X^2Z^4 + Y^2Z^4 + Z^6 + 2X^2Y^2Z^2) \\ & \text{for } \mathbf{C}_s, \end{aligned} \tag{28}$$

$$\begin{aligned} b_1 b_3 = {} & (X^3 + X^2Y + XY^2 + Y^3 \\ & + X^2Z + Y^2Z + XZ^2 + YZ^2 + Z^3 + 2XYZ) \\ & \times (X^9 + X^6Y^3 + X^3Y^6 + Y^9 + X^6Z^3 + Y^6Z^3 \end{aligned}$$

$$+ X^3Z^6 + Y^3Z^6 + Z^9 + 2X^3Y^3Z^3)$$

$$\text{for } \mathbf{C}_3, \tag{29}$$

$$c_4 = X^{12} + X^8Y^4 + X^4Y^8 + Y^{12} + X^8Z^4$$
$$+ Y^8Z^4 + X^4Z^8 + Y^4Z^8 + Z^{12} + 2X^4Y^4Z^4$$
$$\text{for } \mathbf{S}_4, \tag{30}$$

$$b_4 = X^{12} + X^8Y^4 + X^4Y^8 + Y^{12} + X^8Z^4$$
$$+ Y^8Z^4 + X^4Z^8 + Y^4Z^8 + Z^{12} + 2X^4Y^4Z^4$$
$$\text{for } \mathbf{D}_2 \text{ and } \mathbf{T}, \tag{31}$$

$$a_2^2 = (X^6 + X^4Y^2 + X^2Y^4 + Y^6$$
$$+ X^4Z^2 + Y^4Z^2 + X^2Z^4 + Y^2Z^4 + Z^6)^2$$
$$\text{for } \mathbf{C}_{2v}, \tag{32}$$

$$a_1a_3 = (X^3 + X^2Y + XY^2 + Y^3$$
$$+ X^2Z + Y^2Z + XZ^2 + YZ^2 + Z^3)$$
$$\times (X^9 + X^6Y^3 + X^3Y^6 + Y^9 + X^6Z^3 + Y^6Z^3$$
$$+ X^3Z^6 + Y^3Z^6 + Z^9)$$
$$\text{for } \mathbf{C}_{3v}, \tag{33}$$

and

$$a_4 = X^{12} + X^8Y^4 + X^4Y^8 + Y^{12}$$
$$+ X^8Z^4 + Y^8Z^4 + X^4Z^8 + Y^4Z^8 + Z^{12}$$
$$\text{for } \mathbf{D}_{2d} \text{ and for } \mathbf{T}_d, \tag{34}$$

according to Eqs. 47 and 48. These equations are expanded and the terms of the same powers are collected. In the present case, the terms are classified into 19 types, which are designated by a *type index* $[l,m,n]$ for $X^lY^mZ^n$, $X^mY^nZ^l$ and so on. The terms of the same type have equal coefficients. Table 3 collects such coefficients for each type index and each subsymmetry of $\mathbf{T}_d$.

Step 7 is the multiplication of Table 3 by the inverse of the mark table for $\mathbf{T}_d$.[15] The resulting matrix (Table 4) shows the number of isomers of each type and each subsymmetry.

Figure 6 depicts [9,2,1]-isomers, each of which is denoted by the symmetry of the corresponding rigid skeleton.

The total values at the bottom of Table 4 are

Table 3. Coefficients for Enumeration

Index	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$
[12,0,0]	1	1	1	1	1	1	1	1	1	1	1
[11,1,0]	4	0	2	1	0	0	0	1	0	0	0
[10,2,0]	10	2	4	1	0	0	2	1	0	0	0
[10,1,1]	20	0	2	2	0	0	0	0	0	0	0
[9,3,0]	20	0	6	2	0	0	0	2	0	0	0
[9,2,1]	52	0	6	1	0	0	0	1	0	0	0
[8,4,0]	31	3	7	1	1	1	3	1	1	1	1
[8,3,1]	100	0	6	1	0	0	0	1	0	0	0
[8,2,2]	138	6	14	0	0	0	2	0	0	0	0
[7,5,0]	40	0	8	1	0	0	0	1	0	0	0
[7,4,1]	152	0	8	2	0	0	0	0	0	0	0
[7,3,2]	256	0	16	1	0	0	0	1	0	0	0
[6,6,0]	44	4	8	2	0	0	4	2	0	0	0
[6,5,1]	184	0	8	1	0	0	0	1	0	0	0
[6,4,2]	364	8	22	1	0	0	4	1	0	0	0
[6,3,3]	448	0	16	4	0	0	0	2	0	0	0
[5,5,2]	408	0	20	0	0	0	0	0	0	0	0
[5,4,3]	584	0	20	2	0	0	0	0	0	0	0
[4,4,4]	682	10	30	4	2	2	6	0	0	2	0

Table 4. Number of Non-Rigid Isomers Derived from **2**

Type index	Number of isomers of											Total
	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$	
[12,0,0]	0	0	0	0	0	0	0	0	0	0	1	1
[11,1,0]	0	0	0	0	0	0	0	1	0	0	0	1
[10,2,0]	0	0	0	0	0	0	1	1	0	0	0	2
[10,1,1]	0	0	1	1	0	0	0	0	0	0	0	2
[9,3,0]	0	0	1	0	0	0	0	2	0	0	0	3
[9,2,1]	1	0	2	0	0	0	0	1	0	0	0	4
[8,4,0]	0	0	2	0	0	0	1	0	0	0	1	4
[8,3,1]	3	0	2	0	0	0	0	1	0	0	0	6
[8,2,2]	2	1	6	0	0	0	1	0	0	0	0	10
[7,5,0]	0	0	3	0	0	0	0	1	0	0	0	4
[7,4,1]	4	0	4	1	0	0	0	0	0	0	0	9
[7,3,2]	7	0	7	0	0	0	0	1	0	0	0	15
[6,6,0]	1	0	0	0	0	0	2	2	0	0	0	5
[6,5,1]	6	0	3	0	0	0	0	1	0	0	0	10
[6,4,2]	10	1	8	0	0	0	2	1	0	0	0	22
[6,3,3]	15	0	6	1	0	0	0	2	0	0	0	24
[5,5,2]	12	0	10	0	0	0	0	0	0	0	0	22
[5,4,3]	19	0	10	1	0	0	0	0	0	0	0	30
[4,4,4]	21	0	12	1	1	0	3	0	0	1	0	39
Total	411	9	333	19	1	0	36	72	0	1	9	891

alternatively calculated in the light of Lemma 6 and Corollary 3 (Appendix 3). Thus, Lemma 6 for this case yields a row vector $(11^4,11^2,9^2\times11,11^2,11,11,9^2,9^2,11,9)$. According to Corollary 3, this vector is multiplied by the inverse of the mark table for $\mathbf{T}_d$ to afford (411,9,333,19,1,0,36,72,0,1,9), each value of which is identical with that obtained by the summation of each column of Table 4.

The total value of each row of Table 4 can be alternatively obtained in the form of a generating function (a cycle index) if we apply Theorem 2 to the present case. The cycle index (CI) of this case is given as

$$\sum_{\theta} A_\theta W_\theta = (1/24)b_1^4 + (1/8)b_2^2 + (1/4)a_1^2c_2 + (1/3)b_1b_3 + (1/4)c_4, \qquad (35)$$

into which Eqs. 23 to 25 are introduced.

For calculating non-rigid isomers containing at least one chiral moiety, Corollary 2 sould be applied to this case. A similar procedure as above affords Table 5.

For illustrating the result of Table 5, several selected examples are depicted in Fig. 7.

Note that the point groups assigned in Fig. 7 are concerned with the rigid skeletons, not with the molecules themselves. For example, the [6,3,3], $\mathbf{C}_3$-isomer in Fig. 7 belongs to $\mathbf{C}_3$-point group. On the other hand, the other isomers are restricted within $\mathbf{C}_1$ point group, even if they have conformations of the highest symmetries. The [4,4,4], **T**-molecule belongs to $\mathbf{D}_2$ symmetry, strictly speaking. In contrast to this, a full symmetry is realized in the [4,4,4], $\mathbf{S}_4$-molecule. Several remarks have been made on such problems.[25)]

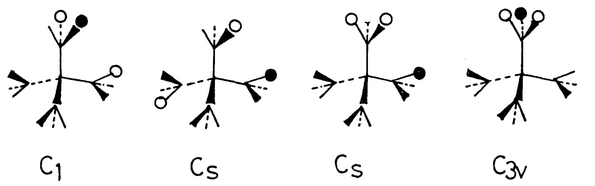


Fig. 6. Isomers with the index[9,2,1] based on **2**.

Conclusion

Unit subduced cycle indices (USCIs) are applied to the enumeration of non-rigid molecules such as 2,2-diphenyl- and 2,2-dimethylpropane. Non-rigid molecules are regarded as a combination of a rigid skeleton and mobile moieties. This formulation allows us to treat non-rigidity in the same line as rigid molecules, since both the rigid skeleton and the mobile moiety

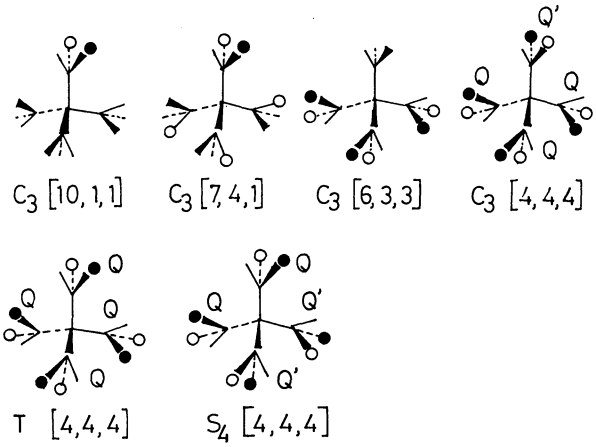


Fig. 7. Selected isomers with chiral moieties based on **2**.

Table 5. Number of Non-Rigid Isomers with Chiral Moieties Based on **2**

Type index	Number of isomers of											Total
	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	**T**	$\mathbf{T}_d$	
[12,0,0]	0	0	0	0	0	0	0	0	0	0	0	0
[11,1,0]	0	0	0	0	0	0	0	0	0	0	0	0
[10,2,0]	0	0	0	0	0	0	0	0	0	0	0	0
[10,1,1]	0	0	0	1	0	0	0	0	0	0	0	1
[9,3,0]	0	0	0	0	0	0	0	0	0	0	0	0
[9,2,1]	1	0	0	0	0	0	0	0	0	0	0	1
[8,4,0]	0	0	0	0	0	0	0	0	0	0	0	0
[8,3,1]	2	0	0	0	0	0	0	0	0	0	0	2
[8,2,2]	2	1	1	0	0	0	0	0	0	0	0	4
[7,5,0]	0	0	0	0	0	0	0	0	0	0	0	0
[7,4,1]	3	0	0	1	0	0	0	0	0	0	0	4
[7,3,2]	5	0	2	0	0	0	0	0	0	0	0	7
[6,6,0]	0	0	0	0	0	0	0	0	0	0	0	0
[6,5,1]	4	0	0	0	0	0	0	0	0	0	0	4
[6,4,2]	7	1	3	0	0	0	0	0	0	0	0	11
[6,3,3]	10	0	2	1	0	0	0	0	0	0	0	13
[5,5,2]	8	0	4	0	0	0	0	0	0	0	0	12
[5,4,3]	13	0	4	1	0	0	0	0	0	0	0	18
[4,4,4]	15	0	6	1	1	0	0	0	0	1	0	24

can be treated as *rigid*. Several propositions useful for isomer enumeration are presented.

Appendix 1.

Enumeration of Mobile Moieties. A mathematical treatment is essentially the same as described for rigid molecules in a previous paper.[15] Suppose that a given moiety of **H**-symmetry consists of several atoms whose symmetrical properties are characterized by a permutation representation ($\mathbf{P_H}$). Then, $\mathbf{P_H}$ can be reduced into the sum of coset representations, i.e.,

$$\mathbf{P_H} = \sum_{p=1}^{c_\mathbf{H}} \gamma_p \mathbf{H}(/\mathbf{H}_p), \tag{36}$$

where the symbol $\mathbf{H}_p$ (p=1,2,..., $c_\mathbf{H}$) denotes a representative of conjugate subgroups and the multiplicity, γ_p, is a non-negative integer. The multiplicity γ_p can be algebraically obtained by using the table of marks for **H** group.[15] Eq. 2 is a simple example of this formulation.

According to the subduction of the CRs ($\mathbf{H}(/\mathbf{H}_p)\downarrow\mathbf{H}_q$), we have defined unit subduced cycle indices (USCIs) as

$$Z(\mathbf{H}(/\mathbf{H}_p)\downarrow\mathbf{H}_q;\, t_{d_{qr}}) = \prod_{r=1}^{v_q} (t_{d_{qr}})^{\delta_{pqr}} \tag{37}$$

for p=1,2,...,$c_\mathbf{H}$ and q=1,2,..., $c_\mathbf{H}$, where the symbol $\mathbf{H}_{qr}$ (r=1,2,...,v_q) denotes a representative of conjugate subgroups of $\mathbf{H}_q$.[15] Note that the t variables are just dummy symbols. The symbol d_{qr} denotes the length of the $\mathbf{H}_q(/\mathbf{H}_{qr})$ orbit which is in turn represented by

$$d_{qr} = |\mathbf{H}_q|/|\mathbf{H}_{qr}|. \tag{38}$$

In terms of the USCIs (Eq. 37), a subduced cycle index (SCI) for each subgroup ($\mathbf{H}_q$) is defined as:

$$\begin{aligned} ZI(\mathbf{H}_q;t_{d_{qr}}) &= \prod_{p=1}^{c_\mathbf{H}} [Z(\mathbf{H}(/\mathbf{H}_p)\downarrow\mathbf{H}_q;t_{d_{qr}})]^{\gamma_p} \\ &= \prod_{p=1}^{c_\mathbf{H}} [\prod_{r=1}^{v_q} (t_{d_{qr}})^{\delta_{pqr}}]^{\gamma_p} \\ &= \prod_{r=1}^{v_q} (t_{d_{qr}})^{\sum_{p=1}^{c_\mathbf{H}} \gamma_p\delta_{pqr}} \end{aligned} \tag{39}$$

for q=1,2,...,$c_\mathbf{H}$.[15]

Suppose that mobile moieties belonging to an equivalence class have the same molecular formula, $w_\xi = X_1^{n1} X_2^{n2} \cdots X_{|\mathbf{X}|}^{n|\mathbf{X}|}$, where $|\psi|$ is the number of positions in a mobile moiety and $n_1+n_2+\cdots n_{|\mathbf{X}|}$. The number of isomeric moieties is regarded as the number of such equivalence classes with the same molecular formula. Let $\rho_{\xi q}$ be the number of such isomeric moieties with the weight w_ξ and $\mathbf{H}_q$. Then, ρ_{ξ_q} is obtained by means of generating functions,[15] i.e.,

Lemma 1. (Calculation of $\rho_{\xi q}$).

$$\sum_\xi \rho_{\xi q} \omega_\xi = ZI(\mathbf{H}_q;t_{d_{qr}}) \tag{40}$$

for q=1,2,...,$c_\mathbf{H}$, in which every term of the right-hand side is substituted by a figure-inventory:

$$t_{d_{qr}} = \sum_{r=1}^{|\mathbf{X}|} x_r^{d_{qr}}. \tag{41}$$

In the light of this lemma, the net number of mobile moieties ($B_{\xi p}$) is obtained by

Lemma 2. (Enumeration of mobile moieties). When $\overline{m}_{qp}$ is an element of the inverse of the mark table, the net number of mobile moieties ($B_{\xi p}$) is obtained by

$$B_{\xi p} = \sum_{q=1}^{c_\mathbf{H}} \rho_{\xi q} \overline{m}_{qp}. \tag{42}$$

Note that we count every pair of antipodes ($y_{\xi q}$ and $\bar{y}_{\xi q}$).

Appendix 2.

Enumeration of Non-Rigid Isomers. Suppose that the rigid skeleton of a non-rigid molecule of **G**-symmetry has $|\phi|$ substitution positions. If a permutation group $\mathbf{P_G}$ acts on the positions, the action is expressed by

$$\mathbf{P_G} = \sum_{i=1}^{c_\mathbf{G}} \alpha_i \mathbf{G}(/\mathbf{G}_i), \tag{43}$$

wherein α_i is the multiplicity of the CR, $\mathbf{G}(/\mathbf{G}_i)$. According to the subduction of the CR,

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{u_j} \beta_{ijk} \mathbf{G}_j(/\mathbf{G}_{jk}), \tag{44}$$

we define a USCI with chirality fittingness as

$$Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\$_{d_{jk}}) = \prod_{k=1}^{u_j} (\$_{d_{jk}})^{\beta_{ijk}}, \tag{46}$$

for i=1,2,...,$c_\mathbf{G}$ and j=1,2,...,$c_\mathbf{G}$. This USCI is essentially equivalent to that described for a mobile moiety. In a similar way, the subscript for \$ is calculated by

$$d_{jk} = |\mathbf{G}_j|/|\mathbf{G}_{jk}|. \tag{46}$$

The dummy variable *\$* is replaced by the variable (a, b, or c) in accord with the chirality fittingness of the participating CR. The variable (a) is selected when both $\mathbf{G}_j$ and $\mathbf{G}_{jk}$ are improper. The variable (b) is adopted, if both $\mathbf{G}_j$ and $\mathbf{G}_{jk}$ are proper. The variable (c) is for the case $\mathbf{G}_j$ is improper and $\mathbf{G}_{jk}$ is proper. Since the dummy variable is dependent upon the $i\alpha$-th *orbit* through the corresponding CR, this dependence is designated by the symbol $\$_{d_{jk}}^{(i\alpha)}$. The SCI for this case is obtained in a similar way described in the preceding sections, i.e.,

$$\begin{aligned} ZI(\mathbf{G}_j;\$_{d_{qr}}^{(i\alpha)}) &= \prod_{\substack{i=1 \\ (\alpha_i\neq 0)}}^{c_\mathbf{G}} \prod_{\alpha=1}^{\alpha_i} Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\$_{d_{qr}}^{(i\alpha)}) \\ &= \prod_{\substack{i=1 \\ (\alpha_i\neq 0)}}^{c_\mathbf{G}} \prod_{\alpha=1}^{\alpha_i} [\prod_{k=1}^{u_j} (\$_{d_{qr}}^{(i\alpha)})^{\beta_{ijk}}] \end{aligned} \tag{47}$$

$$(j = 1,2\ldots,c_\mathbf{G}).$$

A non-rigid compound is regarded as a derivative of a **G** rigid skeleton, in which the α-th $\mathbf{G}(/\mathbf{G}_i)$ *orbit* is substituted by the moieties of $\mathbf{H}_p^{(i\alpha)}$ that have been enumerated in the preceding sections.

Suppose that non-rigid molecules belonging to an equivalence class have the same molecular formula, $W_\theta = X_1^{n1} X_2^{n2} \cdots X_{|\mathbf{X}|}^{n|\mathbf{X}|}$, where $|\phi|$ is the number of positions (roots) in the rigid skeleton and $n_1 + n_1 + \cdots + n_{|\mathbf{X}|} = |\phi|$.

If all the mobile moieties ($y_{\xi p}^{(i\alpha)}$) and their antipodes ($\bar{y}_{\xi p}^{(i\alpha)}$'s) ($p = 1, 2, \ldots, c_{\mathbf{H}^{(i\alpha)}}$) have the same weight ($w_\xi^{(i\alpha)}$) the following lemma can be obtained by a slight modification of the method described elsewhere.[24] We arrive at

Lemma 3. (Calculation of $\sigma_{\theta j}$). Let $\sigma_{\theta j}$ be the number of such derivatives with weight (W_θ) that are invariant (of fixed) on the operation of $\mathbf{G}_j$. We can estimate $\sigma_{\theta j}$ in terms of generating functions,[15]

$$\sum_\theta \sigma_{\theta j} W_\theta = ZI(\mathbf{G}_j; \$_{d_{jk}}^{(i\alpha)}) \tag{48}$$

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

$$a_{d_{jk}}^{(i\alpha)} = \sum_\xi \kappa_{\xi a} (w_\xi^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = a \tag{49}$$

$$b_{d_{jk}}^{(i\alpha)} = \sum_\xi \kappa_{\xi a} (w_\xi^{(i\alpha)})^{d_{jk}} + 2\sum_\xi \kappa_{\xi c} (w_\xi^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = b \tag{50}$$

and

$$c_{d_{jk}}^{(i\alpha)} = \sum_\xi \kappa_{\xi a} (w_\xi^{(i\alpha)})^{d_{jk}} + 2\sum_\xi \kappa_{\xi c} (w_\xi^{(i\alpha)})^{d_{jk}} \quad \text{for} \quad \$ = c, \tag{51}$$

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

$$\kappa_{\xi a} = \underset{\text{improper}}{\sum_{p=1}^{c_{\mathbf{H}^{(i\alpha)}}}} B_{\xi p}^{(i\alpha)} \tag{52}$$

and

$$\kappa_{\xi c} = \underset{\text{proper}}{\sum_{p=1}^{c_{\mathbf{H}^{(i\alpha)}}}} B_{\xi p}^{(i\alpha)}. \tag{53}$$

By means of this lemma, we end up with

Theorem 1. (Enumeration of W_θ, $\mathbf{G}_i$-isomers). Let $A_{\theta i}$ be the number of W_θ, $\mathbf{G}_i$-isomers. This is calculated by using $\sigma_{\theta j}$ (Lemma 3) by means of

$$\sigma_{\theta j} = \sum_{i=1}^{c_\mathbf{G}} A_{\theta i} M_{ij} \quad \text{for} \quad j = 1, 2, \ldots, c_\mathbf{G} \tag{54}$$

or inversely,

$$A_{\theta i} = \sum_{j=1}^{c_\mathbf{G}} \sigma_{\theta j} \overline{M}_{ji} \quad \text{for} \quad i = 1, 2, \ldots, c_\mathbf{G} \tag{55}$$

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

If we restrict the mobile moieties within achiral ones as above, we arrive at

Lemma 4. (Calculation of $\hat{\sigma}_{\theta j}$). Let $\hat{\sigma}_{\theta j}$ by the number of such derivatives with weight (W_θ) that are invariant (or fixed) on the operation of $\mathbf{G}_j$, when only achiral mobile moieties are allowed. We can estimate $\hat{\sigma}_{\theta j}$ in terms of generating functions,[15]

$$\sum_\theta \hat{\sigma}_{\theta j} W_\theta = ZI(\mathbf{G}_j; s_{d_{jk}}^{(i\alpha)}) \tag{56}$$

for $j = 1, 2, \ldots, c_\mathbf{G}$, in which every variable of the right-hand side is substituted by a figure-inventory,

$$s_{d_{jk}}^{(i\alpha)} = \sum_\xi \kappa_{\xi a} (w_\xi^{(i\alpha)})^{d_{jk}}. \tag{57}$$

Using Lemma 4, we can enumerate non-rigid molecules without any chiral mobile moieties. For this purpose, we obtain

Corollary 1. (Enumeration of non-rigid isomers with achiral mobile moieties). Let $\hat{A}_{\theta i}$ be the number of W_θ, $\mathbf{G}_i$-isomers without any chiral mobile moieties. This is calculated from $\hat{\sigma}_{\theta j}$ (Lemma 4) by means of

$$\hat{\sigma}_{\theta j} = \sum_{i=1}^{c_\mathbf{G}} \hat{A}_{\theta i} M_{ij} \quad \text{for} \quad j = 1, 2, \ldots, c_\mathbf{G}, \tag{58}$$

or inversely,

$$\hat{A}_{\theta i} = \sum_{j=1}^{c_\mathbf{G}} \hat{\sigma}_{\theta i} \overline{M}_{ji} \quad \text{for} \quad i = 1, 2, \ldots, c_\mathbf{G}, \tag{59}$$

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

Lemmas 3 and 4 affords foundation to the enumeration of the case concerning derivatives with at least one chiral mobile moiety. That is to say,

Lemma 5. (Calculation of $\tilde{\sigma}_{\theta j}$). Let $\tilde{\sigma}_{\theta j}$ be the number of such derivatives with weight (W_q) that are invariant (or fixed) on the operation of $\mathbf{G}_j$, when permitting achiral as well as chiral mobile moieties. Then,

$$\sum_\theta \tilde{\sigma}_{\theta j} W_\theta = ZI(\mathbf{G}_j; \$_{d_{jk}}^{(i\alpha)}) - ZI(\mathbf{G}_j; s_{d_{jk}}^{(i\alpha)}) \tag{60}$$

for $j = 1, 2, \ldots, c_\mathbf{G}$, in which every variable of the right-hand side is given by Lemmas 3 and 4.

In the light of Lemma 5, we can enumerate non-rigid molecules having at least one chiral mobile moiety. We arrive at

Corollary 2. (Enumeration of non-rigid isomers with at least one chiral mobile moiety). Let $\tilde{A}_{\theta i}$ be the number of W_θ, $\mathbf{G}_i$-isomers with at least one chiral mobile moiety. This is calculated from $\tilde{\sigma}_{\theta j}$ (Lemma 5) by menas of

$$\tilde{\sigma}_{\theta j} = \sum_{i=1}^{c_\mathbf{G}} \tilde{A}_{\theta i} M_{ij} \quad \text{for} \quad j = 1, 2, \ldots, c_\mathbf{G}, \tag{61}$$

or inversely,

$$\tilde{A}_{\theta i} = \sum_{j=1}^{c_G} \tilde{\sigma}_{\theta i}\overline{M}_{ji} \quad (62)$$
$$\text{for} \quad i = 1,2,...,c_G,$$

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

Appendix 3.

The Total Numbers for Every Weight and for Every Subsymmetry. When we sum up all $A_{\theta i}$ over $\mathbf{G}_i$, we obtain the total number (A_θ) of isomers with W_θ-weight. That is to say,

$$A_\theta = \sum_{i=1}^{c_G} A_{\theta i} = \sum_{i=1}^{c_G}\sum_{j=1}^{c_G} \sigma_{\theta i}\overline{M}_{ji}. \quad (63)$$

Enumeration of A_θ can be accomplished by using the generating function represented by $\sum_\theta A_\theta W_\theta$. This term is converted as follows:

$$\sum_\theta A_\theta W_\theta = \sum_\theta (\sum_{i=1}^{c_G}\sum_{j=1}^{c_G} \sigma_{\theta i}\overline{M}_{ji})W_\theta$$
$$= \sum_\theta \sum_{j=1}^{c_G} (\sum_{i=1}^{c_G} \overline{M}_{ji})\sigma_{\theta j}W_\theta$$
$$= \sum_{j=1}^{c_G} (\sum_{i=1}^{c_G} \overline{M}_{ji})\sum_\theta \sigma_{\theta j}W_\theta.$$

Since the last sum of the last side has been given by Eq. 48, we end up with

Theorem 2. (The total number of non-rigid isomers for every weight).

$$\sum_\theta A_\theta W_\theta = \sum_{j=1}^{c_G} (\sum_{i=1}^{c_G} \overline{M}_{ji})ZI(\mathbf{G}_j;\$_{d_{jk}}^{(i\alpha)}), \quad (64)$$

in which the SCIs are generated as shown in Lemma 3.

It should be noted that the term, $\sum_{i=1}^{c_G} \overline{M}_{ji}$, is calculated by summing up each row of the inverse of the mark table for **G**. This terms is zero if **G** is not a cyclic group. The right-hand side of Eq. 64 is a cycle index (CI) that is an alternative form to what is described by Pólya.[1] It should be emphasized that the present procedure generating USCIs ⟶ SCIs ⟶ CI provides us with a systematic tool for enumeration.[24]

If we sum up all $A_{\theta i}$ over W_θ, we are able to calculate the total number (A_i) of non-rigid isomers with $\mathbf{G}_i$-symmetry. This is expressed by

$$A_i = \sum_\theta A_{\theta i} = \sum_\theta \sum_{j=1}^{c_G} \sigma_{\theta i}\overline{M}_{ji} = \sum_{j=1}^{c_G} (\sum_\theta \sigma_{\theta j})\overline{M}_{ji}. \quad (65)$$

The term in the inner parentheses of the rightmost side can be estimated by introducing

$$w_\xi^{(i\alpha)} = 1 \text{ for all } \xi \text{ and all } i\alpha;\ W_\theta = 1 \quad (66)$$

into the equations of Lemma 3. This operation affords

Lemma 6. (Calculation of σ_j). Let σ_j be the number of derivatives that are invariant (or fixed) on the operation of $\mathbf{G}_j$. We can estimate σ_j in the light of

$$\sigma_j \equiv \sum_\theta \sigma_{\theta j} = ZI(\mathbf{G}_j;\$_{d_{jk}}^{(i\alpha)}) \quad (67)$$

for j=1,2,...,c_G, in which every variable of the right-hand side is substituted by

$$a_{d_{jk}}^{(i\alpha)} = \sum_\xi \kappa_{\xi_a} = \sum_\xi \underbrace{\sum_{p=1}^{c_{H^{(i\alpha)}}}}_{\text{improper}} B_{\xi p}^{(i\alpha)} \quad \text{for} \quad \$ = a \quad (68)$$

$$b_{d_{jk}}^{(i\alpha)} = c_{d_{jk}}^{(i\alpha)} = \sum_\xi (\kappa_{\xi_a} + 2\kappa_{\xi_c})$$
$$= \sum_\xi (\underbrace{\sum_{p=1}^{c_{H^{(i\alpha)}}}}_{\text{improper}} B_{\xi p}^{(i\alpha)} + 2 \underbrace{\sum_{p=1}^{c_{H^{(i\alpha)}}}}_{\text{proper}} B_{\xi p}^{(i\alpha)}) \quad (69)$$
$$\text{for} \quad \$ = b \text{ and } \$ = c.$$

By means of this lemma, we end up with

Corollary 3. (The total number of non-rigid isomers for every subsymmetry). Let A_i be the total number of $\mathbf{G}_i$-isomers. This is calculated by using σ_j (Lemma 6) by means of

$$A_i = \sum_{j=1}^{c_G} \sigma_j\overline{M}_{ji} \quad (70)$$
$$\text{for} \quad i = 1,2,...,c_G,$$

wherein the symbol $(\overline{M}_{ji})$ denotes the inverse of the matrix (M_{ji}).

References

1) a) G. Pólya, *Acta Math.*, **68**, 145 (1937). b) G. Pólya and R. C. Read, "Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds," Springer-Verlag, New York (1987).

2) a) J. H. Redfield, *Am. J. Math.*, **49**, 433 (1927). b) R. C. Read, *J. London Math. Soc.*, **34**, 417 (1959); **35**, 344 (1960). c) R. A. Davidson, *J. Am. Chem. Soc.*, **103**, 312 (1981).

3) E. Ruch, W. Hässelbarth and B. Richter, *Theor. Chim. Acta*, **19**, 288 (1970).

4) A. Kerber and K.-J. Thürling, in "Lecture Note in Mathematics," Springer, New York (1982), Vol. 969, p. 191.

5) W. Hässelbarth, *Theor. Chim. Acta*, **67**, 427 (1985).

6) a) D. H. Rouvary, *Chem. Soc. Rev.*, **3**, 355 (1974). b) D. H. Rouvary, *Endeavour*, **34**, 28 (1975).

7) A. T. Balaban, "Chemical Application of Graph Theory," Academic Press, London (1976).

8) K. Balasubramanian, *Chem. Rev.*, **85**, 599 (1985).

9) R. J. Hansen and P. C. Jurs, *J. Chem. Ed.*, **65**, 661 (1988).

10) E. Ruch and D. J. Klein, *Theor. Chim. Acta*, **63**, 447 (1983).

11) a) S. Fujita, *J. Chem. Inf. Comput. Sci.*, **26**, 212 (1986). b) S. Fujita, *J. Chem. Inf. Comput. Sci.*, **27**, 99 (1987). c) S. Fujita, *Bull. Chem. Soc. Jpn.*, **61**, 4189 (1988). d) S. Fujita,

Bull. Chem. Soc. Jpn., **62**, 662 (1989). e) S. Fujita, *J. Chem. Inf. Comput. Sci.*, **29**, 22 (1989).

12) W. Hässelbarth, *Theor. Chim. Acta*, **67**, 339 (1985).

13) C. A. Mead, *J. Am. Chem. Soc.*, **109**, 2130 (1987).

14) J. Brocas, *J. Am. Chem. Soc.*, **108**, 1135 (1986).

15) a) S. Fujita, *Theor. Chim. Acta*, **76**, 247 (1989). b) S. Fujita, *Bull. Chem. Soc. Jpn.*, **62**, 3771 (1989). c) S. Fujita, *Bull. Chem. Soc. Jpn.*, **63**, 203 (1990). d) S. Fujita, *Tetrehedron*, **46**, 365 (1990).

16) a) J. E. Leonard, G. S. Hammond, and H. E. Simmons, *J. Am. Chem. Soc.*, **97**, 5052 (1975). b) J. E. Leonard, *J. Phys. Chem.*, **81**, 2212 (1977). 17) R. L. Flurry, Jr., *J. Chem. Ed.*, **61**, 663 (1984).

18) K. Balasubramanian, *Theor. Chim. Acta*, **51**, 37 (1979).

19) S. Fujita, *Theor. Chim. Acta*, in press.

20) C. M. Woodmann, *Mol. Phys.*, **19**, 753 (1970).

21) B. Baumslag and B. Chandler, "Theory and Problems of Group Theory," McGraw-Hill, New York (1968).

22) M. A. Armstrong, "Groups and Symmetry," Springer-Verlag, New York (1988).

23) W. Burnside, "Theory of Groups of Finite Order (2nd ed.)," Cambridge Univ. Press, Cambridge (1911).

24) S. Fujita, *J. Math. Chem.*, in press.

25) a) K. Mislow, *J. Chem. Soc., Chem. Commun.*, **1981**, 234. b) M. Farina and C. Morandi, *Tetrahedron*, **30**, 1819 (1974).