Systematic Enumeration of High Symmetry Molecules by Means of Unit Subduced Cycle Indices with and without Chirality Fittingness

Shinsaku FUJITA
Research Laboratories, Ashigara, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa 250-01
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A novel method of enumerating isomers is presented by using adamantane as a parent skeleton. This method is based on unit subduced cycle indices with and without chirality fittingness, the indices being derived from the subduction of coset representations. The chirality fittingness, which is determined by examining the relationship between a point group and its subgroup, controls the mode of substitution by achiral and chiral substituents. The method provides detailed enumerations concerning symmetries and molecular formulas, whereas Pólya's theorem takes only the latter into consideration.

An attractive problem in the field of molecular symmetry is how to realize a chiral (or achiral) molecule of a given symmetry. Thus, there have appeared various approaches to the synthesis of chiral or achiral molecules of a high symmetry.[1] One of the most versatile strategies for such approaches is a vertex strategy in which the generation of new compounds is based on the substitution of an achiral skeleton with appropriate ligands.[2] Adamantane, which has $\mathbf{T}_d$ symmetry, has been successfully utilized as such an achiral skeleton. For example, Nakazaki et al. have reported the syntheis of a **T** molceule by starting from an adamantane skeleton.[3]

The adamantane skeleton has also attracted theoretical attention. Farina et al. have pointed out that substitution by chiral units creates molecules of a high symmetry.[4] We ourselves have recently examined modes of substitution on the adamantane skeleton;[5] chiral substituents, in addition to achiral ones, should be considered in order to realize all of the subsymmetries of $\mathbf{T}_d$. Although this approach has manually revealed which subsymmetries are allowed or forbidden, there have emerged no systematic rationalization of the results.

Other approaches treating an adamantane skeleton have been devoted to combinatorial enumerations of isomers.[6] These enumerations stem from Pólya's theorem, which counts isomers with respect only to molecular formulas. In other words, they have taken no account of the symmetries of the isomers.

Hässelbarth reported a method of enumeration concerning symmetry.[7] This method, however, disregarded the concrete forms of the coset representations that control the symmetry of a parent skeleton. Brocas proposed an alternative method, in which a combination of double cosets and framework groups made it possible to enumerate isomers concerning their symmetries.[8] Mead compared these methods using common problems of enumerations.[9]

The above discussions indicate the necessity of systematic enumerations of isomers with respect not only to their molecular formulas but also to their symmetries. In a previous paper, we have discussed the edge strategy and indicated the importance of the subduction of coset representations.[10] We have also provided a new method of isomer enumeration based upon unit subduced cycle indices (USCIs).[11] As a continuation of that work, the present paper deals with an extension of the method and its application to an enumeration by the vertex strategy, with achiral and chiral substituents allowed.

Construction of the Mark Table of $\mathbf{T}_d$ Point Group. The mark table of a group can be based on Burnside's textbook.[12] However, such tables have been prepared for only a limited number of point groups. This section illustrates the constructions of coset representations (CRs) of $\mathbf{T}_d$ and of its mark table.

The $\mathbf{T}_d$ group is decomposed to the corresponding cosets by any subgroup (Appendix 1). For example, if we select $\mathbf{C}_{3v}$ as the subgroup, we obtain

$$\mathbf{T}_d = \mathbf{C}_{3v} + \mathbf{C}_{3v}C_{2(1)} + \mathbf{C}_{3v}C_{2(2)} + \mathbf{C}_{3v}C_{2(3)},$$

as a decomposition. In accord with this decomposition, let us consider a set of cosets: $\{\mathbf{C}_{3v}, \mathbf{C}_{3v}C_{2(1)}, \mathbf{C}_{3v}C_{2(2)}, \mathbf{C}_{3v}C_{2(3)}\}$. When we assign integers 1 to 4 to these cosets, we obtain a set of integers {1, 2, 3, 4}. These cosets are multiplied by $C_{3(1)}$ to give these equations:

$$\begin{aligned}
\mathbf{C}_{3v}C_{3(1)} &= \mathbf{C}_{3v}, \\
\mathbf{C}_{3v}C_{2(1)}C_{3(1)} &= \mathbf{C}_{3v}C_{2(3)}, \\
\mathbf{C}_{3v}C_{2(2)}C_{3(1)} &= \mathbf{C}_{3v}C_{2(1)}, \text{ and} \\
\mathbf{C}_{3v}C_{2(3)}C_{3(1)} &= \mathbf{C}_{3v}C_{2(2)}.
\end{aligned}$$

The resulting cosets afford the set, {1, 4, 2, 3}. Hence, we obtain a permutation represented by

$$\pi_{C_{3(1)}} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 4 & 2 & 3 \end{pmatrix} = (1)(2\ 4\ 3),$$

which corresponds to the $C_{3(1)}$ operation. This manipulation is repeated over all the operations of $\mathbf{T}_d$ to give the corresponding coset representation, $\mathbf{T}_d(/\mathbf{C}_{3v})$, as is shown in Table 1. Each element of the CR is expressed in the form of a product of cycles. The degree of

Table 1. $\mathbf{T}_d(/\mathbf{C}_{3v})$ and the Subgroups

$\mathbf{T}_d$	$\mathbf{T}_d(/\mathbf{C}_{3v})$	Subgroups										
		$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$
I	(1)(2)(3)(4)	x	x	x	x	x	x	x	x	x	x	x
$C_{2(1)}$	(1 2)(3 4)		x			x	x			x	x	x
$C_{2(2)}$	(1 3)(2 4)						x			x	x	x
$C_{2(3)}$	(1 4)(2 3)						x	x		x	x	x
$C_{3(1)}$	(1)(2 4 3)	·	·	·	x	·	·	·	x	·	x	x
$C_{3(3)}$	(1 2 3)(4)										x	x
$C_{3(2)}$	(1 3 4)(2)										x	x
$C_{3(4)}$	(1 4 2)(3)										x	x
$C^3_{3(1)}$	(1)(2 3 4)	·	·	·	x	·	·	·	x	·	x	x
$C^2_{3(4)}$	(1 2 3)(3)										x	x
$C^2_{3(3)}$	(1 3 2)(4)										x	x
$C^2_{3(2)}$	(1 4 3)(2)										x	x
$\sigma_{d(1)}$	(1)(2 3)(4)	·	·	x	·	·	·	x	x	x	·	x
$S_{4(3)}$	(1 2 4 3)									x		x
$S^3_{4(3)}$	(1 3 4 2)									x		x
$\sigma_{d(6)}$	(1 4)(2)(3)							x		x		x
$\sigma_{d(2)}$	(1)(2)(3 4)								x			x
$\sigma_{d(4)}$	(1 2)(3)(4)											x
$S_{4(1)}$	(1 3 2 4)					x						x
$S^3_{4(1)}$	(1 4 2 3)					x						x
$\sigma_{d(3)}$	(1)(2 4)(3)								x			x
$S^3_{4(2)}$	(1 2 3 4)											x
$\sigma_{d(5)}$	(1 3)(2)(4)											x
$S_{4(2)}$	(1 4 3 2)											x
	Mark	4	0	2	1	0	0	0	1	0	0	0

Table 2. Mark Table of $\mathbf{T}_d$

$i \setminus j$	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$
$\mathbf{T}_d(/\mathbf{C}_1)$	24	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_2)$	12	4	0	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_s)$	12	0	2	0	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_3)$	8	0	0	2	0	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{S}_4)$	6	2	0	0	2	0	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{D}_2)$	6	6	0	0	0	6	0	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_{2v})$	6	2	2	0	0	0	2	0	0	0	0
$\mathbf{T}_d(/\mathbf{C}_{3v})$	4	0	2	1	0	0	0	1	0	0	0
$\mathbf{T}_d(/\mathbf{D}_{2d})$	3	3	1	0	1	3	1	0	1	0	0
$\mathbf{T}_d(/\mathbf{T})$	2	2	0	2	0	2	0	0	0	2	0
$\mathbf{T}_d(/\mathbf{T}_d)$	1	1	1	1	1	1	1	1	1	1	1

$\mathbf{T}_d(/\mathbf{C}_{3v})$ is $|\mathbf{T}_d|/|\mathbf{C}_{3v}|=24/6=4$. The $\mathbf{T}_d(/\mathbf{C}_{3v})$ symbol comes from the fact that the $\mathbf{T}_d$ group is divided by the $\mathbf{C}_{3v}$ subgroup in a geometrical sense. This fact is essential for deriving a novel concept 'chirality fittingness of an orbit' (Appendix 2). We consider each number appearing in the cycles to be a point that is either mobile (that changes to another number) or immobile (fixed) during an operation of the group. The mark of a group by a given subgroup is defined as a number of such fixed points during all of the operations due to the elements of the subgroup. The marks of the subgroups in $\mathbf{T}_d(/\mathbf{C}_{3v})$ are obtained by using Table 1, in which fixed points are counted over the elements marked with 'x' for each of the subgroups. Thus, we obtain the $\mathbf{T}_d(/\mathbf{C}_{3v})$ row of marks shown at the bottom of Table 1. The other CRs can be examined; the collection of the results gives the mark table shown in Table 2. For the present purpose, the inverse of the mark table is also important (Table 3).

Classification of Vertices of a Skeleton into Orbits. The adamantane skeleton ($C_{10}H_{16}$) has 26 vertices, all of which can be regarded as substitution positions. Among them, the four vertices (**1**) marked with heavy circles construct a set of chemically equivalent positions. We call such a set *an orbit*, according to the terminology of permutation groups. In a similar way, the other vertices are classified into the respective sets (orbits) of equivalent vertices (**2**, **3**, and **4**), as is shown in Table 4. The orbits are characterized by coset representations (CRs),[10] each of which controls the symmetry behavior of the equivalent vertices.

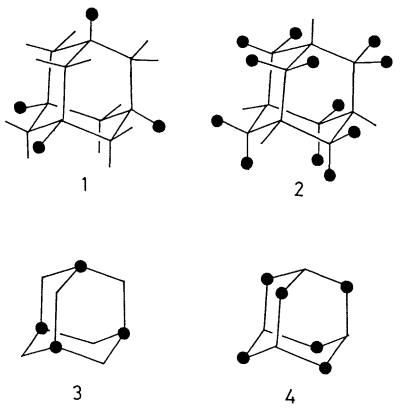
The assignment of a CR to every orbit can be

Table 3. The Inverse of the Mark Table of $\mathbf{T_d}$

	$\mathbf{T_d}(/\mathbf{C_1})$	$\mathbf{T_d}(/\mathbf{C_2})$	$\mathbf{T_d}(/\mathbf{C_s})$	$\mathbf{T_d}(/\mathbf{C_3})$	$\mathbf{T_d}(/\mathbf{S_4})$	$\mathbf{T_d}(/\mathbf{D_2})$	$\mathbf{T_d}(/\mathbf{C_{2v}})$	$\mathbf{T_d}(/\mathbf{C_{3v}})$	$\mathbf{T_d}(/\mathbf{D_{2d}})$	$\mathbf{T_d}(/\mathbf{T})$	$\mathbf{T_d}(/\mathbf{T_d})$	$\sum_{i=1}^{s} \overline{m}_{ji}$
$\mathbf{C_1}$	1/24	0	0	0	0	0	0	0	0	0	0	1/24
$\mathbf{C_2}$	−1/8	1/4	0	0	0	0	0	0	0	0	0	1/8
$\mathbf{C_s}$	−1/4	0	1/2	0	0	0	0	0	0	0	0	1/4
$\mathbf{C_3}$	−1/6	0	0	1/2	0	0	0	0	0	0	0	1/3
$\mathbf{S_4}$	0	−1/4	0	0	1/2	0	0	0	0	0	0	1/4
$\mathbf{D_2}$	1/12	−1/4	0	0	0	1/6	0	0	0	0	0	0
$\mathbf{C_{2v}}$	1/4	−1/4	−1/2	0	0	0	1/2	0	0	0	0	0
$\mathbf{C_{3v}}$	1/2	0	−1	−1/2	0	0	0	1	0	0	0	0
$\mathbf{D_{2d}}$	0	1/2	0	0	−1/2	−1/2	−1/2	0	1	0	0	0
$\mathbf{T}$	1/6	0	0	−1/2	0	−1/6	0	0	0	1/2	0	0
$\mathbf{T_d}$	−1/2	0	1	1/2	0	1/2	0	−1	−1	−1/2	1	0

Table 4. Orbits of an Adamantane Skeleton

Orbit	No. of positions	FPV	Coset representation
1	4	(4 0 2 1 0 0 0 1 0 0 0)	$\mathbf{T_d}(/\mathbf{C_{3v}})$
2	12	(12 0 2 0 0 0 0 0 0 0 0)	$\mathbf{T_d}(/\mathbf{C_s})$
3	4	(4 0 2 1 0 0 0 1 0 0 0)	$\mathbf{T_d}(/\mathbf{C_{3v}})$
4	6	(6 2 2 0 0 0 2 0 0 0 0)	$\mathbf{T_d}(/\mathbf{C_{2v}})$



conducted by comparing a fixed-point vector (FPV) of the orbit with a table of marks.[11] The fixed-point vector (FPV) is defined as a row vector that collects the numbers of fixed points with respect to every subgroup. For example, a mirror plane of $\mathbf{C_s}$ group fixes two bridgehead methines which lie on the plane. Hence, the number of fixed points is 2 in this case. Thus, the FPVs for the orbits (**1** and **3**) are counted to be (4 0 2 1 0 0 0 1 0 0 0), the elements of which are aligned in the order of a set of subgroups (SSG), i.e., $\{\mathbf{C_1}, \mathbf{C_2}, \mathbf{C_s}, \mathbf{C_3}, \mathbf{S_4}, \mathbf{D_2}, \mathbf{C_{2v}}, \mathbf{C_{3v}}, \mathbf{D_{2d}}, \mathbf{T}, \mathbf{T_d}\}$.[13] Since the FPV is identical with the $\mathbf{T_d}(/\mathbf{C_{3v}})$ row of the mark table of the $\mathbf{T_d}$ group (Table 2), the orbits (**1** and **3**) are determined to be subject to $\mathbf{T_d}(/\mathbf{C_{3v}})$. Similarly, the six vertices of **2** and the twelve vertices of **4** are concluded to be subject to $\mathbf{T_d}(/\mathbf{C_{2v}})$ and $\mathbf{T_d}(/\mathbf{C_s})$ respectively by a comparison of the FPVs (Table 4) with the data in Table 2.

Let $\mathbf{P_A}$ be a permutation group for the 26 vertices of adamantane. Then the above result can be formulated as follows:

$$\mathbf{P_A} = \mathbf{T_d}(/\mathbf{C_s}) + \mathbf{T_d}(/\mathbf{C_{2v}}) + 2\mathbf{T_d}(/\mathbf{C_{3v}}). \quad (1)$$

This result can alternatively be obtained by an algebraic method (Appendix 1). Thus, the FPV of the set of 26 vertices is (26 2 8 2 0 0 2 2 0 0 0), which is multiplied by the inverse of the mark table (Table 3)[14] to provide a multiplicity vector (0 0 1 0 0 0 1 2 0 0 0). This vector indicates the multiplicities of the CRs involved in:

$$\begin{aligned}\mathrm{SCR} = \{&\mathbf{T_d}(/\mathbf{C_1}), \mathbf{T_d}(/\mathbf{C_2}), \mathbf{T_d}(/\mathbf{C_s}), \mathbf{T_d}(/\mathbf{C_3}), \mathbf{T_d}(/\mathbf{S_4}),\\ &\mathbf{T_d}(/\mathbf{D_2}), \mathbf{T_d}(/\mathbf{C_{2v}}), \mathbf{T_d}(/\mathbf{C_{3v}}), \mathbf{T_d}(/\mathbf{D_{2d}}), \mathbf{T_d}(/\mathbf{T}),\\ &\mathbf{T_d}(/\mathbf{T_d})\}.\end{aligned}$$

This result is identical with Eq. 1.

Construction of a Table of Unit Subduced Cycle Indices for the $\mathbf{T_d}$ Point Group. In the present enumerations, *unit subduced cycle indices (USCIs)* play an important role in the derivation of generating functions (Appendix 1). A collection in the form of a *table of USCIs* is convenient in solving problems of

enumerations.[15]

For illustrating a process of subduction, let us examine the subduction of $\mathbf{T}_d(/\mathbf{C}_{3v})$ by $\mathbf{C}_{2v}$. If we select the element of $\mathbf{C}_{2v}$ from Table 1, we obtain a subduced representation:

$$\mathbf{T}_d(/\mathbf{C}_{3v})\downarrow\mathbf{C}_{2v} = \{(1)(2)(3)(4),\ (1\ 4)(2\ 3),\ (1)(2\ 3)(4),\ (1\ 4)(2)(3)\},$$

which can be regarded as a permutation representation for the $\mathbf{C}_{2v}$ group. Note that $\mathbf{T}_d(/\mathbf{C}_{3v})$ is transitive, while $\mathbf{T}_d(/\mathbf{C}_{3v})\downarrow\mathbf{C}_{2v}$ is intransitive. Hence, the latter is reduced into transitive coset representations of the $\mathbf{C}_{2v}$ group. The marks of its subgroups ($\mathbf{C}_1$, $\mathbf{C}_2$, $\mathbf{C}_s$, $\mathbf{C}_s'$, and $\mathbf{C}_{2v}$) are obtained as (4 0 2 2 0) by counting fixed points. This row vector is then multiplied by the inverse of the mark table of the $\mathbf{C}_{2v}$ group (see Eq. 1.6 of Appendix 1):

$$(\beta_{C_1}\ \beta_{C_2}\ \beta_{C_s}\ \beta_{C_s'}\ \beta_{C_{2v}}) = (4\,0\,2\,2\,0)\begin{bmatrix} 1/4 & 0 & 0 & 0 & 0 \\ -1/4 & 1/2 & 0 & 0 & 0 \\ -1/4 & 0 & 1/2 & 0 & 0 \\ -1/4 & 0 & 0 & 1/2 & 0 \\ 1/2 & -1/2 & -1/2 & -1/2 & 1 \end{bmatrix} = (0\,0\,1\,1\,0).$$

We then obtain the reduction of the subduced representation:

$$\mathbf{T}_d(/\mathbf{C}_{3v})\downarrow\mathbf{C}_{2v} = \mathbf{C}_{2v}(/\mathbf{C}_s) + \mathbf{C}_{2v}(/\mathbf{C}_s').$$

This result allows us to ascribe a USCI (s_2^2) to the reduction, since each of the coset representations (CRs) of the right-hand side has a degree of 2. If we take account of the chirality fittingness of each CR (Appendix 2), we obtain a_2^2 as the unit subduced cycle index with chirality fittingness. In a similar way, other USCIs with and without chirality fittingness are obtained (Table 5).

Enumeration of Isomers Based on an Adamantane Skeleton in Which Only Achiral Substituents Are Permitted. For the enumeration of this type, we use the USCIs described above. (We consider achiral substituents only in the discussion of this section.) The vertex strategy for producing molecules of various symmetries consists of a substitution onto the vertices of a parent skeleton with a given set of substituents. For simplicity of discussion, we will work out the orbits (**1** and **2**) of the adamantane skeleton. We thus consider 16 positions in all. The first problem is the counting of the isomers derived by the substitution of the 16 positions with H, X, and/or Y. Because the two orbits are subject to $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$, respectively, the corresponding rows of USCIs in Table 5 are adopted to give subduced cycle indices (SCIs).

A figure inventory for substitution with H, X, and Y is represented by $s_k = 1 + x^k + y^k$, which is introduced into the SCIs (Appendix 1). Thus, we obtain the following FP-counting polynomials as generating functions:

for $\mathbf{C}_1$,	$(s_1^4)(s_1^{12}) = (1 + x + y)^{16}$	(3^{16})
for $\mathbf{C}_2$,	$(s_2^2)(s_2^6) = (1 + x^2 + y^2)^8$	(3^8)
for $\mathbf{C}_s$,	$(s_1^2s_2)(s_1^2s_2^5) = (1 + x + y)^4(1 + x^2 + y^2)^6$	(3^{10})
for $\mathbf{C}_3$,	$(s_1s_3)(s_3^4) = (1 + x + y)(1 + x^3 + y^3)^5$	(3^6)
for $\mathbf{S}_4$,	$(s_4)(s_4^3) = (1 + x^4 + y^4)^4$	(3^4)
for $\mathbf{D}_2$,	$(s_4)(s_4^3) = (1 + x^4 + y^4)^4$	(3^4)
for $\mathbf{C}_{2v}$,	$(s_2^2)(s_2^2s_4^2) = (1 + x^2 + y^2)^4(1 + x^4 + y^4)^2$	(3^6)

Table 5. Unit Subduced Cycle Indices for $\mathbf{T}_d$

$i \setminus j$	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$
$\mathbf{T}_d(/\mathbf{C}_1)$	s_1^{24}	s_2^{12}	s_2^{12}	s_3^8	s_4^6	s_4^6	s_4^6	s_6^4	s_8^3	s_{12}^2	s_{24}
	(b_1^{24})	(b_2^{12})	(c_2^{12})	(b_3^8)	(c_4^6)	(b_4^6)	(c_4^6)	(c_4^6)	(c_8^3)	(b_{12}^2)	(c_{24})
$\mathbf{T}_d(/\mathbf{C}_2)$	s_1^{12}	$s_1^4s_2^4$	s_2^6	s_3^4	$s_2^2s_4^2$	s_2^6	$s_2^2s_4^2$	s_6^2	s_4^3	s_6^2	s_{12}
	(b_1^{12})	$(b_1^4b_2^4)$	(c_2^6)	(b_3^4)	$(c_2^2c_4^2)$	(b_2^6)	$(c_2^2c_4^2)$	(c_6^2)	(c_4^3)	(b_6^2)	(c_{12})
$\mathbf{T}_d(/\mathbf{C}_s)$	s_1^{12}	s_2^6	$s_1^2s_2^5$	s_3^4	s_4^3	s_4^3	$s_2^2s_4^2$	$s_3^2s_6$	s_4s_8	s_{12}	s_{12}
	(b_1^{12})	(b_2^6)	$(a_1^2c_2^5)$	(b_3^4)	(c_4^3)	(b_4^3)	$(a_2^2c_4^2)$	$(a_3^2c_6)$	(a_4c_8)	(b_{12})	(a_{12})
$\mathbf{T}_d(/\mathbf{C}_3)$	s_1^8	s_2^4	s_2^4	$s_1^2s_3^2$	s_4^2	s_4^2	s_4^2	s_2s_6	s_8	s_4^2	s_8
	(b_1^8)	(b_2^4)	(c_2^4)	$(b_1^2b_3^2)$	(c_4^2)	(b_4^2)	(c_4^2)	(c_2c_6)	(c_8)	(b_4^2)	(c_8)
$\mathbf{T}_d(/\mathbf{S}_4)$	s_1^6	$s_1^2s_2^2$	s_2^3	s_2^3	$s_1^2s_4$	s_2^3	s_2s_4	s_6	s_2s_4	s_6	s_6
	(b_1^6)	$(b_1^2b_2^2)$	(c_2^3)	(b_3^2)	$(a_1^2c_4)$	(b_2^3)	(c_2c_4)	(c_6)	(a_2c_4)	(b_6)	(a_6)
$\mathbf{T}_d(/\mathbf{D}_2)$	s_1^6	s_1^6	s_2^3	s_3^2	s_2^3	s_1^6	s_2^3	s_6	s_2^3	s_3^2	s_6
	(b_1^6)	(b_1^6)	(c_2^3)	(b_3^2)	(c_2^3)	(b_1^6)	(c_2^3)	(c_6)	(c_2^3)	(b_3^2)	(c_6)
$\mathbf{T}_d(/\mathbf{C}_{2v})$	s_1^6	$s_1^2s_2^2$	$s_1^2s_2^2$	s_3^2	s_2s_4	s_2^3	$s_1^2s_4$	s_3^2	s_2s_4	s_6	s_6
	(b_1^6)	$(b_1^2b_2^2)$	$(a_1^2c_2^2)$	(b_3^2)	(c_2c_4)	(b_2^3)	$(a_1^2c_4)$	(a_3^2)	(a_2c_4)	(b_6)	(a_6)
$\mathbf{T}_d(/\mathbf{C}_{3v})$	s_1^4	s_2^2	$s_1^2s_2$	s_1s_3	s_4	s_4	s_2^2	s_1s_3	s_4	s_4	s_4
	(b_1^4)	(b_2^2)	$(a_1^2c_2)$	(b_1b_3)	(c_4)	(b_4)	(a_2^2)	(a_1a_3)	(a_4)	(b_4)	(a_4)
$\mathbf{T}_d(/\mathbf{D}_{2d})$	s_1^3	s_1^3	s_1s_2	s_3	s_1s_2	s_1^3	s_1s_2	s_3	s_1s_2	s_3	s_3
	(b_1^3)	(b_1^3)	(a_1c_2)	(b_3)	(a_1c_2)	(b_1^3)	(a_1c_2)	(a_3)	(a_1c_2)	(b_3)	(a_3)
$\mathbf{T}_d(/\mathbf{T})$	s_1^2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2	s_1^2	s_2
	(b_1^2)	(b_1^2)	(c_2)	(b_1^2)	(a_2)	(b_1^2)	(c_2)	(c_2)	(c_2)	(b_1^2)	(c_2)
$\mathbf{T}_d(/\mathbf{T}_d)$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1
	(b_1)	(b_1)	(a_1)	(b_1)	(a_1)	(b_1)	(a_1)	(a_1)	(a_1)	(b_1)	(a_1)
$\sum_i^s \bar{m}_{ji}$	1/24	1/8	1/4	1/3	1/4	0	0	0	0	0	0

Table 6. Enumeration of Isomers with Achiral Substituents

Index[a] term	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	Total
x^{16} ; y^{16}	0	0	0	0	0	0	0	0	0	0	1	1
$x^{15}y$; xy^{15}	0	0	1	0	0	0	0	1	0	0	0	2
x^{15} ; y^{15}	0	0	1	0	0	0	0	1	0	0	0	2
$x^{14}y^2$; x^2y^{14}	2	1	4	0	0	0	2	0	0	0	0	9
$x^{14}y$; xy^{14}	7	0	6	0	0	0	0	1	0	0	0	13
x^{14} ; y^{14}	2	1	4	0	0	0	2	0	0	0	0	9
$x^{13}y^3$; x^3y^{13}	17	0	11	1	0	0	0	3	0	0	0	32
$x^{13}y^2$; x^2y^{13}	61	0	18	0	0	0	0	0	0	0	0	79
$x^{13}y$; xy^{13}	61	0	18	0	0	0	0	0	0	0	0	79
x^{13} ; y^{13}	17	0	11	1	0	0	0	3	0	0	0	32
$x^{12}y^4$; x^4y^{12}	62	4	20	1	1	0	3	2	1	0	1	95
$x^{12}y^3$; x^3y^{12}	285	0	35	1	0	0	0	3	0	0	0	324
$x^{12}y^2$; x^2y^{12}	424	11	48	0	0	0	6	0	0	0	0	489
$x^{12}y$; xy^{12}	285	0	35	1	0	0	0	3	0	0	0	324
x^{12} ; y^{12}	62	4	20	1	1	0	3	2	1	0	1	95
$x^{11}y^5$; x^5y^{11}	161	0	42	0	0	0	0	0	0	0	0	203
$x^{11}y^4$; x^4y^{11}	877	0	66	0	0	0	0	0	0	0	0	943
$x^{11}y^3$; x^3y^{11}	1766	0	108	0	0	0	0	0	0	0	0	1874
$x^{11}y^2$; x^2y^{11}	1766	0	108	0	0	0	0	0	0	0	0	1874
$x^{11}y$; xy^{11}	877	0	66	0	0	0	0	0	0	0	0	943
x^{11} ; y^{11}	161	0	42	0	0	0	0	0	0	0	0	203
$x^{10}y^6$; x^6y^{10}	301	11	48	3	0	0	6	4	0	0	0	373
$x^{10}y^5$; x^5y^{10}	1951	0	102	0	0	0	0	0	0	0	0	2053
$x^{10}y^4$; x^4y^{10}	4896	37	176	0	0	0	10	0	0	0	0	5119
$x^{10}y^3$; x^3y^{10}	6571	0	198	7	0	0	0	6	0	0	0	6782
$x^{10}y^2$; x^2y^{10}	4896	37	176	0	0	0	10	0	0	0	0	5119
$x^{10}y$; xy^{10}	1951	0	102	0	0	0	0	0	0	0	0	2053
x^{10} ; y^{10}	301	11	48	3	0	0	6	4	0	0	0	373
x^9y^7 ; x^7y^9	442	0	66	3	0	0	0	4	0	0	0	515
x^9y^6 ; x^6y^9	3272	0	126	3	0	0	0	4	0	0	0	3405
x^9y^5 ; x^5y^9	9875	0	270	0	0	0	0	0	0	0	0	10145
x^9y^4 ; x^4y^9	16518	0	324	7	0	0	0	6	0	0	0	16855
x^9y^3 ; x^3y^9	16518	0	324	7	0	0	0	6	0	0	0	16855
x^9y^2 ; x^2y^9	9875	0	270	0	0	0	0	0	0	0	0	10145
x^9y ; xy^9	3272	0	126	3	0	0	0	4	0	0	0	3405
x^9 ; y^9	442	0	66	3	0	0	0	4	0	0	0	515
x^8y^8	494	12	68	0	2	0	6	0	2	0	0	584
x^8y^7 ; x^7y^8	4215	0	150	0	0	0	0	0	0	0	0	4365
x^8y^6 ; x^6y^8	14822	63	316	0	0	0	14	0	0	0	0	15215
x^8y^5 ; x^5y^8	29805	0	450	0	0	0	0	0	0	0	0	30255
x^8y^4 ; x^4y^8	37239	92	494	0	5	1	15	0	2	0	0	37848
x^8y^3 ; x^3y^8	29805	0	450	0	0	0	0	0	0	0	0	30255
x^8y^2 ; x^2y^8	14822	63	316	0	0	0	14	0	0	0	0	15215
x^8y ; xy^8	4215	0	150	0	0	0	0	0	0	0	0	4365
x^8 ; y^8	494	12	68	0	2	0	6	0	2	0	0	584
x^7y^7	16980	0	360	0	0	0	0	0	0	0	0	17340
x^7y^6 ; x^6y^7	39778	0	514	12	0	0	0	6	0	0	0	40310
x^7y^5 ; x^5y^7	59730	0	660	0	0	0	0	0	0	0	0	60390
x^7y^4 ; x^4y^7	59730	0	660	0	0	0	0	0	0	0	0	60390
x^7y^3 ; x^3y^7	39778	0	514	12	0	0	0	6	0	0	0	40310
x^7y^2 ; x^2y^7	16980	0	360	0	0	0	0	0	0	0	0	17340
x^7y ; xy^7	4215	0	150	0	0	0	0	0	0	0	0	4365
x^7 ; y^7	442	0	66	3	0	0	0	4	0	0	0	515
x^6y^6	69658	130	674	12	0	0	20	6	0	0	0	70500
x^6y^5 ; x^5y^6	83694	0	780	0	0	0	0	0	0	0	0	84474
x^6y^4 ; x^4y^6	69658	130	674	12	0	0	20	6	0	0	0	70500
x^6y^3 ; x^3y^6	39788	0	514	12	0	0	0	6	0	0	0	40310
x^6y^2 ; x^2y^6	14822	63	316	0	0	0	14	0	0	0	0	15215
x^6y ; xy^6	3272	0	126	3	0	0	0	4	0	0	0	3405
x^6 ; y^6	301	11	48	3	0	0	6	4	0	0	0	373
x^5y^5	83694	0	780	0	0	0	0	0	0	0	0	84474
x^5y^4 ; x^4y^5	59730	0	660	0	0	0	0	0	0	0	0	60390
x^5y^3 ; x^3y^5	29805	0	450	0	0	0	0	0	0	0	0	30255
x^5y^2 ; x^2y^5	9875	0	270	0	0	0	0	0	0	0	0	10145
x^5y ; xy^5	1951	0	102	0	0	0	0	0	0	0	0	2053
x^5 ; y^5	161	0	42	0	0	0	0	0	0	0	0	203

Table 6. (Continued)

Index[a] term	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d	Total
x^4y^4	37239	92	494	0	5	1	15	0	2	0	0	37848
x^4y^3 ; x^3y^4	16518	0	324	7	0	0	0	6	0	0	0	16855
x^4y^2 ; x^2y^4	4896	37	176	0	0	0	10	0	0	0	0	5119
x^4y ; xy^4	877	0	66	0	0	0	0	0	0	0	0	943
x^4 ; y^4	62	4	20	1	1	0	3	2	1	0	1	95
x^3y^3	6571	0	198	7	0	0	0	6	0	0	0	6782
x^3y^2 ; x^2y^3	1766	0	108	0	0	0	0	0	0	0	0	1874
x^3y ; xy^3	285	0	35	1	0	0	0	3	0	0	0	324
x^3 ; y^3	17	0	11	1	0	0	0	3	0	0	0	32
x^2y^2	424	11	48	0	0	0	6	0	0	0	0	489
x^2y ; xy^2	61	0	18	0	0	0	0	0	0	0	0	79
x^2 ; y^2	2	1	4	0	0	0	2	0	0	0	0	9
xy	7	0	6	0	0	0	0	0	0	0	0	13
x ; y	0	0	1	0	0	0	0	1	0	0	0	2
1	0	0	0	0	0	0	0	0	0	0	1	1
Total	1778217	1431	28926	243	27	3	351	234	18	0	9	1809459

a) The index term x^my^n corresponds to the molecular formula: $(C_{10}H_{16-m-n}X_mY_n)$.

for $\mathbf{C}_{3v}$, $(s_1s_3)(s_3^2s_6) = (1+x+y)(1+x^3+y^3)^3(1+x^6+y^6)$ (3^5)
for $\mathbf{D}_{2d}$, $(s_4)(s_4s_8) = (1+x^4+y^4)^2(1+x^8+y^8)$ (3^3)
for $\mathbf{T}$, $(s_4)(s_{12}) = (1+x^4+y^4)(1+x^{12}+y^{12})$ (3^2)
and
for $\mathbf{T}_d$, $(s_4)(s_{12}) = (1+x^4+y^4)(1+x^{12}+y^{12})$. (3^2)

The left-hand side of each equation denotes an SCI for each subsymmetry, in which the first set of parentheses contains the USCI of the $\mathbf{T}_d(/\mathbf{C}_{3v})$ row, and the second, the USCI of the $\mathbf{T}_d(/\mathbf{C}_s)$ row.

The expansion of the right-hand sides of the equations gives the generating functions, in which the coefficient of the x^my^n term indicates the number of fixed points with x^my^n and the respective subsymmetry.

For the purpose of illustrating a procedure for obtaining the numbers of isomers, we deal with the case of x^8y^4. Thus, after the expansion, we collect the resulting coefficients of the x^8y^4 term of the polynomials. Thereby, we obtain the FPV of x^8y^4: FPV=(900900 420 1020 0 12 12 32 0 2 0 0). This is multiplied by the inverse (Table 3) to give a vector, (37239 92 494 0 5 1 15 0 2 0 0), which indicates the multiplicities in the order of the SSG. Thus, the $C_{10}H_4X_8Y_4$ isomers are classified into 37239 assymmetric ($\mathbf{C}_1$) isomers, 92 isomers of $\mathbf{C}_2$ subsymmetry, 494 isomers of $\mathbf{C}_s$, 5 of $\mathbf{S}_4$, one isomer of $\mathbf{D}_2$, 15 of $\mathbf{C}_{2v}$, and two isomers of $\mathbf{D}_{2d}$. Similarly, the isomers with x^my^n (which corresponds to the formula of $C_{10}H_{16-m-n}X_mY_n$) were enumerated. Table 6 lists the results, in which the intersection between x^my^n and a subsymmetry indicates the number of isomers with $C_{10}H_{16-m-n}X_mY_n$ and with the subsymmetry.

The $\mathbf{D}_{2d}$ column of Table 6 indicates that the $\mathbf{D}_{2d}$ isomers of the present enumeration should have molecular formulas of $C_{10}X_{12}Y_4$ (1 isomer for the $x^{12}y^4$ term), $C_{10}X_4Y_{12}$ (1 for x^4y^{12}), $C_{10}H_4X_{12}$ (1 for x^{12}), $C_{10}H_4Y_{12}$ (1 for y^{12}), $C_{10}X_8Y_8$ (2 for x^8y^8), $C_{10}H_4X_8Y_4$ (2 for x^8y^4), $C_{10}H_4X_4Y_8$ (2 for x^4y^8), $C_{10}H_8X_8$ (2 for x^8), $C_{10}H_8Y_8$ (2 for y^8), $C_{10}H_8X_4Y_4$ (2 for x^4y^4), $C_{10}H_{12}X_4$ (1 for x^4), or $C_{10}H_{12}Y_4$ (1 for y^4). Thus, there exist 18 $\mathbf{D}_{2d}$ isomers in all. These results are verified by the manual enumeration depicted in Fig. 1. The present enumeration thus clarifies both the symmetry and the molecular formula of an isomer; thereby, we can easily draw a concrete structure of the isomer.

The $\mathbf{D}_2$ column of Table 6 shows that there emerge 3 molecules with the $\mathbf{D}_2$ symmetry. Figure 2 depicts these $\mathbf{D}_2$ molecules.

The $\mathbf{T}$ column of Table 6 suggests the non-existence of $\mathbf{T}$ isomers. In fact, no $\mathbf{T}$ isomers can exist if only achiral substituents are considered. It will be proved that $\mathbf{T}$ isomers are realized on the adamantane skeleton only if chiral substituents in addition to achiral ones are allowed.

A total number regarding each subsymmetry is obtained by summing up the corresponding column of Table 6. Alternatively, the total number can be calculated as a whole. We first obtain an FPV= (43046721 6561 59049 729 81 81 729 243 27 9 9) by the substitution of $x=y=1$ into the above-mentioned FP-counting polynominals (e.g., $3^{16}=43046721$, as is shown in the rightmost parentheses). Then the FPV is multiplied by the inverse of the mark table (Table 3) to give a vector, (1778217 1431 28926 243 27 3 351 234 18 0 9). This result is identical with the values shown at the bottom of Table 6, which are, in turn, derived from the direct summation.

The total number of isomer with x^my^n can alternatively be calculated by using a cycle index derived from a table of USCIs (Appendix 1). Thus, we obtain the cycle index (CI):

$$\begin{aligned} &ZI(\mathbf{T}_d;\, s_k) \\ &= (1/24)(s_1^4)(s_1^{12}) + (1/8)(s_2^2)(s_2^6) + (1/4)(s_1^2s_2)(s_1^2s_2^5) \\ &\quad + (1/3)(s_1s_3)(s_3^4) + (1/4)(s_4)(s_4^3) \\ &= (1/24)(s_1^{16} + 3s_2^8 + 6s_1^4s_2^6 + 8s_1s_3^5 + 6s_4^4), \end{aligned} \quad (2)$$

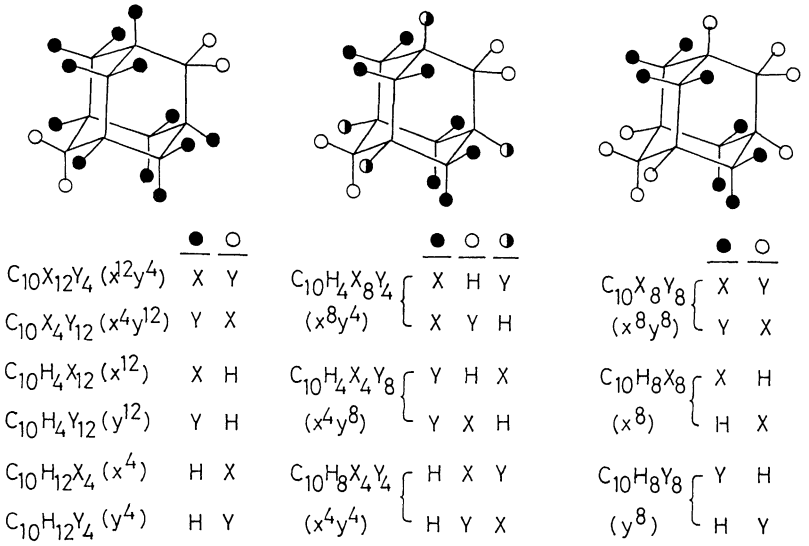


Fig. 1. Isomers of $\mathbf{D}_{2d}$ symmetry with achiral substituents on an adamantane skeleton.

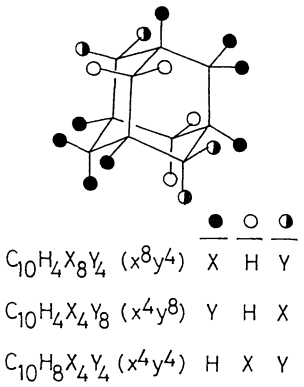


Fig. 2. Isomers of $\mathbf{D}_2$ symmetry with achiral substituents on an adamantane skeleton.

which uses the rows of $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$ and involves the factors (1/24, etc.) at the bottom of the table of USCIs (Table 5). The factors have been obtained by summing up every row of Table 3, as is shown in the rightmost column. Note that the factors are positive only if the corresponding subgroups are cyclic. The resulting cycle index (Eq. 2) can be proved to be identical to that derived alternatively from Pólya's theorem.[16] After the introduction of the figure inventory and the expansion of the resulting equation, we obtain a generating function which counts the total number of isomers with the $x^m y^n$ term. The coefficient of the term is found in the rightmost column of Table 6.

It should be emphasized here that Pólya's theorem, which gives a result equivalent to Eq. 2, takes no account of molecular symmetry. On the other hand, the present method provides detailed results that can be itemized regarding molecular symmetry (Table 6).

Enumeration of Isomers Permitting Achiral and Chiral Substituents. If we permit chiral substituents in addition to achiral ones, we should use *unit subduced cycle indices with chirality fittingness (USCI-CFs)* in place of the USCIs described in the previous section (Appendix 2). Table 5 also lists the USCI-CFs for the $\mathbf{T}_d$ symmetry. The USCI-CFs contain variables (a, b, and c) which indicate the chirality fittingness of the respective coset representation (in other words, of the corresponding orbit).

Let us work out the same adamantane skeleton except that we will now consider chiral substituents as well as achiral ones. The $\mathbf{T}_d(/\mathbf{C}_{3v})$ and $\mathbf{T}_d(/\mathbf{C}_s)$ rows of USCI-CFs (Table 5) are applied to two orbits (**1** and **2**), thus affording the following subduced cycle indices with chirality fittingness (SCI-CFs):

$$\text{for } \mathbf{C}_1, \quad (b_1^{12})(b_1^4) = (1+x)^{12}(1+x+r+s)^4,$$
$$\text{for } \mathbf{C}_2, \quad (b_2^6)(b_2^2) = (1+x^2)^6(1+x^2+r^2+s^2)^2,$$
$$\text{for } \mathbf{C}_3, \quad (a_1^2c_2^5)(a_1^2c_2) = (1+x)^4(1+x^2)^5(1+x^2+2rs),$$
$$\text{for } \mathbf{S}_4, \quad (c_4^3)(c_4) = (1+x^4)^3(1+x^4+2r^2s^2),$$
$$\text{for } \mathbf{D}_2, \quad (b_4^3)(b_4) = (1+x^4)^3(1+x^4+r^4+s^4),$$
$$\text{for } \mathbf{C}_{2v}, \quad (a_2^2c_4^2)(a_2^2) = (1+x^2)^4(1+x^4)^2,$$
$$\text{for } \mathbf{C}_{3v}, \quad (a_3^2c_6)(a_1a_3) = (1+x)(1+x^3)^3(1+x^6),$$
$$\text{for } \mathbf{D}_{2d}, \quad (a_4c_8)(a_4) = (1+x^4)^2(1+x^8),$$
$$\text{for } \mathbf{T}, \quad (b_{12})(b_4) = (1+x^{12})(1+x^4+r^4+s^4), \text{ and}$$
$$\text{for } \mathbf{T}_d, \quad (a_{12})(a_4) = (1+x^{12})(1+x^4),$$

in which the left-hand sides denote the SCI-CFs for the respective subsymmetries. Note that the first parentheses on the left-hand side of each equation contain the USCI-CF of $\mathbf{T}_d(/\mathbf{C}_{3v})$, while the second ones enclose the USCI-CF of $\mathbf{T}_d(/\mathbf{C}_s)$.

For simplicity of discussion, suppose, for example, that the **1** orbit can take a chiral substituent (R) and its

Table 7. Enumeration of Isomers with Achiral and Chiral Substituents

Index term	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$x^m(r^4+s^4)$:											
m=12; 0	0	0	0	0	0	0	0	0	0	1	0
11; 1	1	0	0	0	0	0	0	0	0	0	0
10; 2	4	3	0	0	0	0	0	0	0	0	0
9; 3	17	0	0	4	0	0	0	0	0	0	0
8; 4	38	6	0	0	0	1	0	0	0	0	0
7; 5	66	0	0	0	0	0	0	0	0	0	0
6	70	10	0	6	0	0	0	0	0	0	0
$x^m(r^3s+rs^3)$:											
m=12; 0	0	0	0	1	0	0	0	0	0	0	0
11; 1	4	0	0	0	0	0	0	0	0	0	0
10; 2	22	0	0	0	0	0	0	0	0	0	0
9; 3	72	0	0	4	0	0	0	0	0	0	0
8; 4	165	0	0	0	0	0	0	0	0	0	0
7; 5	264	0	0	0	0	0	0	0	0	0	0
6	306	0	0	6	0	0	0	0	0	0	0
$x^m(r^3+s^3)$:											
m=13; 0	0	0	0	1	0	0	0	0	0	0	0
12; 1	4	0	0	1	0	0	0	0	0	0	0
11; 2	26	0	0	0	0	0	0	0	0	0	0
10; 3	94	0	0	4	0	0	0	0	0	0	0
9; 4	237	0	0	4	0	0	0	0	0	0	0
8; 5	429	0	0	0	0	0	0	0	0	0	0
7; 6	570	0	0	6	0	0	0	0	0	0	0
$x^m(r^2s^3)$:											
m=12; 0	0	0	0	0	1	0	0	0	0	0	0
11; 1	3	0	0	0	0	0	0	0	0	0	0
10; 2	15	3	0	0	0	0	0	0	0	0	0
9; 3	55	0	0	0	0	0	0	0	0	0	0
8; 4	120	6	0	0	3	0	0	0	0	0	0
7; 5	198	0	0	0	0	0	0	0	0	0	0
6	226	10	0	0	0	0	0	0	0	0	0
$x^m(r^2s+sr^2)$:											
m=13; 0	1	0	0	0	0	0	0	0	0	0	0
12; 1	13	0	0	0	0	0	0	0	0	0	0
11; 2	78	0	0	0	0	0	0	0	0	0	0
10; 3	286	0	0	0	0	0	0	0	0	0	0
9; 4	715	0	0	0	0	0	0	0	0	0	0
8; 5	1287	0	0	0	0	0	0	0	0	0	0
7; 6	1716	0	0	0	0	0	0	0	0	0	0
$x^m(r^2+s^2)$:											
m=14; 0	0	1	0	0	0	0	0	0	0	0	0
13; 1	7	0	0	0	0	0	0	0	0	0	0
12; 2	42	7	0	0	0	0	0	0	0	0	0
11; 3	182	0	0	0	0	0	0	0	0	0	0
10; 4	490	21	0	0	0	0	0	0	0	0	0
9; 5	1001	0	0	0	0	0	0	0	0	0	0
8; 6	1484	35	0	0	0	0	0	0	0	0	0
7	1716	0	0	0	0	0	0	0	0	0	0
$x^m(rs)$:											
m=14; 0	0	0	1	0	0	0	0	0	0	0	0
13; 1	5	0	4	0	0	0	0	0	0	0	0
12; 2	40	0	11	0	0	0	0	0	0	0	0
11; 3	170	0	24	0	0	0	0	0	0	0	0
10; 4	480	0	41	0	0	0	0	0	0	0	0
9; 5	971	0	60	0	0	0	0	0	0	0	0
8; 6	1464	0	75	0	0	0	0	0	0	0	0
7	1676	0	80	0	0	0	0	0	0	0	0

Table 7. (Continued)

Index term	C_1	C_2	C_s	C_3	S_4	D_2	C_{2v}	C_{3v}	D_{2d}	T	T_d
$x^m(r+s)$:											
m=15; 0	0	0	0	1	0	0	0	0	0	0	0
14; 1	5	0	0	0	0	0	0	0	0	0	0
13; 2	35	0	0	0	0	0	0	0	0	0	0
12; 3	150	0	0	5	0	0	0	0	0	0	0
11; 4	455	0	0	0	0	0	0	0	0	0	0
10; 5	1001	0	0	0	0	0	0	0	0	0	0
9; 6	1665	0	0	10	0	0	0	0	0	0	0
8; 7	2145	0	0	0	0	0	0	0	0	0	0
x^m:											
m=16; 0	0	0	0	0	0	0	0	0	0	0	1
15; 1	0	0	1	0	0	0	0	1	0	0	0
14; 2	2	1	4	0	0	0	2	0	0	0	0
13; 3	17	0	11	1	0	0	0	3	0	0	0
12; 4	62	4	20	1	1	0	3	2	1	0	1
11; 5	161	0	42	0	0	0	0	0	0	0	0
10; 6	301	11	48	3	0	0	6	4	0	0	0
9; 7	442	0	66	3	0	0	0	4	0	0	0
8	494	12	68	0	2	0	6	0	2	0	0

antipode (S) in addition to the achiral ones, while the **2** orbit has two achiral substituents (H and X) only. Then, the figure inventories for this case are represented by:

$$a_k = 1 + x^k$$
$$b_k = 1 + x^k + r^k + s^k \quad \text{and}$$
$$c_k = 1 + x^k + 2(rs)^{k/2} \qquad \text{for the orbit (1),}$$

and:

$$a_k = b_k = c_k = 1 + x^k \qquad \text{for the orbit (2).}$$

These equations are introduced into the above SCIs and expanded into generating functions for counting the number of fixed points. Note that the $x^l r^m s^n$ and $x^l r^n s^m$ terms express a pair of antipodes. Hence, the coefficients of the paired terms are summed up to give the number of fixed points. If m is equal to n, the coefficient of $x^l r^m s^m$ represents the number. For example, the pair of x^9r^3s and x^9rs^3 has an FPV as follows.

$$\text{FPV} = (1760\ 0\ 0\ 8\ 0\ 0\ 0\ 0\ 0\ 0\ 0)$$

This vector is multiplied by the inverse (Table 3), giving a row vector, (72 0 0 4 0 0 0 0 0 0 0). The resulting vector indicates that there exist 72 C_1 molecules and 4 C_3 molecules both of which correspond to x^9r^3s (or x^9rs^3). Table 7 summarizes the results of the present enumerations.

In order to illustrate the results of Table 7, Fig. 3 collects C_3 molecules with $x^{15}r$ (or r), $x^{12}r$ (or x^3r), and x^9r (or x^6r), in which only one antipode is selected from every racemic pair. Their numbers appear in the C_3 column of Table 7.

Figure 4 shows another type of C_3 molecules, consisting of achiral substituents only. Their numbers also appear in the C_3 column of Table 7.

Table 7 indicates that there are two D_2 molecules in the present enumeration. These molecules have the x^8r^4 and x^4r^4 terms. The concrete forms are found in Fig. 5. Figure 5 also contains **T** molecules which are predicted by the systematic enumeration shown in Table 7. It should be noted that the enumeration of the previous section created no **T** isomers.

A Selection Rule for the Existence of Molecules with a Subsymmetry. The above procedure reveals which subsymmetries of a present skeleton exist if a set of substituents is given. However, the results vary with the set of substituents. This section aims at showing that USCIs and USCI-CFs are versatile tool for predicting the existence or non-existence of the subsymmetries.

Let us consider the first case in which the $T_d(/C_s)$ and $T_d(/C_{3v})$ orbits of the adamantane skeleton are replaced with achiral ligands. An index for a subsymmetry is defined as a set of USCIs punctuated with semicolons. Figure 6 depicts the subgroup lattice of T_d, which also contains indices for the subsymmetry of T_d. The indices are obtained from the $T_d(/C_s)$ and $T_d(/C_{3v})$ rows of Table 5.

The indices collected in Fig. 6 indicate the modes of the substitution of the respective subsymmetry. For example, the index $(s_4s_8; s_4)$ for D_{2d} corresponds to the $(X_4Y_8; Z_4)$ substitution, in which Z may be the same as X or Y; however X must be different from Y. For example, all of the D_{2d} molecules collected in Fig. 1 satisfy this criterion.

The discussions of the previous paragraph afford a selection rule for the allowance of subsymmetries. Thus, the **T** symmetry of Fig. 6 has an index of $s_{12}; s_4$,

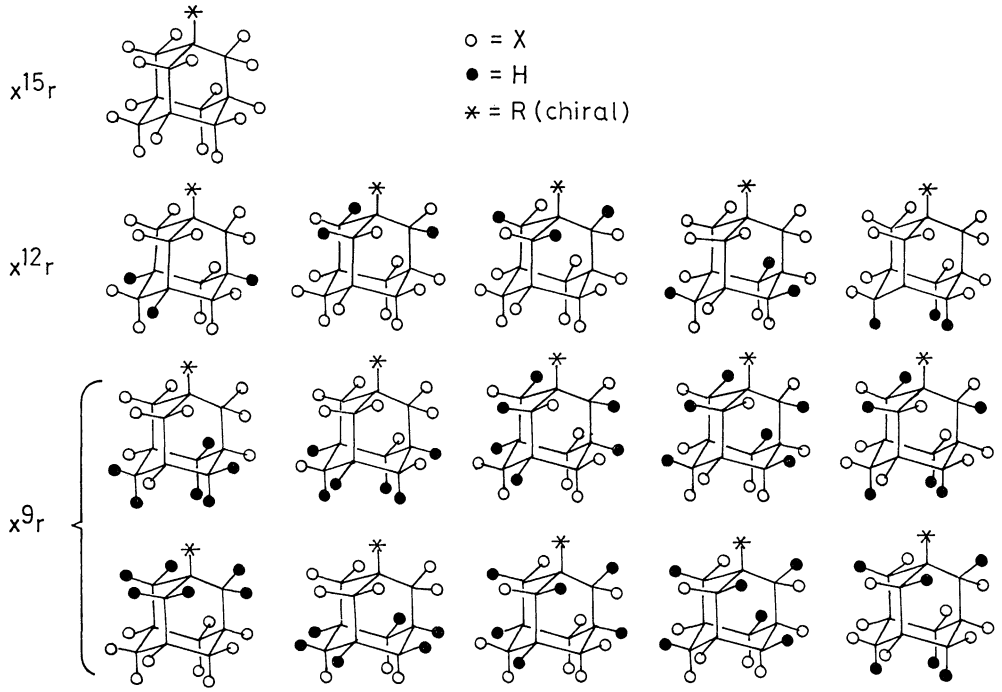


Fig. 3. Selected isomers of C_3 symmetry with chiral and achiral substituents on an adamantane skeleton.

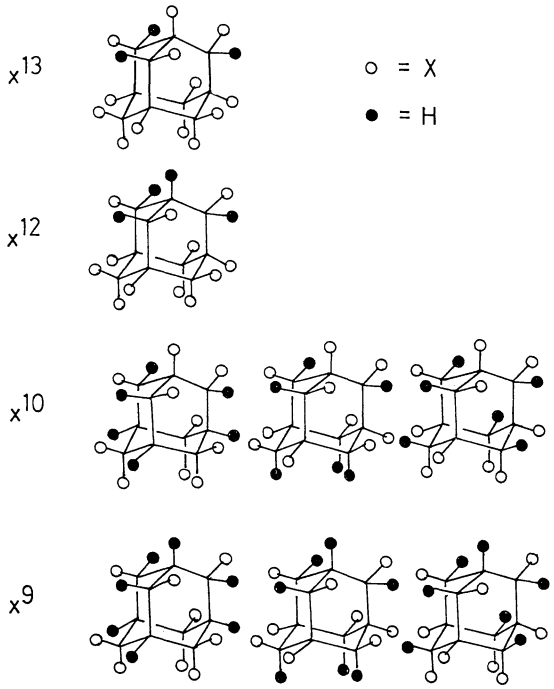


Fig. 4. Selected isomers of C_3 symmetry with achiral substituents on an adamantane skeleton.

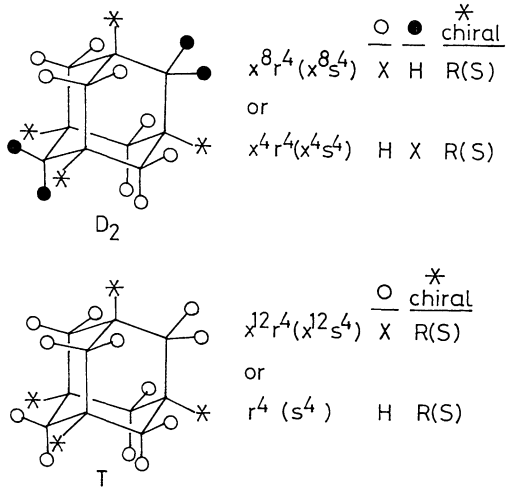


Fig. 5. Isomers of D_2 and T symmetry with achiral and chiral substituents on an adamantane skeleton.

which is identical with that of the T_d symmetry. This fact indicates that no **T** molecules are allowed in this series. It is possible that molecules with other subsymmetries of this series exist, since the respective indices are different from those of the supergroups.

On the other hand, if we permit additional chiral substituents, **T** molecules can exist, as is shown in Table 7.[17] This can be explained by the fact that the **T** symmetry has an index, $b_{12}; b_4$, which is different from that $(a_{12}; a_4)$ of the T_d symmetry.

Conclusion

The subduction of coset representations (SCR) and a unit subduced cycle index are introduced to enumerate isomers based on T_d skeletons. The enumeration is concerned with the molecular symmetry as well as

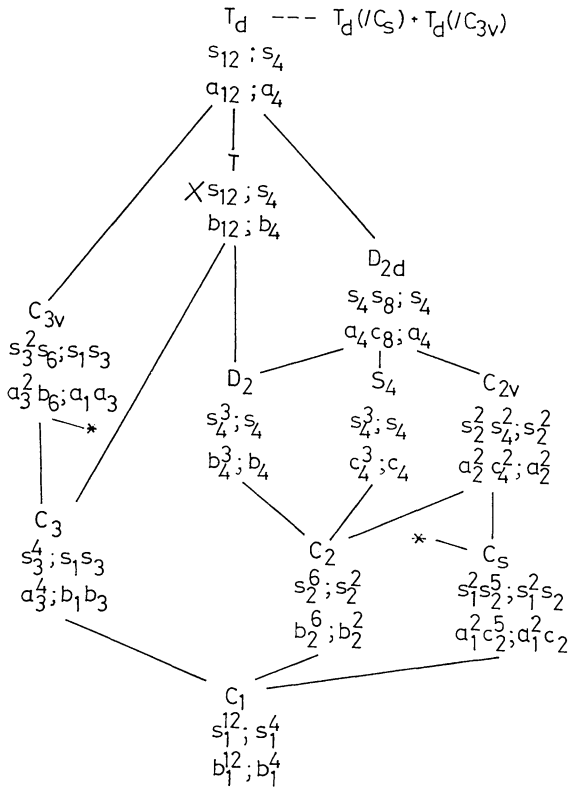


Fig. 6. Allowed and forbidden subsymmetries of an adamantane skeleton ($\mathbf{T}_d$). The x-ed subsymmetry is forbidden.

with the molecular formulas. A vertex strategy is illustrated to produce isomers of various subsymmetries. A unit subduced cycle index with chirality fittingness is also discussed in an attempt to enumerate isomers having chiral in addition to achiral substituents. Although we have restricted ourselves to the enumeration based on an adamantane skeleton, the present method can be applied to other $\mathbf{T}_d$ skeletons as well as to those of other point groups.

Appendix 1

This appendix affords a method of enumerating isomers with achiral substituents only. The enumeration is done taken into account the constitutions of the isomers as well as their symmetries.

Coset Representations. Let $\mathbf{G}$ be a group of a finite order. Suppose that a set of subgroups is defined as

$$\mathrm{SSG} = \{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_s\},$$

the elements of which are representatives of the respective conjugate subgroups, wherein $\mathbf{G}_1$ is an identity group and $\mathbf{G}_s$ is equal to $\mathbf{G}$. The corresponding set of coset representations (CR), i.e.,

$$\mathrm{SCR} = \{\mathbf{G}(/\mathbf{G}_1), \mathbf{G}(/\mathbf{G}_2), \cdots, \mathbf{G}(/\mathbf{G}_s)\},$$

is a full list of the transitive permutation representations of the group ($\mathbf{G}$).

Let $\mathbf{P}_A$ be a permutation representation of $\mathbf{G}$. Then, $\mathbf{P}_A$ can be reduced in terms of:

$$\mathbf{P}_A = \sum_{i=1}^{s} \alpha_i \mathbf{G}(/\mathbf{G}_i). \tag{1.1}$$

The multiplicities α_i are calculated by means of the following equations:

$$\mu_j = \sum_{i=1}^{s} \alpha_i m_{ij} \qquad (j = 1, 2, \cdots, s). \tag{1.2}$$

The matrix (m_{ij}) is called *a table of marks*, which is denoted as M. We define a multiplicity vector (MV) and a fixed-point vector (FPV) as:

$$\mathrm{MV} = (\alpha_1\ \alpha_2 \cdots \alpha_s)$$

and

$$\mathrm{FPV} = (\mu_1\ \mu_2 \cdots \mu_s).$$

Equation 1.2 is thereby transformed into

$$\underset{\mathrm{MV}}{(\alpha_1\ \alpha_2 \cdots \alpha_s)} = \underset{\mathrm{FPV}}{(\mu_1\ \mu_2 \cdots \mu_s)} \underbrace{\begin{bmatrix} \overline{m}_{11} & \overline{m}_{12} & \cdots & \overline{m}_{1s} \\ \overline{m}_{21} & \overline{m}_{22} & \cdots & \overline{m}_{2s} \\ & \cdots & & \\ \overline{m}_{s1} & \overline{m}_{s2} & \cdots & \overline{m}_{ss} \end{bmatrix}}_{\overline{\mathrm{M}}}, \tag{1.3}$$

wherein the matrix $(\overline{\mathrm{M}})$ is the inverse of the table of marks.

Subduction of Coset Representations and Unit Subduced Cycle Indices. Although a coset representation $\mathbf{G}(/\mathbf{G}_i)$ is transitive, a subduced representation (SR) by a subgroup $\mathbf{G}_j \leqslant \mathbf{G}$ is generally intransitive. Let the symbol $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ denote the subduced representation. Let us consider the set of subgroups of $\mathbf{G}_j$ represented by:

$$\mathrm{SSG}_j = \{\mathbf{G}_1^{(j)}, \mathbf{G}_2^{(j)}, \cdots, \mathbf{G}_{v_j}^{(j)}\} \qquad (j = 1, 2, \cdots, s), \tag{1.4}$$

where the first element, $\mathbf{G}_1^{(j)}$, is an identity group, while the last one, $\mathbf{G}_{v_j}^{(j)}$, is identical with $\mathbf{G}_j$. Then, Eqs. 1.1 and 1.3 are converted so as to apply in the SR. The SR is thus reduced into coset representations in the light of:

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j = \sum_{k=1}^{v_j} \beta_k^{(ij)} \mathbf{G}_j(/\mathbf{G}_k^{(j)}) \qquad (j = 1, 2, \cdots, s) \tag{1.5}$$

and:

$$(\beta_1^{(ij)}\ \beta_2^{(ij)} \cdots \beta_{v_j}^{(ij)}) = (\nu_1^{(ij)}\ \nu_2^{(ij)} \cdots \nu_{v_j}^{(ij)})\overline{\mathrm{M}}^{(j)} \qquad (j = 1, 2, \cdots, s), \tag{1.6}$$

where $\beta_k^{(ij)}$ is the multiplicity of $\mathbf{G}_j(/\mathbf{G}_k^{(j)})$ in the SR and where the symbol $\overline{\mathrm{M}}^{(j)}$ denotes the inverse of a table of marks for the $\mathbf{G}_j$ group.

Equation 1.1 provides a division of the positions of a skeleton into a set of orbits, $\Delta_{i\alpha}$. Equation 1.5 indicates subdivision of the $\Delta_{i\alpha}$ orbit into a set of suborbits, $\Delta_{k\beta}^{(i\alpha)}$. Since the $\Delta_{k\beta}^{(i\alpha)}$ suborbit is subject to $\mathbf{G}_j(/\mathbf{G}_k^{(j)})$, its length is equal to the degree of $\mathbf{G}_j(/\mathbf{G}_k^{(j)})$. Hence, it is represented by:

$$d_{jk} = |\mathbf{G}_j| / |\mathbf{G}_k^{(j)}|. \tag{1.7}$$

Suppose that a variable $s_{d_{jk}}^{(i\alpha)}$ is assigned to the suborbit. Thereby, we successively introduce these new concepts, *unit subduced cycle index (USCI), subduced cycle index (SCI)*, and

cycle index (CI), in terms of:

Definition 1.

(1) A unit subduced cycle index (USCI) is defined as:

$$Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\ s_{d_{jk}{}^{(i\alpha)}}) = \prod_{k=1}^{\nu_j} (s_{d_{jk}{}^{(i\alpha)}})^{\beta_k{}^{(ij)}} \quad (1.8)$$
$$(\text{for } i = 1, 2, \cdots, s \text{ and } j = 1, 2, \cdots, s).$$

(2) A subduced cycle index (SCI) is defined as:

$$Z(\mathbf{G}_j;\ s_{d_{jk}{}^{(i\alpha)}}) = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\ s_{d_{jk}{}^{(i\alpha)}}) \quad (1.9)$$
$$(\text{for } j = 1, 2, \cdots, s),$$

where the term on the right-hand side is equal to 1 if α_i is equal to 0.

(3) A cycle index (CI) is defined as:

$$ZI(\mathbf{G};\ s_{d_{jk}{}^{(i\alpha)}}) = \sum_{j=1}^{s} (\sum_{i=1}^{s} \overline{m}_{ji}) Z(\mathbf{G}_j;\ s_{d_{jk}{}^{(i\alpha)}}).$$

Enumeration of Isomers with Achiral Substituents Only. Let $\Delta=\{\delta_1, \delta_2, \cdots, \delta_{|\Delta|}\}$ be a domain, the elements of which are called *positions*. Consider that the m_r values of figures (X_r) selected from a codomain, $\mathbf{X}=\{X_1, X_2, \cdots, X_r, \cdots, X_{|\mathbf{X}|}\}$, occupy the positions of Δ. In a chemical sense, the figures are called *substituents* or *ligands*. The positions are divided and subdivided in the way described in the last section. We assign a weight, $w_{i\alpha}(X_r)$, to a figure (substituent) on the suborbit ($\Delta_{i\alpha}$). The resulting isomers have a molecular formula (or weight), W_θ, which is represented by a monomial of $w_{i\alpha}(X_r)$. The number of fixed points ($\rho_{\theta j}$) concerning $\mathbf{G}_j$ and W_θ is obtained by a generating function as is shown in:

Lemma 1.[11]

$$\sum_{\theta} \rho_{\theta j} W_\theta = Z(\mathbf{G}_j;\ s_{d_{jk}{}^{(i\alpha)}}) \quad (1.11)$$
$$(j = 1, 2, \cdots, s),$$

which is substituted by:

$$s_{d_{jk}{}^{(i\alpha)}} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha}(X_r)^{d_{jk}}. \quad (1.12)$$

The number of isomers with W_θ and $\mathbf{G}_i$ is obtained by the use of

Theorem 1. Let $A_{\theta i}$ be the number of $\mathbf{G}_i$-isomers with W_θ. Then,

$$\begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1s} \\ A_{21} & A_{22} & \cdots & A_{2s} \\ & \cdots & & \\ A_{|\theta|1} & A_{|\theta|2} & \cdots & A_{|\theta|s} \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1s} \\ \rho_{21} & \rho_{22} & \cdots & \rho_{2s} \\ & \cdots & & \\ \rho_{|\theta|1} & \rho_{|\theta|2} & \cdots & \rho_{|\theta|s} \end{bmatrix} \overline{\mathrm{M}}, \quad (1.13)$$

where $\overline{\mathrm{M}}$ is the inverse denoted in Eq. 1.3.

Let A_θ be the total number of isomers with W_θ. This can be calculated by means of the summation:

$$A_\theta = \sum_{i=1}^{s} A_{\theta i}, \quad (1.14)$$

in which the $A_{\theta i}$'s are calculated by means of Eq. 1.12.

The A_θ value is alternatively obtained by the use of

Corollary 1.

$$\sum_{\theta} A_\theta W_\theta = ZI(\mathbf{G};\ s_{d_{jk}{}^{(i\alpha)}}), \quad (1.15)$$

which is replaced by the figure inventory (Eq. 1.12). Corollary 1 can be proved to be equivalent to Pólya's theorem. The proof will be reported elsewhere.

Appendix 2

This appendix is devoted to the enumeration of isomers with achiral and chiral substituents. The chirality fittingness of an orbit is a key concept for deriving theorems for the enumeration.

Chirality Fittingness of an Orbit. Suppose that $\mathbf{G}$ is a point group and that $\mathbf{G}_i$ is its subgroup. An orbit is subject to a coset representation, $\mathbf{G}(/\mathbf{G}_i)$, as has been shown in Appendix 1. The relationship between $\mathbf{G}$ and $\mathbf{G}_i$ determines the mode of substitution on the orbit according to Theorem 2. (The proof will be reported elsewhere.[11b])

Theorem 2. A coset representation, $\mathbf{G}(/\mathbf{G}_i)$, can act on:

a) an orbit that takes only achiral substituents if both $\mathbf{G}$ and $\mathbf{G}_i$ contain improper rotations (an achiral part),

b) an orbit that takes achiral as well as chiral substituents if both $\mathbf{G}$ and $\mathbf{G}_i$ contain only proper rotations (a neutral part), and

c) an orbit that takes achiral as well as chiral ligands if $\mathbf{G}$ contains improper rotations, while $\mathbf{G}_i$ contains only proper rotations (a chiral part).

In a neutral part, the same kind of achiral or chiral substituents freely occupy the orbit. In a chiral part, however, achiral substituents are capable of occupying freely, but chiral ones fulfill the orbit in such a way that a half of the orbit involves the same kind of substituents of a given chirality, while the remaining half contains their antipodes.

Unit Subduced Cycle Indices with Chirality Fittingness. If we consider chiral substituents along with achiral ones, we should assign three types of variables to the suborbits ($\Delta_{k\beta}{}^{(i\alpha)}$) in agreement with their chirality fittingness. Therefore, we then use these variables:

$$a_{d_{jk}{}^{(i\alpha)}},\ b_{d_{jk}{}^{(i\alpha)}},\ \text{and}\ c_{d_{jk}{}^{(i\alpha)}},$$

for achiral, neutral, and chiral parts respectively. Thereby, we can define unit subduced cycle indices with chirality fittingness (USCI-CFs) and so forth as follows.

Definition 2.

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

$$Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\ \$_{d_{jk}{}^{(i\alpha)}}) = \prod_{k=1}^{\nu_j} (\$_{d_{jk}{}^{(i\alpha)}})^{\beta_k{}^{(ij)}} \quad (2.1)$$
$$(\text{for } i = 1, 2, \cdots, s \text{ and } j = 1, 2, \cdots, s),$$

wherein the symbol ($\$) denotes a, b, or c in accord with the chirality fittingness of $\mathbf{G}_j(/\mathbf{G}_k{}^{(j)})$.

(2) A subduced cycle index with chirality fittingness (SCI-CF) is defined as

$$Z(\mathbf{G}_j;\ \$_{d_{jk}{}^{(i\alpha)}}) = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} Z(\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j;\ \$_{d_{jk}{}^{(i\alpha)}}) \quad (2.2)$$
$$(\text{for } j = 1, 2, \cdots, s),$$

where the term of the right-hand side is equal to 1 if α_i is equal to 0.

(3) A cycle index with chirality fittingness (CI-CF) is defined as

$$ZI(\mathbf{G};\ \$_{d_{jk}{}^{(i\alpha)}}) = \sum_{j=1}^{s} (\sum_{i=1}^{s} \overline{m}_{ji}) Z(\mathbf{G}_j;\ \$_{d_{jk}{}^{(i\alpha)}}). \quad (2.3)$$

Enumeration of Isomers with Achiral and Chiral Substituents. Using these indices, we can obtain the number of

fixed points ($\rho_{\theta j}$) in terms of:

Lemma 2.

$$\sum_{\theta} \rho_{\theta j} W_\theta = Z(\mathbf{G}_j; \$_{d_{jk}}{}^{(i\alpha)}) \quad (j = 1, 2, \cdots, s), \tag{2.4}$$

which is substituted by:

$$a_{d_{jk}}{}^{(i\alpha)} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha}(X_r{}^{(a)})^{d_{jk}} \quad \text{for } \$ = a, \tag{2.5}$$

$$b_{d_{jk}}{}^{(i\alpha)} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha}(X_r)^{d_{jk}} \quad \text{for } \$ = b, \tag{2.6}$$

and:

$$c_{d_{jk}}{}^{(i\alpha)} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha}(X_r{}^{(a)})^{d_{jk}} + 2\sum_{r=1}^{|\mathbf{X}|} [w_{i\alpha}(X_r{}^{(c)}) w_{i\alpha}(X_r{}^{(c\#)})]^{d_{jk}/2} \quad \text{for } \$ = c, \tag{2.7}$$

wherein the symbol ($X_r{}^{(a)}$) denotes an achiral substituent, the symbol (X_r) denotes any substituent, and $X_r{}^{(c)}$ is the antipode of $X_r{}^{(c\#)}$.

If achiral and chiral substituents are considered, the number of isomers with W_θ and $\mathbf{G}_i$ is obtained by

Corollary 2. Let $B_{\theta i}$ be the number of $\mathbf{G}_i$-isomers with W_θ. Then,

$$\begin{bmatrix} B_{11} & B_{12} & \cdots & B_{1s} \\ B_{21} & B_{22} & \cdots & B_{2s} \\ & \cdots & & \\ B_{|\theta|1} & B_{|\theta|2} & \cdots & B_{|\theta|s} \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1s} \\ \rho_{21} & \rho_{22} & \cdots & \rho_{2s} \\ & \cdots & & \\ \rho_{|\theta|1} & \rho_{|\theta|2} & \cdots & \rho_{|\theta|s} \end{bmatrix} \overline{\mathrm{M}}, \tag{2.8}$$

where $\overline{\mathrm{M}}$ is the inverse denoted in Eq. 1.3.

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13) The FPV can be easily obtained by inspection. For the symmetry operations of $\mathbf{T}_d$ and the subgroups, see Ref. 5.

14) The summation of a row of the inverse provides a positive value only if the corresponding subgroup is cyclic; otherwise, the value vanishes.

15) The construction of the table of USCIs is a rather laborious task; however, the methodology of the construction is straight-forward. The tables of the USCIs for the other point groups will be reported elsewhere.

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