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Systematic Enumerations of Highly Symmetric Cage-Shaped Molecules by Unit Subduced Cycle Indices

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Cage-shaped hydrocarbons are enumerated, starting from the tetrahedron skeleton (**T**$_d$ symmetry). This enumeration stems from an edge strategy in which six edges of the skeleton are substituted by m methylene and n ethylene units. This is accomplished by a new method based on unit subduced cycle indices. This is a versatile methodology for counting cage-shaped hydrocarbons that have a given subsymmetry and an index term, $x^m y^n$, the latter of which corresponds to the molecular formula $C_{4+m+2n}H_{4+2m+4n}$.

Chiral and achiral molecules of high symmetry have been studied both synthetically[1)] and theoretically.[2)] Two strategies have been applied to the derivation of new compounds of given symmetries. The first is a vertex strategy in which substituents are placed on vertices (nodes) of a parent skeleton.[3)] The second (edge strategy) consists of the insertion of methylene or other units into the edges (bonds) of a parent skeleton. In particular, the latter is a versatile methodology used to guide synthetical studies concerning cage-shaped compounds of high symmetry.[4)] However, there have emerged no comprehensive studies concerning the following problems: *what symmetries are realized and how many isomers are allowed on the basis of a skeleton of a given symmetry.*

In order to settle the former problem, we now report on the applications of unit subduced cycle indices (USCIs), which are drived by the subduction of coset representations (CRs). In addition, the USCIs are also useful for the latter problem, i.e., an enumeration of isomers with a given symmetry as well as a given molecular formula.

A Set of Equivalent Positions Classified by a Coset Representation. In this paper we choose as an example tetrahedrane (**1**), whose skeleton has **T**$_d$ symmetry. The symmetry of the skeleton controls the behavior of its vertices as well as that of its edges. As a result, the vertices and edges are partitioned into several sets of equivalent positions. These sets are called *orbits* according to the terminology of permutation groups. Although all of these orbits are subject to the same **T**$_d$ symmetry, they behave differently. The characterization of such behaviors is important for a comprehensive understanding of the molecular symmetry.

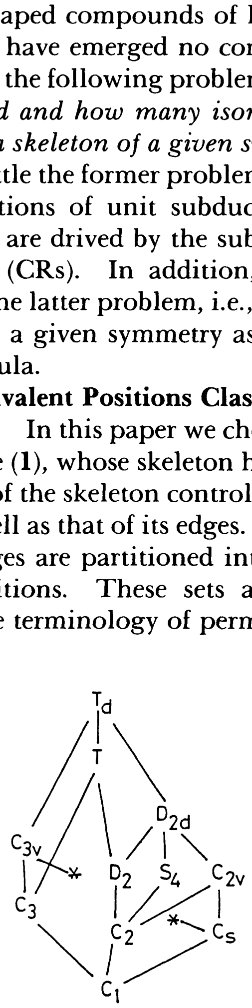
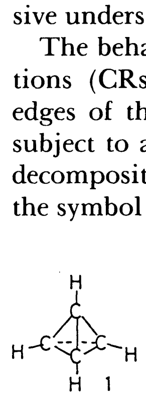


Fig. 1. Subgroup lattice of **T**$_d$ group.

The behaviors can be specified by coset representations (CRs) (Appendix A). For example, the six edges of the skeleton (**1**) belong to an orbit that is subject to a CR obtained by the corresponding coset decomposition of **T**$_d$ by **C**$_{2v}$. The CR is denoted by the symbol (**T**$_d$(/**C**$_{2v}$)) in the present paper.



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6 bonds (edges) on which **T**$_d$(/**C**$_{2v}$) acts,
4 hydrogens (nodes) on which **T**$_d$(/**C**$_{3v}$) acts,
and
4 carbons (nodes) on which **T**$_d$(/**C**$_{3v}$) acts

For the purpose of assigning such a CR to an orbit, we define a set of subgroups (SSG) as a list in which the representative subgroups of a given point group are aligned in ascending order of the orders of the subgroups. Note that the respective representatives are selected in such a way that only one is adopted from every set of conjugate subgroups. For the **T**$_d$ group, the SSG is represented by

$$\mathrm{SSG}=\{\mathbf{C}_1,\mathbf{C}_2,\mathbf{C}_s,\mathbf{C}_3,\mathbf{S}_4,\mathbf{D}_2,\mathbf{C}_{2v},\mathbf{C}_{3v},\mathbf{D}_{2d},\mathbf{T},\mathbf{T}_d\}.$$

The group-subgroup relationship is clarified by the subgroup lattice shown in Fig. 1.

In general, a set of equivalent positions (i.e. an orbit) of a **T**$_d$ skeleton is subject to one of the eleven CRs that are associated with the eleven subgroups collected in the SSG. Thus, a set of CRs for **T**$_d$ symmetry is obtained as follows:

$$\mathrm{SCR}=\{\mathbf{T}_d(/\mathbf{C}_1),\mathbf{T}_d(/\mathbf{C}_2),\mathbf{T}_d(/\mathbf{C}_s),\mathbf{T}_d(/\mathbf{C}_3),\mathbf{T}_d(/\mathbf{S}_4),\mathbf{T}_d(/\mathbf{D}_2),\mathbf{T}_d(/\mathbf{C}_{2v}),\mathbf{T}_d(/\mathbf{C}_{3v}),\mathbf{T}_d(/\mathbf{D}_{2d}),\mathbf{T}_d(/\mathbf{T}),\mathbf{T}_d(/\mathbf{T}_d)\}.$$

Equivalent positions contained in an orbit are interchangeable with each other, if all of the operations of the **T**$_d$ point group are considered. On the other hand, if the operations are restricted to those of a subgroup, several positions of the orbit become fixed. The number of the fixed points is obtained for each of the subgroups collected in the SSG; the number of fixed points is called a *mark* by Burnside.⁵⁾ A row vector which lists these numbers in the same order of the SSG is called a *fixed-point vector* (FPV) in the present paper. The FPV is a clue to the assignment of a CR to an orbit.

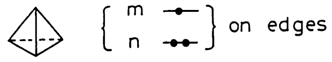
A table of marks (Appendix B), which comes from Burnside's textbook,⁵⁾ is utilized to determine what CR governs an orbit. The table of marks for the $\mathbf{T}_d$ group (Table 1) lists the marks of each CR, the numbers of the fixed points for the operations of the respective subgroups of the SSG. Note that each row of a mark table denotes the FPV of the corresponding CR.

An algorithm for choosing a CR contains the following steps: (1) select a set of equivalent positions (i.e. an orbit), (2) calculate the FPV for each of the orbits, and (3) refer to Table 1 (a mark table) and select the CR in which the row of the table is identical to the FPV. For example, the six edges of the skeleton (**1**) afford the FPV, (62200020000). This is identical to the row of $\mathbf{T}_d(/\mathbf{C}_{2v})$ in Table 1; therefore, the six positions of **1** are subject to $\mathbf{T}_d(/\mathbf{C}_{2v})$. Thus, if we consider a given skeleton, the classification of the positions into orbits and their assignment to CRs (steps 1 to 3) are easily acccomplished by inspection. A more mathematical treatment of steps 1 to 3 is given in Appendix B.

Table 1. Mark Table of $\mathbf{T}_d$

i/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

Enumeration of Cage-Shaped Hydrocarbons. Let us consider the insertion of methylene (—●—) or ethylene units (-●-●-) into C–C bonds of the skeleton (**1**). For example, the insertion of six methylenes affords adamantane (**2**).



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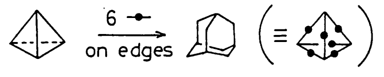


1 (T_d) 2 (T_d)

Although the methodology described in the last paragraph has been widely applied to synthetic studies,⁴⁾ an important problem still remains unsolved: how many isomers with given molecular formula and symmetry are allowed by this methodology? This problem is ascribed to an edge-coloring problem which enumerates the isomers substituted by three colors onto the six edges of **1** (e.g., one color to no substitution, a second color for *m* of —●— and a third color for *n* of -●-●-). We call this type of formulation and *edge strategy* for producing molecules of a given symmetry.⁶⁾

A solution to the problem requires a table of unit subduced cycle indices (Appendices C and D) and the inverse of a mark table. These are given as Tables 2 and 3 for $\mathbf{T}_d$ symmetry.⁷⁾

An algorithm to solve the problem contains the following steps: (1) classify the positions of a skeleton into orbits, (2) find the corresponding CR for each of the orbits, as shown in the last section, (3) read the rows of the obtained CRs from the table of unit subduced cycle indices (USCIs) (e.g., Table 2), (4) construct a subduced cycle index (SCI) from the set of USCIs for each subgroup (Appendix D), (5) introduce a figure inventory into the SCI and expand the result-

Table 2. Unit subduced Cycle Indices for $\mathbf{T}_d$

i/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}
$\mathbf{T}_d(/\mathbf{C}_2)$	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}
$\mathbf{T}_d(/\mathbf{C}_s)$	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}
$\mathbf{T}_d(/\mathbf{C}_3)$	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
$\mathbf{T}_d(/\mathbf{S}_4)$	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
$\mathbf{T}_d(/\mathbf{D}_2)$	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
$\mathbf{T}_d(/\mathbf{C}_{2v})$	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
$\mathbf{T}_d(/\mathbf{C}_{3v})$	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
$\mathbf{T}_d(/\mathbf{D}_{2d})$	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
$\mathbf{T}_d(/\mathbf{T})$	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
$\mathbf{T}_d(/\mathbf{T}_d)$	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1	s_1
$\sum_{i=1}^{s}\overline{m}_{ji}$	1/24	1/8	1/4	1/3	1/4	0	0	0	0	0	0

a) The value of each factor is the summation appearing in the rightmost column of Table 3.

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

j/i	$\mathbf{T}_d(/\mathbf{C}_1)$	$\mathbf{T}_d(/\mathbf{C}_2)$	$\mathbf{T}_d(/\mathbf{C}_s)$	$\mathbf{T}_d(/\mathbf{C}_3)$	$\mathbf{T}_d(/\mathbf{S}_4)$	$\mathbf{T}_d(/\mathbf{D}_2)$	$\mathbf{T}_d(/\mathbf{C}_{2v})$	$\mathbf{T}_d(/\mathbf{C}_{3v})$	$\mathbf{T}_d(/\mathbf{D}_{2d})$	$\mathbf{T}_d(/\mathbf{T})$	$\mathbf{T}_d(/\mathbf{T}_d)$	$\sum_{i=1}^{s} \overline{m}_{ji}$
$\mathbf{C}_1$	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

ing equation to give a fixed-point (FP)-counting polynomial for each subgroup (Appendix E), (6) construct a fixed-point matrix (FPM), the each row of which is the FPV for the monomial term of given powers appearing in the polynomials, and (7) multiply the FPM by the inverse of a mark table (e.g., Table 3) to give a matrix, each element of which indicates the number of isomers of a given molecular formula and a given symmetry. The mathematical foundation of these steps is found in Appendices C, D, and E.

The steps listed above are illustrated by using the skeleton (**1**) as an example. The six edges of **1** are subject to $\mathbf{T}_d(/\mathbf{C}_{2v})$. Hence, the $\mathbf{T}_d(/\mathbf{C}_{2v})$ row of Table 2 is selected in order to construct subduced cycle indices (SCIs). A figure inventory is $s_r = 1 + x^r + y^r$, where x and y are used to count the methylenes and ethylenes, respectively. We then introduce it into the SCIs:

$$\mathbf{C}: s_1^6 = (1+x+y)^6, \qquad (3^6)$$

$$\mathbf{C}_2: s_1^2 s_2^2 = (1+x+y)^2(1+x^2+y^2)^2, \qquad (3^4)$$

$$\mathbf{C}_s: s_1^2 s_2^2 = (1+x+y)^2(1+x^2+y^2)^2, \qquad (3^4)$$

$$\mathbf{C}_3: s_3^2 = (1+x^3+y^3)^2, \qquad (3^2)$$

$$\mathbf{S}_4: s_2 s_4 = (1+x^2+y^2)(1+x^4+y^4), \qquad (3^2)$$

$$\mathbf{D}_2: s_2^3 = (1+x^2+y^2)^3, \qquad (3^3)$$

$$\mathbf{C}_{2v}: s_1^2 s_4 = (1+x+y)^2(1+x^4+y^4), \qquad (3^3)$$

$$\mathbf{C}_{3v}: s_3^2 = (1+x^3+y^3)^2, \qquad (3^2)$$

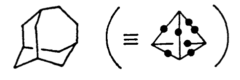
$$\mathbf{D}_{2d}: s_2 s_4 = (1+x^2+y^2)(1+x^4+y^4), \qquad (3^2)$$

$$\mathbf{T}: s_6 = 1+x^6+y^6, \qquad (3)$$

and

$$\mathbf{T}_d: s_6 = 1+x^6+y^6. \qquad (3)$$

These equations are expanded to give the corresponding FP-counting polynomials as generating functions. For example, the FPV for x^5y is (62200020000), the coefficients of the terms (x^5y) of the respective polynomials. Multiplication of FPV by the inverse (Table 3) gives an isomer-counting vector (IMV),(00000010000). The vector shows that there is only one isomer which corresponds to homoadamantane (**3**) with x^5y and $\mathbf{C}_{2v}$ symmetry. Similarly, the IMVs for the other $x^m y^n$ terms are obtained as shown in Table 4. The $x^m y^n$ term is called an *index term*. The resulting isomer is called an *$x^m y^n$ isomer*. The intersection of a subsymmetry column and an $x^m y^n$ row (Table 4) indicates the number of $x^m y^n$ isomers with the subsymmetry.


3 (C_{2v}) [x^5y]

Since the term ($x^m y^n$) indicates the substitution of m of —●— and n of -●-●-, it corresponds to the molecular formula $C_{4+m+2n}H_{4+2m+4n}$.

The total number of isomers is 64, among which 21 belong to chiral subgroups ($\mathbf{C}_1$, $\mathbf{C}_2$, and $\mathbf{D}_2$). Figure 2 depicts $\mathbf{C}_2$ molecules (**4** to **12**), the number of which emerges in the $\mathbf{C}_2$ column of Table 4.

There is only one $\mathbf{D}_2$ molecule which corresponds to the term (x^2y^2), as shown in Table 4. An example of

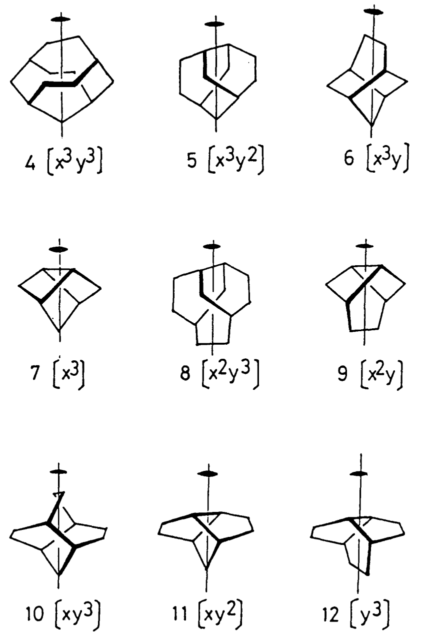

4 [x^3y^3] 5 [x^3y^2] 6 [x^3y]
7 [x^3] 8 [x^2y^3] 9 [x^2y]
10 [xy^3] 11 [xy^2] 12 [y^3]

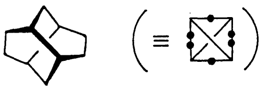
Fig. 2. $\mathbf{C}_2$ Molecules based on a tetrahedron skeleton (**1**).

Table 4. The Numbers of Cage-Shaped Compounds Derived Form the Skeleton (**1**) by an Edge Strategy

Index term	Number of isomers											Total for $x^m y^n$
	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_3$	$\mathbf{S}_4$	$\mathbf{D}_2$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{D}_{2d}$	$\mathbf{T}$	$\mathbf{T}_d$	
x^6; y^6	0	0	0	0	0	0	0	0	0	0	1	1
x^5y; xy^5	0	0	0	0	0	0	1	0	0	0	0	1
x^5; y^5	0	0	0	0	0	0	1	0	0	0	0	1
x^4y^2; x^2y^4	0	0	1	0	0	0	0	0	1	0	0	2
x^4y; xy^4	1	0	0	0	0	0	1	0	0	0	0	2
x^4; y^4	0	0	1	0	0	0	0	0	1	0	0	2
x^3y^3	0	1	0	0	0	0	0	2	0	0	0	3
x^3y^2; x^2y^3	1	1	2	0	0	0	0	0	0	0	0	4
x^3y; xy^3	1	1	2	0	0	0	0	0	0	0	0	4
x^3; y^3	0	1	0	0	0	0	0	2	0	0	0	3
x^2y^2	2	0	3	0	0	1	0	0	0	0	0	6
x^2y; xy^2	1	1	2	0	0	0	0	0	0	0	0	4
x^2; y^2	0	0	1	0	0	0	0	0	1	0	0	2
xy	1	0	0	0	0	0	1	0	0	0	0	2
x; y	0	0	0	0	0	0	1	0	0	0	0	1
1	0	0	0	0	0	0	0	0	0	0	1	1
Total[a)]	11	9	21	0	0	1	9	6	6	0	1	64

a) The total number is the sum of the numbers in each column over all the index terms. Note that the number of $x^m y^n$ isomers is equal to that of $x^n y^m$.

this type is twistane (**13**), which can be derived by the substitution of 2 methylenes and 2 ethylenes on the edges of the skeleton (**1**) in accordance with the index term. It should be noted that neither $\mathbf{C}_3$ nor **T** molecules can exist. This fact will be discussed later.


13 (D_2) $[x^2y^2]$

Among the total 64 isomers, there exist 43 achiral isomers ($\mathbf{C}_s$, $\mathbf{C}_{2v}$, $\mathbf{C}_{3v}$, $\mathbf{D}_{2d}$, and $\mathbf{T}_d$). Figure 3 lists all of the $\mathbf{D}_{2d}$ molecules, the number of which appears in the $\mathbf{D}_{2d}$ column of Table 4. Other achiral isomers can be listed in terms of the index terms. There exist no $\mathbf{S}_4$ isomers, as shown in Table 4. It should be emphasized that the results of Table 4 have been obtained by mathematical manipulation. Hence, they are the probes for verifying manual enumerations, which may sometimes contain duplicated or incomplete counting.

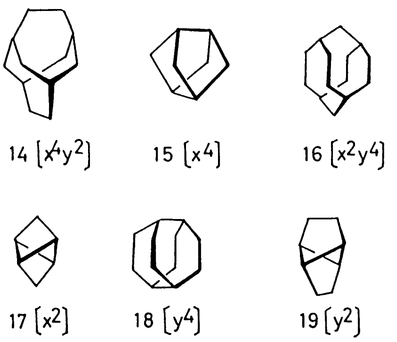
The summation in each column of Table 4 (the bottom) affords the total number of molecules having the corresponding subsymmetry. The number can be obtained by an alternative method (Appendix E). The total number of fixed points concerning each subsymmetry is obtained by introducing $x=y=1$ to the corresponding FP-counting polynomials in order to construct an FPV=(3^6 3^4 3^4 3^2 3^2 3^3 3^3 3^2 3^2 3 3), each element of which is the total number. Multiplication of FPV by the inverse (Table 3) affords an IMV=(11 9 21 0 0 1 9 6 6 0 1), the elements of which are identical to those shown in the bottom row of Table 4.

The total number of molecules with the index term ($x^m y^n$) is calculated in the form of a generating function (Appendix E). We use the $\mathbf{T}_d(/\mathbf{C}_{2v})$ row of Table 2 and the factors collected in the bottom of the same table. We then obtain a cycle index,

$$\mathbf{Z}(\mathbf{T}_d;\, s_r) = (1/24)s_1^6+(1/8)s_1^2s_2^2+(1/4)s_1^2s_2^2+(1/3)s_3^2+(1/4)s_2s_4$$
$$=(1/24)(s_1^6+9s_1^2s_2^2+8s_3^2+6s_2s_4).$$

The mathematical foundation of this derivation is found in Appendix E. This can be proven to be identical to that obtained alternatively by Pólya's theorem.[8,9] After the introduction of a figure inventory, $s_r=1+x^r+y^r$, into the cycle index, the expansion of the resulting equation provides the following generating function,

$$G(x,y)=\mathbf{Z}(\mathbf{T}_d;\, 1+x^r+y^r)$$
$$=(1/24)((1+x+y)^6+9(1+x+y)^2(1+x^2+y^2)^2+8(1+s^3+y^3)^2+6(1+x^2+y^2)(1+x^4+y^4))$$
$$=x^6+x^5y+x^5+2x^4y^2+2x^4y+2x^4+3x^3y^3+4x^3y^2+4x^3y+3x^3+\cdots,$$


14 $[x^4y^2]$ 15 $[x^4]$ 16 $[x^2y^4]$

17 $[x^2]$ 18 $[y^4]$ 19 $[y^2]$

Fig. 3. $\mathbf{D}_{2d}$ Molecules based on a tetrahedron skeleton (**1**).

in which the coefficient of $x^m y^n$ indicates the total number of molecules with $x^m y^n$. These values are identical to those collected in the right-most column of Table 4, which are obtained alternatively by summing up the values in the respective rows.

Selection Rule for Subsymmetries. Table 4 shows that molecules of $\mathbf{C}_3$, $\mathbf{S}_4$, and **T** point groups are absent in the above enumeration.[10] Why are these subsymmetries forbidden? This section is devoted to a rationalization of the problem. Note that we consider only achiral substituents.

The existence and nonexistence of molecules having special subgroups can be predicted by examining USCIs. Figure 4 depicts the subgroup lattice of the $\mathbf{T}_\mathrm{d}$ point group which contains the USCI of each subgroup in the case of $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{2\mathrm{v}})$. The USCI indicates the mode of subdivision of the orbit that is subject to $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{2\mathrm{v}})$. In order to realize a subsymmetry, substituents should occupy the resulting suborbits in accord with the USCI. For example, the USCI (s_3^2) of $\mathbf{C}_{3\mathrm{v}}$ is in agreement with the fact that the mode of substitution is A_3B_3 (Fig. 4), where A and B are achiral substituents.

More concretely, let us examine homoadamantane (**3**) of $\mathbf{C}_{2\mathrm{v}}$ symmetry that has one ethylene (-●-●-), one methylene (—●—) and four methylenes as respective equivalent positions. This subsitution is in accord with the USCI ($s_1^2 s_4$), which appears in Fig. 4. Further examples are found in Fig. 2, in which each molecule of $\mathbf{C}_2$ symmetry has substituents (—●— and/or -●-●-) in the form of $s_1^2 s_2^2$. Figure 3 depicts various $s_2 s_4$ substitutions that lead to $\mathbf{D}_{2\mathrm{d}}$ symmetry.

Since the USCI (s_6) of **T** is identical to that of $\mathbf{T}_\mathrm{d}$ in the case of $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{2\mathrm{v}})$, as shown in Fig. 4, the substitution of A_6 onto the suborbit of **T** produces no **T** but, rather, a superior $\mathbf{T}_\mathrm{d}$ molecule. The same reasoning is applicable to $\mathbf{C}_3$ and $\mathbf{S}_4$ cases. Hence, **T**, $\mathbf{C}_3$, and $\mathbf{S}_4$ subsymmetries are forbidden in case of $\mathbf{T}_\mathrm{d}(/\mathbf{C}_{2\mathrm{v}})$.

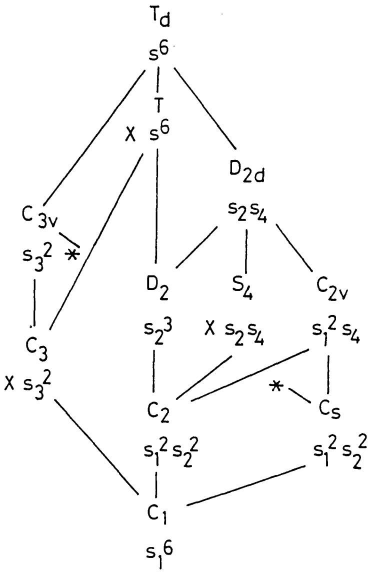


Fig. 4. Allowed and forbidden subsymmetries on the basis of a tetrahedron skeleton (**1**).

In general, because a given skeleton is represented by a set of CRs, a subsymmetry of the skeleton is characterized by a set of USCIs in which the multiplicity of the latter set is identical to that of the former set of CRs. Therefore, if the USCIs of a subgroup are identical to that of any subgroup appearing in an upper level of a subgroup lattice, the former subgroup is forbidden.

Conclusion

Enumerations based on the edge strategy are presented. Thus, a tetrahedrane of $\mathbf{T}_\mathrm{d}$ symmetry gives various cage-shaped hydrocarbons of the subsymmetries of $\mathbf{T}_\mathrm{d}$ by considering substitution on its edges. The enumerations with respect to subsymmetries and to molecular formulas are accomplished by a novel procedure in which unit subduced cycle indices are utilized. Although we have restricted ourselves to manipulating a tetrahedron skeleton ($\mathbf{T}_d$), we can apply the present method to other $\mathbf{T}_\mathrm{d}$ skeletons as well as various skeletons of other symmetries than $\mathbf{T}_\mathrm{d}$.

Appendix A. Coset Representations

Let **H** be a subgroup of a given finite group **G**. Then, the elements of **G** are partitioned into a set of cosets:

$$\Gamma=\{\mathbf{H}g_1, \mathbf{H}g_2, \cdots, \mathbf{H}g_m\}, \qquad \text{(A.1)}$$

where g_1 ($=I$), $\cdots$, and g_m are representatives of the cosets. Any element g ($\in \mathbf{G}$) is multiplied onto each coset of Γ to afford

$$\Gamma'=\{\mathbf{H}g_1g, \mathbf{H}g_2g, \cdots, \mathbf{H}g_mg\}. \qquad \text{(A.2)}$$

The transformation $\Gamma \rightarrow \Gamma'$ is considered to be a permutation represented by

$$\pi_g= \begin{pmatrix} \mathbf{H}g_1, \mathbf{H}g_2, \cdots, \mathbf{H}g_m \\ \mathbf{H}g_1g, \mathbf{H}g_2g, \cdots, \mathbf{H}g_mg \end{pmatrix}, \qquad \text{(A.3)}$$

which constructs a permutation group homomorphic to the group **G**. We call this a coset representation (CR) of **G** by **H**, which is denoted as $\mathbf{G}(/\mathbf{H})$. The degree of $\mathbf{G}(/\mathbf{H})$ is $m=|\mathbf{G}|/|\mathbf{H}|$. The coset representation is transitive, so that it has one orbit.

Appendix B. A Table of Marks

Burnside pointed out the importance of a table of marks.[5] Suppose that $\mathbf{G}_i$ ($i=1, 2, \cdots, s$) are an irredundant set of conjugate subgroups of **G**, where $\mathbf{G}_1=\mathbf{C}_1$ and $\mathbf{G}_s=\mathbf{G}$. We define a set of subgroups as a series of the conjugate subgroups represented by

$$\mathrm{SSG}=\{\mathbf{G}_1, \mathbf{G}_2, \cdots, \mathbf{G}_s\}, \qquad \text{(B.1)}$$

the elements of which are aligned in the ascending order of $|\mathbf{G}_i|$. The corresponding set of coset representations:

$$\mathrm{SCR}=\{\mathbf{G}(/\mathbf{G}_1), \mathbf{G}(/\mathbf{G}_2), \cdots, \mathbf{G}(/\mathbf{G}_s)\} \qquad \text{(B.2)}$$

contains all possible transitive representations of the finite group **G**.

Let the mark of a subgroup **H** in **G** be the number of fixed points of a **G**-set on the action by **H**. When the symbol m_{ij} incidates the mark of subgroup $\mathbf{G}_j$ in $\mathbf{G}(/\mathbf{G}_i)$, we obtain a fixed point vector as

$$\mathrm{FPV}_i=(m_{i1}, m_{i2}, \cdots, m_{is}) \qquad \text{(B.3)}$$

for each $\mathbf{G}(/\mathbf{G}_i)$. If we collects FPVs for all $\mathbf{G}_j$ $(J=1, 2, \cdots, s)$ as row vectors, we arrive at a matrix,

$$\mathrm{MT}=\ (m_{ij})=\begin{pmatrix} m_{11}m_{12} \cdots m_{1s} \\ m_{21}m_{22} \cdots m_{2s} \\ \cdots \\ m_{s1}m_{s2} \cdots m_{ss} \end{pmatrix}, \qquad \text{(B.4)}$$

which is called a table of marks by Burnside and denoted as a mark table in the present paper.

If a set (Δ) of positions appearing in a given skeleton is a **G**-set in the form of a permutation group ($\mathbf{P}_\mathbf{G}$) acting on the set, it is partitioned into several orbits (i.e. sets of equivalent positions) in accord with

$$\mathbf{P}_\mathbf{G}=\sum_{i=1}^{s} \alpha_i\mathbf{G}(/\mathbf{G}_i), \qquad \text{(B.5)}$$

where $\mathbf{G}_i$ $(i=1, 2, \cdots, s)$ belong to the SSG of **G** and $\mathbf{G}(/\mathbf{G}_i)$ are the corresponding coset representations. The multiplicity α_i is obtained by

$$(\mu_1\mu_2\cdots\mu_s)=(\alpha_1\alpha_2\cdots\alpha_s)\mathrm{MT}, \qquad \text{(B.6)}$$

where $(\mu_1\mu_2\cdots\mu_s)$ is a FPV for the set (Δ) and the s×s matix is the mark table represented by Eq. B.4. When we define $\bar{m}_{ji}$ as a ji element of an inverse of the mark table (IMT) derived from Eq. B.4, i.e.,

$$\mathrm{IMT}=\ (\bar{m}_{ji})=\begin{pmatrix} \bar{m}_{11}\bar{m}_{12} \cdots \bar{m}_{1s} \\ \bar{m}_{21}\bar{m}_{22} \cdots \bar{m}_{2s} \\ \cdots \\ \bar{m}_{s1}\bar{m}_{s2} \cdots \bar{m}_{ss} \end{pmatrix}, \qquad \text{(B.7)}$$

Eq. B.6 is converted to

$$(\alpha_1\alpha_2\cdots\alpha_s)=(\mu_1\mu_2\cdots\mu_s)\mathrm{IMT}. \qquad \text{(B.8)}$$

Appendix C. Subduced Representations of a Coset Representation

Let us consider a coset representation $\mathbf{G}(/\mathbf{G}_i)$, the element of which homomorphically corresponds to $|\mathbf{G}|$ elements of **G**. Suppose that we restrict the elements of $\mathbf{G}(/\mathbf{G}_i)$ into a set of elements corresponding to a subgroup ($\mathbf{G}_j$). The restricted set is a representation of the subgroup ($\mathbf{G}_j$). This is called a subduced representation (SR) and is denoted by $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ in the present paper. Although $\mathbf{G}(/\mathbf{G}_i)$ is a transitive representation of **G**, the SR, $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, is an intransitive representation of the subgroup $\mathbf{G}_j$. Equation B.5 is applicable to this case and can be transformed into

$$\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j=\sum_{k=1}^{v_j}\beta_k{}^{(ij)}\mathbf{G}_j(/\mathbf{H}_k{}^{(j)}), \qquad \text{(C.1)}$$

wherein $\mathbf{H}_k{}^{(j)}$ $(k=1, 2, \cdots, v_j)$ are conjugate subgroups of the group $\mathbf{G}_j$. The multiplicity $\beta_k{}^{(ij)}$ $(k=1, 2, \cdots, v_j)$ are obtained by

$$\nu_1=\sum_{k=1}^{v_j}\beta_k{}^{(ij)}m_{k1}{}^{(j)}. \qquad \text{(C.2)}$$

On the basis of this equation, the $k1$ elements, $m_{k1}{}^{(j)}$, construct a table of marks for the subgroup $\mathbf{G}_j$. It should be noted that each $\beta_k{}^{(ij)}$ is constant because $\mathbf{G}(/\mathbf{G}_i)$ and $\mathbf{G}_j(/\mathbf{H}_k{}^{(i)})$ are strictly decided by their components. On the other hand, the term α_i in Eq. B.5 is dependent on **G**-set even if the group **G** is given.

Appendix D. Table of Unit Subduced Cycle Indices and a Subduced Cycle Index

Let us consider $\mathbf{G}_j(/\mathbf{H}_k{}^{(j)})$ appearing in Eq. C.1. An orbit that is subject to $\mathbf{G}_j(/\mathbf{H}_k{}^{(j)})$ has a length represented by

$$d_{jk}=|\mathbf{G}_j|/|\mathbf{H}_k{}^{(j)}|. \qquad \text{(D.1)}$$

Hence, we can ascribe a variable $s_{d_{jk}}$ to $\mathbf{G}_j(/\mathbf{H}_k{}^{(j)})$. The variable $s_{d_{jk}}$ is an index representing a behavior of the orbit on which $\mathbf{G}_j(/\mathbf{H}_k{}^{(j)})$ acts. We then define *a unit subduced cycle index (USCI)* as being

$$\prod_{k=1}^{v_j}(s_{d_{jk}})^{\beta_k{}^{(ij)}}. \qquad \text{(D.2)}$$

The USCI corresponds to Eq. C.1 that represents the subdivision provided by $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$. A collection of the USCIs over all i and all j as shown in Table 5 is useful to various applications. We call such a table *a table of unit subduced cycle indices (USCIs).*

By using USCIs, we define a *subduced cycle index (USCI)* for a subgroup $\mathbf{G}_j$ as follows:

$$Z(\mathbf{G}_j;\ s_{d_{jk}})=\prod_{i=1}^{s}\ [\prod_{k=1}^{v_j}(s_{d_{jk}})^{\beta_k{}^{(ij)}}]^{\alpha_i} \qquad \text{(D.3)}$$

$$=\prod_{k=1}^{v_j}(s_{d_{jk}})^{\sum_{i=1}^{s}\alpha_i\beta_k{}^{(ij)}} \qquad \text{(D.4)}$$

(for $j=1, 2, \cdots, s$),

where each α_i is the multiplicity of $\mathbf{G}(/\mathbf{G}_i)$ obtained by Eq. B.8.

Appendix E. Enumeration of Isomers with a
$\mathbf{G}_i$-Symmetry and a $\mathbf{W}_\theta$-Formula

Suppose that a given skeleton of **G** symmetry has $|\Delta|$ positions (vertices or edges) which construct a domain,

$$\Delta=\{\delta_1, \delta_2, \cdots, \delta_{|\Delta|}\}.$$

Consider that m_r figures of X_r selected from a codomain,

$$\mathbf{X}=\{X_1, X_2, \cdots, X_r, \cdots, X_{|\mathbf{X}|}\},$$

occupy the positions of Δ. The resulting isomers have a molecular formula (or a weight) represented by

Table 5. Table of Unit Subduced Cycle Indices

	$\downarrow\mathbf{G}_1$	$\downarrow\mathbf{G}_2$	$\cdots$	$\downarrow\mathbf{G}_j$	$\cdots$	$\downarrow\mathbf{G}_s$
$\mathbf{G}(/\mathbf{G}_1)$						
$\mathbf{G}(/\mathbf{G}_2)$				$\cdots$		
$\cdots$						
$\mathbf{G}(/\mathbf{G}_i)$	$\cdots$			$\prod_{k=1}^{v_j}(s_{d_{jk}})^{\beta_k{}^{(i,j)}}$	$\cdots$	
$\cdots$						
$\mathbf{G}(/\mathbf{G}_s)$				$\cdots$		

$$W_\theta=\prod_{r=1}^{|\mathbf{X}|}X_r^{m_r}, \tag{E.1}$$

wherein the subscript θ runs over all partitions of $m_1+m_2+\cdots+m_r+m_{|\mathbf{X}|}=|\Delta|$. Our objective is an enumeration of isomers with W_θ and of a given subsymmetry. Suppose that the domain Δ, which is originally a **G**-set, is now considered to be a $\mathbf{G}_j$-set. Thus, the domain, which is divided by the action of **G** (Eq. B.5), is further subdivided into suborbits by $\mathbf{G}_j$. The accumulated actions are characterized by the subduced cycle index (SCI) represented by Eqs. D.3 and D.4. Hence, the number ($\rho_{\theta j}$) of $\mathbf{G}_j$-isomers with a W_θ formula is obtained by a generating function,

$$\sum_\theta \rho_{\theta j}W_\theta=Z(\mathbf{G}_j;\, s_{d_{jk}}) \tag{E.2}$$

$$\text{for } j=1, 2, \cdots, s,$$

which is substituted by

$$s_{d_{jk}}=\sum_{r=1}^{|\mathbf{X}|}X_r^{d_{jk}}. \tag{E.3}$$

We call the generating function *a fixed-point-couting polynomial.* Since the number $\rho_{\theta j}$ suffers from duplicated counting, its correction is accomplised by

$$\rho_{\theta j}=\sum_{i=1}^{s}A_{\theta i}m_{ij} \tag{E.4}$$

$$(\text{for } j=1, 2, \cdots, s),$$

where $A_{\theta i}$ is the number of $\mathbf{G}_i$-isomers with W_θ and m_{ji} is the mark defined in Eq. B.4. The θj-elements ($\rho_{\theta j}$) coonstruct a matrix, which is called a *fixed-point matrix (FPM).* Each row of the FPM is an FPV.

Suppose that $X_r=1$ ($r=1, 2, \cdots$, and $|\mathbf{X}|$) are introduced into Eq. E.3. This operation results in the transformation of Eq. 2 into

$$\sum_\theta \rho_{\theta j}=|\mathbf{X}|^{\sum_{i=1}^{s}\alpha_i\beta_{ij}} \tag{E.5}$$

$$(\text{for } j=1, 2, \cdots, s),$$

where

$$\beta_{ij}=\sum_{k=1}^{v_j}\beta_k^{(ij)}. \tag{E.6}$$

The term β_{ij} represents the number of suborbits. The summation of Eq. E.4 over all θ gives

$$\sum_\theta \rho_{\theta j}=\sum_\theta\sum_{i=1}^{s}A_{\theta i}m_{ij}=\sum_{i=1}^{s}(\sum_\theta A_{\theta i})m_{ij} \tag{E.7}$$

$$(\text{for } j=1, 2, \cdots, s).$$

Since the term $A_i=\sum_\theta A_{\theta i}$ is the total number of $\mathbf{G}_i$-isomers, Eqs. E.5 and E.7 provide

$$|\mathbf{X}|^{\sum_{i=1}^{s}\alpha_i\beta_{ij}}=\sum_{i=1}^{s}A_i m_{ij} \tag{E.8}$$

$$(\text{for } j=1, 2, \cdots, s).$$

When the symbol ρ_j denotes the number of fixed points on the action of $\mathbf{G}_j$, i.e.

$$\rho_j=|\mathbf{X}|^{\sum_{i=1}^{s}\alpha_i\beta_{ij}} \tag{E.9}$$

Equation E.8 can be rewritten by following matrix representation:

$$(\rho_1\rho_2\cdots\rho_s)=(A_1A_2\cdots A_s)\mathrm{MT}, \tag{E. 10}$$

where MT is a table of marks.

The total number (A_θ) of W_θ-isomers is represented by

$$A_\theta=\sum_{i=1}^{s}A_{\theta i}=\sum_{i=1}^{s}\sum_{j=1}^{s}\rho_{\theta i}\bar{m}_{ji}, \tag{E.11}$$

the latter term of which comes from Eq. E.4. Note that $\bar{m}_{ji}$ is the inverse of a table of marks. Hence, a generating function of A_θ takes the following form:

$$\sum_\theta A_\theta W_\theta=\sum_{j=1}^{s}[(\sum_{i=1}^{s}\bar{m}_{ji})\sum_\theta\rho_{\theta j}W_\theta]. \tag{E.12}$$

Because of Eq. E.2,

$$\sum_\theta A_\theta W_\theta=\sum_{j=1}^{s}[(\sum_{i=1}^{s}\bar{m}_{ji})Z(\mathbf{G}_j;\, s_{d_{jk}})], \tag{E.13}$$

where Eq. E.3 is effective. Equation E.13 can be proved to be identical to that obtained alternatively by Polya's theorem; however, the present formulation is quite different and have some advantages over Pólya's theorem. The term

$$\sum_{i=1}^{s}\bar{m}_{ji}$$

is the sum of the $\mathbf{G}_j$-row of the inverse of a table of marks. This term is positive if and only if $\mathbf{G}_j$ is a cyclic group. Otherwise, it vanishes to zero. The relationship between the present method and Polya's method will be discussed elsewhere.[9]

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6) The present enumeration is not concerned with exact conformations. In other words, it is based on the presumption that a molecule has an average conformation. For example, tricyclo[5.5.2.2$^{4.10}$]hexadecane (y^6) is assigned to T_d symmetry in this paper. If we take account of conformation, we find M- and P-conformers of **T** symmetry, which are determined by their helicity. These conformers can be enumerated by using unit subduced cycle indices *with chirality fittingness* (or with helicity fittingness). We will report this type of enumeration later. See S. Fujita, *Bull. Chem. Soc. Jpn.,* in press and S. Fujita, *J. Math. Chem.,* in press.

7) For further applications, tables of USCIs of other point groups should be prepared. The full lists will be

reported elsewhere. For the proof of the equations appearing in Appendices, see S. Fujita, *Theor. Chim. Acta,* in press.

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9) For the proof, S. Fujita *J. Math. Chem.*, in press.

10) The non-existence of the three subsymmetries was reported in a different context. See Ref. 2b.