Systematic Enumerations of Compounds Derived from D_{3h} Skeletons. An Application of Unit Subduced Cycle Indices

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The table of unit subduced cycle indices (USCIs) for D_{3h} is constructed and applied to the enumerations of chemical structures by starting from various parent skeletons of D_{3h} symmetry i.e., a trigonal bipyramid, an iceane skeleton, and a pirsmane skeleton. The substitution positions of these skeletons are divided into orbits governed by coset representations. According to the division of such a skeleton, subduced cycle indices (SCIs) are constructed to enumerate chemical structures with respect to their symmetries. The introduction of figure inventories into the SCIs and the subsequent expansion give generating functions for counting fixed points. The resulting matrix of fixed points is multiplied by the inverse of a mark table to afford the number of isomers with each molecular formula and each subsymmetry.

Since the original introduction of Pólya's theorem,[1] the enumeration of chemical compounds has been one of the major fields that provide a number of exercises exemplifying the capabilities of the theorem.[2] Recently, there have emerged several effective methods of enumerating compounds.[3] These methods allow us to count compounds with respect to molecular formulas as well as to symmetries. In previous papers, we have reported systematic enumerations of compounds by means of unit subduced cycle indices (USCIs).[4] This method would become a general method with great potentialities, if we have prepared a table of USCIs concerning point groups to be examined. However, such tables have been reported for a limited number of point groups: C_2, D_2, D_{2h}, D_3, and T_d.[4,5] Hence, the construction of such a table of USCIs for every point group is an important task in order to make the USCI approach popular. In this connection, the present paper aims at showing the merit of the USCI approach by examining enumerations based on various D_{3h} skeletons.

Results and Discussion

Orbits of D_{3h} skeletons. Although various D_{3h}-molecules have been attracting the attention of organic chemists,[6] there have appeared a few systematic approaches to enumerate their derivatives.[7] Figure 1 lists several D_{3h} molecules. Although all of these molecules belong to the D_{3h}-symmetry, they are quite different in their shapes. This means that the D_{3h} point group itself is insufficient to manipulate their discrete symmetrical properties.

For the purpose of remedying the inherent drawback of the point groups, we have already reported the SCR notation (the notation based on the subduction of coset representations).[8] This notation stems from the fact that an orbit is subject to the corresponding coset representation (CR). For example, the molecule (**1**) is represented by the SCR notation, $D_{3h}[/C_{2v}(X_3); /C_{3v}(Y_2); /D_{3h}(P)]$, which means that three Xs construct an orbit governed by the CR ($D_{3h}(/C_{2v})$), two Ys are subject to the CR ($D_{3h}(/C_{3v})$), and P is governed by the CR ($D_{3h}(/D_{3h})$). Each of these symbols stems from its mode of construction, in which, for example, $D_{3h}(/C_{2v})$ is obtained through a coset decomposition of D_{3h} by C_{2v}.

In order to assign such an SCR notation to a given molecule, we should introduce some mathematical concepts utilized in the permutation-group theory. The D_{3h} group has a set of subgroups,

$$\mathrm{SSG}=\{C_1, C_2, C_s, C's, C_3, C_{2v}, C_{3h}, D_3, D_{3h}\}, \quad (1)$$

in which each subgroup is a representative of all conjugate subgroups. According to this SSG, the full list of coset representations (CRs) is represented by

$$\mathrm{SCR}=\{D_{3h}(/C_1), D_{3h}(/C_2), D_{3h}(/C_s), D_{3h}(/C's), D_{3h}(/C_3), D_{3h}(/C_{2v}), D_{3h}(/C_{3v}), D_{3h}(/C_{3h}), D_{3h}(/D_3), D_{3h}(/D_{3h})\}. \quad (2)$$

The substitution positions (vertices, edges, and faces) of a given skeleton can be divided into orbits which are subject to CRs. Let us examine the trigonal bipyramid (**9**). The assignment of an orbit to the corresponding CR is accomplished by a fixed-point vector (FPV), which lists the number of fixed points for each subgroup during all of the operations appearing in the

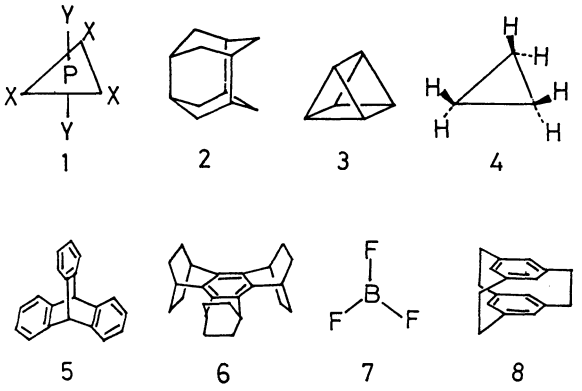

Fig. 1. Several D_{3h} molecules as parent skeletons.

Table 1. The Inverse of the Mark Table for D_{3h} Point Group

	D_{3h} ($/C_1$)	D_{3h} ($/C_2$)	D_{3h} ($/C_s$)	D_{3h} ($/C_s'$)	D_{3h} ($/C_3$)	D_{3h} ($/C_{2v}$)	D_{3h} ($/C_{3v}$)	D_{3h} ($/C_{3h}$)	D_{3h} ($/D_3$)	D_{3h} ($/D_{3h}$)	Sum[a]
C_1	1/12	0	0	0	0	0	0	0	0	0	1/12
C_2	−1/4	1/2	0	0	0	0	0	0	0	0	1/4
C_s	−1/4	0	1/2	0	0	0	0	0	0	0	1/4
C_s'	−1/12	0	0	1/6	0	0	0	0	0	0	1/12
C_3	−1/12	0	0	0	1/4	0	0	0	0	0	1/6
C_{2v}	1/2	−1/2	−1/2	−1/2	0	1	0	0	0	0	0
C_{3v}	1/4	0	−1/2	0	−1/4	0	1/2	0	0	0	0
C_{3h}	1/12	0	0	−1/6	−1/4	0	0	1/2	0	0	1/6
D_3	1/4	−1/2	0	0	−1/4	0	0	0	1/2	0	0
D_{3h}	−1/2	1/2	1/2	1/2	1/2	−1	−1/2	−1/2	−1/2	1	0

a) $\text{sum}=\sum_{i=1}^{s}\overline{m}_{ji}$.

subgroup. We obtain an FPV, (6,2,4,4,3,2,3,1,1,1), for the skeleton (**9**). This vector is multiplied by the inverse of the mark table for the D_{3h} group (Table 1). The resulting vector, (0,0,0,0,0,0,1,1,0,0,1), indicates the multiplicity of each subgroup collected in the SSG. Hence, there appear $D_{3h}(/C_{2v})$, $D_{3h}(/C_{3v})$, and $D_{3h}(/D_{3h})$ in the case of **9**. Obviously, the $D_{3h}(/C_{2v})$ CR governs the set (orbit) of 3 equatorial positions of **9** (●), the $D_{3h}(/C_{3v})$ controls the orbit of 2 axial positions (○) and the $D_{3h}(/D_{3h})$ corresponds to the central position (◓). If we fill up these orbits separately with X_3, Y_2, and P, we can obtain the molecule (**1**). This situation is strictly denoted by the SCR notation, $D_{3h}[/C_{2v}(X_3); /C_{3v}(Y_2); /D_{3h}(P)]$.

With respect to the 12 carbon and 18 hydrogen atoms of iceane (**2**), we have an FPV, (30,0,10,0,0,0,0, 0,0,0,0). This vector is multiplied by the inverse (Table 1) to produce a row vector, (0,0,5,0,0,0,0,0,0,0,0), which indicates the appearance of 5 orbits governed by $D_{3h}(/C_s)$: 6 methine carbons, 6 methylene carbons, 6 methine hydrogens, 6 equatorial methylene hydrogens, and 6 axial methylene hydrogens. Hence, we obtain the SCR notation for iceane (**2**): $D_{3h}[/C_s(2C_6, 3H_6)]$.

In a similar way, the other compounds depicted in Fig. 1 are designated by SCR notations, i.e., $D_{3h}[/C_s(C_6, 3H_6)]$ for prismane (**3**), $D_{3h}[/C_s(H_6); /C_{2v}(C_3)]$ for cyclopropane (**4**), $D_{3h}[/C_s(3C_6, 2H_6); /C_{3v}(C_2, H_2)]$ for triptycene (**5**), $D_{3h}[/C_1(C_{12}, 2H_{12}); /C'_s(2C_6, H_6)]$ for 1,2:3,4:5,6-tris(bicyclo[2.2.2]oct-2-eno)benzene (**6**), $D_{3h}[/C_{2v}(F_3), /D_{3h}(B)]$ for trifluoroborane (**3**), and $D_{3h}[/C_1(H_{12}); /C_s(3C_6)]$ for [2.2.2](1,3,5)cyclophane (**8**).[8]

Construction of a Table of USCIs for D_{3h} Group. The mathematical foundation of USCIs has been reported in the previous paper.[4] A table of USCIs constructed by the following steps: (1) construction of the concrete form of every coset representation ($\mathbf{G}(/\mathbf{G}_i)$), where $\mathbf{G}_i$ is a subgroup listed in the SSG, (2) selection of elements corresponding to another subgroup ($\mathbf{G}_j$) from the elements of $\mathbf{G}(/\mathbf{G}_i)$, affording a subduced representation, $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$, (3) reduction of $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$ into a sum of CRs for $\mathbf{G}_j$, and (4) assignment of dummy variables according to the sum, providing a USCI for $\mathbf{G}(/\mathbf{G}_i)\downarrow\mathbf{G}_j$. This procedure is programed with FORTRAN77 and executed on a VAX11-750 computer. This program is applicable to any point group and will be reported elsewhere. The results are collected in Table 2, which also contains USCIs with chirality fittingness[9] in parentheses. For the purpose of obtaining a cycle index[10], this table at the bottom also involves a factor for every subgroup, each of which is obtained by summing up the corresponding row of Table 1.[11]

Enumeration of Derivatives Based on a Trigonal Bipyramid (9). In the preceding section, the trigonal bipyramid (**9**) has shown to have a $D_{3h}(/C_{2v})$ orbit (●), a $D_{3h}(/C_{3v})$ orbit (○), and a $D_{3h}(/D_{3h})$ orbit (◓). Let us examine $PX_lY_mZ_n$ isomers on this skeleton. Since the phosphorus atom always occupies the $D_{3h}(/D_{3h})$ orbit, we can here take into consideration the remaining two orbits without losing generality.

After the above assignment of the CRs to the orbits, we construct a subduced cycle index (SCI) for every subgroup by means of a table of unit subduced cycle indices (USCIs) preestimated in Table 2.

In this case, we use the $D_{3h}(/C_{2v})$ and $D_{3h}(/C_{3v})$ rows of this table for preparing SCIs. When we introduce a figure inventory:

$$s_d = x^d + y^d + z^d \tag{3}$$

into the SCIs, we obtain generating functions for FPV (ρ_{θ_j}),

$$(s_1^3)(s_1^2) = (x + y + z)^5 \text{ for } \mathbf{C}_1,$$

$$(s_1s_2)(s_2) = (x + y + z)(x^2 + y^2 + z^2)^2 \text{ for } \mathbf{C}_2,$$

$$(s_1s_2)(s_1^2) = (x + y + z)^3(x^2 + y^2 + z^2) \text{ for } \mathbf{C}_s,$$

$$(s_1^3)(s_2) = (x + y + z)^3(x^2 + y^2 + z^2) \text{ for } \mathbf{C}_s',$$

Table 2. Unit Subduced Cycle Indices of $\mathbf{D}_{3h}$

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}'_s$	$\mathbf{C}_3$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{C}_{3h}$	$\mathbf{D}_3$	$\mathbf{D}_{3h}$
$\mathbf{D}_{3h}(/\mathbf{C}_1)$	s_1^{12}	s_2^6	s_2^6	s_2^6	s_3^4	s_4^3	s_6^2	s_6^2	s_6^2	s_{12}
	(b_1^{12})	(b_2^6)	(c_2^6)	(c_2^6)	(b_3^4)	(c_4^3)	(c_6^2)	(c_6^2)	(b_6^2)	(c_{12})
$\mathbf{D}_{3h}(/\mathbf{C}_2)$	s_1^6	$s_1^2s_2^2$	s_2^3	s_2^3	s_3^2	s_2s_4	s_6	s_6	s_3^2	s_6
	(b_1^6)	$(b_1^2b_2^2)$	(c_2^3)	(c_2^3)	(b_3^2)	(c_2c_4)	(c_6)	(c_6)	(b_3^2)	(c_6)
$\mathbf{D}_{3h}(/\mathbf{C}_s)$	s_1^6	s_2^3	$s_1^2s_2^2$	s_2^3	s_3^2	s_2s_4	s_3^2	s_6	s_6	s_6
	(b_1^6)	(b_2^3)	$(a_2^2c_2^2)$	(c_2^3)	(b_3^2)	(a_2c_4)	(a_3^2)	(c_6)	(b_6)	(a_6)
$\mathbf{D}_{3h}(/\mathbf{C}'_s)$	s_1^6	s_2^3	s_2^3	s_1^6	s_3^2	s_2^3	s_6	s_3^2	s_3^2	s_6
	(b_1^6)	(b_2^3)	(c_2^3)	(a_1^6)	(b_3^2)	(a_2^3)	(c_6)	(a_3^2)	(b_3^2)	(a_6)
$\mathbf{D}_{3h}(/\mathbf{C}_3)$	s_1^4	s_2^2	s_2^2	s_2^2	s_1^4	s_4	s_2^2	s_2^2	s_2^2	s_4
	(b_1^4)	(b_2^2)	(c_2^2)	(c_2^2)	(b_1^4)	(c_4)	(c_2^2)	(c_2^2)	(b_2^2)	(c_4)
$\mathbf{D}_{3h}(/\mathbf{C}_{2v})$	s_1^3	s_1s_2	s_1s_2	s_1^3	s_3	s_1s_2	s_3	s_3	s_3	s_3
	(b_1^3)	(b_1b_2)	(a_1c_2)	(a_1^3)	(b_3)	(a_1a_2)	(a_3)	(a_3)	(b_3)	(a_3)
$\mathbf{D}_{3h}(/\mathbf{C}_{3v})$	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_1^2	s_2	s_2	s_2
	(b_1^2)	(b_2)	(a_1^2)	(c_2)	(b_1^2)	(a_2)	(a_1^2)	(c_2)	(b_2)	(a_2)
$\mathbf{D}_{3h}(/\mathbf{C}_{3h})$	s_1^2	s_2	s_2	s_1^2	s_1^2	s_2	s_2	s_1^2	s_2	s_2
	(b_1^2)	(b_2)	(c_2)	(a_1^2)	(b_1^2)	(a_2)	(c_2)	(a_1^2)	(b_2)	(a_2)
$\mathbf{D}_{3h}(/\mathbf{D}_3)$	s_1^2	s_1^2	s_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)	(c_2)	(b_1^2)	(c_2)	(c_2)	(c_2)	(b_1^2)	(c_2)
$\mathbf{D}_{3h}(/\mathbf{D}_{3h})$	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)	(a_1)	(b_1)	(a_1)	(a_1)	(a_1)	(b_1)	(a_1)
$\sum_{i=1}^{s} \overline{m}_{ji}$	1/12	1/4	1/4	1/12	1/6	0	0	1/6	0	0

$(s_3)(s_1^2) = (x + y + z)^2(x^3 + y^3 + z^3)$ for $\mathbf{C}_3$,

$(s_1s_2)(s_2) = (x + y + z)(x^2 + y^2 + z^2)^2$ for $\mathbf{C}_{2v}$,

$(s_3)(s_1^2) = (x + y + z)^2(x^3 + y^3 + z^3)$ for $\mathbf{C}_{3v}$,

and

$(s_3)(s_2) = (x^2 + y^2 + z^2)(x^3 + y^3 + z^3)$ for $\mathbf{C}_{3h}$, $\mathbf{D}_3$, and $\mathbf{D}_{3h}$,

where the first parentheses in the left-hand side of each equation is concerned with the $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ row of Table 2 and the second with the $\mathbf{D}_{3h}(/\mathbf{C}_{3v})$ row. The generating functions are expanded to give the number (ρ_{θ_j}) of fixed points as the coefficient of the term $(x^l y^m z^n)$. These are collected in Table 3, in which each column is concerned with a subsymmetry and each row with an $x^l y^m z^n$-weight. This weight corresponds to the molecular formula, $PX_lY_mZ_n$.

Table 3 is regarded as a matrix, which is in turn multiplied by the inverse (Table 1) to give a matrix shown in Table 4. The value at each intersection indicates the number of $PX_lY_mZ_n$-isomers with the corresponding subsymmetry. In the case of any chiral group ($\mathbf{C}_1$, $\mathbf{C}_2$, $\mathbf{C}_3$, or $\mathbf{D}_3$), each estimated number is concerned with every recemic pair throughout the present paper.

Figure 2 illustrates all PX_2Y_2Z-isomers enumerated in Table 4, in which the numbers for respective subsymmetries appear in the [2,2,1] row. Note that an arbitrary antipode from each racemic pair is depicted here.

Table 3. Coefficients for Enumeration Based on the Skeleton (**9**)

j,m,n	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}'_s$	$\mathbf{C}_3$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{C}_{3h}$	$\mathbf{D}_3$	$\mathbf{D}_{3h}$
5,0,0	1	1	1	1	1	1	1	1	1	1
4,1,0	5	1	3	3	2	1	2	0	0	0
4,0,1	5	1	3	3	2	1	2	0	0	0
3,2,0	10	2	4	4	1	2	1	1	1	1
3,1,1	20	0	6	6	2	0	2	0	0	0
3,0,2	10	2	4	4	1	2	1	1	1	1
2,3,0	10	2	4	4	1	2	1	1	1	1
2,2,1	30	2	6	6	0	2	0	0	0	0
2,1,2	30	2	6	6	0	2	0	0	0	0
2,0,3	10	2	4	4	1	2	1	1	1	1
1,4,0	5	1	3	3	2	1	2	0	0	0
1,3,1	20	0	6	6	2	0	2	0	0	0
1,2,2	30	2	6	6	0	2	0	0	0	0
1,1,3	20	0	6	6	2	0	2	0	0	0
1,0,4	5	1	3	3	2	1	2	0	0	0
0,5,0	1	1	1	1	1	1	1	1	1	1
0,4,1	5	1	3	3	2	1	2	0	0	0
0,3,2	10	2	4	4	1	2	1	1	1	1
0,2,3	10	2	4	4	1	2	1	1	1	1
0,1,4	5	1	3	3	2	1	2	0	0	0
0,0,5	1	1	1	1	1	1	1	1	1	1

The total number of each row of Table 4 can be obtained by the direct summation of the row and alternatively by meas of a generation function.[9] The latter method requires a cycle index,

$$\mathrm{CI}(\mathbf{D}_{3h}; s_d) = (1/12)(s_1^3)(s_1^2) + (1/4)(s_1s_2)(s_2) + (1/4)(s_1s_2)(s_1^2) + (1/12)(s_1^3)(s_2) + (1/6)(s_3)(s_1^2) + (1/6)(s_3)(s_2), \quad (4)$$

where the coefficients of the right-hand side are

Table 4. The Number of $X_lY_mZ_n$-Isomers Based on the Skeleton (**9**)

l,m,n	C_1	C_2	C_s	C_s'	C_3	C_{2v}	C_{3v}	C_{3h}	D_3	D_{3h}	Total
5,0,0	0	0	0	0	0	0	0	0	0	1	1
4,1,0	0	0	0	0	0	1	1	0	0	0	2
4,0,1	0	0	0	0	0	1	1	0	0	0	2
3,2,0	0	0	1	0	0	1	0	0	0	1	3
3,2,1	0	0	2	1	0	0	1	0	0	0	4
3,0,2	0	0	1	0	0	1	0	0	0	1	3
2,3,0	0	0	1	0	0	1	0	0	0	1	3
2,2,1	1	0	2	0	0	2	0	0	0	0	5
2,1,2	1	0	2	0	0	2	0	0	0	0	5
2,0,3	0	0	1	0	0	1	0	0	0	1	3
1,4,0	0	0	0	0	0	1	1	0	0	0	2
1,3,1	0	0	2	1	0	0	1	0	0	0	4
1,2,2	1	0	2	0	0	2	0	0	0	0	5
1,1,3	0	0	2	1	0	0	1	0	0	0	4
1,0,4	0	0	0	0	0	1	1	0	0	0	2
0,5,0	0	0	0	0	0	0	0	0	0	1	1
0,4,1	0	0	0	0	0	1	1	0	0	0	2
0,3,2	0	0	1	0	0	1	0	0	0	1	3
0,2,3	0	0	1	0	0	1	0	0	0	1	3
0,1,4	0	0	0	0	0	1	1	0	0	0	2
0,0,5	0	0	0	0	0	0	0	0	0	1	1
Total	3	0	18	3	0	18	9	0	0	9	60

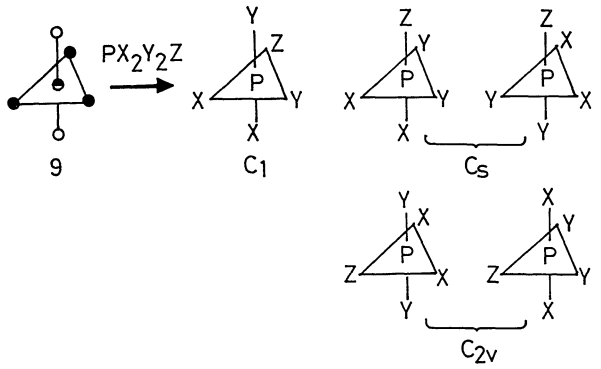

Fig. 2. PX_2Y_2Z-isomers derived from the skeleton **9**.

adopted from the values listed at the bottom of Table 2; and the USCIs used in each term are those of the $D_{3h}(/C_{2v})$ and $D_{3h}(/C_{3v})$ rows.[12] The figure inventory (Eq. 3) is introduced into Eq. 4 to give

$$\begin{aligned} G(x,y,z) &= CI(D_{3h};\ x^d + y^d + z^d) \\ &= x^5 + 2x^4y + 2x^4y + 3x^3y^2 + 4x^3yz + 3x^3z^2 \\ &+ 3x^2y^3 + 5x^2y^2z + 5x^2yz^2 + 3x^2yz^2 + 2xy^4 \\ &+ 4xy^3z + 5xy^2z^2 + 4xyz^3 + 2xz^4 + y^5 + 2y^4z \\ &+ 3y^3z^2 + 3y^2z^3 + 2yz^4 + z^5. \end{aligned} \quad (5)$$

The coefficient of each term ($x^ly^mz^n$) is identical with the rightmost value of the [*l*, *m*, *n*] row which is obtained by the direct summation.

The total value for every subsymmetry is obtained from an FPV: (3^5,3^3,3^4,3^4,3^3,3^3,3^3,3^2,3^2,3^2), which is obtained by introducing $x=y=z=1$ into the above SCIs.[13] The FPV is multiplied by the inverse (Table 1) to afford (3,0,18,3,0,18,9,0,0,0,9). These values are indentical with those appearing at the bottom of Table 4.

Enumeration of Derivatives Based on an Iceane Skeleton (2). In chemical enumerations, there are several cases that should take accoumt of obligatory minimum valency (OMV).[14] The present USCI approach can easily treat such enumeration problems. Let us work out an iceane skeleton (**2**) of D_{3h}-symmetry, in which we take 12 vertices (carbon atoms) into consideration. Obviously, the bridgehead vertices can take tri- or more-valent atoms but cannot take mono- or di-valent atoms in the light of the OMV restriction. On the other hand, di- or more-valent atoms can occupy the bridge positions. The SCR notation for **2**, $D_{3h}[/C_s(2C_6, 3H_6)]$, indicates that the orbits of 6 bridgehead positions (methines: Δ_1) and of 6 bridge positions (methylenes: Δ_2) are both subjects to $D_{3h}(/C_s)$. Let X={C,N,O} be a codomain which contains all substituents. According to the OMV restriction, the orbit (Δ_1) can take C and N; on the other hand, Δ_2 can take O in addition to C and N. We thereby determine weights for the orbits,

$$w_1(C) = x,\ w_1(N) = y,\ w_1(O) = 0,$$

and

$$w_2(C) = x,\ w_2(N) = y,\ w_2(O) = z,$$

which afford two figure inventories,

$$s_d^{(1)} = x^d + y^d, \quad (6)$$

and

$$s_d^{(2)} = x^d + y^d + z^d, \quad (7)$$

where the superscripts (1) and (2) are concerned with Δ_1 and Δ_2. Since the same $\mathbf{D}_{3h}(/\mathbf{C}_s)$ row of Table 2 is adopted for Δ_1 and Δ_2, the SCIs of this case are obtained as follows,

$$(s_1^6)^{(1)}(s_1^6)^{(2)} = (x+y)^6(x+y+z)^6 \text{ for } \mathbf{C}_1,$$

$$(s_2^3)^{(1)}(s_2^3)^{(2)} = (x^2+y^2)^3(x^2+y^2+z^2)^3 \text{ for } \mathbf{C}_2,$$

$$(s_1^2s_2^2)^{(1)}(s_1^2s_2^2)^{(2)} = (x+y)^2(x^2+y^2)^2(x+y+z)^2 \times (x^2+y^2+z^2)^2 \text{ for } \mathbf{C}_s,$$

$$(s_2^3)^{(1)}(s_2^3)^{(2)} = (x^2+y^2)^3(x^2+y^2+z^2)^3 \text{ for } \mathbf{C}_s',$$

$$(s_3^2)^{(1)}(s_3^2)^{(2)} = (x^3+y^3)^2(x^3+y^3+z^3)^2 \text{ for } \mathbf{C}_3,$$

$$(s_2s_4)^{(1)}(s_2s_4)^{(2)} = (x^2+y^2)(x^4+y^4)(x^2+y^2+z^2) \times (x^4+y^4+z^4) \text{ for } \mathbf{C}_{2v},$$

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

and

$$(s_6)^{(1)}(s_6)^{(2)} = (x^6+y^6)(x^6+y^6+z^6) \text{ for } \mathbf{C}_{3h}, \mathbf{D}_3, \text{ and } \mathbf{D}_{3h},$$

in which superscripts (1) and (2) indicates Δ_1 and Δ_2. The right-hand side of each of the SCIs is a generating function, which is obtained by introducing the figure inventories (Eqs. 6 and 7).

Table 5. The Number of $C_lN_mO_n$- and $C_mN_lO_n$-Isomers Based on **2**

l,m,n	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_s$	$\mathbf{C}_s'$	$\mathbf{C}_3$	$\mathbf{C}_{2v}$	$\mathbf{C}_{3v}$	$\mathbf{C}_{3h}$	$\mathbf{D}_3$	$\mathbf{D}_{3h}$	Total
12,0,0	0	0	0	0	0	0	0	0	0	1	1
11,1,0	0	0	2	0	0	0	0	0	0	0	2
11,0,1	0	0	1	0	0	0	0	0	0	0	1
10,2,0	2	2	4	0	0	2	0	0	0	0	10
10,1,1	4	0	3	0	0	0	0	0	0	0	7
10,0,2	0	1	1	0	0	1	0	0	0	0	3
9,3,0	14	0	8	0	0	0	2	0	0	0	24
9,2,1	24	0	7	0	0	0	0	0	0	0	31
9,1,2	10	0	5	0	0	0	0	0	0	0	15
9,0,3	1	0	1	0	0	0	1	0	0	0	3
8,4,0	30	6	14	1	0	3	0	0	0	0	54
8,3,1	76	0	13	0	0	0	0	0	0	0	89
8,2,2	46	7	11	2	0	1	0	0	0	0	67
8,1,3	12	0	6	0	0	0	0	0	0	0	18
8,0,4	0	1	1	0	0	1	0	0	0	0	3
7,5,0	56	0	20	0	0	0	0	0	0	0	76
7,4,1	156	0	18	0	0	0	0	0	0	0	174
7,3,2	140	0	20	0	0	0	0	0	0	0	160
7,2,3	54	0	12	0	0	0	0	0	0	0	66
7,1,4	8	0	4	0	0	0	0	0	0	0	12
7,0,5	0	0	1	0	0	0	0	0	0	0	1
6,60	62	8	18	2	0	2	2	0	0	2	96
6,5,1	220	0	22	0	0	0	0	0	0	0	242
6,4,2	240	14	26	4	0	2	0	0	0	0	286
6,3,3	131	0	17	0	0	0	3	0	0	0	151
6,2,4	28	5	7	1	0	2	0	0	0	0	43
6,1,5	2	0	3	0	0	0	0	0	0	0	5
6,0,6	0	0	0	0	0	0	0	0	0	1	1
5,5,2	300	0	30	0	0	0	0	0	0	0	330
5,4,3	198	0	24	0	0	0	0	0	0	0	222
5,3,4	64	0	12	0	0	0	0	0	0	0	76
5,2,5	8	0	5	0	0	0	0	0	0	0	13
5,1,6	0	0	1	0	0	0	0	0	0	0	1
4,4,4	76	8	12	2	0	2	0	0	0	0	100
4,3,5	14	0	7	0	0	0	0	0	0	0	21
4,2,6	0	1	1	0	0	1	0	0	0	0	3
3,3,6	1	0	1	0	0	0	1	0	0	0	3
0,12,0	0	0	0	0	0	0	0	0	0	1	1
0,11,1	0	0	1	0	0	0	0	0	0	0	1
0,10,2	0	1	1	0	0	1	0	0	0	0	3
0,9,3	1	0	1	0	0	0	1	0	0	0	3
0,8,4	0	1	1	0	0	1	0	0	0	0	3
0,7,5	0	0	1	0	0	0	0	0	0	0	1
0,6,6	0	0	0	0	0	0	0	0	0	1	1

Expanding these generating functions, we obtain a coefficent for each term ($x^l y^m z^n$) and each subsymmetry in the form of a table similar to Table 3. For example, the $x^{10}y^2$ row of the table is calculated to be (66,6,10,6,0,2,0,0,0,0,), which is alligned according to the SSG. This row vector is multiplied by the inverse (Table 1) to yield a vector, (2,2,4,0,0,2,0,0,0,0), which indicates that the set of $C_{10}N_2$ isomers consists of two C_1-, two C_2-, 4C_s-, and two C_{2v}-isomers. Other results are obtained similarly and shown in Table 5. Note that the index [l,m,n] corresponds to the term $x^l y^m z^n$ ($C_lN_mO_n$) and $x^m y^l z^n$ ($C_mN_lO_n$).

In order to exemplify the effect of OMVs, Fig. 3 collects $C_{10}N_2$-, $C_{10}NO$- and $C_{10}O_2$-isomers derived from (**2**), the numbers of which appear at [10,2,0]-, [10,1,1]- and [10,0,2]-rows of Table 5. Compare the $C_{10}N_2$-isomers with $C_{10}O_2$-ones; the total number of the former is 10, whereas that of the latter is 3. This difference is because an oxygen atom is forbidden to occupy any bridgehead position.

The sum of each row of Table 5 shown at the rightmost column can be obtained in terms of a generating function. A cycle index for this case is obtained in a similar way as Eq. 4, i.e.,

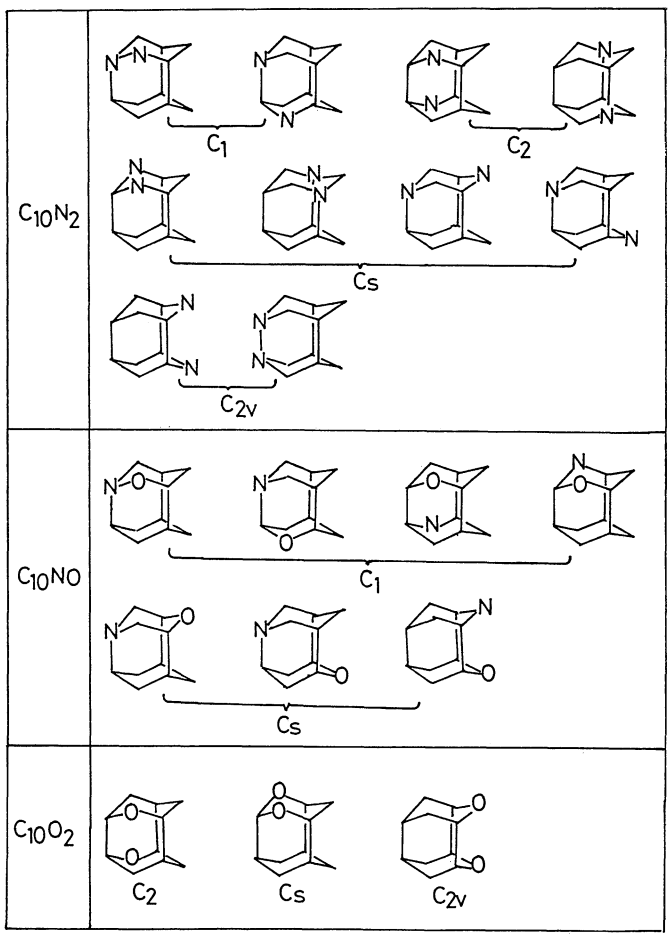

Fig. 3. $C_{10}N_2$-, $C_{10}NO$-, and $C_{10}O_2$-isomers derived from **2**.

$$\mathrm{CI}(\mathbf{D}_{3h};\, s_d^{(1)},\, s_d^{(2)}) = (1/12)(s_1^6)^{(1)}(s_1^6)^{(2)} + (1/4)(s_2^3)^{(1)}(s_2^3)^{(2)} + (1/4)(s_1^2s_2^2)^{(1)}(s_1^2s_2^2)^{(2)} + (1/12)(s_2^3)^{(1)}(s_2^3)^{(2)} + (1/6)(s_3^2)^{(1)}(s_3^2)^{(2)} + (1/6)(s_6)^{(1)}(s_6)^{(2)}, \quad (8)$$

where the coefficients of the right-hand side are adopted from the values listed at the bottom of Table 2.[12] Note that each term of Eq. 8 contains twice the USCI of $\mathbf{D}_{3h}(/\mathbf{C}_s)$ row and that the two USCIs are differentiated by the superscripts (1) and (2) according to the orbits Δ_1 and Δ_2). The figure inventories (Eqs. 6 and 7) are introduced into Eq. 8 to give a generating function, in which the coefficient of the term ($x^l y^m z^n$) is identical with the total value appearing at the corresponding [l,m,n] row of Table 5.

Enumeration of Cage-Shaped Molecules Derived from Prismane (3). In previous papers,[5] we have reported enumerations in terms of an edge strategy, where $\mathbf{T}_d$ and $\mathbf{D}_{2h}$ skeletons are manipulated. This methodology is effective generally for enumerating cage-shaped molecules of high symmetries. Figure 4 depicts its application to a prismane skeleton (**3**). Suppose that an appropriate number of methylenes (●) occupy (or insert) the edges of this skeleton. For example, if six methylenes occupy all the edges of the top and bottom triangles, there emerges an iceane molecule of $\mathbf{D}_{3h}$-symmetry with the term x^6. The latter term corresponds to the molecular formula of $(CH)_6$-$(CH_2)_6$. Our target is the enumeration of such isomers as having x^m (i.e., $(CH_6(CH_2)_m)$ and a given subsymmetry.

The edges of prismane (**3**) construct two orbits that are subject to $\mathbf{D}_{3h}(/\mathbf{C}_s)$ and $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$, whereas the vertices otherwise behave according to the SCR notation, $\mathbf{D}_{3h}[\mathbf{C}_s(\mathbf{C}_6,\mathbf{H}_6)]$. As a result, we use the $\mathbf{D}_{3h}(/\mathbf{C}_s)$ and $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ rows of Table 2 for preparing SCIs. When we introduce a figure inventory:

$$s_d = 1 + x^d \quad (9)$$

into theSCIs, we obtain generating functions for FPV (ρ_{θ_j}),

$(s_1^6)(s_1^3) = (1 + x)^9$ for $\mathbf{C}_1$,

$(s_2^3)(s_1s_2) = (1 + x)(1 + x^2)^4$ for $\mathbf{C}_2$,

$(s_1^2s_2^2)(s_1s_2) = (1 + x)^3(1 + x^2)^3$ for $\mathbf{C}_s$,

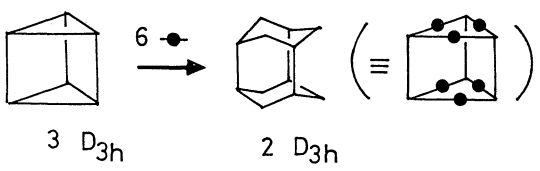

Fig. 4. An edge strategy for enumerating cage-shaped molecules derived from a prismane skeleton.

$(s_2^3)(s_1^3) = (1 + x)^3(1 + x^2)^3$ for $\mathbf{C}_s'$,

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

$(s_2s_4)(s_1s_2) = (1 + x)(1 + x^2)^2(1 + x^4)$ for $\mathbf{C}_{2v}$,

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

and

$(s_6)(s_3) = (1 + x^3)(1 + x^6)$ for $\mathbf{C}_{3h}$, $\mathbf{D}_3$, and $\mathbf{D}_{3h}$,

where the first parentheses in the left-hand side of each equation are concerned with the $\mathbf{D}_{3h}(/\mathbf{C}_s)$ row of Table 2 and the second with the $\mathbf{D}_{3h}(/\mathbf{C}_{2v})$ row. The procedure described in the preceding sections is repeated for this case to afford Table 6, in which the intersection between an m row and an subsymmetry column indicates the number of the corresponding cage-shaped molecules.

Figure 5 illustrates all of the cage-shaped molecules counted in Table 6, where we take no account of their conformations. Since this method clarifies the molecular formulas (or constitutions) of the enumerated molecules as well as their symmetries, we can depict such molecules without duplication nor overlooking.

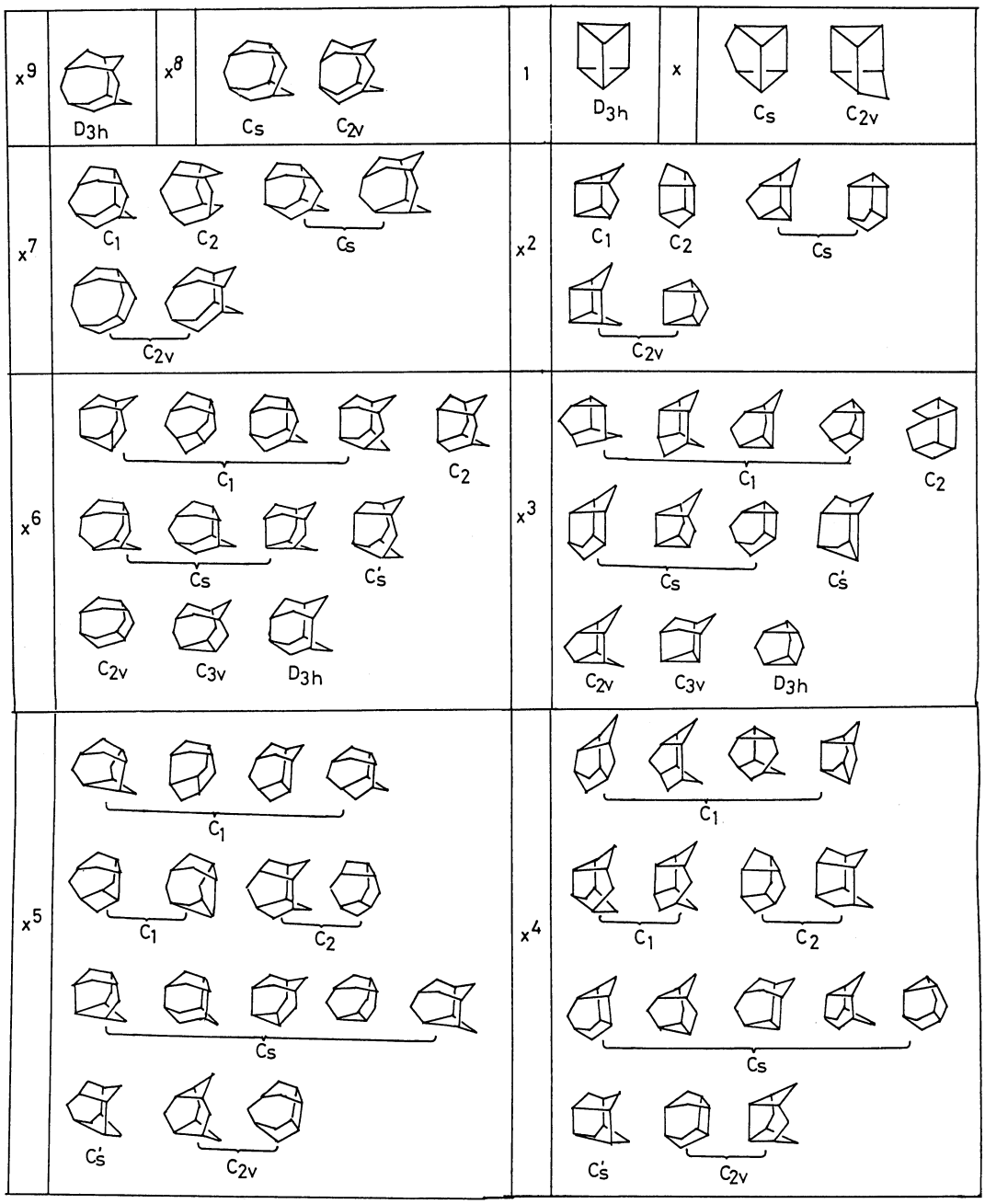

Fig. 5. Cage-shaped molecules derived from a prismane skeleton.

Table 6. The Number of $(CH)_6(CH_2)_m$-Molecules Based on **3**

m	C_1	C_2	C_s	C_s'	C_3	C_{2v}	C_{3v}	C_{3h}	D_3	D_{3h}	Total
9	0	0	0	0	0	0	0	0	0	1	1
8	0	0	1	0	0	1	0	0	0	0	2
7	1	1	2	0	0	2	0	0	0	0	6
6	4	1	3	1	0	1	1	0	0	1	12
5	6	2	5	1	0	2	0	0	0	0	16
4	6	2	5	1	0	2	0	0	0	0	16
3	4	1	3	1	0	1	1	0	0	1	12
2	1	1	2	0	0	2	0	0	0	0	6
1	0	0	1	0	0	1	0	0	0	0	2
0	0	0	0	0	0	0	0	0	0	1	1

Although we do not manipulate the other D_{3h}-skeletons (Fig. 1) in the present paper, the USCI method is applicable not only to the remaining skeletons but also to D_{3h}-skeletons to which we have not referred here.

Conclusion

We have clarified the usefulness of the USCI (unit subduced cycle index) approach in the enumeration of isomers derived from various D_{3h} skeletons. Since any skeleton is considered to consist of several orbits governed by coset representations, a preestimated table of USCIs provides us with a general method for enumeration of compounds, graphs and other geometrical objects.

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11) Only the factor of a cyclic group has a positive value. Otherwise, it vanishes to zero. See Ref. 10.

12) This cycle index can be proven to be identical to that obtained by Pólya's theorem. For the correlation of USCIs to Pólya's cycle index, see Ref. 10.

13) Note that the power of each element in the FPV is the number of suborbits to be considered. We have already reported a slightly different formulation for solving this type of enumeration problems. See Ref. 4a.

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