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Subduction of coset representations

An application to enumeration of chemical structures

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Summary. Enumerations of compounds based on a parent skeleton with and without the influence of obligatory minimum valency (OMV) are reported. The effect of the OMV is formulated by assigning different weights to the respective orbits of the parent skeleton. This type of enumeration requires introduction of several new concepts that are derived from the subduction of coset representations, e.g., a unit subduced cycle index, a subduced cycle index and the number of suborbits.

Key words: Enumeration of compounds — Table of marks — Coset representation — Unit subduced cycle index

1. Introduction

Enumeration of compounds in chemistry is one of the most important fields to which Pólya's theorem [1] has been applied. Ruch et al. [2] and later Brocas [3] have proved the concept of double coset to be very convenient for such compound-counting problems. More recently, Hässelbarth [4] has developed an important method in this field. This is based on the concept of "table of marks" that goes back to Burnside [5]. Mead [6] has discussed the relationship between these methods by using common problems as examples.

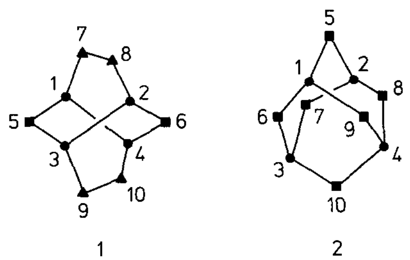
In previous papers [7] we have reported the counting of organic reactions. The enumeration is based on the manipulation of reaction graphs that are subgraphs of imaginary transition structures. A more specific enumeration has also been accomplished by counting reaction-center graphs. In this enumeration we encountered a problem concerned with obligatory minimum valency (OMV) as discussed below. We have solved the problem by using two or more different weights that are assigned to the respective orbits of a domain [8]. Although we have restricted ourselves to the case of organic reactions, our results are applicable to the enumeration of chemical structures under the influence of the OMV. A remaining problem is the counting of chemical structures with a given symmetry as well as a given weight, not only in the reaction counting but also in the compound counting.

The present paper deals with the remaining problem, which requires a more general approach than Hässelbarth's one in order to meet the OMV restriction. For this purpose, we clarify the usefulness of subduced representations of a transitive coset representation and of their further reduction into transitive permutation ones. This method provides novel concepts such as a *unit subduced cycle index* and a *subduced cycle index*, which are versatile guides for solving enumeration problems.

2. A parent skeleton characterized by a permutation representation and its equivalent positions specified by coset representations

A chemical compound can be considered to be a derivative of a given skeleton which has a skeletal symmetry. The skeleton has several sets (orbits) of equivalent positions. Each orbit is characterized by an obligatory minimum valency. For example, a twistane skeleton (**1**) has $\boldsymbol{D}_2$ symmetry, which creates three orbits that have different OMVs. Each bridgehead position of the orbit marked with a solid circle has an OMV of 3 and can take C and N from a set of C, N, and O. The other orbits (bridge positions) permit the substitution of all the three atoms because of their OMV of 2. The OMV thus affects the counting of organic structures. The adamantane skeleton (**2**) has two orbits, one with OMV = 3 and the other with OMV = 2. Hence, substitution patterns on **2** should be restricted by the OMVs.

As a result of the above discussion, our question is formulated as follows: what is the number of compounds, with a given set of substituents (atoms or ligands), on a given skeleton with a specified subsymmetry of the skeleton under the restricting conditions of OMV?



1 2

The above discussion shows that our first object is the classification of substitution positions into equivalence classes. This is formulated to obtain the number of orbits for a given set of positions and to assign a transitive permutation representation (i.e., a coset representation) to each of the orbits.

A permutation representation (PR) of a finite group $\boldsymbol{G}$ is produced when the group $\boldsymbol{G}$ acts on a finite set $\Delta = \{\delta_1, \delta_2, \ldots, \delta_{|\Delta|}\}$. In a chemical sense, the set Δ is regarded as containing all the positions of a given skeleton, the symmetry of which is represented by the point group $\boldsymbol{G}$. The PR ($\boldsymbol{P_G}$) is a set of permutations (P_g) on Δ, each of which is associated with an element $g \in \boldsymbol{G}$ so that $\boldsymbol{P_G}$ and $\boldsymbol{G}$ are homomorphic. That is

$$P_g P_{g'} = P_{gg'} \quad \text{for any } g,\ g' \in \boldsymbol{G}. \tag{1}$$

Let $\boldsymbol{H}$ be a subgroup of $\boldsymbol{G}$. The set of (left) cosets of $\boldsymbol{H}$ in $\boldsymbol{G}$ provides a partition of $\boldsymbol{G}$. That is,

$$\boldsymbol{G} = \boldsymbol{H}g_1 + \boldsymbol{H}g_2 + \cdots + \boldsymbol{H}g_m, \tag{2}$$

where $g_1 = I$ (identity) and $g_i \in \boldsymbol{G}$. A set of $\{g_1, g_2, \ldots, g_m\}$ is called a transversal (i.e., a system of representatives). Then we consider the set of the cosets:

$$\{\boldsymbol{H}g_1, \boldsymbol{H}g_2, \ldots, \boldsymbol{H}g_m\}. \tag{3}$$

For any $g \in \boldsymbol{G}$, the set of permutations of degree m:

$$G(/H)_g = \begin{pmatrix} \boldsymbol{H}g_1, \boldsymbol{H}g_2, \ldots, \boldsymbol{H}g_m \\ \boldsymbol{H}g_1g, \boldsymbol{H}g_2g, \ldots, \boldsymbol{H}g_mg \end{pmatrix}, \tag{4}$$

constructs a permutation representation of $\boldsymbol{G}$, which is called a coset representation (CR) of $\boldsymbol{G}$ by $\boldsymbol{H}$ and notified as $\boldsymbol{G}(/\boldsymbol{H})$. The degree of $\boldsymbol{G}(/\boldsymbol{H})$ is $m = |\boldsymbol{G}|/|\boldsymbol{H}|$ where $|\boldsymbol{G}|$ is the number of elements in $\boldsymbol{G}$. Obviously, the coset representation $\boldsymbol{G}(/\boldsymbol{H})$ is transitive and, in other words, has one orbit. When $\boldsymbol{H}$ and $\boldsymbol{H}'$ are conjugate subgroups of $\boldsymbol{G}$, the corresponding coset representations $\boldsymbol{G}(/\boldsymbol{H})$ and $\boldsymbol{G}(/\boldsymbol{H}')$ are equivalent.

A stabilizer $\boldsymbol{G}_{\langle\delta_i\rangle}$ is defined as a subgroup of $\boldsymbol{G}$ which fixes one (δ_i) of the elements of Δ. If $\boldsymbol{P_G}$ is a transitive PR on Δ, $\boldsymbol{P_G}$ of degree $|\Delta|$ is identical to the coset representation $\boldsymbol{G}(/\boldsymbol{G}_{\langle\delta_i\rangle})$ that is based on an appropriate stabilizer $\boldsymbol{G}_{\langle\delta_i\rangle}$. Since two stabilizers $\boldsymbol{G}_{\langle\delta_i\rangle}$ and $\boldsymbol{G}_{\langle\delta_j\rangle}$ are conjugate, the corresponding CRs $\boldsymbol{G}(/\boldsymbol{G}_{\langle\delta_i\rangle})$ and $\boldsymbol{G}(/\boldsymbol{G}_{\langle\delta_j\rangle})$ are equivalent. The following theorems have already been proven in Burnside's excellent book [6].

Theorem 1. *Suppose that the number of subgroups in a finite group $\boldsymbol{G}$ is s (where a set of conjugate subgroups should be counted one time). We select a complete set:*

$$\boldsymbol{G}_1, \boldsymbol{G}_2, \ldots, \boldsymbol{G}_s$$

in an ascending order of their orders, i.e.

$$|\boldsymbol{G}_1| \leqslant |\boldsymbol{G}_2| \leqslant \cdots \leqslant |\boldsymbol{G}_s|,$$

wherein $\boldsymbol{G}_1 =$ identity and $\boldsymbol{G}_s = \boldsymbol{G}$. The set of the corresponding CRs: $\boldsymbol{G}(/\boldsymbol{G}_i)$ *($i = 1, 2, \ldots, s$) is the complete set of different transitive representations of $\boldsymbol{G}$.* □

Obviously, $\boldsymbol{G}(/\boldsymbol{G}_l)$ is the regular representation and $\boldsymbol{G}(/\boldsymbol{G}_s)$ is an identity representation.

Theorem 2. *Any permutation representation $\boldsymbol{P_G}$ of a finite group $\boldsymbol{G}$ acting on Δ can be reduced into transitive* CRs *in accord with the following equation*:

$$\boldsymbol{P_G} = \sum_{i=1}^{s} \alpha_i \boldsymbol{G}(/\boldsymbol{G}_i), \tag{5}$$

wherein the multiplicity α_i is a non-negative integer. The multiplicities are obtained by using a table of marks:

$$\mu_j = \sum_{i=1}^{s} \alpha_i m_j^{(i)} \quad (j = 1, 2, \ldots, s), \tag{6}$$

where μ_j is the mark (the number of fixed points) of $\boldsymbol{G}_j$ in $\boldsymbol{P_G}$. The symbol $m_j^{(i)}$ denotes the mark of $\boldsymbol{G}_j$ in $\boldsymbol{G}(/\boldsymbol{G}_i)$.

For the present purpose, transitive coset representations (CRs) are as important as their multiplicities. This is in contrast to the previous Hässelbarth's method [4] which pays no attention to the concrete forms of the CRs. Tables 1 to 10 collect several examples of them, which will be used in the discussion below. The odd-numbered tables contain the symmetry operations of each point group and the products of cycles of the corresponding CRs. The even-numbered ones are tables of marks which contain all $m_j^{(i)}$.

Since $\boldsymbol{P_G}$ is a permutation representation of $\boldsymbol{G}$ acting on Δ, the representation can be reduced to a sum of CRs in the light of Eq. (5). This action provides a

Table 1. CRs of $\boldsymbol{C}_2$

	$\boldsymbol{C}_2(/\boldsymbol{C}_1)$	$\boldsymbol{C}_2(/\boldsymbol{C}_2)$
I	(1)(2)	(1)
C_2	(1 2)	(1)

Table 2. Mark table of $\boldsymbol{C}_2$

	$\boldsymbol{C}_1$	$\boldsymbol{C}_2$
$\boldsymbol{C}_2(/\boldsymbol{C}_1)$	2	0
$\boldsymbol{C}_2(/\boldsymbol{C}_2)$	1	1

Table 3. CRs of $\boldsymbol{C}_3$

	$\boldsymbol{C}_3(/\boldsymbol{C}_1)$	$\boldsymbol{C}_3(/\boldsymbol{C}_3)$
I	(1)(2)(3)	(1)
C_3	(1 2 3)	(1)
C_3^2	(1 3 2)	(1)

Table 4. Mark table of $\boldsymbol{C}_3$

	$\boldsymbol{C}_1$	$\boldsymbol{C}_3$
$\boldsymbol{C}_3(/\boldsymbol{C}_1)$	3	0
$\boldsymbol{C}_3(/\boldsymbol{C}_3)$	1	1

Table 5. Coset representation of $\boldsymbol{D}_2$

	$\boldsymbol{D}_2(/\boldsymbol{C}_1)$	$\boldsymbol{D}_2(/\boldsymbol{C}_2)$	$\boldsymbol{D}_2(/\boldsymbol{C}_2')$	$\boldsymbol{D}_2(/\boldsymbol{C}_2'')$	$\boldsymbol{D}_2(/\boldsymbol{D}_2)$
I	(1)(2)(3)(4)	(1)(2)	(1)(2)	(1)(2)	(1)
$C_{2(1)}$	(1 2)(3 4)	(1)(2)	(1 2)	(1 2)	(1)
$C_{2(2)}$	(1 2)(3 4)	(1)(2)	(1 2)	(1 2)	(1)
$C_{2(2)}$	(1 3)(2 4)	(1 2)	(1)(2)	(1 2)	(1)
$C_{2(3)}$	(1 4)(2 3)	(1 2)	(1 2)	(1)(2)	(1)

Table 6. Mark table of D_2

	C_1	C_2	C_2'	C_2''	D_2
$D_2(/C_1)$	4	0	0	0	0
$D_2(/C_2)$	2	2	0	0	0
$D_2(/C_2')$	2	0	2	0	0
$D_2(/C_2'')$	2	0	0	2	0
$D_2(/D_2)$	1	1	1	1	1

Table 8. Mark table of D_3

	C_1	C_2	C_3	D_3
$D_3(/C_1)$	6	0	0	0
$D_3(/C_2)$	3	1	0	0
$D_3(/D_3)$	2	0	2	0
$D_3(/D_3)$	1	1	1	1

Table 7. Coset representations of D_3

	$D_3(/C_1)$	$D_3(/C_2)$	$D_3(/C_3)$	$D_3(/D_3)$
I	(1)(2)(3)(4)(5)(6)	(1)(2)(3)	(1)(2)	(1)
C_3	(1 2 3)(4 5 6)	(1 2 3)	(1)(2)	(1)
C_3^2	(1 3 2)(4 6 5)	(1 3 2)	(1)(2)	(1)
$C_{2(1)}$	(1 4)(2 6)(3 5)	(1)(2 3)	(1 2)	(1)
$C_{2(2)}$	(1 5)(2 4)(3 6)	(1 2)(3)	(1 2)	(1)
$C_{2(3)}$	(1 6)(2 5)(3 4)	(1 3)(2)	(1 2)	(1)

Table 9. Coset representation of T

T	$T(/C_1)$	$T(/C_2)$	$T(C_3)$	$T(/D_2)$	$T(/T)$
I	(1)(2)(3)(4)(5)(6) (7)(8)(9)(10)(11)(12)	(1)(2)(3)(4)(5)(6)	(1)(2)(3)(4)	(1)(2)(3)	(1)
$C_{2(1)}$	(1 2)(3 4)(5 6)(7 8) (9 10)(11 12)	(1)(2)(3 4)(5 6)	(1 2)(3 4)	(1)(2)(3)	(1)
$C_{2(2)}$	(1 3)(2 4)(5 7)(6 8) (9 11)(10 12)	(1 2)(3 4)(5)(6)	(1 3)(2 4)	(1)(2)(3)	(1)
$C_{2(3)}$	(1 4)(2 3)(5 8)(6 7) (9 12)(10 11)	(1 2)(3)(4)(5 6)	(1 4)(23)	(1)(2)(3)	(1)
$C_{3(1)}$	(1 5 9)(2 8 11) (3 6 12)(4 7 10)	(1 3 5)(2 4 6)	(1)(2 4 3)	(1 2 3)	(1)
$C_{3(3)}$	(1 6 11)(2 7 9) (3 5 10)(4 8 12)	(1 4 5)(2 3 6)	(1 2 3)(4)	(1 2 3)	(1)
$C_{3(2)}$	(1 7 12)(2 6 10) (3 8 9)(4 5 11)	(1 4 6)(2 3 5)	(1 3 4)(2)	(1 2 3)	(1)
$C_{3(4)}$	(1 8 10)(2 5 12) (3 7 11)(4 6 9)	(1 3 6)(2 4 5)	(1 4 2)(3)	(1 2 3)	(1)
$C_{3(1)}^2$	(1 9 5)(2 11 8) (3 12 6)(4 10 7)	(1 5 3)(2 6 4)	(1)(2 3 4)	(1 3 2)	(1)
$C_{3(4)}^2$	(1 10 8)(2 12 5) (3 11 7)(4 9 6)	(1 6 3)(2 5 4)	(1 2 4)(3)	(1 3 2)	(1)
$C_{3(2)}^2$	(1 11 6)(2 9 7) (3 10 5)(4 12 8)	(1 5 4)(2 6 3)	(1 3 2)(4)	(1 3 2)	(1)
$C_{3(3)}^2$	(1 12 7)(2 10 6) (3 9 8)(4 11 5)	(1 6 4)(2 5 3)	(1 4 3)(2)	(1 3 2)	(1)

Table 10. Mark table of $\boldsymbol{T}$

	C_1	C_2	C_3	D_2	T
$T(/C_1)$	12	0	0	0	0
$T(/C_2)$	6	2	0	0	0
$T(/C_3)$	4	0	1	0	0
$T(/D_2)$	3	3	0	3	0
$T(/T)$	1	1	1	1	1

partition of the elements of Δ into a set of orbits so that a transitive $\boldsymbol{G}(/\boldsymbol{G}_i)$ acts on each of the α_i orbits:

$$\Delta_{i1}, \Delta_{i2}, \ldots, \Delta_{i\alpha_i} \quad (i = 1, 2, \ldots, s). \tag{7}$$

Chemically speaking, each orbit ($\Delta_{i\alpha}$) represents a set of equivalent positions. The symmetry properties of the set are induced by $\boldsymbol{G}$ and are controlled by $\boldsymbol{G}(/\boldsymbol{G}_i)$. Obviously the total number of such orbits is

$$\sum_{i=1}^{s} \alpha_i.$$

The mark μ_j of $\boldsymbol{G}_j$ in any permutation group $\boldsymbol{P}_G$ is the number of fixed points. This is easily available from the explicit form of $\boldsymbol{P}_G$ or if we apply the symmetry operations of $\boldsymbol{G}_j$ to the parent skeleton. The following examples illustrate the procedure of decomposition into transitive representations to generate a set of orbits.

Example 1: $\boldsymbol{D}_2$ *skeleton of twistane* (**1**)

The number of (μ_j) of fixed points are obtained by a geometrical examination of **1**. Equation (6) then gives

$$(10 \quad 0 \quad 0 \quad 2 \quad 0) = (\alpha_{C_1} \quad \alpha_{C_2} \quad \alpha_{C_2'} \quad \alpha_{C_2''} \quad \alpha_{D_2}) \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 & 0 \\ 2 & 0 & 2 & 0 & 0 \\ 2 & 0 & 0 & 2 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix},$$

which produces

$$\alpha_{C_1} = 2, \quad \alpha_{C_2} = 0, \quad \alpha_{C_2'} = 0, \quad \alpha_{C_2''} = 1, \quad \text{and } \alpha_{D_2} = 0.$$

Hence,

$$\boldsymbol{P}_{D_2} = 2\boldsymbol{D}_2(/\boldsymbol{C}_1) + \boldsymbol{D}_2(/\boldsymbol{C}_2'').$$

The CRs on the right-hand side are shown in Table 5. This decomposition corresponds to a partition into three orbits:

$$\Delta_{11} = \{1 \quad 2 \quad 3 \quad 4\}, \qquad \Delta_{21} = \{5 \quad 6\}, \qquad \Delta_{12} = \{7 \quad 8 \quad 9 \quad 10\},$$

on which $\boldsymbol{D}_2(/\boldsymbol{C}_1)$, $\boldsymbol{D}_2(/\boldsymbol{C}_2'')$, and $\boldsymbol{D}_2(/\boldsymbol{C}_1)$ respectively act. This partition is identical to that obtained by the direct inspection of the skeleton (**1**). For example, when we apply any symmetry operation of $\boldsymbol{D}_2$ to the orbit (Δ_{11}), we can obtain the corresponding permutation of the four elements (positions) which emerge at the $\boldsymbol{D}_2(/\boldsymbol{C}_1)$ column of Table 5.

Example 2: The $\boldsymbol{T}$ *part of the adamantane skeleton* (**2**)

The marks of a subgroup in $\boldsymbol{P_T}$ are obtained by counting fixed points on all the symmetry operations of the respective subgroup. A detailed description of the operations of the $\boldsymbol{T}$ point group has appeared elsewhere [9]. The values of marks are put into Eq. (5) giving the following representation.

$$(10 \quad 2 \quad 1 \quad 0 \quad 0) = (\alpha_{\boldsymbol{C}_1} \quad \alpha_{\boldsymbol{C}_2} \quad \alpha_{\boldsymbol{C}_3} \quad \alpha_{\boldsymbol{D}_2} \quad \alpha_{\boldsymbol{T}}) \begin{bmatrix} 12 & 0 & 0 & 0 & 0 \\ 6 & 2 & 0 & 0 & 0 \\ 4 & 0 & 1 & 0 & 0 \\ 3 & 3 & 0 & 3 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

That is $\alpha_{\boldsymbol{C}_1} = 0$, $\alpha_{\boldsymbol{C}_2} = 1$, $\alpha_{\boldsymbol{C}_3} = 1$, $\alpha_{\boldsymbol{D}_2} = 0$ and $\alpha_{\boldsymbol{T}} = 0$, which indicates

$$\boldsymbol{P_T} = \boldsymbol{T}(/\boldsymbol{C}_2) + \boldsymbol{T}(/\boldsymbol{C}_3).$$

The concrete forms of these transitive CRs are collected in Table 9. The equation is in agreement with the fact that the vertices 1 to 10 are divided into two orbits, i.e. $\Delta_1 = \{1, 2, 3, 4\}$ and $\Delta_2 = \{5, 6, 7, 8, 9, 10\}$, which are associated with $\boldsymbol{T}(/\boldsymbol{C}_3)$ and $\boldsymbol{T}(/\boldsymbol{C}_2)$, respectively.

3. Subduced representations of a coset representation

As a basis for solving enumeration problems, we introduce subductions of coset representations. This section deals with a mathematical formulation of the topic as well as its chemical meanings. The set of the coset representations of a given group $\boldsymbol{G}$ is determined only by $\boldsymbol{G}$ by Theorem 1. This means that the properties of $\boldsymbol{G}(/\boldsymbol{G}_i)$ ($i = 1, 2, \ldots, s$) can be preexamined irrespective of the $\boldsymbol{G}$-sets. In this section, we discuss the subduced representations of them.

Let $\boldsymbol{G}_i$ and $\boldsymbol{G}_j$ be any subgroups of $\boldsymbol{G}$ that are selected as in Theorem 1. The representation $\boldsymbol{G}(/\boldsymbol{G}_i)$ denotes the coset representation (CR) of $\boldsymbol{G}$ by $\boldsymbol{G}_i$. Then we define a subduced representation (SR) $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ as the subgroup of $\boldsymbol{G}(/\boldsymbol{G}_i)$ that contains only the elements associated with the elements of $\boldsymbol{G}_j$. The SR $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ can be regarded as a permutation representation of $\boldsymbol{G}_j$ and can be considered to act on each of the orbits $\Delta_{i\alpha}$ ($\alpha = 1, 2, \ldots, \alpha_i$) on which the group $\boldsymbol{G}(/\boldsymbol{G}_i)$ also acts. Although the action of $\boldsymbol{G}(/\boldsymbol{G}_i)$ on the orbit $\Delta_{i\alpha}$ is transitive, that of the SR $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ is intransitive. Hence, the orbit $\Delta_{i\alpha}$ is subdivided by the action of $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ (Fig. 1). This subdivision can also be accomplished by means of Eqs. (5) and (6). Thus, we arrive at

Corollary 2.1. *Let* $\boldsymbol{G}(/\boldsymbol{G}_i)$ *be a coset representation of* $\boldsymbol{G}$ *by* $\boldsymbol{G}_i$. *Let* $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ *be a subduced representation of* $\boldsymbol{G}(/\boldsymbol{G}_i)$ *by* $\boldsymbol{G}_j \leqslant \boldsymbol{G}$. *The* SR $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ *can be reduced*

$$\begin{tikzcd}
\Delta \arrow[r, dash, dashed] \arrow[d, "\boldsymbol{G}"] & \boldsymbol{G} \\
\Delta_{i\alpha} \arrow[r, dash, dashed] \arrow[d, "\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow \boldsymbol{G}_j"] & \boldsymbol{G}(/\boldsymbol{G}_i) \\
\Delta^{i\alpha}_{k\beta} \arrow[r, dash, dashed] & \boldsymbol{G}_j(/\boldsymbol{H}_k)
\end{tikzcd}$$

Fig. 1. Orbits and suborbits generated during the action by $\boldsymbol{G}$ and the subsequent subduction by $\boldsymbol{G}_j$

by the following equation:

$$\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow \boldsymbol{G}_j = \sum_{k=1}^{v} \beta^{ij}_k \boldsymbol{G}_j(/\boldsymbol{H}_k) \quad \text{for } i = 1, 2, \ldots, s \text{ and } j = 1, 2, \ldots, s, \tag{8}$$

where $\boldsymbol{H}_k$ is a subgroup of $\boldsymbol{G}_j$ and $\boldsymbol{G}_j(/\boldsymbol{H}_k)$ is the CR *of $\boldsymbol{G}_j$ by $\boldsymbol{H}_k$. The multiplicities, the β^{ij}_k's, are non-negative integers and the symbol v* is the number of $\boldsymbol{H}_k$ *conjugate classes. The coefficients are obtained from the following equation.*

$$v_l = \sum_{k=1}^{v} \beta^{ij}_k m^{(k)}_l \quad \text{for } l = 1, 2, \ldots, v, \tag{9}$$

where v_l is the mark of $\boldsymbol{H}_l$ in $\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow \boldsymbol{G}_j$. □

The subgroup $\boldsymbol{H}_k$ and the number v depend upon $\boldsymbol{G}_j$; however, for simplicity of the notation, this dependence is not expressed explicitly.

Since the degree of $\boldsymbol{G}_j(/\boldsymbol{H}_k)$ is $d_{jk} = |\boldsymbol{G}_j|/|\boldsymbol{H}_k|$, each subdivided orbit,

$$\Delta^{i\alpha}_{k\beta} \quad (\beta = 1, 2, \ldots, \beta^{ij}_k),$$

has a length of d_{jk}. Then we assign a variable $s^{(\alpha)}_{d_{jk}}$ to $\Delta^{i\alpha}_{k\beta}$. The superscript (α) indicates the dependence on the corresponding orbit, $\Delta_{i\alpha}$ ($\alpha = 1, 2, \ldots$, or α_i), since the α_i orbits can take different sets of substituents. Note that all the suborbits ($\Delta^{i\alpha}_{k\beta}$) take the same set of substituents as that of the parent orbit. These requisites are introduced to meet the OMV restriction described in Sect. 2. Since the multiplicity of this suborbit is β^{ij}_k, we define a unit subduced cycle index (USCI) as follows:

Definition 1. A unit subduced cycle index (USCI):

$$Z(\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow \boldsymbol{G}_j; s^{(\alpha)}_{d_{jk}}) = \prod_{k=1}^{v} (s^{(\alpha)}_{d_{jk}})^{\beta^{ij}_k}, \tag{10}$$

for each action of $\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow \boldsymbol{G}_j$ on $\Delta_{i\alpha}$. Another useful constant is the number of suborbits (NSO):

$$\beta_{ij} = \sum_{k=1}^{v} \beta^{ij}_k. \tag{11}$$

It should be emphasized that the USCI and the NSO do not depend upon a particular $\boldsymbol{G}$-set but only on the subduction by Eqs. (8) and (9). Hence, they are commonly useful for any problem. The full tabulation of USCIs and β_{ij}'s for every point group would be a valuable tool for enumeration problems. Tables 11 to 14 collect several examples of them, where the NSOs are in the parentheses.

Table 11. $Z(G(/G_i) \downarrow G_j; s)$ and β_{ij} for C_2

$i\backslash j$	C_1	C_2
$C_2(/C_1)$	s_1^2 (2)	s_2 (1)
$C_2(/C_2)$	s_1 (1)	s_1 (1)

Table 12. $Z(G(/G_i) \downarrow G_j; s)$ and β_{ij} for D_2

$i\backslash j$	C_1	C_2	C_2'	C_2''	D_2
$D_2(/C_1)$	s_1^4 (4)	s_2^2 (2)	s_2^2 (2)	s_2^2 (2)	s_4 (1)
$D_2(/C_2)$	s_1^2 (2)	s_1^2 (2)	s_2 (1)	s_2 (1)	s_2 (1)
$D_2(/C_2')$	s_1^2 (2)	s_2 (1)	s_1^2 (2)	s_2 (1)	s_2 (1)
$D_2(/C_2'')$	s_1^2 (2)	s_2 (1)	s_2 (1)	s_1^2 (2)	s_2 (1)
$D_2(/D_2)$	s_1 (1)	s_1 (1)	s_1 (1)	s_1 (1)	s_1 (1)

Table 13. $Z(G/(G_i) \downarrow G_j; s)$ and β_{ij} for D_3

$i\backslash j$	C_1	C_2	C_3	D_3
$D_3(/C_1)$	s_1^6 (6)	s_2^3 (3)	s_3^2 (2)	s_6 (1)
$D_3(/C_2)$	s_1^3 (3)	$s_1 s_2$ (2)	s_3 (1)	s_3 (1)
$D_3(/C_3)$	s_1^2 (2)	s_2 (1)	s_1^2 (2)	s_2 (1)
$D_3(/D_3)$	s_1 (1)	s_1 (1)	s_1 (1)	s_1 (1)

Table 14. $Z(G(/G_i) \downarrow G_j; s)$ and β_{ij} for T

$i\backslash j$	C_1	C_2	C_3	D_2	T
$T(/C_1)$	s_1^{12} (12)	s_2^6 (6)	s_3^4 (4)	s_4^3 (3)	s_{12} (1)
$T(/C_2)$	s_1^6 (6)	$s_1^2 s_2^2$ (4)	s_3^2 (2)	s_2^3 (3)	s_6 (1)
$T(/C_3)$	s_1^4 (4)	s_2^2 (2)	$s_1 s_3$ (2)	s_4 (1)	s_4 (1)
$T(/D_2)$	s_1^3 (3)	s_1^3 (3)	s_3 (1)	s_1^3 (3)	s_3 (1)
$T(/T)$	s_1 (1)	s_1 (1)	s_1 (1)	s_1 (1)	s_1 (1)

Example 3

In Example 2, we have already found the two orbits of the adamantane skeleton (**2**), i.e., $\Delta_1 = \{1, 2, 3, 4\}$ and $\Delta_2 = \{5, 6, 7, 8, 9, 10\}$, on which $T(/C_3)$ and $T(/C_2)$, respectively, act in a transitive fashion. Subductions to subsymmetries provide the subdivision of the orbits, Δ_1 and Δ_2, into the corresponding suborbits. Table 14 assigns unit subduced cycle indices to the suborbits. The total profile of the subdivision is illustrated in Fig. 2, which also contains USCIs assigned to the respective orbits on which the corresponding CRs act. Note that the degree of the CR is equal to the length of the suborbit. Figure 2 gives an insight into the meaning of the USCI (Eq. 10). For example, the orbit $\Delta_1(|\Delta_1| = 4)$ is divided during the operation $(T/(C_3) \downarrow C_2)$ into two suborbits of length 2. This fact is in agreement with the assigned USCI (s_2^2).

4. Orbits of configurations

For the formulation of the restriction by the OMVs described above, we introduce a set of weights for each orbit. Let Δ be a domain which consists of $|\Delta|$

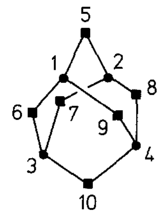
$\Delta = \{1\ 2\ 3\ 4\ 5\ 6\ 7\ 8\ 9\ 10\} \cdots \boldsymbol{T}$

$\Delta_1 = \{1\ 2\ 3\ 4\} \cdots \boldsymbol{T}(/\boldsymbol{C}_3)$

$\downarrow \boldsymbol{C}_1$	$\{1\}\{2\}\{3\}\{4\}$	s_1^4
$\downarrow \boldsymbol{C}_2$	$\{1\ 2\}\{3\ 4\}$	s_2^2
$\downarrow \boldsymbol{C}_3$	$\{1\}\{2\ 3\ 4\}$	$s_1 s_3$
$\downarrow \boldsymbol{D}_2$	$\{1\ 2\ 3\ 4\}$	s_4
$\downarrow \boldsymbol{T}$	$\{1\ 2\ 3\ 4\}$	s_4

$\Delta_2 = \{5\ 6\ 7\ 8\ 9\ 10\} \cdots \boldsymbol{T}(/\boldsymbol{C}_2)$

$\downarrow \boldsymbol{C}_1$	$\{5\}\{6\}\{7\}\{8\}\{9\}\{10\}$	s_1^6
$\downarrow \boldsymbol{C}_2$	$\{5\}\{6\ 8\}\{7\ 9\}\{10\}$	$s_1^2 s_2^2$
$\downarrow \boldsymbol{C}_3$	$\{5\ 6\ 9\}\{7\ 10\ 8\}$	s_3^2
$\downarrow \boldsymbol{D}_2$	$\{5\ 10\}\{6\ 8\}\{7\ 9\}$	s_2^3
$\downarrow \boldsymbol{T}$	$\{5\ 6\ 7\ 8\ 9\ 10\}$	s_6



2

Fig. 2. Orbits and suborbits of the adamantane skeleton (**2**)

elements called *positions*:

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

Let $\boldsymbol{G}$ (order $|\boldsymbol{G}|$) act on the domain (Δ) to provide a permutation representation $\boldsymbol{P}_G$ on Δ. Suppose that the action of $\boldsymbol{G}$ provides a partition into orbits:

$$\Delta_{i\alpha} \quad \text{for } i = 1, 2, \ldots, s \text{ and } \alpha = 1, 2, \ldots, \alpha_i,$$

where the number of orbits is

$$\sum_{i=1}^{s} \alpha_i.$$

Let X be a codomain that contains $|X|$ elements called *figures*. The mathematical term "figure" can be translated into a chemical term "substituent", "ligand", or "atom",

$$\boldsymbol{X} = \{X_1, X_2, \ldots, X_{|X|}\}.$$

Suppose that f is a *function* (*configuration*) from Δ to $\boldsymbol{X}$:

$$f: \Delta \to \boldsymbol{X}, \tag{12}$$

in which the mode of the mapping is restricted in light of *weights*. Equation (12) corresponds to a chemical procedure in which the positions of Δ (or of a given skeleton) are replaced by appropriate substituents selected from X. Hence, each of the functions (configurations) derived from Eq. (12) represents an appropriate compound in a chemical sense. For the purpose of considering OMVs, different sets of the weights are assigned to the respective orbits, i.e.,

$$w_{i\alpha}(X_r) \quad \text{for } \Delta_{i\alpha} \ (r = 1, 2, \ldots, |\mathbf{X}|). \tag{13}$$

Then we define a weight of the function $W(f)$ as follows.

$$W(f) = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} \prod_{\delta \in \Delta_{i\alpha}} w_{i\alpha}(f(\delta)), \tag{14}$$

wherein $w_{i0}(X_r) = 1$. Obviously the multiplication over $\delta \in \Delta_{i\alpha}$ affords a monomial of a total power of

$$\sum_{k=1}^{v} d_{jk}\beta_k^{ij}. \tag{15}$$

In most chemical enumerations, the weight of a function (configuration) represented by Eq. (14) can be regarded as the molecular formula of the configuration.

A set of all the functions $(f: \Delta \rightarrow \mathbf{X})$ is notified as

$$\boldsymbol{F} = \{f_1, f_2, \ldots, f_\gamma, \ldots, f_\varepsilon, \ldots, f_{|\boldsymbol{F}|}\}. \tag{16}$$

Let f_γ and f_ε be two functions belonging to $\boldsymbol{F}$. A binary relation between f_γ and f_ε is defined as $f_\gamma \sim f_\varepsilon$, if the following equation is fulfilled for $\exists P_g$ $(\in \boldsymbol{P_G})$:

$$f_\gamma(\delta) = f_\varepsilon(P_g(\delta)) \quad \text{for } \forall\delta \in \Delta. \tag{17}$$

The binary relation is an equivalence one, which provides a partition of $\boldsymbol{F}$ into equivalence classes.

If this relationship is considered to be a mapping $f_\varepsilon \rightarrow f_\gamma$, i.e. $f_\gamma P_g^{-1} \rightarrow f_\gamma$, we find a permutation:

$$\begin{aligned}\pi_g &= \begin{pmatrix} f_1 P_g^{-1}, \ldots, f_{|\boldsymbol{F}|} P_g^{-1} \\ f_1, \ldots, f_{|\boldsymbol{F}|} \end{pmatrix} \\ &= \begin{pmatrix} f_1, \ldots, f_{|\boldsymbol{F}|} \\ f_1 P_g, \ldots, f_{|\boldsymbol{F}|} P_g \end{pmatrix}. \end{aligned} \tag{18}$$

The set of $(\Pi_{\boldsymbol{G}})$ of π_g for $^{\forall}g \in \boldsymbol{G}$ is a permutation group on $\boldsymbol{F}$ [8]. A significant standpoint of Pólya's theorem is the fact that an equivalence class of configurations with respect to Eq. (17) is an orbit of $\boldsymbol{F}$ which is induced by the action of $\Pi_{\boldsymbol{G}}$. This formulation enables us to apply Theorem 2 (Eqs. 5 and 6) to the present case. Thus, we arrive at

Theorem 3. *Let a group $\boldsymbol{G}$ act on $\boldsymbol{F}$ via a permutation representation $\Pi_{\boldsymbol{G}}$. The multiplicity (A_i) of each transitive representation $\boldsymbol{G}(/\boldsymbol{G}_i)$ in $\Pi_{\boldsymbol{G}}$ is determined by the following equation,*

$$\Pi_{\boldsymbol{G}} = \sum_{i=1}^{s} A_i \boldsymbol{G}(/\boldsymbol{G}_i), \tag{19}$$

wherein A_i is a non-negative integer. The multiplicity A_i constitutes the solution of *the system of linear equations,*

$$\rho_j = \sum_{i=1}^{s} A_i m_j^{(i)} \quad \text{for } j = 1, 2, \ldots, s. \tag{20}$$

where ρ_j is the mark of $\boldsymbol{G}_j$ in Π_G.

Although the marks (the fixed points) in the previous Eqs. (6) and (9) are easily traceable because of the concrete nature of positions, the mark ρ_j is somewhat difficult to understand due to the abstract nature of functions or configurations. Equation (19) provides a partition of $\boldsymbol{F}$ by Π_G to create the corresponding orbits of $\boldsymbol{F}$. Suppose that one of the orbits is

$$\boldsymbol{F}_i = \{f_1^{(i)}, f_2^{(i)}, \ldots, f_\varepsilon^{(i)}\} \tag{21}$$

which is associated with $\boldsymbol{G}(/\boldsymbol{G}_i)$. The definition of $\boldsymbol{G}(/\boldsymbol{G}_i)$ indicates that the group $\boldsymbol{G}(/\boldsymbol{G}_i)$ acts on $\boldsymbol{F}_i$ in a transitive fashion. Since $\boldsymbol{G}(/\boldsymbol{G}_i)$ is a coset representation of $\boldsymbol{G}$ by $\boldsymbol{G}_i$, the subgroup $\boldsymbol{G}_i$ is a stablizer on $\boldsymbol{F}_i$ (Theorem 1). This fact indicates that there is an appropriate $f_k^{(i)} (\in \boldsymbol{F}_i)$ which is a fixed configuration with respect to action by $\boldsymbol{G}_i$. In other words, the fixed configuration $f_k^{(i)}$ has a symmetry of $\boldsymbol{G}_i$. It is to be noted that $f_k^{(i)}$ is invariant with respect to action of $\boldsymbol{G}_i$ but variant with respect to that of $\boldsymbol{G}(/\boldsymbol{G}_i)$. Hence, all configurations of $\boldsymbol{F}_i$ have the same symmetry, $\boldsymbol{G}_i$. As a result, A_i in Eq. (19) also indicates the number of different configurations of symmetry $\boldsymbol{G}_i$. We summarize the discussion in the form of

Corollary 3.1. *Let a group $\boldsymbol{G}$ act on $\boldsymbol{F}$ by acting on Δ. Then the numbers (A_i) of configurations of symmetry $\boldsymbol{G}_i \leqslant \boldsymbol{G}$ constitute the solution of the system of linear equations expressed by Eq.* (20).

The next important problem is the evaluation of ρ_j of Eq. (20). The mark (ρ_j) of $\boldsymbol{G}_j$ in Π_G is the number of fixed functions (or fixed configurations) of $\boldsymbol{F}$ on the action of $\boldsymbol{G}_j$. In order for an appropriate $f^{(j)}$ ($\in \boldsymbol{F}$) to be a fixed configuration with respect to $^\forall g \in \boldsymbol{G}_j$, the following equation is required to hold:

$$f^{(j)}(P_g(\delta)) = f^{(j)}(\delta) \quad (\text{for } ^\forall\delta \in \Delta \text{ and } ^\forall g \in \boldsymbol{G}_j). \tag{22}$$

In other words, $f^{(j)}$ has to be constant on the $\boldsymbol{G}_j$-orbit of Δ. Since Δ is divided into orbits $\Delta_{i1}, \Delta_{i2}, \ldots, \Delta_{i\alpha_i}$ ($i = 1, 2, \ldots, s$) by the action of $\boldsymbol{G}$ and each orbit $\Delta_{i\alpha}$ ($\alpha = 1, 2, \ldots, \alpha_i$) is subdivided by the action $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ (Fig. 1), the number (β_{ij}) of orbits for each $\Delta_{i\alpha}$ is given by Eq. (11).

In order for $^\exists f^{(j)}$ ($\in \boldsymbol{F}$) to be constant, all positions of each suborbit have to take the same figure (or substituent). This means that there are $|\boldsymbol{X}_{i\alpha}|$ ways of substitution for each suborbit subduced from $\Delta_{i\alpha}$, where

$$|\boldsymbol{X}_{i\alpha}| = \text{no. of non-zero } w_{i\alpha}(\boldsymbol{X}_r) \text{ for each } \Delta_{i\alpha}.$$

Since the number of the suborbits from $\Delta_{i\alpha}$ is β_{ij} in the subdivision by $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$, the term,

$$\prod_{\alpha=0}^{\alpha_i} |X_{i\alpha}|^{\beta_{ij}}, \tag{23}$$

is the number of fixed configurations corresponding to $\Delta_{i\alpha}$, where $|X_{i0}| = 1$. Finally, the total number of fixed configurations is obtained by collecting the terms (23) through all the subgroups, i.e.

$$\rho_j = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} |X_{i\alpha}|^{\beta_{ij}}. \tag{24}$$

Equations (20) and (24) lead to

Corollary 3.2. *Let a group $\boldsymbol{G}$ act on $\boldsymbol{F}$ by acting on Δ. Then the numbers (A_i) of orbits with symmetry $\boldsymbol{G}_i$ are obtained by the following equation*:

$$\prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} |X_{i\alpha}|^{\beta_{ij}} = \sum_{i=1}^{s} A_1 m_j^{(i)} \quad (j = 1, 2, \ldots, s), \tag{25}$$

where the action of $\boldsymbol{G}$ on Δ is restricted by the weights of Eq. (13) *and* $|X_{i0}| = 1$.

Example 4

We examine two cases in the enumeration of compounds based on the adamatane skeleton (**2**). In order to simplify the problem, we use $\boldsymbol{T}$ symmetry rather than $\boldsymbol{T}_d$ for the skeleton. This simplification retains the essential aspects of the present procedure. Figure 2 indicates a partition of the vertices of **2**, i.e., $\Delta_1 = \{1 \text{ to } 4\}$ on which $\boldsymbol{T}(/\boldsymbol{C}_3)$ acts and $\Delta_2 = \{5 \text{ to } 10\}$ on which $\boldsymbol{T}(/\boldsymbol{C}_2)$ acts. Suppose that Case 1 adopts a codomain $\boldsymbol{X} = \{\mathrm{C}, \mathrm{O}\}$. Because of the OMV of each orbit, Case 1 permits only C substitution on Δ_1 but C and O substitution on Δ_2. In Case 2, assumed to have a codomain $\boldsymbol{X} = \{\mathrm{C}, \mathrm{N}, \mathrm{O}\}$, the orbit Δ_1 can take C and N as substitutents and Δ_2 is capable of taking C, N and O. These situations can be formulated by the following weights:

Case 1

$$w_1(\mathrm{C}) = x, \qquad w_1(\mathrm{O}) = 0 \quad \text{for the orbit } \Delta_1$$

and

$$w_2(\mathrm{C}) = x, \qquad w_2(\mathrm{O}) = z \quad \text{for the orbit } \Delta_2.$$

Hence, $|X_1| = 1$ and $|X_2| = 2$.

Case 2

$$w_1(\mathrm{C}) = x, \qquad w_1(\mathrm{N}) = y, \qquad w_1(\mathrm{O}) = 0 \quad \text{for the orbit } \Delta_1$$

and

$$w_2(\mathrm{C}) = x, \qquad w_2(\mathrm{N}) = y, \qquad w_2(\mathrm{O}) = z \quad \text{for the orbit } \Delta_2.$$

Hence, $|X_1| = 2$ and $|X_2| = 3$.

For the calculation of marks, we use the $\boldsymbol{T}(/\boldsymbol{C}_2)$ and $\boldsymbol{T}(/\boldsymbol{C}_3)$ rows of Table 14. Thus, we find

Case 1

$$\rho_{C_1} = 2^6 1^4 = 64, \qquad \rho_{C_2} = 2^4 1^2 = 16, \qquad \rho_{C_3} = 2^2 1^2 = 4,$$
$$\rho_{D_2} = 2^3 1^1 = 8, \quad \text{and } \rho_{T} = 2^1 1^1 = 2,$$

Case 2

$$\rho_{C_1} = 3^6 2^4 = 11664, \qquad \rho_{C_2} = 3^4 2^2 = 324, \qquad \rho_{C_3} = 3^2 2^2 = 36,$$
$$\rho_{D_2} = 3^3 2^1 = 54, \quad \text{and } \rho_{T} = 3^1 2^1 = 6.$$

For Case 1, we find Eq. (20) as

$$(64 \quad 16 \quad 4 \quad 8 \quad 2) = (A_{C_1} \quad A_{C_2} \quad A_{C_3} \quad A_{D_2} \quad A_{T}) \begin{bmatrix} 12 & 0 & 0 & 0 & 0 \\ 6 & 2 & 0 & 0 & 0 \\ 4 & 0 & 1 & 0 & 0 \\ 3 & 3 & 0 & 3 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix},$$

which affords

Case 1

$$A_{C_1} = 2, \qquad A_{C_2} = 4, \qquad A_{C_3} = 2, \qquad A_{D_2} = 2, \quad \text{and } A_{T} = 2.$$

Similarly, case 2

$$A_{C_1} = 890, \qquad A_{C_2} = 135, \qquad A_{C_3} = 30, \qquad A_{D_2} = 16, \quad \text{and } A_{T} = 6.$$

Figure 3 illustrates the result of Case 1. It should be noted that, since we have chosen $\boldsymbol{T}$ symmetry rather than $\boldsymbol{T}_d$, each of the isomers has a lower symmetry than they would under $\boldsymbol{T}_d$ symmetry.

Example 5

Twistane (**1**) has $\boldsymbol{D}_2$ symmetry and affords three orbits, i.e., $\Delta_1 = \{1, 2, 3, 4\}$ on which $\boldsymbol{D}_2(/\boldsymbol{C}_1)$ acts; $\Delta_2 = \{5, 6\}$ on which $\boldsymbol{D}_2(/\boldsymbol{C}_2'')$; and $\Delta_3 = \{7, 8, 9, 10\}$ on which $\boldsymbol{D}_2(/\boldsymbol{C}_1)$ acts (see Example 1). Let us select a codomain $\boldsymbol{X} = \{\mathrm{C, N, O}\}$. The OMVs of the orbits afford a set of weights as follows.

$$w_1(\mathrm{C}) = x, \qquad w_1(\mathrm{N}) = y, \qquad w_1(\mathrm{O}) = 0 \quad \text{for the orbit } \Delta_1,$$
$$w_2(\mathrm{C}) = x, \qquad w_2(\mathrm{N}) = y, \qquad w_2(\mathrm{O}) = z \quad \text{for the orbit } \Delta_2,$$

and

$$w_3(\mathrm{C}) = x, \qquad w_3(\mathrm{N}) = y, \qquad w_3(\mathrm{O}) = z \quad \text{for the orbit } \Delta_3.$$

Hence, $|\boldsymbol{X}_1| = 2$, $|\boldsymbol{X}_2| = 3$, and $|\boldsymbol{X}_3| = 3$.
By using the values collected in the $\boldsymbol{D}_2(/\boldsymbol{C}_1)$ and $\boldsymbol{D}_2(/\boldsymbol{C}_2'')$ rows of Table 12, we obtain the marks for Eq. (24):

$$\rho_{C_1} = 2^4 3^4 3^2 = 11664, \qquad \rho_{C_2} = 2^2 3^2 3^1 = 108, \qquad \rho_{C_2'} = 2^2 3^2 3^1 = 108,$$
$$\rho_{C_2''} = 2^2 3^2 3^2 = 324, \quad \text{and } \rho_{D_2} = 2^1 3^1 3^1 = 18,$$

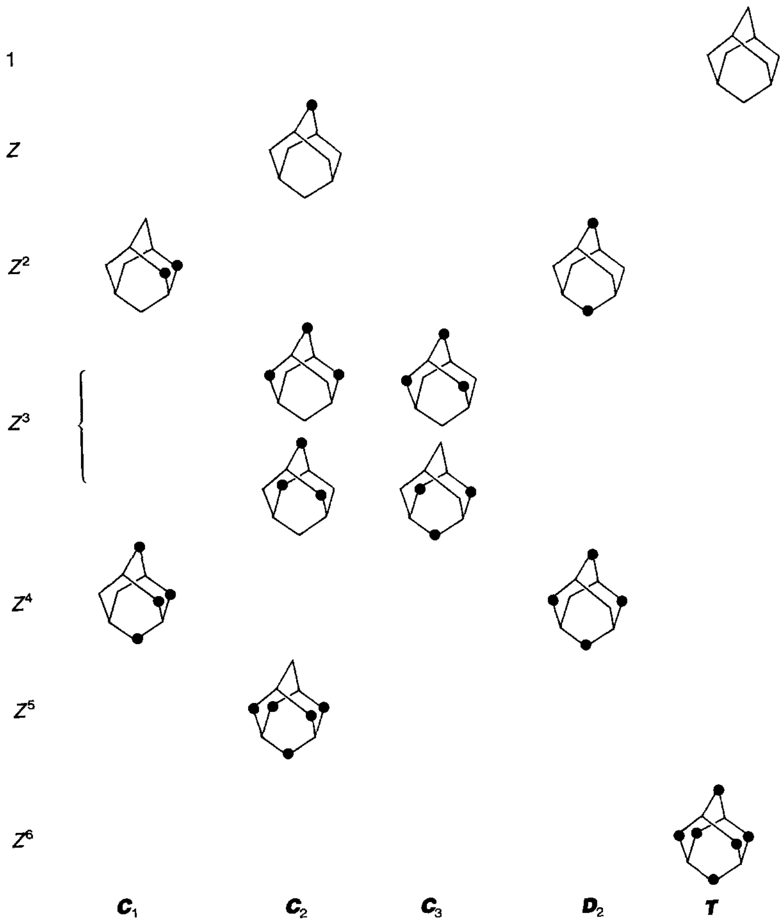


Fig. 3. Compounds derived from the adamantane skeleton (**2**). See Examples 4 and 6. The *solid circle* denotes an oxygen atom. Unmarked vertices are replaced by carbon atoms. Note that we take account of the $\boldsymbol{T}$ part only. Hence, the column of $\boldsymbol{C}_2$ symmetry contains molecules that should strictly be classified under $\boldsymbol{C}_{2v}$ symmetry, and so on

which are in turn introduced to Eq. (24) to afford

$$\begin{aligned}(11664 \quad 108 \quad 108 \quad 324 \quad 18)\\ =(A_{\boldsymbol{C}_1} \quad A_{\boldsymbol{C}_2} \quad A_{\boldsymbol{C}'_2} \quad A_{\boldsymbol{C}''_2} \quad A_{\boldsymbol{D}_2})\end{aligned} \begin{bmatrix} 4 & 0 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 & 0 \\ 2 & 0 & 2 & 0 & 0 \\ 2 & 0 & 0 & 2 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix}.$$

Hence, we arrive at

$$A_{\boldsymbol{C}_1} = 2790, \quad A_{\boldsymbol{C}_2} = 45, \quad A_{\boldsymbol{C}'_2} = 45, \quad A_{\boldsymbol{C}''_2} = 153, \quad \text{and } A_{\boldsymbol{D}_2} = 18.$$

These values are verified by a more intuitive treatment. In order to realize the $\boldsymbol{D}_2$ symmetry, every orbit in **1** must be filled with atoms of the same kind. Hence, the orbit (Δ_1 marked by the solid circle) takes four atoms of C or of N. Thereby, there appear two cases (i.e., C_4 and N_4). Since Δ_2 (solid square) can take two atoms of C, N, or O, there are three cases (i.e., C_2, N_2, and O_2). Similarly, there are three cases in the occupation of the orbit (Δ_3 (solid triangle)). Therefore, the combinatorial examination produces $2 \times 3 \times 3$ ($=18$) cases, which is equal to the number (A_{D_2}) obtained above.

5. Orbits of configurations with a given symmetry and with a given weight

In the previous sections, we have answered the question: what is the number of compounds of a subsymmetry based on a skeleton of a given symmetry under the OMV restriction? In the previous paper, we have also enumerated compounds of a given weight under the same restriction [8]. A further question is then: what is the number of compounds with a given subsymmetry as well as a given weight under the OMV restriction?

Suppose that the weight of a function is given by Eq. (14). In terms of the equivalence relation (Eq. 17), two equivalent functions are easily proved to have an equal weight [8]. It should be noted that the converse is not always true. Let $\boldsymbol{F}^{(\theta)}$ be a set of functions ($f: \Delta \rightarrow \boldsymbol{X}$) all of which have the same weight $W_\theta(f)$.

$$\boldsymbol{F}^{(\theta)} = \{f_1^{(\theta)}, f_2^{(\theta)}, \ldots, f_{|\boldsymbol{F}\theta|}^{(\theta)}\}. \tag{26}$$

Suppose that $P_g \in \boldsymbol{P_G}$ acts on $f_\gamma^{(\theta)} \in \boldsymbol{F}^{(\theta)}$ by Eq. (17). The resulting $f_\varepsilon^{(\theta)}$ is also a member of $\boldsymbol{F}^{(\theta)}$ by definition. Hence we obtain a permutation,

$$\begin{aligned} \lambda_g^{(\theta)} &= \begin{pmatrix} f_1^{(\theta)} P_g^{-1} \cdots f_{|\boldsymbol{F}\theta|}^{(\theta)} P_g^{-1} \\ f_1^{(\theta)} \cdots f_{|\boldsymbol{F}\theta|}^{(\theta)} \end{pmatrix} \\ &= \begin{pmatrix} f_1^{(\theta)} \cdots f_{|\boldsymbol{F}\theta|}^{(\theta)} \\ f_1^{(\theta)} P_g \cdots f_{|\boldsymbol{F}\theta|}^{(\theta)} P_g \end{pmatrix} \end{aligned} \tag{27}$$

The set $\Lambda_{\boldsymbol{G}}^{(\theta)}$ of $\lambda_g^{(\theta)}$ for $^\forall g \in \boldsymbol{G}$ can be proved to be a permutation group on $\boldsymbol{F}^{(\theta)}$ [8]. This formulation permits us to apply the general theorem (Eqs. 5 and 6) to this case.

Theorem 4.

$$\Lambda_{\boldsymbol{G}}^{(\theta)} = \sum_{i=1}^{s} A_{\theta i} \boldsymbol{G}(/\boldsymbol{G}_i) \tag{28}$$

and

$$\rho_{\theta j} = \sum_{i=1}^{s} A_{\theta i} m_j^{(i)} \tag{29}$$

where $\rho_{\theta j}$ is the mark of $\boldsymbol{G}_j$ in $\Lambda_{\boldsymbol{G}}^{(\theta)}$. The subscript or superscript θ is concerned with all different values of weights W_θ. The number of different weights is denoted $|\theta|$.

Equation (29) is equivalent to the following matrix equation

$$\begin{bmatrix} \rho_{11} & \cdots & \rho_{1j} & \cdots & \rho_{1s} \\ \rho_{21} & \cdots & \rho_{2j} & \cdots & \rho_{2s} \\ & & \cdots & & \\ \rho_{\theta 1} & \cdots & \rho_{\theta j} & \cdots & \rho_{\theta s} \\ & & \cdots & & \\ \rho_{|\theta|1} & \cdots & \rho_{|\theta|j} & \cdots & \rho_{|\theta|s} \end{bmatrix} = \begin{bmatrix} A_{11} & \cdots & A_{1s} \\ A_{21} & \cdots & A_{2s} \\ & \cdots & \\ & \cdots & \\ A_{|\theta|1} & \cdots & A_{|\theta|s} \end{bmatrix} \begin{bmatrix} m_1^{(1)} & \cdots & m_s^{(1)} \\ m_1^{(2)} & \cdots & m_s^{(2)} \\ & \cdots & \\ m_1^{(s)} & \cdots & m_s^{(s)} \end{bmatrix} \tag{30}$$

We call $(\rho_{\theta j})$ a fixed-point (FP) matrix and $(A_{\theta i})$ an isomer-counting matrix. The third matrix of Eq. (30) is the matrix representation of a table of marks. Obviously, the following equations hold:

$$A_i = \sum_{\theta} A_{\theta i}, \tag{31}$$

$$\rho_j = \sum_{\theta} \rho_{\theta j}. \tag{32}$$

The next problem is the evaluation of $\rho_{\theta j}$. We shall discuss a column of the mark matrix $(\rho_{\theta j})$. The series of elements:

$$\rho_{1j}, \rho_{2j}, \ldots, \rho_{\theta j}, \ldots, \quad \text{and } \rho_{|\theta|j}$$

of the jth column is concerned with configurations of symmetry $\boldsymbol{G}_j$. Suppose that $\boldsymbol{F}_j$ is a set of such configurations of symmetry $\boldsymbol{G}_j$.

A subduced representation $\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow\boldsymbol{G}_j$ acts on $\Delta_{i\alpha}$ $(\alpha = 1, 2, \ldots, \alpha_i)$ to produce the subdivision of $\Delta_{i\alpha}$ into β_k^{ij} suborbits of length d_{jk}, each of which satisfies Eqs. (8) and (9). In order for $f^{(j)} \in \boldsymbol{F}_j$ to be constant, each suborbit of length d_{jk} has to take the same figure (or ligand), i.e., $d_{jk}X_1$, or $d_{jk}X_2, \ldots$, or $d_{jk}X_{|X|}$. Hence, for each suborbit of $\Delta_{i\alpha}$, the corresponding generating function (figure inventory) is obtained,

$$\sum_{r=1}^{|X|} w_{i\alpha}(X_r)^{d_{jk}}. \tag{33}$$

Since this equation holds for all suborbits of $\Delta_{i\alpha}$, the multiplication over all the suborbits of the orbit $\Delta_{i\alpha}$ (i.e., over all subgroups $\boldsymbol{H}_k$) affords a generating function,

$$\prod_{k=1}^{v} \left(\sum_{r=1}^{|X|} w_{i\alpha}(X_r)^{d_{jk}} \right)^{\beta_k^{ij}}, \tag{34}$$

wherein β_k^{ij} is concerned with $\boldsymbol{H}_k$. Alternatively Eq. (34) follows from Eqs. (33) and (10). Note that Eq. (34) is concerned with $\boldsymbol{G}(/\boldsymbol{G}_i)\downarrow\boldsymbol{G}_j$ (or with $\Delta_{i\alpha}$). Since Eq. (34) is true for all orbits of Δ, the multiplication over all α and i provides a generating function,

$$\prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} \prod_{k=1}^{v} \left(\sum_{r=1}^{|X|} w_{i\alpha}(X_r)^{d_{jk}} \right)^{\beta_k^{ij}}, \quad (j = 1, 2, \ldots, s), \tag{35}$$

where $\beta_k^{ij} = 0$ if $\alpha_i = 0$.

Expansion of Eq. (35) leads to a polynomial that contains monomials expressed by Eq. (14). Since the multiplication over k in Eq. (35) contains monomials of total powers $(d_{j1}\beta_1^{ij} + d_{j2}\beta_2^{ij} + \cdots + d_{jk}\beta_k^{ij})$, we arrive at a generating function giving $\rho_{\theta j}$ as the coefficients of W_θ,

$$\sum_{\theta} \rho_{\theta j} W_\theta = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} \prod_{k=1}^{v} \left(\sum_{r=1}^{|X|} w_{i\alpha}(X_r)^{d_{jk}} \right)^{\beta_k^{ij}} \quad (j = 1, 2, \ldots, s), \tag{36}$$

where $\beta_k^{ij} = 0$ if $\alpha_i = 0$.

To formulate the above discussion, we define a subduced cycle index $Z(\boldsymbol{G}_j; s_{d_{jk}}^{(\alpha)})$ for $\boldsymbol{G}_j \leqslant \boldsymbol{G}$ by using USCIs (Eq. 10).

Definition 3 (subduced cycle index).

$$Z(\boldsymbol{G}_j;\, s_{d_{jk}}^{(\alpha)}) = \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} Z(\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j;\, s_{d_{jk}}^{(\alpha)})$$

$$= \prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} \prod_{k=1}^{v} (s_{d_{jk}}^{(\alpha)})^{\beta_k^{ij}} \quad (j = 1, 2, \ldots, s), \tag{37}$$

where $\beta_k^{ij} = 0$ if $\alpha_i = 0$. The superscript (α) is associated with the corresponding orbit $\Delta_{i\alpha}$.

The subduced cycle index can be obtained from a table of USCIs that has been preestimated by examining the reducible subduced representations of a transitive coset representation (Sect. 3). We summarize the above results expressed in Eq. (36) in the form of the following lemma.

Lemma 1. *If $\boldsymbol{G}_j \leqslant \boldsymbol{G}$ acts on Δ under the restriction of weights (Eq. 14), the generating function for marks $\rho_{\theta j}$ with a weight W_θ is given by the following generating function*:

$$\sum_{\theta} \rho_{\theta j} W_\theta = Z(\boldsymbol{G}_j;\, s_{d_{jk}}^{(\alpha)}) \quad (j = 1, 2, \ldots, s), \tag{38}$$

where the right-hand side is replaced by

$$s_{d_{jk}}^{(\alpha)} = \sum_{r=1}^{|X|} w_{i\alpha}(X_r)^{d_{jk}}. \tag{39}$$

Equation (39) *is a kind of generating function, which we call a figure inventory. The following example illustrates an application of Lemma* 1.

Example 6

Let us reexamine Case 1 of Example 4. The use of the following weights,

$$w_1(\mathrm{C}) = 1, \qquad w_1(\mathrm{O}) = 0 \quad \text{for the orbit } \Delta_1$$

and

$$w_2(\mathrm{C}) = 1, \qquad w_2(\mathrm{O}) = z \quad \text{for the orbit } \Delta_2,$$

in Eq. (39) provides two inventories, i.e.,

$$s_t^{(1)} = 1 \qquad \text{for the orbit } \Delta_1$$

and

$$s_t^{(2)} = 1 + z^t \quad \text{for the orbit } \Delta_2.$$

Note that the orbits Δ_1 and Δ_2 correspond to $\boldsymbol{T}(/\boldsymbol{C}_3)$ and $\boldsymbol{T}(/\boldsymbol{C}_2)$, respectively. Hence, we use the $\boldsymbol{T}(/\boldsymbol{C}_3)$ and $\boldsymbol{T}(/\boldsymbol{C}_2)$ rows of Table 14 to find

$$\begin{aligned}
(s_1^4)^{(1)}(s_1^6)^{(2)} &= (1+z)^6 && \text{for } \boldsymbol{G}_1 = \boldsymbol{C}_1\\
(s_2^2)^{(1)}(s_1^2 s_2^2)^{(2)} &= (1+z)^2(1+z^2)^2 && \text{for } \boldsymbol{G}_2 = \boldsymbol{C}_2\\
(s_1 s_3)^{(1)}(s_3^2)^{(2)} &= (1+z^3)^2 && \text{for } \boldsymbol{G}_3 = \boldsymbol{C}_3\\
(s_4)^{(1)}(s_2^3)^{(2)} &= (1+z^2)^3 && \text{for } \boldsymbol{G}^4 = \boldsymbol{D}_2\\
(s_4)^{(1)}(s_6)^{(2)} &= 1+z^6 && \text{for } \boldsymbol{G}_5 = \boldsymbol{T},
\end{aligned}$$

where the superscripts (1) and (2) denote Δ_1 and Δ_2, respectively. These expressions are the explicit forms of Eq. (38) for this example. The expansion of them yields the columns of the corresponding FP matrix $(\rho_{\theta j})$. We now obtain

$$\begin{array}{c} \\ 1 \\ z \\ z^2 \\ z^3 \\ z^4 \\ z^5 \\ z^6 \end{array}
\begin{array}{c} \begin{array}{ccccc} \boldsymbol{C}_1 & \boldsymbol{C}_2 & \boldsymbol{C}_3 & \boldsymbol{D}_2 & \boldsymbol{T} \end{array} \\
\begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 6 & 2 & 0 & 0 & 0 \\ 15 & 3 & 0 & 3 & 0 \\ 20 & 4 & 2 & 0 & 0 \\ 15 & 3 & 0 & 3 & 0 \\ 6 & 2 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \end{array}
= A \begin{pmatrix} 12 & 0 & 0 & 0 & 0 \\ 6 & 2 & 0 & 0 & 0 \\ 4 & 0 & 1 & 0 & 0 \\ 3 & 3 & 0 & 3 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

which provides the number of isomers with a given symmetry as well as a given weight in the form of an isomer-counting matrix:

$$A = \begin{array}{c} \\ 1 \\ z \\ z^2 \\ z^3 \\ z^4 \\ z^5 \\ z^6 \end{array}
\begin{array}{c} \begin{array}{ccccc} \boldsymbol{C}_1 & \boldsymbol{C}_2 & \boldsymbol{C}_3 & \boldsymbol{D}_1 & \boldsymbol{T} \end{array} \\
\begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 2 & 2 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix} \end{array}$$

Figure 3 illustrates the results appearing in this matrix.

7. Special cases

In Sects. 4 to 6, we have taken account of OMVs. There are, however, many cases where it is not necessary to consider the OMVs. These cases are formulated here as special cases of the treatment described above. Suppose that all the weights given previously by Eq. (13) are defined by the following equations for this situation:

$$w_{i\alpha}(X_r) = X_r \quad \text{for } i = 1, 2, \ldots, s,\ \alpha = 1, 2, \ldots, \alpha_i, \text{ and } r = 1, 2, \ldots, |X|. \tag{40}$$

Then the weight of a function (configuration) is represented by the equation,

$$W(f) = \prod_{\delta \in \Delta} w_{i\alpha}(f(\delta)). \tag{41}$$

The first object of this section is to obtain a solution when Corollary 3.2 is applied to this case. Because all $|X_{i\alpha}|$'s are equal to $|X|$, the left-hand side of Eq. (25) is transformed as follows:

$$\prod_{i=1}^{s} |X|^{\alpha_i \beta_{ij}} = |X|^{\sum_{i=1}^{s} \alpha_i \beta_{ij}}.$$

Hence, by using Eq. (25), we end up with the following corollary:

Corollary 3. *Let a group of* $\boldsymbol{G}$ *act on* $\boldsymbol{F}$ *by acting on* Δ. *Then the number of* A_i *of orbits with symmetry* $\boldsymbol{G}_i$ *constitutes the solution of linear equations,*

$$|X|^{\sum_{i=1}^{s} \alpha_i \beta_{ij}} = \sum_{i=1}^{s} A_i m_j^{(i)} \quad (j = 1, 2, \ldots, s). \tag{42}$$

This corollary is the counterpart of Hässelbarth's Corollary 1 [4]. However, Eq. (42) contains the number of orbits as a concrete power, i.e.

$$\sum_{i=1}^{s} \alpha_i \beta_{ij},$$

where α_i is obtained by Eq. (5) and β_{ij} is derived from Eq. (11). It should be emphasized that the introduction of subduced representations results in the present approach being more detailed than Hässelbarth's.

The second problem of this section is the determination of the number of fixed configurations with symmetry $\boldsymbol{G}_j$ as well as a weight W_θ without consideration of OMV. The left-hand side of Eq. (37) is transformed under the condition of Eqs. (39) and (40),

$$\begin{aligned}
\prod_{i=1}^{s} \prod_{\alpha=0}^{\alpha_i} \prod_{k=1}^{v} (s_{d_{jk}}^{(\alpha)})^{\beta_k^{ij}} &= \prod_{i=1}^{s} \prod_{k=1}^{v} \prod_{\alpha=0}^{\alpha_i} (s_{d_{jk}}^{(\alpha)})^{\beta_k^{ij}} \\
&= \prod_{i=1}^{s} \prod_{k=1}^{v} (s_{d_{jk}})^{\alpha_i \beta_k^{ij}} \\
&= \prod_{k=1}^{v} \prod_{i=1}^{s} (s_{d_{jk}})^{\alpha_i \beta_k^{ij}} \\
&= \prod_{k=1}^{v} (s_{d_{jk}})^{\sum_{i=1}^{s} \alpha_i \beta_k^{ij}},
\end{aligned}$$

in which the superscript (α) can be omitted, since $s_{d_{jk}}^{(\alpha)}$ is independent upon $\Delta_{i\alpha}$. This provides a new form of subduced cycle index suitable to the special case. That is

Definition 4 (subduced cycle index).

$$Z'(G_j;\, s_{d_{jk}}) = \prod_{k=1}^{v} (s_{d_{jk}})^{\sum_{i=1}^{s} \alpha_i \beta_k^{ij}} \tag{43}$$

By the use of the definition, Lemma 1 can be converted into Lemma 2 to meet the present requirement. Note that all $w_{i\alpha}(X_r) = X_r$.

Lemma 2. *If $\boldsymbol{G}_j \leqslant \boldsymbol{G}$ acts on Δ, a generating function for marks $\rho_{\theta j}$ with a weight W_θ is given by the equation,*

$$\sum_{\theta} \rho_{\theta j} W_\theta = Z'(\boldsymbol{G}_j;\, s_{d_{jk}}) \tag{44}$$

$$(j = 1, 2, \ldots, s)$$

$$s_{d_{jk}} = \sum_{r=1}^{|X|} X_r^{d_{jk}}. \tag{45}$$

This lemma is more informative than Hässelbarth's counterpart [4], since the former is based on the subduced cycle index. Thus, the power of the cycle index,

$$\sum_{i=1}^{s} \alpha_i \beta_k^{ij}$$

comes from the subduced representation $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ in the present method.

Finally, it is worthwhile mentioning the differences between our approach and Hässelbarth's one. Figure 1 illustrates an essence of our approach, in which the first division of a domain by $\boldsymbol{G}$ and the subsequent subdivision by a subduced representation $\boldsymbol{G}(/\boldsymbol{G}_i) \downarrow \boldsymbol{G}_j$ enable us to realize precise classification of the positions of a domain (Δ). Thus a suborbit $\Delta_{k\beta}^{ij}$ is ascribed to the corresponding orbit $\Delta_{i\alpha}$, which is in turn determined by the coset representation $\boldsymbol{G}(/\boldsymbol{G}_i)$. Hence, we have arrived at the concept of subduced cycle index, which is effective in the enumeration under the influence of the obligatory minimum valency (OMV).

By way of contrast, Hässelbarth's approach considers each subgroup $\boldsymbol{G}_j$ ($\leqslant \boldsymbol{G}$) acting directly on the domain (Δ). In other words, it disregards the action of the group $\boldsymbol{G}$ on Δ in the evaluation process of fixed points. As a result, it shows less discrimination in its classification of the positions. Hence, it is limited to the cases on which the OMV has no effect.

8. Conclusion

We have reported the enumeration of compounds with and without the influence of obligatory minimum valence (OMV). To solve the problem concerned with the restriction by the OMV, different weights are assigned to respective orbits of a parent skeleton. Several new concepts associated with subduced representations are the essential parts of the present work.

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