

## ENUMERATION OF ORGANIC REACTIONS BY COUNTING SUBSTRUCTURES OF IMAGINARY TRANSITION STRUCTURES. IMPORTANCE OF ORBITS GOVERNED BY COSET REPRESENTATIONS

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### Abstract

Two methods for the enumeration of organic reactions are presented in order to take obligatory minimum valencies of a given skeleton into consideration. The first method is a generalization of Pólya's theorem, in which the transitivity of the positions of the skeletons is explicitly considered. Thus, a permutation representation acting on the positions is reduced into coset representations (CRs). In accord with this reduction, unit cycle indices derived from the CRs construct a generalized cycle index. The second method is based on the subduction of the coset representations. This contains useful concepts such as unit subduced cycle indices and subduced cycle index that afford a new type of generating functions.

### 1. Introduction

The systematic enumeration of reactions of inorganic complexes has been thoroughly investigated by several authors in terms of effective mathematical formulations [1]. On the other hand, mathematical approaches to the systematic enumeration of *organic* reactions have long remained unchallenged, whereas there have appeared a vast number of manual enumerations and classification methods of organic reactions [2]. This is mainly because there have been no effective formulations suitable to mathematical treatments. In previous papers [3,4], we have formulated individual organic reactions as imaginary transition structures (ITSs) having three kinds of bonds (par-bonds, out-bonds and in-bonds) [5]. A set of individual reactions is thereby classified into a reaction type which is designated as a reaction-center graph (RCG) or a reaction graph (RG) abstracted from such ITSs. This formulation allows us to regard the enumeration of organic reactions as the counting of RCGs or RGs. Thus, the RGs are counted by placing par-bonds on the edges of a basic reaction graph (BRG) as a parent skeleton [6]; the RCGs are enumerated by substituting appropriate atoms for the vertices of an RG as a parent [7].

In the enumeration of the RCGs, we have encountered the restriction due to obligatory minimum valencies (OMVs) [8]. The consideration of the OMV requires careful attention to the transitivity of positions contained in a skeleton. It affords more general results than those of conventional methods. Thus, we have already

reported an enumeration of reaction types under the OMV restriction [7]. As a continuation of this work, the present paper [9] deals with an extension of Pólya's theorem to more general cases in which the positions of a given skeleton construct one or more orbits governed by coset representations (CRs). Although the mathematical foundation of this method has been reported elsewhere [10], its scope and applications to reaction enumerations have not been investigated; these are the first issues of the present paper. Another issue of the present report is an application of a novel theorem that has been developed for the enumeration of organic compounds [11]. Such an application to reaction enumerations indicates the merits of this theorem. Both of these methods are based on the concept of coset representations (CRs), which has attracted little attention in chemical enumerations. We also discuss the relationship between the two methods and emphasize the importance of CRs. We will restrict ourselves to problems in chemistry, and our results will be applicable to other combinatorial enumerations [12–14].

## 2. Formulation

### 2.1. GLOSSARY FOR THE ITS (IMAGINARY TRANSITION STRUCTURE) APPROACH

This glossary is devoted to the definition of terms and acronyms used in the present approach [3].

An *imaginary transition structure (ITS)* is defined as a structure in which molecules in the starting stage of a given reaction are superposed onto the corresponding products (contained in the product stage), and three kinds of bonds (par-bonds, out-bonds, and in-bonds) are distinguished.

The term *par-bond* (–) denotes a bond that appears both in one of the starting molecules and in one of the products. In other words, the par-bond is kept intact during the reaction. An *out-bond* (–||–) is defined as a bond that appears only in one of the starting molecules. This means that the out-bond is a bond cleaved during the reaction. The term *in-bond* (–○–) is used to refer to a bond that appears only in one of the products. In other words, the in-bond is a bond formed during the reaction.

A *reaction-center graph (RCG)* is defined as a substructure (or subgraph) of such an imaginary transition structure (ITS), where all atoms and bonds (par-, out-, and in-bonds) participating in a reaction are selected. A *reaction graph (RG)* is defined as a simplified reaction-center graph in which all of the atoms are replaced by abstract balls (or unmarked vertices). Note the distinction between the RCG and the RG. For example, the RCG of a Cope rearrangement is different from that of a Claisen rearrangement; however, they afford the same RG. A *basic reaction graph (BRG)* is defined as a simplified reaction graph in which all par-bonds are omitted.

The *obligatory minimum valency (OMV)* is a valency that is permitted for a vertex of an RG. For example, if the OMV of a vertex is equal to 3, the vertex can take an atom having tri- or more-valency (e.g. C and N), but cannot take a mono- or di-valent atom such as H and O.

A *projection to the starting stage (PS)* is defined as an operation that deletes all in-bonds. This operation affords the molecules of the starting stage. A *projection to the product stage (PP)* is defined as an operation that deletes all out-bonds, which gives the corresponding products.

## 2.2. CLASSIFICATION AND ENUMERATION

An imaginary transition structure (ITS) contains a reaction-center graph (RCG) as a substructure or subgraph. If we take no account of atoms of the RCG, we can obtain a more generic subgraph, i.e. a reaction graph (RG). For example, ITS 1 represents a reaction belonging to a category of Claisen's rearrangement (fig. 1). This

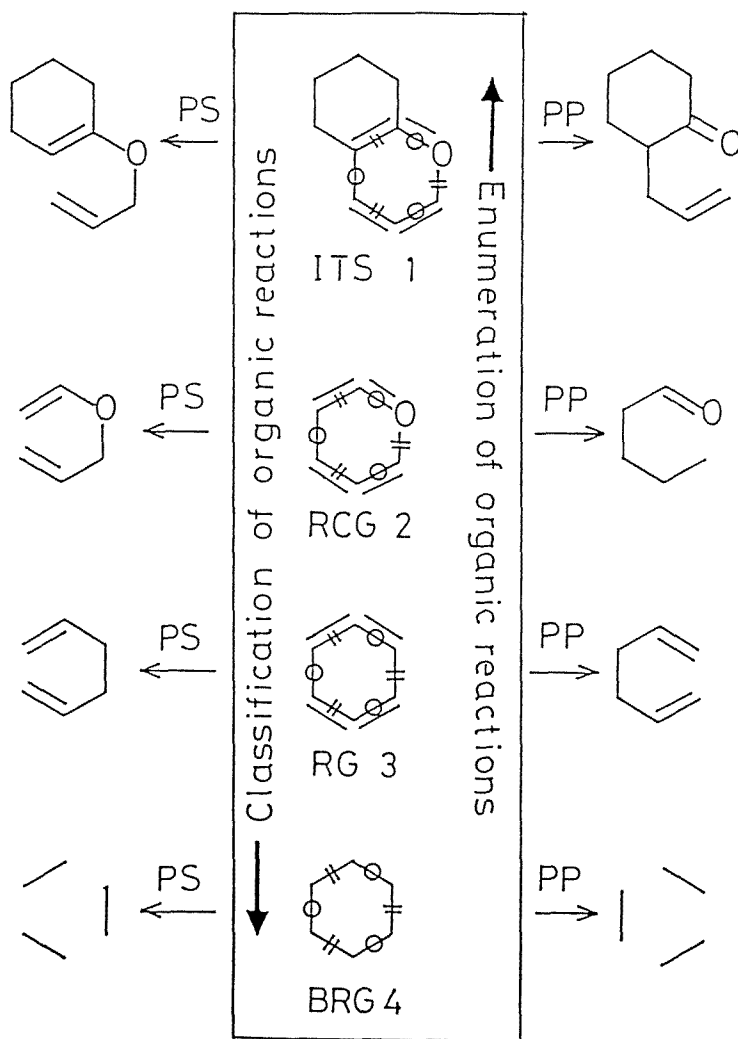


Fig. 1. ITS, RCG and RG for a [3,3]-sigmatropic reaction.

is verified by two operations, PS and PP. Thus, the deletion of all in-bonds of **1** (projection to the starting stage: PS) affords the corresponding starting molecule. On the other hand, the deletion of all out-bonds of **1** (projection to the product stage: PP) creates a product. The ITS **1** contains an RCG **2** that corresponds to a reaction type called Claisen's rearrangement. A more generic name, a [3, 3]-sigmatropic reaction, is assigned to the RG **3**. When we take no account of par-bonds, we obtain a basic reaction graph **4**, which represents a mode of bond switching.

It should be noted that the concepts RCG and RG are distinct from each other in spite of their apparent resemblance. Thus, the RCG **2** contains  $C_5O$  on its vertices, although the five carbon atoms are not explicitly shown according to a chemist's convention. This RCG represents a set of Claisen rearrangements. In contrast, each vertex of the RG **3** has a ball in an abstract fashion. This RG represents a set of [3, 3]-sigmatropic reactions, which involves Cope rearrangements, oxy-Cope rearrangements, N-analogs of the Claisen rearrangement and so on, in addition to the Claisen rearrangement.

As we have shown in fig. 1, the process of abstraction (ITS  $\rightarrow$  RCG  $\rightarrow$  RG  $\rightarrow$  BRG) provides a general method of classifying organic reactions, since this corresponds to the conventional process of constructing a reaction hierarchy, i.e. an individual organic reaction  $\rightarrow$  a reaction type  $\rightarrow$  a generic reaction type  $\rightarrow$  a mode of bond switching. The reverse process (BRG  $\rightarrow$  RG  $\rightarrow$  RCG  $\rightarrow$  ITS) provides a versatile methodology for the enumeration of organic reactions [7, 11].

### 2.3. RG-ISOMERS AND RCG-ISOMERS

Since the concept of ITS is an extended concept of usual chemical structure, all concepts in the chemical structure can be extended to apply in the ITS. Hence, the term *isomerism* is extended for the purpose of enumerating RGs and RCGs.

Two RGs are defined as being *isomeric* if they have the same BRG and the same number of par-bonds. For example, the RGs of fig. 2 are isomeric, since they

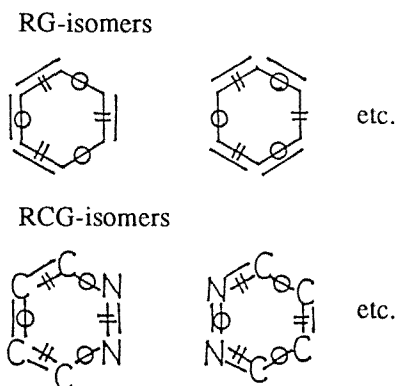


Fig. 2. RG-isomers and RCG-isomers.

are derived from a common basic reaction graph (BRG) by substituting four single par-bonds on its edges. We refer to such isomeric reaction graphs as *RG-isomers*.

Two RCGs are defined as being *isomeric* if they have the same RG and the same set of atoms. For example, the RCGs of fig. 2 are isomeric, since they have the same formula ( $C_4N_2$ ). We call such isomeric reaction-center graphs *RCG-isomers*.

#### 2.4. ORBITS OF A PARENT REACTION GRAPH

We have reported the enumerations of RCGs under the influence of obligatory minimum valencies (OMVs) inherent to the orbits of a parent RG [7], where we have assigned different variables to the different orbits. However, we have taken no account of the correspondence between such an orbit and a coset representation. In this section, we will deal with this correspondence more strictly than in the previous treatment.

In general, let  $G$  be a finite group that keeps a given parent skeleton invariant. The group  $G$  has an irredundant set of subgroups  $G_i$  ( $i = 1, 2, \dots, s$ ), each of which is a representative selected from respective conjugate subgroups, where  $s$  denotes the number of such representatives. The group  $G$  thus acts on the set ( $\Delta$ ) of positions of the skeleton to give a permutation group  $P_G$  on  $\Delta$ . If  $P_G$  is intransitive, the domain  $\Delta$  is divided into orbits. This division is accomplished by theorem 1, which is by Burnside [15].

##### THEOREM 1

Any permutation representation  $P_G$  is reduced to a set of (transitive) coset representations (CRs) in the form of

$$P_G = \sum_{i=1}^s \alpha_i G / G_i, \quad (1)$$

where the symbol  $G/G_i$  denotes a CR derived from a coset decomposition of  $G$  by  $G_i$  [16]. The multiplicities  $\alpha_i$  are non-negative integers determined by solving the following equations:

$$\mu_j = \sum_{i=1}^s \alpha_i m_{ij} \quad (j = 1, 2, \dots, s), \quad (2)$$

where  $\mu_j$  is the mark (the number of fixed points) of  $G_j$  in  $P_G$ , and the symbol  $m_{ij}$  denotes the mark of  $G_j$  in  $G/G_i$ .

An  $s \times s$  matrix or table collecting the  $m_{ij}$ 's is called a *table of marks* for the  $G$  group. Such tables of marks were reported for several groups and applied to enumeration problems [17]. The mark ( $\mu_j$ ) of a subgroup  $G_j$  in  $P_G$  is obtained by counting cycles of length = 1 (invariant members) in  $P_G$  under the action of  $G_j$ . This task is also accomplished by counting immobile positions of the skeleton ( $G$  symmetry) with respect to all symmetry operations of  $G_j$ .

Equation (1) corresponds to the division of the domain  $\Delta$  which affords orbits:  $\Delta_{i\alpha}$  ( $i = 1, 2, \dots, s$  and  $\alpha = 1, 2, \dots, \alpha_i$ ), on which  $G/(G_i)$  acts. The length of  $\Delta_{i\alpha}$  is equal to the degree of the corresponding  $G/(G_i)$ , i.e.  $|\Delta_{i\alpha}| = |G|/|G_i|$ .

*Example 1* (Orbits concerning six vertices in the RG 3)

Let us work out the RG 3 representing a [3, 3]-sigmatropic reaction (fig. 3). We select the  $C_2$  group to describe the symmetry of this skeleton. The six vertices of this skeleton are divided into three equivalence classes ( $\Delta_1 = \{1, 5\}$ ,  $\Delta_2 = \{2, 6\}$ , and  $\Delta_3 = \{3, 4\}$ ), which we refer to as orbits. This division can be easily done by inspection.

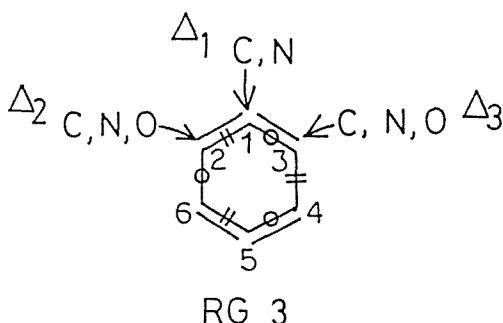


Fig. 3. Orbits of a parent RG for a [3, 3]-sigmatropic reaction.

These orbits are subject to appropriate coset representations (CRs). The assignment of each orbit to a CR is accomplished by using a table of marks [15]. This skeleton (3) is invariant to a permutation group,

$$P_{C_2} = \{(1)(2)(3)(4)(5)(6), (1\ 5)(2\ 6)(3\ 4)\}. \quad (3)$$

The numbers of fixed points ( $\mu_j$ 's) are obtained easily by examining this permutation group as being  $\mu_{C_1} = 6$  and  $\mu_{C_2} = 0$ . In the present case, eq. (2) is obtained as a matrix expression, being

$$(6\ 0) = (\alpha_{C_1}\ \alpha_{C_2}) \begin{pmatrix} 2 & 0 \\ 1 & 1 \end{pmatrix}. \quad (4)$$

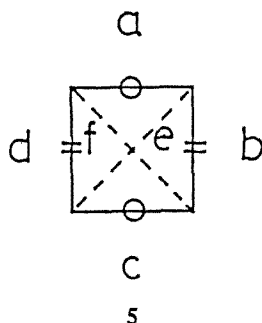
The second matrix on the right-hand side of eq. (4) is a table of marks for the  $C_2$  group. Thereby, we have  $\alpha_{C_1} = 3$  and  $\alpha_{C_2} = 0$ . Three orbits ( $\Delta_1 = \{1, 5\}$ ,  $\Delta_2 = \{2, 6\}$ , and  $\Delta_3 = \{3, 4\}$ ) are concluded to be subject to the same CR,  $C_2/(C_1)$ . This fact is algebraically represented by

$$P_{C_2} = 3C_2/(C_1). \quad (5)$$

The OMV influences the mode of substitution on a given skeleton. The vertices of  $\Delta_1$  have  $OMV = 3$  and, hence, cannot take less than trivalent atoms. However, the other positions, having  $OMV = 2$  ( $\Delta_2$  and  $\Delta_3$ ), can take bi- or more-valent atoms. Thus, even if the same CR governs several orbits, these orbits can take different sets of substituents according to their OMVs.

Example 2 shows orbits concerning edges of a basic reaction graph (BRG).

*Example 2* (Orbits of edges in a square BRG with cross-linked phantom edges (5) of  $D_2$  symmetry)



Let us consider the skeleton (5) to have  $D_2$  symmetry. Its subgroups are represented by  $C_1 = \{I\}$ ,  $C_2 = \{I, C_{2(3)}\}$ ,  $C_2' = \{I, C_{2(1)}\}$ ,  $C_2'' = \{I, C_{2(2)}\}$ , and  $D_2 = \{I, C_{2(3)}, C_{2(1)}, C_{2(2)}\}$ . The permutation representation ( $P_{D_2}$ ) consists of four permutations,  $I \sim (a)(b)(c)(d)(e)(f)$ ,  $C_{2(3)} \sim (a\ c)(b\ d)(e)(f)$ ,  $C_{2(1)} \sim (a)(c)(b\ d)(e\ f)$ , and  $C_{2(2)} \sim (a\ c)(b)(d)(e\ f)$ . When we operate every symmetry operation to this BRG, we obtain the number of fixed points for each subgroup by inspection, i.e.,

$$\mu_{C_1} = 6, \mu_{C_2} = 2, \mu_{C_2'} = 2, \mu_{C_2''} = 2, \text{ and } \mu_{D_2} = 0. \quad (6)$$

These values can also be obtained by counting cycles of length = 1 in  $P_{D_2}$  under the action of every subgroup. These values are introduced into eq. (2), affording

$$\begin{aligned}
 & (\alpha_{C_1} \alpha_{C_2} \alpha_{C_2'} \alpha_{C_2''} \alpha_{D_2}) \\
 & = (6 \ 2 \ 2 \ 2 \ 0) \begin{pmatrix} 1/4 & 0 & 0 & 0 & 0 \\ -1/4 & 1/2 & 0 & 0 & 0 \\ -1/4 & 0 & 1/2 & 0 & 0 \\ -1/4 & 0 & 0 & 1/2 & 0 \\ 1/2 & -1/2 & -1/2 & -1/2 & 1 \end{pmatrix} = (0 \ 1 \ 1 \ 1 \ 0). \quad (7)
 \end{aligned}$$

Note that this expression uses the inverse form of eq. (2), where the  $5 \times 5$  matrix is the inverse of the table of marks for the  $D_2$  group. The resulting row vector (0 1 1 1 0) corresponds to the reduction represented by

$$P_{D_2} = D_2(/C_2) + D_2(/C_2') + D_2(/C_2''), \quad (8)$$

which gives three orbits:  $\Delta_1 = \{e, f\}$ ,  $\Delta_2 = \{a, c\}$ ,  $\Delta_3 = \{b, d\}$ .

### 3. Isomer enumeration under the OMV restriction

#### 3.1. GENERALIZATION OF PÓLYA'S THEOREM

In order to manipulate the OMV restriction, we explicitly consider a partition of positions of a given skeleton. We then provide different sets of weights to different orbits of the skeleton. This idea requires a generalization of Pólya's theorem. Suppose that  $\Delta = \{\delta_1, \delta_2, \dots, \delta_{|\Delta|}\}$  is a domain which contains vertices of the skeleton and  $\mathbf{X} = \{X_1, X_2, \dots, X_{|\mathbf{X}|}\}$  is a co-domain which contains atoms or ligands. Let a finite group  $\mathbf{G}$  act on  $\Delta$  in the form of the permutation representation  $\mathbf{P}_{\mathbf{G}}$  on  $\Delta$ . The action of  $\mathbf{G}$  on  $\Delta$  affords a partition to give  $\Delta_{i\alpha}$  ( $i = 1, 2, \dots, s$  and  $\alpha = 1, 2, \dots, \alpha_i$ ), each of which is governed by  $\mathbf{G}/(G_i)$  according to eq. (1). Suppose that a weight:  $w_{i\alpha}(X_r)$  (for  $i = 1, 2, \dots, s$ ,  $\alpha = 1, 2, \dots, \alpha_i$  and  $r = 1, 2, \dots, |\mathbf{X}|$ ) is assigned to each orbit  $\Delta_{i\alpha}$ . We then define a weight of a function (configuration) as follows.

#### DEFINITION 1

(Weight of function)

$$W(f) = \prod_{i=1}^s \prod_{\substack{\alpha=1 \\ \alpha_i \neq 0}}^{\alpha_i} \prod_{\delta \in \Delta_{i\alpha}} w_{i\alpha}(f(\delta)) \quad (9)$$

for a function  $f: \Delta \rightarrow \mathbf{X}$ .

If two functions  $f_\gamma$  and  $f_\epsilon: \Delta \rightarrow \mathbf{X}$  are equivalent to each other, then  $W(f_\gamma)$  can be proven to be equal to  $W(f_\epsilon)$ . This relation provides us with a more mathematical definition of isomers, in which two functions ( $f_\gamma$  and  $f_\epsilon$ ) are isomeric to each other if  $W(f_\gamma) = W(f_\epsilon)$  and if they are not equivalent [7].

Each CR,  $\mathbf{G}/(G_i)$ , is a transitive permutation representation on  $\Delta_{i\alpha}$ . We can separately treat every orbit governed by such a CR [7]. Suppose that  $G/(G_i)_g \in \mathbf{G}/(G_i)$  corresponds to  $g \in \mathbf{G}$ . The cycle structure of the  $G/(G_i)_g$  permutation is represented by the number  $i_\tau$  of cycles of size  $\tau$  ( $\tau = 1$  to  $m$ ), where  $m = |\Delta_{i\alpha}| = |\mathbf{G}|/|G_i|$ . That is to say,

$$\{i_1, i_2, \dots, i_m\}, \quad (10)$$

where

$$\sum_{\tau=1}^m \tau i_\tau = m. \quad (11)$$

We then assign a variable  $s_\tau$  to a cycle of length  $\tau$ . Thereby, we define a *unit cycle index (UCI)* by the following statement [10].



## DEFINITION 2

A unit cycle index (UCI) for  $G/(G_i)_g$  is represented by

$$z_g^{(i\alpha)} = \left( \sum_{\tau=1}^m s_{\tau}^{i_{\tau}} \right)_{(g)}^{(i\alpha)}. \quad (12)$$

The superscript  $(i\alpha)$  is concerned with the orbit  $\Delta_{i\alpha}$  on which  $G/(G_i)$  acts.

Since every CR is determined algebraically through a coset decomposition of  $G$  by  $G_i$ , we can precalculate UCIs for the elements of the CR. Table 1 lists all of the CRs for the  $D_2$  group, which are obtained by the corresponding coset decompositions. Table 2 collects unit cycle indices for the  $D_2$  symmetry, which are easily obtained by the data of table 1.

Table 1  
Coset representations for the  $D_2$  group

Operation	$D_2/(C_1)$	$D_2/(C_2)$	$D_2/(C_2')$	$D_2/(C_2'')$	$D_2/(D_2)$
$I$	(1) (2) (3) (4)	(1) (2)	(1) (2)	(1) (2)	(1)
$C_{2(3)}$	(1 2) (3 4)	(1) (2)	(1 2)	(1 2)	(1)
$C_{2(1)}$	(1 3) (2 4)	(1 2)	(1) (2)	(1 2)	(1)
$C_{2(2)}$	(1 4) (2 3)	(1 2)	(1 2)	(1) (2)	(1)

Table 2  
Unit cycle indices for the  $D_2$  group

Operation	$D_2/(C_1)$	$D_2/(C_2)$	$D_2/(C_2')$	$D_2/(C_2'')$	$D_2/(D_2)$
$I$	$s_1^4$	$s_1^2$	$s_1^2$	$s_1^2$	$s_1$
$C_{2(3)}$	$s_2^2$	$s_1^2$	$s_2$	$s_2$	$s_1$
$C_{2(1)}$	$s_2^2$	$s_2$	$s_1^2$	$s_2$	$s_1$
$C_{2(2)}$	$s_2^2$	$s_2$	$s_2$	$s_1^2$	$s_1$

Table 3  
Coset representations for the  $D_3$  group

Operation	$D_3/(C_1)$	$D_3/(C_2)$	$D_3/(C_3)$	$D_3/(D_3)$
$I$	(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 3 collects all of the coset representations for the  $D_3$  group. Table 4 indicates unit cycle indices for the  $D_3$  symmetry.

Table 4  
Unit cycle indices for the  $D_3$  group

Operation	$D_3(/C_1)$	$D_3(/C_2)$	$D_3(/C_3)$	$D_3(/D_3)$
$I$	$s_1^6$	$s_1^3$	$s_1^2$	$s_1$
$C_3$	$s_3^2$	$s_3$	$s_1^2$	$s_1$
$C_3^2$	$s_3^2$	$s_3$	$s_1^2$	$s_1$
$C_{2(1)}$	$s_2^3$	$s_1s_2$	$s_2$	$s_1$
$C_{2(2)}$	$s_2^3$	$s_1s_2$	$s_2$	$s_1$
$C_{2(3)}$	$s_2^3$	$s_1s_2$	$s_2$	$s_1$

By using the UCIs ( $z_g^{(i\alpha)}$ ), we obtain the definition of a cycle index [10].

DEFINITION 3

(Cycle index)

$$CI(\mathbf{P}_G; s_\tau^{(i\alpha)}) = \frac{1}{|G|} \sum_{g \in G} \prod_{i=1}^s \prod_{\substack{\alpha_i \\ \alpha_i \neq 0}} z_g^{(i\alpha)}. \quad (13)$$

This definition is essentially equivalent to Pólya's cycle index. However, this has some advantages so that the UCIs in eq. (13) can be precalculated and tabulated, as shown in tables 2 and 4, and so that this equation takes OMVs into consideration.

We can obtain the following theorem, which is a generalization of Pólya's theorem. The proof has been reported elsewhere [10].

THEOREM 2

The number ( $A_\theta$ ) of configurations with a weight  $W_\theta$  is obtained in terms of a generating function:

$$\sum_{\theta} A_{\theta} W_{\theta} = CI(\mathbf{P}_G; s_\tau^{(i\alpha)}), \quad (14)$$

where the corresponding figure-inventories are represented by

$$s_\tau^{(i\alpha)} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha}(X_r)^\tau. \quad (15)$$

## 3.2. THE FIRST PROCEDURE FOR THE ENUMERATION OF ORGANIC REACTIONS

A procedure for the enumeration in terms of the above mentioned method is summarized as follows:

- (1) determination of the symmetry  $G$  of a parent skeleton;
- (2) the counting of fixed points (marks) in the  $G$ -set of the skeleton on each operation of the symmetry  $G$ ;
- (3) determination of orbits of the  $G$ -set and assignment of the corresponding CRs by means of eqs. (1) and (2);
- (4) citation of unit cycle indices (UCIs) from a table of UCIs (e.g. tables 2 and 4) and construction of a cycle index in accord with definition 3; and
- (5) introduction of figure-inventories to the variables of the cycle index (theorem 2).

The advantages of the present procedure stem mainly from step (4) because of precalculated UCIs. This comes from the fact that they are independent of any particular  $G$ -set but dependent only upon the CRs. The full tabulation of UCIs for all point groups is a reasonable task, and will be reported elsewhere.

The following example 3, concerning a parent BRG with phantom edges, is a re-investigation of a previous result [7a] by means of precalculated UCIs. This example shows an OMV restriction in the case of an edge substitution problem.

*Example 3* (A square BRG with cross-linked phantom edges (5) of  $D_2$  symmetry)

Suppose that each pericycle edge ( $a$ ,  $b$ ,  $c$ , or  $d$ ) of the BRG 5 can take single or double par-bonds. On the other hand, each phantom edge ( $e$  or  $f$ ) can take any of single, double, and triple par-bonds. In example 2, we have already obtained the orbits of 5, i.e.  $\Delta_1 = \{e, f\}$ ,  $\Delta_2 = \{a, c\}$ , and  $\Delta_3 = \{b, d\}$ . These orbits are subject to the CRs appearing on the right-hand side of eq. (8). By using the columns of  $D_2(/C_2)$ ,  $D_2(/C_2')$  and  $D_2(/C_2'')$  in table 2, definition 3 (eq. (13)) affords the following cycle index:

$$CI(P_{D_2}; s_\tau^{(1)}, s_\tau^{(2)}, s_\tau^{(3)}) = (1/4) \left( (s_1^2)^{(1)}(s_1^2)^{(2)}(s_1^2)^{(3)} + (s_1^2)^{(1)}(s_2)^{(2)}(s_2)^{(3)} \right. \\ \left. + (s_2)^{(1)}(s_1^2)^{(2)}(s_2)^{(3)} + (s_2)^{(1)}(s_2)^{(2)}(s_1^2)^{(3)} \right). \quad (16)$$

The superscripts (1) to (3) denote the correspondence to  $\Delta_1$ ,  $\Delta_2$ , and  $\Delta_3$ . We select a co-domain:  $X = \{\emptyset, -, =, \equiv\}$  for substitution on the edges of 4. Since  $\Delta_1$  can take a bond selected from single ( $-$ ), double ( $=$ ), and triple ( $\equiv$ ) par-bonds, we adopt the weights:

$$w_1(\emptyset) = 1, \quad w_1(-) = x, \quad w_1(=) = y, \quad w_1(\equiv) = z \quad \text{for } \Delta_1.$$

On the other hand, orbits  $\Delta_2$  and  $\Delta_3$  are incapable of taking triple par-bonds. Hence, we assign the weights:

$$w_2(\emptyset) = 1, \quad w_2(-) = x, \quad w_2(=) = y, \quad w_2(\equiv) = 0 \quad \text{for } \Delta_2,$$

and

$$w_3(\emptyset) = 1, \quad w_3(-) = x, \quad w_3(=) = y, \quad w_3(\equiv) = 0 \quad \text{for } \Delta_3.$$

Hence, we determine figure-inventories:

$$s_{\tau}^{(1)} = 1 + x^{\tau} + y^{\tau} + z^{\tau} \quad \text{for } \Delta_1,$$

$$s_{\tau}^{(2)} = 1 + x^{\tau} + y^{\tau} \quad \text{for } \Delta_2,$$

and

$$s_{\tau}^{(3)} = 1 + x^{\tau} + y^{\tau} \quad \text{for } \Delta_3.$$

These figure-inventories are introduced into the cycle index (eq. (16)). Theorem 2 provides a generating function:

$$\begin{aligned} \sum_{\theta} A_{\theta} W_{\theta} &= CI(\mathbf{P}_{D_2}; 1 + x^{\tau} + y^{\tau} + z^{\tau}, 1 + x^{\tau} + y^{\tau}, 1 + x^{\tau} + y^{\tau}) \\ &= (1/4) \left( (1 + x + y + z)^2 (1 + x + y)^4 + (1 + x + y + z)^2 (1 + x^2 + y^2)^2 \right. \\ &\quad \left. + 2(1 + x^2 + y^2 + z^2)(1 + x^2 + y^2)(1 + x + y)^2 \right) \\ &= x^6 + 3x^5y + x^5z + 3x^5 + 6x^4y^2 + 3x^4yz + 9x^4y + x^4z^2 \\ &\quad + 3x^4z + 6x^4 + 8x^3y^3 + 6x^3y^2z + 18x^3y^3 + 2x^3yz^2 \\ &\quad + 10x^3yz + 18x^3y + 2x^3z^2 + 6x^3z + 8x^3 + 6x^2y^4 \\ &\quad + 6x^2y^3z + 18x^2y^3 + 3x^2y^2z^2 + 16x^2y^2z + 27x^2y^2 \\ &\quad + 4x^2yz^2 + 16x^2yz + 18x^2y + 3x^2z + 6x^2z + 6x^2 \\ &\quad + 3xy^5 + 3xy^4z + 9xy^4 + 2xy^3z^2 + 10xy^3z + 18xy^3 \\ &\quad + 4xy^2z^2 + 16xy^2z + 18xyz^2 + 4xyz^2 + 10xyz + 9xy \\ &\quad + 2xz^2 + 3xz + 3x + y^6 + y^5z + 3y^5 + y^4z^2 + 3y^4z \\ &\quad + 6y^4 + 2y^3z^2 + 6y^3z + 8y^3 + 3y^2z^2 + 6y^2z + 6y^2 \\ &\quad + 2yz^2 + 3yz + 3y + z^2 + z + 1. \end{aligned} \tag{17}$$

The coefficient of  $x^{p_1}y^{p_2}z^{p_3}$  indicates the number of isomers with  $p_1$  single,  $p_2$  double, and  $p_3$  triple par-bonds. For example, the coefficient of  $x^4$  shows that there are 6 RG-isomers having four single par-bonds, which are listed in fig. 4. In terms of PS and PP operations, we find the corresponding reaction diagrams, which are also illustrated on the right-hand side of fig. 4.

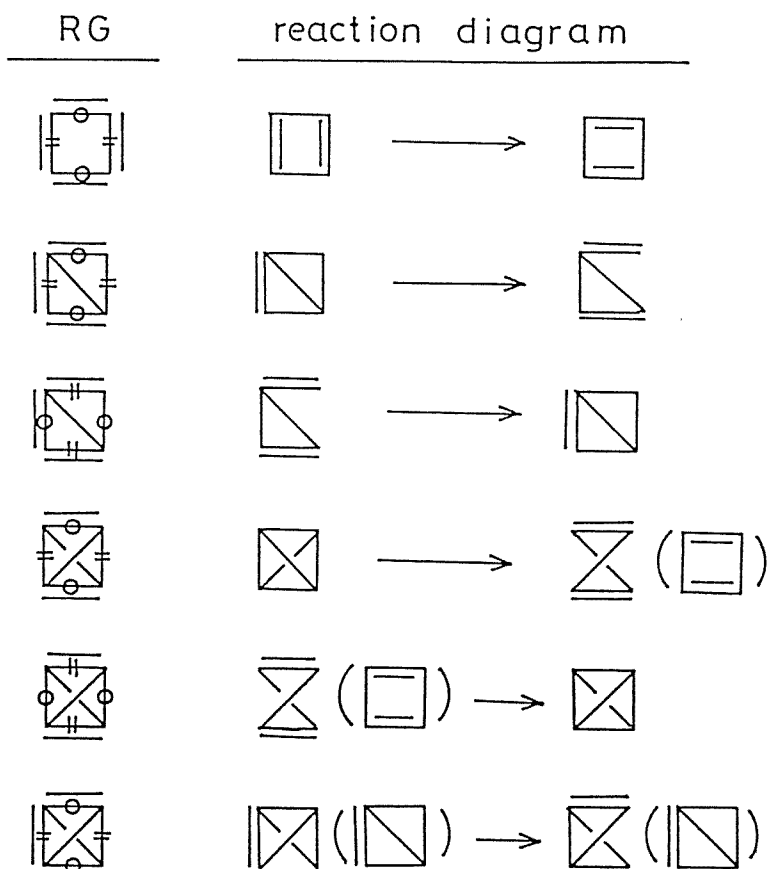


Fig. 4. RGs based on 5 and the corresponding reaction diagrams.

#### 4. Enumeration by means of unit subduced cycle indices

##### 4.1. UNIT SUBDUCED CYCLE INDICES, SUBDUCED CYCLE INDICES, AND CYCLE INDICES

A subduced representation (SR), denoted by  $G/G_i \downarrow G_j$ , is constructed by selecting such elements of  $G/G_i$  that correspond to those of a subgroup  $G_j$ . Obviously, this SR is a permutation representation of  $G_j$ . Although the original CR  $G/G_i$  is transitive, the resulting SR  $(G/G_i) \downarrow G_j$  is intransitive in general. Since theorem 1

is applicable to this case, the SR  $G/(G_i) \downarrow G_j$  is again reduced into the sum of the CRs for  $G_j$ , i.e.

$$G/(G_i) \downarrow G_j = \sum_{k=1}^{v_j} \beta_k^{(ij)} G_j/(G_k^{(j)}), \quad (18)$$

where the  $G_k^{(j)}$ 's ( $k = 1, 2, \dots, v_j$ ) are the subgroups of  $G_j$ . The multiplicities  $\beta_k^{(ij)}$  ( $k = 1, 2, \dots, v_j$ ) are calculated by means of equations equivalent to eq. (2) [11a]. Since the  $\Delta_{i\alpha}$  orbit is subject to the CR  $G/(G_i)$ , the subduction divides the  $\Delta_{i\alpha}$  orbit into suborbits  $\Delta_{jk\beta}^{(i\alpha)}$  ( $\beta = 1, 2, \dots, \beta_k^{(ij)}$ ), each of which is subject to  $G_j/(G_k^{(j)})$ . Note that  $\Delta_{jk\beta}^{(i\alpha)}$  corresponds to a set of cosets contained in a  $(G_i, G_j)$ -double coset. The sum  $\sum_{k=1}^{v_j} \beta_k^{(ij)}$  denotes the total number of such suborbits, which can be proven to be equal to the number of  $(G_i, G_j)$ -double cosets.

If we assign a dummy variable  $s_{d_{jk}}^{(i\alpha)}$  to each of the suborbits

$$\left( \Delta_{jk\beta}^{(i\alpha)}; \beta = 1, 2, \dots, \beta_k^{(ij)} \right),$$

a set of  $\beta_k^{(ij)}$  of these orbits corresponds to a term

$$\left( s_{d_{jk}}^{(i\alpha)} \right)^{\beta_k^{(ij)}},$$

where  $d_{jk} = |G_j| / |G_k^{(j)}|$ . Since this term is concerned with the  $k$ th CR  $(G_j/(G_k^{(j)}))$ , the multiplication over all  $k$  affords a unit subduced cycle index (USCI) for the orbit  $(\Delta_{i\alpha})$ . Hence, we arrive at the following definition [11].

#### DEFINITION 4

*(Unit subduced cycle index)*

The unit subduced cycle index for  $G/(G_i) \downarrow G_j$  is represented by

$$Z(G/(G_i) \downarrow G_j; s_{d_{jk}}^{(i\alpha)}) = \prod_{k=1}^{v_j} \left( s_{d_{jk}}^{(i\alpha)} \right)^{\beta_k^{(ij)}} \quad (19)$$

$$\text{for } i = 1, 2, \dots, s \quad \text{and} \quad j = 1, 2, \dots, s,$$

in which the superscript  $(i\alpha)$  is concerned with the suborbit  $\Delta_{i\alpha}$ .

Table 5 is a full list of unit subduced cycle indices (USCIs) of the  $D_2$  group. The multiplication of USCIs over  $\alpha$  and  $i$  affords the definition of a subduced cycle index (SCI) for every sub-symmetry  $(G_j)$ .

Table 5  
Unit subduced cycle indices for the  $D_2$  group

	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_2'$	$\downarrow C_2''$	$\downarrow D_2$
$D_2(/C_1)$	$s_1^4$	$s_2^2$	$s_2^2$	$s_2^2$	$s_4$
$D_2(/C_2)$	$s_1^2$	$s_1^2$	$s_2$	$s_2$	$s_2$
$D_2(/C_2')$	$s_1^2$	$s_2$	$s_1^2$	$s_2$	$s_2$
$D_2(/C_2'')$	$s_1^2$	$s_2$	$s_2$	$s_1^2$	$s_2$
$D_2(/D_2)$	$s_1$	$s_1$	$s_1$	$s_1$	$s_1$
$\sum_{i=1}^s \bar{m}_{ji}$	1/4	1/4	1/4	1/4	0

## DEFINITION 5

(Subduced cycle index)

The subduced cycle index for  $G_j$  is represented by

$$ZI(G_j; s_{d_{jk}}^{(i\alpha)}) = \prod_{i=1}^s \prod_{\substack{\alpha_i \\ \alpha_i \neq 0}} Z(G(/G_i) \downarrow G_j; s_{d_{jk}}^{(i\alpha)}) \quad \text{for } j = 1, 2, \dots, s. \quad (20)$$

In terms of definition 5, we have obtained the generating function of  $\rho_{\theta_j}$  in the form of the following theorem [11a].

## THEOREM 3

Let  $\rho_{\theta_j}$  be a mark for calculating the number ( $A_{\theta_j}$ ) of configurations with a symmetry of  $G_i$  and a weight  $W_{\theta}$ . A generating function for calculating the mark  $\rho_{\theta_j}$  is expressed by

$$\sum_{\theta} \rho_{\theta_j} W_{\theta} = ZI(G_j; s_{d_{jk}}^{(i\alpha)}), \quad (21)$$

wherein the right-hand side is substituted by

$$s_{d_{jk}}^{(i\alpha)} = \sum_{r=1}^{|\mathbf{X}|} w_{i\alpha} (X_r)^{d_{jk}}. \quad (22)$$

Let  $A_{\theta_j}$  be the number of configurations with a symmetry of  $G_i$  as well as a weight of  $W_{\theta}$ . The derivation of  $A_{\theta_j}$  from the values of  $\rho_{\theta_j}$  is mathematically equivalent to that of  $\alpha_i$  from  $\mu_j$ . Hence, eq. (2) can be converted to

$$A_{\theta_j} = \sum_{j=1}^s \rho_{\theta_j} \bar{m}_{ji}, \quad (23)$$

in terms of the inverse of a mark table. Equation (23) is summed over all  $G_j$  to give the total number of orbits  $A_\theta = \sum_{i=1}^s A_{\theta_i}$ . We then construct a generating function concerning  $A_\theta$ . As a result, we end up with the following theorem [10].

THEOREM 4

A generating function for the total number of orbits is represented by

$$\sum_{\theta} A_{\theta} W_{\theta} = \sum_{j=1}^s \left( \sum_{i=1}^s \bar{m}_{ji} \right) ZI(G_j; s_{d_{jk}}^{(i\alpha)}), \quad (24)$$

where  $s_{d_{jk}}^{(i\alpha)}$  is represented by eq. (22).

The right-hand side of eq. (24) is a novel generating function that is based on the concept of "subduced cycle index". We call this function a cycle index, which is defined as:

DEFINITION 6

A cycle index for the group  $G$  is represented by

$$CI(G; s_{d_{jk}}^{(i\alpha)}) = \sum_{j=1}^s \left( \sum_{i=1}^s \bar{m}_{ji} \right) ZI(G_j; s_{d_{jk}}^{(i\alpha)}). \quad (25)$$

This cycle index can be proven to be equal to eq. (13), which is drawn from Pólya's theorem [10].

### 3.3. THE SECOND PROCEDURE FOR THE ENUMERATION OF ORGANIC REACTIONS

Theorem 4 provides a new method of enumeration. A procedure for this method contains the following steps:

- (1) determination of the symmetry  $G$  of a parent skeleton;
- (2) counting of fixed points (marks) in the  $G$ -set of the skeleton on each operation of symmetry  $G$ ;
- (3) determination of CRs by means of eqs. (1) and (2);
- (4) use of USCIs (definition 4) to the CRs and construction of an SCI for every subgroup in terms of definition 5;
- (5) construction of a cycle index (CI) by definition 6; and
- (6) introduction of figure-inventories into the CI according to theorem 4.

The following examples illustrate the procedure. These examples also reveal flexibilities of the present method, which allow us to treat various modes of reduction.



**Example 4** (The square BRG 5 of  $D_2$  symmetry)

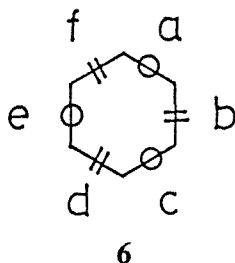
This example is the reexamination of the skeleton discussed in example 3. The inverse of the mark table of  $D_2$  (example 2, the  $5 \times 5$  matrix in eq. (7)) gives

$$\sum_{i=1}^s \bar{m}_{ji} = 1/4 \quad \text{for } C_1, C_2, C'_2, \text{ and } C''_2; \text{ and} \\ = 0 \quad \text{for } D_2$$

by summing the elements of each row. These values are listed at the bottom of table 5. The reduction discussed in example 3 allows us to use the data of table 5 (columns  $D_2/(C_2)$ ,  $D_2/(C'_2)$  and  $D_2/(C''_2)$ ). Hence, the application of definition 6 to this case provides

$$CI(\mathbf{P}_{D_2}; s_d^{(1)}, s_d^{(2)}, s_d^{(3)}) = (1/4) \left( (s_1^{(2)})^{(1)}(s_1^{(2)})^{(2)}(s_1^{(2)})^{(3)} + (s_1^{(2)})^{(1)}(s_2)^{(2)}(s_2)^{(3)} \right. \\ \left. + (s_2)^{(1)}(s_1^{(2)})^{(2)}(s_2)^{(3)} + (s_2)^{(1)}(s_2)^{(2)}(s_1^{(2)})^{(3)} \right). \quad (26)$$

The superscripts (1) to (3) denote the correspondence to  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ . This cycle index is identical to that of example 3.

**Example 5** (A hexagonal BRG 6 of  $D_3$  symmetry)

Let us consider that BRG 6 has  $D_3$  symmetry. We have previously discussed this problem [6]. The present example deals with an application of the new method. The subgroups of the  $D_3$  group are represented by  $C_1 = \{I\}$ ,  $C_2 = \{I, C_{2(1)}\}$ ,  $C_3 = \{I, C_3, C_3^2\}$ , and  $D_3 = \{I, C_3, C_3^2, C_{2(1)}, C_{2(2)}, C_{2(3)}\}$ . The permutation representation ( $\mathbf{P}_{D_3}$ ) consists of six permutations,  $I \sim (a)(b)(c)(d)(e)(f)$ ,  $C_3 \sim (a c e)(b d f)$ ,  $C_3^2 \sim (a e c)(b f d)$ ,  $C_{2(1)} \sim (a)(c e)(d)(b f)$ ,  $C_{2(2)} \sim (a c)(e)(b)(d f)$ , and  $C_{2(3)} \sim (a e)(c)(b f)(d)$ . Table 6 collects the data for the  $D_3$  symmetry.

Consider that each edge can take a single par-bond or a double par-bond. The marks ( $\mu_j$ ) are obtained by counting fixed edges during the operations of each sub-symmetry:

Table 6  
Unit subduced cycle indices for the  $D_3$  group

	$\downarrow C_1$	$\downarrow C_2$	$\downarrow C_3$	$\downarrow D_3$
$D_3(/C_1)$	$s_1^6$	$s_2^3$	$s_3^2$	$s_6$
$D_3(/C_2)$	$s_1^3$	$s_1 s_2$	$s_3$	$s_3$
$D_3(/C_3)$	$s_1^2$	$s_2$	$s_1^2$	$s_2$
$D_3(/D_3)$	$s_1$	$s_1$	$s_1$	$s_1$
$\sum_{i=1}^3 \bar{m}_{ji}$	1/6	1/2	1/3	0

$$\mu_{C_1} = 6, \mu_{C_2} = 2, \mu_{C_3} = 0, \text{ and } \mu_{D_3} = 0. \quad (27)$$

We then write down eq. (2) for this case, i.e.

$$(\alpha_{C_1} \alpha_{C_2} \alpha_{C_3} \alpha_{D_3}) = (6 \ 2 \ 0 \ 0) \begin{pmatrix} 1/6 & 0 & 0 & 0 \\ -1/2 & 1 & 0 & 0 \\ -1/6 & 0 & 1/2 & 0 \\ 1/2 & -1 & -1/2 & 1 \end{pmatrix} = (0 \ 2 \ 0 \ 0), \quad (28)$$

where the  $4 \times 4$  matrix is the inverse of the mark table of the  $D_3$  group. This solution indicates a reduction into two coset representations in the form of

$$P_{D_3} = 2D_3(/C_2). \quad (29)$$

Thus, the edges of the skeleton are divided into two orbits:

$$\Delta_1 = \{a, c, e\} \quad \text{and} \quad \Delta_2 = \{b, d, f\},$$

both of which are subject to the same CR. According to eq. (29), we twice use the row of  $D_3(/C_2)$  of table 6, in accord with definition 6. We thus obtain a cycle index:

$$\begin{aligned} CI(P_{D_3}; s_d) &= (1/6)s_1^3 s_1^3 + (1/2)s_1 s_2 s_1 s_2 + (1/3)s_3 s_3 \\ &= (1/6)(s_1^6 + 3s_1^2 s_2^2 + 2s_3^2). \end{aligned} \quad (30)$$

The coefficient of each term is taken from the bottom of table 6, which is the sum of the corresponding row of the inverse matrix appearing in eq. (28). Equation (30) is identical to the previous result that was derived by Pólya's theorem [6]. We select a co-domain:  $\mathbf{X} = \{\emptyset, -, =\}$ . In this example, we consider a single pattern of substitution at each edge. Hence, we determine a single set of weights:

$$w(\emptyset) = 1, \quad w(-) = x, \quad \text{and} \quad w(=) = y,$$

which affords a figure-inventory:

$$s_d = 1 + x^d + y^d. \quad (31)$$

Theorem 4 yields the following generating function.

$$\begin{aligned} \sum_{\theta} A_{\theta} W_{\theta} &= CI(\mathbf{D}_3; 1 + x^d + y^d) \\ &= (1/6) \left( (1+x+y)^6 + 3(1+x+y)^2(1+x^2+y^2) + 2(1+x^3+y^3)^2 \right) \\ &= x^6 + 2x^5y + 2x^5 + 4x^4y^2 + 6x^4y + 4x^4 + 6x^3y^3 \\ &\quad + 12x^3y^2 + 12x^3y + 6x^3 + 4x^2y^4 + 12x^2y^3 + 18x^2y^2 \\ &\quad + 12x^2y + 4x^2 + 2xy^5 + 6xy^4 + 12xy^3 + 12xy^2 + 6xy \\ &\quad + 2x + y^6 + 2y^5 + 4y^4 + 6y^3 + 4y^2 + 2y + 1. \end{aligned} \quad (32)$$

Figure 5 illustrates 4 isomers (RG isomers) of  $x^4y^0$ , which indicates 4 single par-bonds but no double par-bonds. These reaction graphs (RGs) correspond to well-known reactions. Their names and conventional diagrams are also shown.

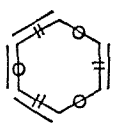

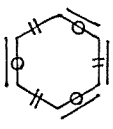
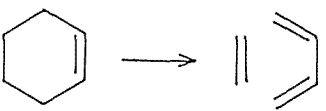
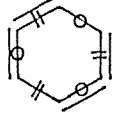

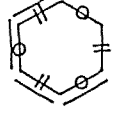
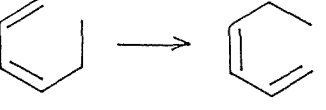
RG	reaction name	reaction diagram
	Diels-Alder addition	
	Retro-Diels-Alder reaction	
	[3,3]Sigmatropic reaction	
	[1,5]Sigmatropic reaction	

Fig. 5. RGs based on 6 and the corresponding reaction diagrams.

## 5. A detailed enumeration

Equation (23) indicates the availability of a more detailed enumeration than those described in the previous sections. Since we have reported applications of this equation to the enumeration of compounds [11], here we deal with an application to the enumeration of reactions.

*Example 6* (The RCGs based on the parent RG 3).

The parent RG 3 has three orbits as obtained in example 1, all of which are associated with  $C_2(/C_1)$ . Suppose that  $\Delta = \{1, 2, 3, 4, 5, 6\}$  and  $X = \{C, N, O\}$ . We adopt the following weights in accord with the OMVs of the orbits:

$$w_1(C) = 1, \quad w_1(N) = x, \quad w_1(O) = 0 \quad \text{for } \Delta_1 = \{1, 5\},$$

$$w_2(C) = 1, \quad w_2(N) = x, \quad w_2(O) = y \quad \text{for } \Delta_2 = \{2, 6\},$$

and

$$w_3(C) = 1, \quad w_3(N) = x, \quad w_3(O) = y \quad \text{for } \Delta_3 = \{3, 4\},$$

which afford inventories for the respective orbits. That is to say,

$$s_d^{(1)} = 1 + x^d \quad \text{for } \Delta_1, \quad (33)$$

$$s_d^{(2)} = 1 + x^d + y^d \quad \text{for } \Delta_2, \quad (34)$$

and

$$s_d^{(3)} = 1 + x^d + y^d \quad \text{for } \Delta_3. \quad (35)$$

Table 7

Unit subduced cycle indices for the  $C_2$  group

	$\downarrow C_1$	$\downarrow C_2$
$C_2(/C_1)$	$s_1^2$	$s_2$
$C_2(/C_2)$	$s_1$	$s_1$
$\sum_{i=1}^j \bar{m}_{ji}$	$1/2$	$1/2$

Since all of the orbits are subject to  $C_2(/C_1)$ , the corresponding row of table 7 is used three times but in different ways. Thus, we obtain

$$(s_1^2)^{(1)}(s_1^2)^{(2)}(s_1^2)^{(3)} = (1+x)^2(1+x+y)^4 \quad \text{for } C_1 \quad (36)$$

and

$$(s_2)^{(1)}(s_2)^{(2)}(s_2)^{(3)} = (1+x^2)(1+x^2+y^2)^2 \quad \text{for } C_2, \quad (37)$$



## 6. Conclusion

A novel enumeration of organic reactions, in which obligatory minimum valencies (OMVs) of a parent reaction graph are explicitly considered, is accomplished by using coset representations. Pólya's theorem is thus generalized to the form that allows us to enumerate isomers under the restriction of OMVs. Another method of enumeration is based on novel concepts such as unit subduced cycle index and subduced cycle index, both of which also stem from the coset representation. These approaches are different in their construction of cycle indices (CIs), which are represented by UCI (unit cycle index)  $\rightarrow$  CI for the former approach and by USCI (unit subduced cycle index)  $\rightarrow$  SCI (subduced cycle index)  $\rightarrow$  CI for the latter approach.

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- [12] For Pólya's theorem, see (a) G. Pólya, *Acta Math.* 68(1937)145; (b) G. Pólya and R.C. Read, *Combinatorial Enumeration of Groups, Graphs, and Chemical Compounds* (Springer, New York, 1987).
- [13] For chemical applications of Pólya's theorem, see (a) A.T. Balaban (ed.), *Chemical Application of Graph Theory* (Academic Press, London, 1976); (b) D.H. Rouvray, *Chem. Soc. Rev.* 3(1974)355; (c) K. Balasubramanian, *Chem. Rev.* 85(1985)588.
- [14] For enumeration methods developed recently, see (a) E. Ruch, W. Hässelbarth and B. Richter, *Theor. Chim. Acta* 19(1979)288; (b) J. Brocas, *J. Amer. Chem. Soc.* 108(1986)1135.
- [15] W. Burnside, *Theory of Groups of Finite Order*, 2nd ed. (Cambridge Univ. Press, Cambridge, 1911).
- [16] Strictly speaking, eq. (1) contains some ambiguity, since  $P_G$  is concerned with a set of positions ( $\Delta$ ) and each  $G/(G_i)$  governs a set of cosets. However, we can regard the  $\Delta$  orbit as a set of positive integers if we number the positions sequentially. Furthermore, we can regard the set of cosets as being a set of positive integers if we number the cosets sequentially. Then we are able to consider  $P_G$  and  $G/(G_i)$  to act on the respective sets of integers. As a result of these presumptions, we have eq. (1). Although this treatment may lack mathematical strictness, it would be suitable for chemists to understand the relationship between the two kinds of sets intuitively. The author appreciates the comments of one of the referees on this point.
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(c) J.H. Redfield, *J. Graph Theory* 8(1984)205;  
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(e) C.A. Mead, *J. Amer. Chem. Soc.* 109(1987)2130.