

# Graphical Models of Marks of Groups

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## Abstract

Two graphical approaches have been presented to obtain marks of a group, where one approach is based on a set of homomers and the other is based on a set of equivalent ligands. These procedures have been illustrated by using the point group  $D_3$  as a common example. Comparison of these approaches has revealed that their foundation comes from the one-to-one correspondence among a homomer set  $\mathcal{H}[\mathbf{G}/(\mathbf{G}_i)]$ , a ligand set  $\mathcal{L}[\mathbf{G}/(\mathbf{G}_i)]$ , and a set of cosets  $\mathbf{G}/\mathbf{G}_i$ , which are all assigned to the coset representations  $\mathbf{G}/(\mathbf{G}_i)$ , where  $\mathbf{G}$  is a group and  $\mathbf{G}_i$  is a subgroup of  $\mathbf{G}$ .

## 1 Historical Background and Definitions

Character tables have long been used in the study of infrared and Raman spectroscopy [1, 2] and in the modeling of molecular movements [3, 4, 5], as found in many textbooks. Mark tables are not, however, so common or popular as character tables. Historically, Burnside (1911) published some mark tables for a few groups in the 2nd edition of his famous book [6] but attracted only little attention. Redfield thought he had (re)discovered these tables in 1937, as found in his article published far after his death [7]. Lloyd [8] pointed out to one of the authors (S.E.) that the copy of Burnside's book used by Redfield was the first edition of Burnside's book which did not contain marks. It seems, then the copy of Burnside's book which was found in Redfield's personal library (after he died) was the *first* edition which did not contain marks! It seems, then, that both mathematicians, Burnside and Redfield, did independently use these functions, viz., marks of a group.

Fujita recently revived interest in these tables and developed a versatile theory of the combinatorial enumeration of (stereo)isomers [9]. Fujita's approach requires people who think mathematically and, consequently, is likely to rule out organic chemists who will certainly benefit from the theory of marks (if they are willing to think in an abstract way).<sup>1</sup>

The objective of this work is to present two graphical (almost nonmathematical) approaches to calculating marks of chemically important groups. These approaches work for all groups that are important to discuss stereoisomerism and stereochemistry. Instead of using abstract algebraic methods we use simple geometric methods such as rotation and/or reflection of (colored or substituted) graphs especially designed according to the symmetry operations of the group. In order to be able to understand the method we need to define cosets and coset representations of a group.

### 1.1 Cosets and Coset Representations of a Group

Normally a group is expressed as a set of symmetry operations. For example, for the chiral dihedral point group  $D_3$  we write:

$$D_3 = \{I, C_2, C_2', C_2'', C_3, C_3^2\}, \quad (1)$$

where the elements (three two-fold axes and one three-fold axis) of symmetry are pictorially illustrated on *trans-transoid-trans-transoid-trans*-perhydrotriphenylene (**1**) and on a fixed cyclohexane derivative with six substituents (Q) of the same chirality (**2**). The substituent Q may be selected from chiral ligands such as *R*-CXYZ, *S*-CXYZ etc. Note that the three two-fold axes which respectively correspond to the rotations  $C_2$ ,  $C_2'$ , and  $C_2''$  are perpendicular to the three-fold axis for the rotations  $C_3$  and  $C_3^2$ .

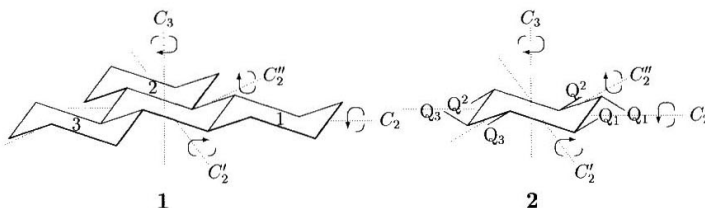


Figure 1: A perhydrotriphenylene and a fixed cyclohexane both of  $D_3$ -symmetry. Each of the terminal cyclohexane rings (1, 2, and 3) in the former molecule belongs to  $C_2$ -symmetry. The symbol Q in the latter molecule represents a chiral substituent. Each of the segments ( $Q_nC-CQ_n$ ,  $n = 1, 2, 3$ ) belongs to  $C_2$ -symmetry.

A more general way of depicting (envisaging) the symmetry operations of a group  $G$  is to construct a geometric object (graph) which remains invariant (stabilized) only under the

<sup>1</sup>One of the authors (S.F.) has recently reported a nonmathematical article to discuss stereochemistry in terms of this approach [10], since he is a synthetic-organic chemist of part-time mathematical thinking.

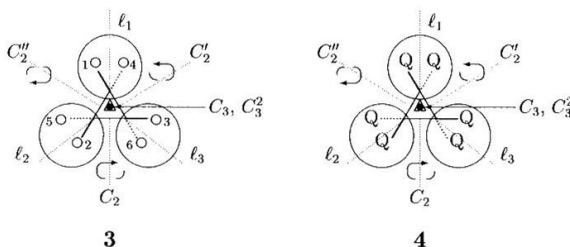


Figure 2: Cyclopropane derivatives of  $D_3$ -symmetry. The symbol  $\blacktriangle$  represents the three-fold axis. Each encircled ligand ( $O-C-O$ ) of **3** belongs to  $C_2$ , because the plain containing the ligand is slightly slanted. The symbol Q represents a chiral substituent. Each of the encircled ligands ( $Q-C-Q$ ) belongs to  $C_2$ -symmetry.

symmetry operations of  $G$ . When  $G = D_3$ , a convenient model (**3** or **4**) is selected as shown in Fig. 2, where a cyclopropane skeleton is used after the reduction of the original  $D_{3h}$ -symmetry. The distorted cyclopropane ring of **3** has  $D_3$ -symmetry, where the planes containing  $H-C-H$  ( $O-C-O$ ) are not perpendicular to the cyclopropane ring but are slanted by the same angle.<sup>2</sup> The other model (**4**) for reducing the original symmetry is obtained by placing six chiral substituents (Q) of the same chirality, e.g.,  $R-CXYZ$  or  $S-CXYZ$ . Construction of such models is the key point-of our graphical approach.

The group  $D_3$  has four subgroups and writes this sequence of subgroups, SSG (a set of subgroups), as follows:

$$SSG(D_3) = \{C_1, C_2, C_3, D_3\}, \quad (2)$$

where  $C_1 = \{I\}$  or  $\{E\}$ ;  $C_2 = \{I, C_2\}$ ; and  $C_3 = \{I, C_3, C_3^2\}$ . Note that the group  $C_2$  is selected as a representative of three conjugate subgroups, because an equivalent SSG can be obtained by selecting another subgroup,  $C_2' = \{I, C_2'\}$  or  $C_2'' = \{I, C_2''\}$ .

The elements of a group can be classified in terms of one of its subgroups, e.g.,

$$D_3 = C_2I + C_2C_3 + C_2C_3^2, \quad (3)$$

where we obtain

$$C_2I = \{I, C_2\}, \quad C_2C_3 = \{C_3, C_3^2\}, \quad \text{and} \quad C_2C_3^2 = \{C_3^2, C_3'\} \quad (4)$$

by referring to the multiplication table of  $D_3$ .<sup>3</sup> The subsets of elements on the right-hand

<sup>2</sup>A thick-line bond and a dotted-line bond incident to the same carbon atom ( $C^*$ ) are contained in a plane, where the bisecting line of the angle of  $H-C^*-H$  is identical with that of the angle of  $C-C^*-C$ . Thus, the thick-line bond is directed upward from the page plane by an angle less than  $90^\circ$ , while the corresponding dotted-line bond sinks by the same angle.

<sup>3</sup>If we take a graphical approach thoroughly, another method of explanation should be considered instead of such a multiplication table. For example, let us consider  $C_2C_3 = C_2''$ , which appears in the derivation,  $C_2C_3 = \{IC_3, C_2C_3\} = \{C_3, C_2''\}$ . Atom 1 in **3** is converted into atom 3 by the operation  $C_3$  (Fig.2). Then atom 3 is converted into atom 2 by the operation  $C_2$ . The total effect of  $C_2C_3$  corresponds to the conversion of atom 1 into atom 2, which is identical with the effect of the operation  $C_2''$ . Thereby, we obtain  $C_2C_3 = C_2''$  without using the multiplication table of  $D_3$ . For the sake of simplicity, however, we sometimes take such a compromised but convenient way as found in the text.

Table 1: Coset Representation  $D_3(/C_2)$ 

Sym. opn.	$C_2I$	$C_2C_3$	$C_2C_3^2$	$D_3(/C_2)$
	(labeled)			
	1	2	3	
$I$	1	2	3	(1)(2)(3)
$C_2$	1	3	2	(1)(2 3)
$C_2'$	3	2	1	(2)(1 3)
$C_2''$	2	1	3	(3)(1 2)
$C_3$	2	3	1	(1 2 3)
$C_3^2$	3	1	2	(1 3 2)

sides of eq. 3 (or eq. 4) are called (right) cosets and one writes them as a set of cosets:

$$D_3/C_2 = \{C_2I, C_2C_3, C_2C_3^2\}, \quad (5)$$

where the cosets are explicitly represented by eq. 4. Equation 5 (or eq. 3) is called a *coset decomposition* of  $D_3$  in terms of  $C_2$ .

When all the symmetry operations are applied to the three cosets on the right-hand sides of eq. 5, one generates a *permutation representation* (PR) called a *coset representation* (CR) of a point group,  $D_3$  in this case, by one of its subgroup, here  $C_2$ . This particular CR is abbreviated as  $D_3(/C_2)$ , since this is concerned with the coset decomposition expressed by eq. 5. Table 1 outlines the resulting permutations, which are expressed as products of cycles after the cosets are labeled as 1, 2, and 3. Note, for example, that the product of cycles (1)(2 3) for the symmetry operation  $C_2$  represents the fixation of 1 (one-cycle) and the interchange between 2 and 3 (two-cycle) and that the product of cycles (1 3 2) for the symmetry operation  $C_3^2$  represents a cyclic rearrangement,  $1 \leftarrow 3 \leftarrow 2 \leftarrow 1$  (three-cycle).

Now to obtain the marks one counts the number of fixed cosets (i.e., fixed points) under the operation of subgroups. This number is called the *mark* of a given subgroup (i.e., corresponding to a given CR). To do this we collect the permutations and list the subgroups in a non-descending order (i.e., find SSG). The elements forming a subgroup are “marked” as the symbol  $\checkmark$  and the fixed points are counted. This is illustrated in Table 2. For example, the mark for  $C_2$  is the number of one-cycles common to its elements marked with  $\checkmark$ , i.e., (1)(2)(3) and (1)(2 3). Then, the mark is obtained to be 1. When the above procedure is repeated for all subgroups and the resulting rows are assembled in the order of SSG, one obtains the mark table (MT) of  $G$ . Table 3 gives the MT for  $D_3$ . Many such tables are collected in the appendix of Fujita’s book [9]. With some concentration and experience of using multiplication tables (cf. keeping track of multiplication—order of elements), an organic chemist may succeed in deriving the above and such tables especially for groups not possessing very large orders.

However, the mathematical description of chemistry or physics, which is necessary to understanding, does not always leave things “flowery”. For example, the mathematical

Table 2: Calculation of the Row of Marks (MR) of  $D_3(/C_2)$ 

Sym. opn.	$D_3(/C_2)$	SSG			
		$C_1$	$C_2$	$C_3$	$D_3$
$I$	(1)(2)(3)	✓	✓	✓	✓
$C_2$	(1)(2 3)		✓		✓
$C'_2$	(2)(1 3)				✓
$C''_2$	(3)(1 2)				✓
$C_3$	(1 2 3)			✓	✓
$C^2_3$	(1 3 2)				✓
MR[ $D_3(/C_2)$ ] =		(3	1	0	0)

Table 3: 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
$D_3(/C_3)$	2	0	2	0
$D_3(/D_3)$	1	1	1	1

description of a given CR is given for a group  $\mathbf{G}$  and a subgroup  $\mathbf{H}$ :

$$\mathbf{G}/(\mathbf{H}) = \{\pi_g \mid \forall g \in \mathbf{G}\}, \quad (6)$$

where  $\pi_g$  is the permutation corresponding to the symmetry element  $g$  is denoted by

$$\pi_g = \begin{pmatrix} \mathbf{H}g_1 & \mathbf{H}g_2 & \cdots & \mathbf{H}g_r \\ \mathbf{H}g_1g & \mathbf{H}g_2g & \cdots & \mathbf{H}g_rg \end{pmatrix}, \quad (7)$$

where  $r = |\mathbf{G}|/|\mathbf{H}|$ . In Table 1,  $g$  is “resolved” into the elements of  $\mathbf{D}_3$  (eq. 1) and  $\mathbf{H}$  into the SSG (eq. 2).

In fact, the degree of abstraction given by eqs. 6 and 7 may be sufficient to repel most experimental chemists of such a topic. However in the presence of “motive” such a chemist may not decide to close the book, instead, does some extra effort. So what is the benefit behind this game? As far as organic chemistry is concerned, the theory of marks opens the door to two important aspects.

- A. *Combinatorial Chemistry*: Enumeration and classification of (stereo)isomers into their subgroups. In contrast to theories of Pólya-Redfield enumeration [11] and Balasubramanian’s wreath-product method [12], only the “Enumeration Journey” of Fujita [9] leads to the so-called Isomer-Counting-Matrix (ICM)<sup>4</sup> which counts how many isomers are there in each subgroup. The former schemes other than the ICM give only total counts. So the “extra” effort of finding out mark tables is rewarded by the generation of the ICM. To illustrate this remarkable difference we cite below the generation function (GF),  $Z(x+y)$ , of all isomers of cyclopropane whose hydrogen atoms (variable  $x$ ) are substituted by one type of substituents (variable  $y$ ):

$$Z(x+y) = x^6 + xy^5 + 4x^2y^4 + 4x^3y^3 + 4x^4y^2 + x^5y + y^6 \quad (8)$$

The above function according to the Pólya-Redfield theory does not say anything about the stereochemistry of these isomers. The ICM of Fujita, on the other hand, looks as follows (Table 4), where the numbers of isomers are itemized with respect to two criteria: formulas ( $x^m y^n$  for  $m_{\text{O}} n_{\text{●}}$  or  $\text{CH}_m \text{Q}_n$ ) and symmetries.

For example, three isomers characterized as  $x^4 y^2$  and  $\mathbf{C}_2$ -symmetry are depicted in Fig. 3. This part of important chemical applications of the theory of marks of groups will not be considered here but Fujita’s book [9] contains many examples of such combinatorial enumerations.

- B. *Characters of Groups*: This is the other vent of chemical applications of the theory of marks. Although mark tables are not popular in chemical every-day use, as, e.g. character tables, yet Fujita demonstrated that a row of marks of a given CR of a group corresponds to the sum of irreducible representations (IR) of that group [19]. This remarkable finding is a “gift” to the experimental chemist who wishes to know more about character tables but being hindered with the very abstract nature of

<sup>4</sup>Called by one of the authors (S.E.), the “Heaven of Fujita” [13]! But the other author (S.F.) calls this the USCI approach in connection with USCIs (unit subduced cycle indices) that have newly been derived from CRs and their subductions. Other approaches have been reported to enumerate isomers with respect also to symmetries of isomers [14]–[18], but they have not put emphasis on CRs and their subductions.

Table 4: ICM of Cyclopropane Derivatives

	$C_1$	$C_2$	$C_3$	$D_3$
$x^6, y^6$	0	0	0	1
$xy^5, x^5y$	1	0	0	0
$x^2y^4, x^4y^2$	1	3	0	0
$x^3y^3$	3	0	1	0

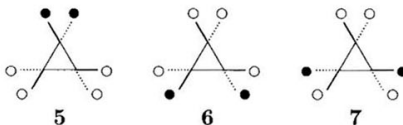


Figure 3: Three isomers of  $C_2$  corresponding to  $x^4y^2$  (four  $\circ$  and two  $\bullet$ ). Isomers **6** and **7** are diastereomers because we use the distorted cyclopropane skeleton (see text).

representation theory. We will elsewhere present a nonmathematical approach to obtaining 1-dimensional characters from marks of a group, since the mark tables are somewhat easier to obtain than character tables.

## 2 Graphical Approaches of Marks

### 2.1 Graphical Approach Based on an Orbit of Homomers

Chapter 15 of Fujita's book [9] has revealed that isomers derived from a skeleton of  $G$ -symmetry are classified into several sets (orbits) of homomers of each subgroup ( $G_i \subset G$ ) on the action of  $G$  and that each orbit of homomers belongs to the CR ( $G/(G_i)$ ). This fact was originally used to combinatorial enumeration in Fujita's book. But, it is applied here to obtain marks of the group  $G$  after introducing an appropriate graph (regular body).<sup>5</sup> Thus, we adopt the following procedure:

**Step 1:** Find a graph (regular body) which remains invariant (fixed) *specifically* under the symmetrical operations of the group.<sup>6</sup> The number of vertices (substitution sites) in such a graph *must* be equal to the order (the number of symmetrical operations) of the group.

The word *specifically* is crucial. Take, e.g. the point group  $D_3$  (eq. 1), where  $|D_3| = 6$ . Strictly speaking, cyclopropane itself is not suitable as a graphical model

<sup>5</sup>For other qualitative applications to stereochemistry, see [20].

<sup>6</sup>One of the authors (S.F.) has referred to this graph as *regular body*, since this graph corresponds to a regular representation  $G/(G_1)$  [19]. A general diagram for such regular bodies has been depicted as Figure 7.1 in Chapter 7 of Fujita's book [9]. Figures 7.2, 7.3 and 7.4 have given illustrative examples of regular bodies for  $D_{2d}$  and  $T_d$ .

for  $D_3$ , although it has six hydrogens as substitution sites. Since cyclopropane belongs to  $D_{3h}$ , it remains fixed also under three dihedral reflections ( $\sigma_d$ 's), one horizontal reflection ( $\sigma_h$ ), and two roto reflections ( $S_3$  and  $S_3^2$ ), which may lead to wrong marks. The two promising ways for reducing the original symmetry have already been described, i.e. the use of the distorted cyclopropane ring of  $D_3$  (**3**) and the substitution with chiral substituents (Q), as shown in **4** (Fig. 2). A further way is illustrated in Fig. 4, in which a model with two superimposed triangles that are slightly rotated to each other. Note that such a model can be obtained as one conformation of ethane.

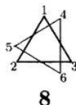


Figure 4: A  $D_3$ -model with superimposed triangles. The line through their centers is perpendicular to their planes, where the triangle drawn in thick lines is an upper one.

**Step 2:** Find the sequence of subgroups, SSG, and order the subgroups in a nondescending way and whence find all CR's:  $\mathbf{G}(/G_i)$ ,  $i = 1, 2, \dots, s$  where  $s$  is the number of subgroups in the SSG. In general,  $\mathbf{G}_1 = \mathbf{C}_1 = \{I\}$  and  $\mathbf{G}_s = \mathbf{G}$ . One recalls here the two "terminal" CR's: i.e. the regular representation  $\mathbf{G}(/C_1)$  and the identity representation  $\mathbf{G}(/G)$ .

**Step 3:** In this step we find a *set of colored graphs* which models (represents) each CR.<sup>7</sup> So the number of these sets is equal to the number of subgroups and to the number of CRs.

The members of each set may be called homomers (h's) and the set itself is an equivalence class (orbit) given by the symbol  $\mathcal{H} \equiv \mathcal{H}[\text{CR}] \equiv \mathcal{H}[\mathbf{G}(/G_i)]$ .

For an extreme case, the identity representation  $\mathbf{G}(/G)$  corresponds to the uncolored graph (h) which generates the symmetry operations of  $\mathbf{G}$ . In general, the cardinality of  $\mathcal{H}[\mathbf{G}(/G)]$  is equal to 1. For example, we can select the graph **3** (Fig. 2) as a single homomer for  $D_3(/D_3)$ , i.e.  $\mathcal{H}[D_3(/D_3)] = \{\mathbf{3}\}$ .

For general cases of  $\mathbf{G}(/G_i)$  ( $i = 1, 2, \dots, s$ ), the symmetry of the graph must be reduced by coloring (substituting) some of the vertices of h ( $\in \mathcal{H}[\mathbf{G}(/G_i)]$ ), i.e. the single homomer which models the identity representation. The colors are used, say, black and white so that the resulting graph is fixed under the operations of  $G_i$ . Conventionally, when there is a choice, the number of black vertices is less than the number of white (open) ones. The resulting colored graph is denoted as  $h_1 \in \mathcal{H}[\mathbf{G}(/G_i)]$ .

**Step 4:** To find marks, we count fixed colored graphs (contained in  $\mathcal{H}[\mathbf{G}(/G_i)]$ ) on the action of each subgroup of the SSG.

<sup>7</sup>One of the authors (S.F.) has once discussed this item in terms of subductive and inductive derivation for designing molecules of high symmetry [21].



**Example 1** [An Orbit of Homomers for  $D_3(/C_2)$ ]:

**(Step 1)** To find one ( $h_1$ ) of the homomers which belongs to  $\mathcal{H}[D_3(/C_2)]$ , we start from **3** as a regular body ( $h \in \mathcal{H}[D_3(/D_3)]$ ), where the six vertices are numbered arbitrarily, as found in Fig. 2.

**(Step 2)** We have obtained the SSG for  $D_3$ , as shown in eq. 2. Now, we select  $C_2 = \{I, C_2\}$  for the next step.

**(Step 3)** When the operations of  $C_2$  are applied to the set of vertices of **3** as  $h$ , one obtains three sets (“color-equalities”) of equivalent vertices:  $\{1, 4\}$ ,  $\{2, 6\}$ , and  $\{3, 5\}$ .<sup>8</sup> It follows that candidate homomers which remain fixed only under  $C_2$  are determined to be **5**, **6**, and **7** shown in Fig. 3. Since these candidates give equivalent results, we tentatively select **5** as  $h_1$  ( $\in \mathcal{H}[D_3(/C_2)]$ ), as shown in Fig. 5.

In order to obtain other members of the set, one applies all of the symmetry operations of the “mother group”  $D_3$  to  $h_1$ , as shown in Fig. 5. The operations  $I$  and  $C_2$  involved in  $C_2$  fix  $h_1$  invariant. The operations  $C_3$  and  $C_3''$  in the coset  $C_2C_3$  produce a homomer  $h_2$  (**5b**), while  $C_3^2$  and  $C_2'$  in the coset  $C_2C_3^2$  produce another homomer  $h_3$  (**5c**). Hence, we obtain  $\mathcal{H}[D_3(/C_2)] = \{h_1, h_2, h_3\}$ , where the homomers are depicted in Fig. 5.

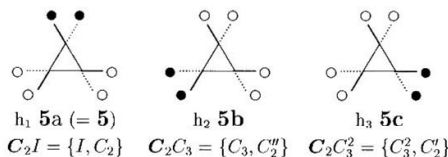


Figure 5: An orbit of homomers  $\mathcal{H}[D_3(/C_2)]$  generated by symmetry operations of  $D_3$ . The symmetry operations of each coset convert  $h_1$  into the corresponding homomer ( $h_1$ ,  $h_2$ , or  $h_3$ ). For a portrayal of symmetry operations, see Fig. 2.

The order of  $\mathcal{H}[D_3(/C_2)]$  is equal to  $|D_3|/|C_2| = 6/2 = 3$ . This is a general result, viz.,

$$|\mathcal{H}[G(/G_i)]| = |G|/|G_i|, \quad (9)$$

which can be easily proved as a corollary of Theorem 15.2 of Fujita’s book [9].

**(Step 4)** It is (almost) trivial to find marks from the colored graphs by inspection, e.g., from  $\mathcal{H}[D_3(/C_2)]$  listed in Fig. 5. List the graphs which remain invariant under the symmetry operations of each subgroup in the order of the SSG of the group  $D_3$ . For the case of  $D_3(/C_2)$ , one obtains the following mark row (MR):

$C_1$	$C_2$	$C_3$	$D_3$
$\{h_1, h_2, h_3\}$	$\{h_1\}$	$\{\emptyset\}$	$\{\emptyset\}$
3	1	0	0

where  $\{\emptyset\}$  represents an empty set, i.e., no homomers belonging to  $\mathcal{H}[D_3(/C_2)]$  are fixed under  $C_2$ . The MR (3 1 0 0) is algebraically the same as the second row of Table 3.

<sup>8</sup>According to the USCI approach [9], this division is ascribed to the subduction of the regular representation, i.e.,  $D_3(/C_1) \downarrow C_2 = 3C_2(/C_1)$ .

The above procedure can be systematically done as follows. Place the individual homomers in a row, and check if a subgroup at issue fixes each homomer. The checks are counted for each row. For the case of  $D_3(/C_2)$ , one obtains the following mark row (MR):<sup>9</sup>

	$h_1$	$h_2$	$h_3$	sum
$C_1$	✓	✓	✓	3
$C_2$	✓			1

$\mathcal{H}[D_3(/C_3)]$				
$h_1$	$h_2$			
$C_1$	$C_2$	$C_3$	$D_3$	
$\{h_1, h_2\}$	$\{\emptyset\}$	$\{h_1, h_2\}$	$\{\emptyset\}$	
2	0	2	0	

$\mathcal{H}[D_3(/C_1)]$				
	...			
$h_1$	...	$h_6$		
$C_1$	$C_2$	$C_3$	$D_3$	
$\{h_1, \dots, h_6\}$	$\{\emptyset\}$	$\{\emptyset\}$	$\{\emptyset\}$	
6	0	0	0	

Figure 6: Orbits of homomers,  $\mathcal{H}[D_3(/C_3)]$  and  $\mathcal{H}[D_3(/C_1)]$ , and the resulting MR's.

In a similar way, other mark rows for  $D_3$  are obtained. The corresponding sets of homomers, i.e.,  $\mathcal{H}[D_3(/C_3)]$  and  $\mathcal{H}[D_3(/C_1)]$ , and the resulting mark rows (MR's) are shown in Fig. 6. The MR's are the same as the corresponding rows of Table 3.  $\square$

Although the theoretical foundation of the above procedure has been discussed in general in Chapter 15 of Fujita's book [9], it is worthy to mention the detailed features of the present case. As found in Fig. 5, the action of the symmetry operation  $C_3$  on the set  $\mathcal{H}[D_3(/C_2)] = \{h_1, h_2, h_3\}$ , for example, produces another ordered set  $\{h_2, h_3, h_1\}$ . This operation corresponds to the following permutation or cycle (or generally the product of cycles):

$$\begin{pmatrix} h_1 & h_2 & h_3 \\ h_2 & h_3 & h_1 \end{pmatrix} \sim \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \equiv (1\ 2\ 3). \quad (10)$$

Thus, we obtain permutations:  $(1)(2)(3)$  for  $I$ ,  $(1)(2\ 3)$  for  $C_2$ ,  $(2)(1\ 3)$  for  $C'_2$ ,  $(3)(1\ 2)$  for  $C''_2$ ,  $(1\ 2\ 3)$  for  $C_3$ , and  $(1\ 3\ 2)$  for  $C'_3$ , when we apply every symmetry operations of  $D_3$

<sup>9</sup>It should be noted here that this systematic way has been used in the enumeration of isomers. See Table 15.2 of Fujita's book [9].

to the set  $\mathcal{H}[\mathbf{D}_3(/C_2)]$ . These permutations are identical with those collected in Table 1 that has been calculated by the algebraic consideration of cosets. Here we replace such algebraic symbols with objects (colored graphs) whose rotations and/or reflections can be more easily envisaged from the chemists' point of view.

The replacement can be verified by the fact the set  $\mathcal{H}[\mathbf{D}_3(/C_2)] = \{h_1, h_2, h_3\}$  corresponds to the cosets in eq. 5 in one-to-one fashion via their labels ( $h_1 \leftrightarrow 1$ ;  $h_2 \leftrightarrow 2$ ; and  $h_3 \leftrightarrow 3$ ). More concretely speaking, the cosets listed in Fig. 5 linked with the respective homomers involved in the set  $\mathcal{H}[\mathbf{D}_3(/C_2)]$ . In other words, the set  $\mathcal{H}[\mathbf{D}_3(/C_2)]$  is ascribed to the CR  $\mathbf{D}_3(/C_2)$ .<sup>10</sup> Thereby, the stabilizer of  $h_1$  is determined to be  $C_2$ , which indicates that the homomer  $h_1$  belongs to the  $C_2$ -symmetry. In a similar way,  $h_2$  belongs to the  $C'_2$ -symmetry and  $h_3$  belongs to the  $C''_2$ -symmetry. They are homomeric so that the three groups ( $C_2$ ,  $C'_2$ , and  $C''_2$ ) are conjugate to each other within  $\mathbf{D}_3$ .

## 2.2 Graphical Approach Based on Orbits of Ligands

According to Lemma 7.1 of Fujita's book [9], a regular body characterized by a regular representation  $\mathbf{G}/(\mathbf{C}_1)$  has blocks (ligands) of  $\mathbf{G}_i$ -symmetry so that they construct an orbit governed by  $\mathbf{G}/(\mathbf{G}_i)$ . This fact is applied here to give an alternative method for obtaining marks of the group  $\mathbf{G}$ .

**Step 1:** The same procedure described in the preceding subsection is followed. The substitution sites of the selected graph (regular body) construct an orbit governed by  $\mathbf{G}/(\mathbf{C}_1)$ .

**Step 2:** The same procedure described in the preceding subsection is followed.

**Step 3:** We select a set of blocks of  $\mathbf{G}_i$  symmetry from the substitution sites of the selected graph. The set models the corresponding CR  $\mathbf{G}/(\mathbf{G}_i)$ . The members (blocks) of each set may be called ligands or segments ( $\ell$ 's) and the set itself is an equivalence class (orbit) given by the symbol  $\mathcal{L} \equiv \mathcal{L}[\text{CR}] \equiv \mathcal{L}[\mathbf{G}/(\mathbf{G}_i)]$ .

**Step 4:** To find marks, we count fixed ligands ( $\in \mathcal{L}[\mathbf{G}/(\mathbf{G}_i)]$ ) on the action of each subgraph of the SSG.

**Example 2** [An Orbit of Ligands for  $\mathbf{D}_3(/C_2)$ ]:

**(Step 1)** Let us now consider the distorted cyclopropane **3** shown in Fig. 2, where the six substitution sites numbered as 1 to 6.

**(Step 2)** The same procedure in Step 2 of Example 1 is followed.

**(Step 3)** When the operations of  $C_2$  are applied to the set of vertices of **3** as the regular body, one obtains three sets of equivalent vertices:  $\{1, 4\}$ ,  $\{2, 6\}$ , and  $\{3, 5\}$ . Since these candidates of a ligand set give equivalent results, we tentatively select  $\{1, 4\}$  as a ligand  $\ell_1 (\in \mathcal{L}[\mathbf{D}_3(/C_2)])$ , as encircled in Fig. 2.

In order to obtain other members of the set, one applies all of the symmetry operations of the group  $\mathbf{D}_3$  to  $\ell_1$ , as shown in Fig. 2. The operations  $I$  and  $C_2$  involved in  $C_2$  fix  $\ell_1$  invariant. The operations  $C_3$  and  $C'_2$  in the coset  $C_2C_3$  produce a ligand  $\ell_2 (= \{2, 5\})$ , while  $C_3^2$  and  $C''_2$  in the coset  $C_2C_3^2$  produce another ligand  $\ell_3 (= \{3, 6\})$ . Hence, we obtain

<sup>10</sup>This has been generally proved as Theorem 15.2 and Corollary 15.1 of Fujita's book [9].

$\mathcal{L}[\mathbf{D}_3(/C_2)] = \{\ell_1, \ell_2, \ell_3\}$ . If more organic meanings are required, each encircled ligand labeled as  $\ell_1, \ell_2$ , or  $\ell_3$  may be considered to be a segment of  $\text{O}-\text{C}-\text{O}$  (i.e., a substituted methylene).

(Step 4) In a parallel way as described in Step 4 of Example 1, we list the ligands ( $\in \mathcal{L}[\mathbf{D}_3(/C_2)]$ ) which remain invariant under the symmetry operations of each subgroup in the order of the SSG of the group  $\mathbf{D}_3$ . By referring to Fig. 2, one obtains the following mark row (MR):

$C_1$	$C_2$	$C_3$	$D_3$
$\{\ell_1, \ell_2, \ell_3\}$	$\{\ell_1\}$	$\{\emptyset\}$	$\{\emptyset\}$
3	1	0	0

where  $\{\emptyset\}$  represents an empty set, i.e., no ligands belonging to  $\mathcal{L}[\mathbf{D}_3(/C_2)]$  are fixed under  $C_2$ . The MR (3 1 0 0) is algebraically the same as the second row of Table 3.

$\mathcal{L}[\mathbf{D}_3(/C_3)]$		$C_1$	$C_2$	$C_3$	$D_3$
$\{1, 2, 3\}$	$\{4, 5, 6\}$	$\{\ell_1, \ell_2\}$	$\{\emptyset\}$	$\{\ell_1, \ell_2\}$	$\{\emptyset\}$
$\ell_1$	$\ell_2$	2	0	2	0

$\mathcal{L}[\mathbf{D}_3(/C_1)]$			$C_1$	$C_2$	$C_3$	$D_3$
$\{1\}$	$\cdots$	$\{6\}$	$\{\ell_1, \dots, \ell_6\}$	$\{\emptyset\}$	$\{\emptyset\}$	$\{\emptyset\}$
$\ell_1$	$\cdots$	$\ell_6$	6	0	0	0

Figure 7: Orbits of ligands,  $\mathcal{L}[\mathbf{D}_3(/C_3)]$  and  $\mathcal{L}[\mathbf{D}_3(/C_1)]$ , and the resulting MR's. For a portrayal of symmetry operations, see Fig. 2.

According to this approach, other mark rows for  $\mathbf{D}_3$  are also obtained. The corresponding sets of ligands, i.e.,  $\mathcal{L}[\mathbf{D}_3(/C_3)]$  and  $\mathcal{L}[\mathbf{D}_3(/C_1)]$ , and the resulting mark rows (MR's) are shown in Fig. 7. The MR's are the same as the corresponding rows of Table 3.  $\square$

Although the above procedure is based on the discussion described in Chapter 7 of Fujita's book [9], it is worthy to mention of the present case in comparison with Example 1. When we apply the symmetry operations of  $\mathbf{D}_3$  to the set of the three ligands, we obtain permutations: (1)(2)(3) for  $I$ , (1)(2 3) for  $C_2$ , (2)(1 3) for  $C_2'$ , (3)(1 2) for  $C_2''$ , (1 2 3) for  $C_3$ , and (1 3 2) for  $C_3'$ . These permutations are identical with those collected in Table 1. This means that the cosets in eq. 5 correspond to the ligand set  $\mathcal{L}[\mathbf{D}_3(/C_2)]$  in **3** (Fig. 2) in one-to-one fashion via their labels. In other words, the set of the ligand set is ascribed to the CR  $\mathbf{D}_3(/C_2)$ . Thereby, the stabilizer of  $\ell_1$  in **3** is determined to be  $C_2$ , which indicates that the ligand  $\ell_1$  belongs to the  $C_2$ -symmetry.<sup>11</sup> In a similar way, the ligand  $\ell_2$  belongs to the  $C_2'$ -symmetry and the ligand  $\ell_3$  belongs to the  $C_2''$ -symmetry.

<sup>11</sup>If one considers an unsubstituted cyclopropane ring ( $\mathbf{D}_{3h}$ ), each ligand  $\text{CH}_2$  belongs to  $C_{2v}$ -symmetry (local symmetry). The introduction of the distortion reduces the symmetry of the ring so as to restrict the symmetry of the ligand ( $\ell_1$  or  $\text{O}-\text{C}-\text{O}$ ) to  $C_2$ .

Similarly, the symmetry operations of  $D_3$  are applied to the set of the terminal cyclohexane rings (numbered as 1, 2, and 3) in the perhydrotriphenylene **1** (Fig. 1), to the set of the ligands ( $Q_nC - CQ_n$ ,  $n = 1, 2, 3$ ) in the fixed cyclohexane **2** (Fig. 1), and to the set of the ligands ( $CQ_2$  numbered as 1, 2, and 3) in the cyclopropane derivative **4** (Fig. 2), where each of the sets is ascribed to the CR  $D_3(/C_2)$ . Obviously, the symmetry of each object (each terminal cyclohexane ring in **1**, each ligand in **2**, or each ligand in **4**) is determined to be  $C_2$ -symmetry. This treatment has been discussed in general cases [19].

### 2.3 Comparison of Two Graphical Approaches

As found in the above procedures and examples, the two graphical approaches are closely related. The parallelism between the two approaches is illustrated in Fig. 8. It should be noted that the distinct coloring of ligands  $\ell_1$ ,  $\ell_2$ , and  $\ell_3$  generates homomers  $h_1$ ,  $h_2$ , and  $h_3$  respectively. This means that the homomer set  $\mathcal{H}[D_3(/C_2)]$  as an ordered set corresponds to the ligand set  $\mathcal{L}[D_3(/C_2)]$  in one-to-one fashion. Moreover, they correspond to the coset decomposition  $D_3/C_2$  (eq. 5) as an ordered set:

$\mathcal{H}[D_3(/C_2)]$		$\mathcal{L}[D_3(/C_2)]$		$D_3/C_2$
$h_1$	$\leftrightarrow$	$\ell_1$	$\leftrightarrow$	$C_2I$
$h_2$	$\leftrightarrow$	$\ell_2$	$\leftrightarrow$	$C_2C_3$
$h_3$	$\leftrightarrow$	$\ell_3$	$\leftrightarrow$	$C_2C_3^2$

Thereby,  $\mathcal{H}[D_3(/C_2)]$ ,  $\mathcal{L}[D_3(/C_2)]$ , and, of course,  $D_3/C_2$  are ascribed to the coset representation  $D_3(/C_2)$ . This is the foundation to the fact that  $\mathcal{H}[D_3(/C_2)]$ ,  $\mathcal{L}[D_3(/C_2)]$ , and  $D_3/C_2$  give the same marks as collected in Table 3.<sup>12</sup>

Such relationships as illustrated in Fig. 8 hold true for any groups by virtue of the discussions described in Chapters 7 and 15 of Fujita's book [9]. The present results provide us not only with practical methods for obtaining marks but also with a deeper insight into stereochemistry and stereoisomerism. It is useful to summarize the results in the form of a theorem: *A homomer set  $\mathcal{H}[G(/G_i)]$ , a ligand set  $\mathcal{L}[G(/G_i)]$ , and a set of cosets  $G/G_i$  are all governed by the same coset representation  $G(/G_i)$ .*

## 3 Conclusion

The correspondence among a set of homomers  $\mathcal{H}[G(/G_i)]$ , a set of equivalent ligands  $\mathcal{L}[G(/G_i)]$ , and a set of cosets  $G/G_i$  is discussed by virtue of coset representations  $G(/G_i)$ , where  $G$  is a group and  $G_i$  is a subgroup of  $G$ . This correspondence provides us with two graphical approaches for obtaining marks of the group  $G$ . The procedures of the two approaches are illustrated by using  $D_3$  as examples.

<sup>12</sup>One of the authors (S.F.) has referred to this fact in his correspondence to the other author (S.E.) as follows: 'An organic chemist demanded to know the riddle and the Sphinx said "What is it that controls elements in a group, controls atoms in a compound, and finally isomers in organic chemistry?" "Is it a coset representation or a mark?" replied the organic chemist. The Sphinx found that her riddle was at last answered and died as was fated. The organic chemist received his reward and he was made King of the heaven.' Of course, this is a parody of a famous Greek myth [22].

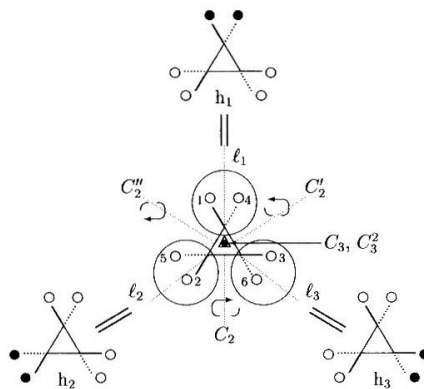


Figure 8: An orbit of ligands ( $\mathcal{L}[\mathbf{D}_3(/C_2)] = \{\ell_1, \ell_2, \ell_3\}$ ) in a regular body (center, i.e. **3**) and an orbit of homomers ( $\mathcal{H}[\mathbf{D}_3(/C_2)] = \{h_1, h_2, h_3\}$ ), which are assigned to the same CR  $\mathbf{D}_3(/C_2)$ .

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