A Model for Combinatorial Organic Chemistry

Sherif El-Basil†

Faculty of Pharmacy, Kasr El-Aini Street, Cairo 11562, Egypt

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The set of coset representations, CR's, of a group **G**, {**G**(/**G**$_1$), **G**(/**G**$_2$), ..., **G**(/**G**$_s$)}, where **G**$_1$ = {I}, **G**$_s$ = **G**, the marks, m_{ij} of subgroup **G**$_j$ on a given **G**(/**G**$_i$), $1 \le i \le s$, and the subduction of **G**(/**G**$_i$) by **G**$_j$, $j \le i$, **G**(/**G**$_i$) ↓ **G**$_j$, are essential tools for the enumeration of stereoisomers and their classification according to their subgroup symmetry (Fujita, S. *Symmetry and Combinatorial Enumeration in Chemistry;* Springer−Verlag: Berlin, 1991). In this paper, each **G**(/**G**$_i$) is modeled by a set of colored equivalent configurations (called homomers), $H = \{h_1, h_2, ..., h_r\}$, $r = |\mathbf{G}|/|\mathbf{G}_i|$, such that a given homomer, h_k, remains invariant *only* under all $g \in \mathbf{G}_i$, where g is an element of symmetry. The resulting homomers generate the corresponding set of marks almost by inspection. The symmetry relations among a set H can be conveniently stored in a Cayley-like diagram (Chartrand, G. *Graphs as Mathematical Models*; Prindle, Weber and Schmidt Incorporated: Boston, MA, 1977; Chapter 10), which is a complete digraph on r vertices so that an arc from vertex v_i to vertex v_j is colored with the set **S**$_{ij}$ of symmetry elements such that $h_i \xrightarrow{g_{ij}} h_j, g_{ij} \in \mathbf{S}_{ij}$. In addition, each vertex, v_i, is associated with a loop that is colored with a set **S**$_{ii}$ so that $g_{ii} \in \mathbf{S}_{ii}$ stabilizes h_i. A Cayley-like diagram of a given CR, G [**G**(/**G**$_i$)], leads to graphical generation of **G**(/**G**$_i$) ↓ **G**$_j$ for all values of j and also to all **m**$_{ij}$'s. Several group-theoretical results are rederived and/or became more envisagable through this modeling. The approach is examplified using **C**$_2$, **C**$_3$, **D**$_2$, **T**, and **D**$_3$ point groups and is applied to trishomocubane, a molecule that belongs to the **D**$_3$ point group.

1. INTRODUCTION AND BACKGROUND

Suppose a parent skeleton that belongs to a given point group, **G**, is subjected to a particular substitution pattern leading to a number of structures. Let **G**$_1$ = **C**$_1$ (=={I}), **G**$_2$, ..., **G**$_s$, be the sequence of representative subgroups,[1] where **G**$_s$ = **G**. One may ask: How many derivatives are there that belong to each subgroup?

In the past few years, Fujita has published a number of papers[2−9] in which he developed powerful group-theoretical methods that answer the above and such questions. While conventional treatments consider linear representations and character tables of groups,[10] Fujita's approach is based on **coset representations**, CR's, and **table of marks**.[11] Namely, each element of symmetry, $g \in \mathbf{G}$, applied to a coset of **G**$_i$, $1 \le i \le s$, gives another coset, and thus each element of **G** can be considered as a certain permutation of the cosets, leading to a representation of **G** in terms of these permutations, called **coset representations**, **G**(/**G**$_i$). Formally

$$\mathbf{G}(/\mathbf{G}_i) = \{\pi_g \mid \forall\, g \in \mathbf{G}\} \tag{1}$$

$$\pi_g = \begin{pmatrix} \mathbf{G}_i g_1 & \mathbf{G}_i g_2 & ... & \mathbf{G}_i g_r \\ \mathbf{G}_i g_1 g & \mathbf{G}_i g_2 g & ... & \mathbf{G}_i g_r g \end{pmatrix} \tag{2}$$

In eq 2, $r = |\mathbf{G}|/|\mathbf{G}_i|$, $|\mathbf{G}|$ = order of **G**. The **mark** m_{ij} of **G**$_j$ on **G**(/**G**$_i$), **G**$_j$ being another subgroup of **G**, is the number of cosets left invariant (fixed) by **G**$_j$. The set of vertices of the molecular graph that undergoes substitution is called the **orbit** of substitution. Essential to the treatment of Fujita is to classify the orbit that undergoes substitution according to the CR that governs its substitution.[6] This orbit is then **subduced** by all subgroups of the parent point group in order to obtain the required structural counts that are expressed in the so-called isomer-count matrix.[1] The subduction of a CR, **G**(/**G**$_i$), by **G**$_j$ is expressed by eq 3, which is related to eq 1 by just attaching the subscript j to **G** in braces, viz.

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j = \{\pi_g \forall \mid g \in \mathbf{G}_j\} \tag{3}$$

The basic tools here (cosets, marks, subduction tables, etc.,) are indeed rather abstract in nature and may not draw the attention of an organic chemist who benefits most from the **results** of this algebra.[12] Here we propose a graphical modeling of mark and subduction tables of CR's using "Cayley[13]-like color graphs" (or simply, Cayley diagrams, for brevity). Owing to their diagrammatic nature, graphs are more appealing to chemists, and in addition the suggested graphical model rederives many of the group theoretical results that are conventionally obtained using purely algebraic methods.

2. MODELING COSET REPRESENTATIONS AND MARKS OF A GROUP

First a molecular graph is drawn that remains fixed under all of the symmetry operations of **G**. In Figure 1 several graphs are drawn that represent models of some of the simpler point groups. When all the vertices are open, the model is said (here) to be "uncolored", and by definition

† E-mail: sherifelbasil@hotmail.com.

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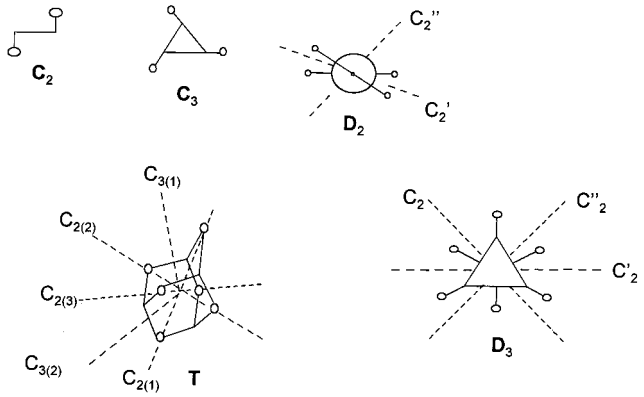


Figure 1. Model graphs of five point groups. Some elements of symmetry are shown. The (open) vertices represent orbits of substitution. The indicated graphs model the identity coset representations, **G**(/**G**), of point groups.

such a model represents the **regular** coset representation, **G**(/**G**), since it remains fixed under all $g \in \mathbf{G}$. For the other CR's, **G**(/**G**$_i$), $1 \le i \le s$, one is dealing with fewer symmetry operations, viz., only those that belong to **G**$_i$, and whence a particular "coloring" of the original model of **G**(/**G**) is adopted so that the colored graph remains fixed **only** under **G**$_i$. Arbitrarily the number of black (≡closed) vertices is chosen to be a minimum. Further, one must search for all such colored **equivalent configurations** that reproduce the permutation properties for the cosets of **G**$_i$. The chemical term for equivalent configurations is **homomers**.[14] For a given CR, **G**(/**G**$_i$), this set will be denoted as H [**G**(/**G**$_i$)] where

$$H\,[\mathbf{G}(/\mathbf{G}_i)] \equiv H = \{h_1, h_2, ..., h_r\} \qquad (4)$$

in which h_i is an ith homomer and r is defined by eq 2. To find $h_1 \in H$ [**G**(/**G**$_i$)], we apply all g's $\in \mathbf{G}_i$ and express the result in cyclic notation[15] such as (ab)(cdef)(...), where the letters in parentheses refer to the labels of vertices of the orbit. Since h_1 remains fixed under **G**$_i$ it must yield the following "vertex-color" identities:

$$a = b;\ c = d = e = f, ... \qquad (5)$$

We then select **just one** such equality that involves the smallest number of vertices and color them in black. The resulting (colored) configuration is (arbitrarily) called h_1. The other $r-1$ elements of the set H are deduced so that they generate the same cyclic structures of the permutations representing **G**(/**G**$_i$).

Figure 2 models some of the CR's of the **T** point group.

To find the marks, one lists below each homomer the subgroups that leave it fixed and then arranges the results in the form of a row vector, the entries of which are the representative[1] subgroups of **G** ordered in a nonascending order, viz.

$$|\mathbf{G}_1| \le |\mathbf{G}_2| \le ... \le |\mathbf{G}_s|$$

3. INTERRELATIONS AMONG A SET OF HOMOMERS

To further our knowledge of the properties of a set H [**G**(/**G**$_i$)], the interrelations among the individual members (homomers) can be outlined either graphically or in matrix form.

3.1. Graphical Representation of H: "Cayley[13]-like Color Diagrams".

The set of r homomers $\{h_1, h_2, ..., h_r\} \equiv H$, which is associated with a given CR, **G**(/**G**$_i$), can be represented by a complete digraph (directed graph) on r vertices with arcs and loops. Each arc from h_i to h_j is "colored" with a **set** of symmetry elements, **S**$_{ij}$, such that

$$h_i \xrightarrow[g_{ij} \in \mathbf{S}_{ij}]{g_{ij}} h_j \qquad (6)$$

Each vertex, v_i, is associated with a loop that is also colored with a set of elements **S**$_{ii}$ so that a given $g_{ii} \in \mathbf{S}_{ii}$ stabilizes h_i. The resulting digraphs, G [H (**G**/**G**$_i$)], are reminiscent of "Cayley color graphs" of groups.[13] We shall demonstrate that the G graphs contain information on

(a) coset decomposition of **G** by **G**$_i$,

(b) marks of **G**(/**G**$_i$), and

(c) **G**(/**G**$_i$) ↓ **G**$_j$ (cf. eq 3) for all **G**$_j$ of **G**$_i$, where **G**$_j$ is a subgroup of **G**$_i$.

Furthermore, the above information can be extracted almost immediately from these digraphs.

3.2. Matrix Representation of H.

If $|H$ [**G**(/**G**$_i$)]| is large (>4) it may be more convenient to work with **G** in its matrix form, **M**[**G**(/**G**$_i$)]. The matrix is defined as an $r \times r$ matrix whose diagonal and off-diagonal elements are the sets **S**$_{ii}$ and **S**$_{ij}$, respectively.

3.3. Graphical Representation of Eq 3: Subduced Representations.

G(/**G**$_i$) ↓ **G**$_j$ is usually expressed as a sum of CR's of **G**$_j$, viz.

$$\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j = \alpha_{jk}\mathbf{G}_j(/\mathbf{G}_k) + \alpha_{jl}\mathbf{G}_j(/\mathbf{G}_l) + ... \qquad (7)$$

where **G**$_k$, **G**$_l$, ... are subgroups of **G**$_j$ and the α's are nonnegative multiplication factors.

The "subduction" set of equivalent configurations described above may be obtained graphically by the following steps:

(a) Find the Cayley-like color graph of **G**(/**G**$_i$), G [**G**(/**G**$_i$)], as described in section 3.1.

(b) An arc (or a loop) in G [**G**(/**G**$_i$)] is annihilated (i.e., pruned out) unless one of its color components belongs to **G**$_j$, the subducing group.

(c) The result of (b) is, in general, a set of disconnected G's of the general form

$$\{G\,[\mathbf{G}_j(/\mathbf{G}_k)]\cdot G\,[\mathbf{G}_j(/\mathbf{G}_l)]...\} \qquad (8)$$

where, in general, each component of the above set may be repeated α_{jk}, α_{jl}, ... times (cf. eq 7).

Figure 3 illustrates such a graphical subduction of the CR: **T**(/**C**$_3$) by **C**$_2$ and by **C**$_3$.

Alternatively the set **G**(/**G**$_i$) ↓ **G**$_j$ might be obtained by subducing the matrix **M**[**G**(/**G**$_i$)] in the following steps:

(a) Annihilate from **M**[**G**(/**G**$_i$)] all $g \notin \mathbf{G}_j$ to give **M**[**G**(/**G**$_i$) ↓ **G**$_j$].

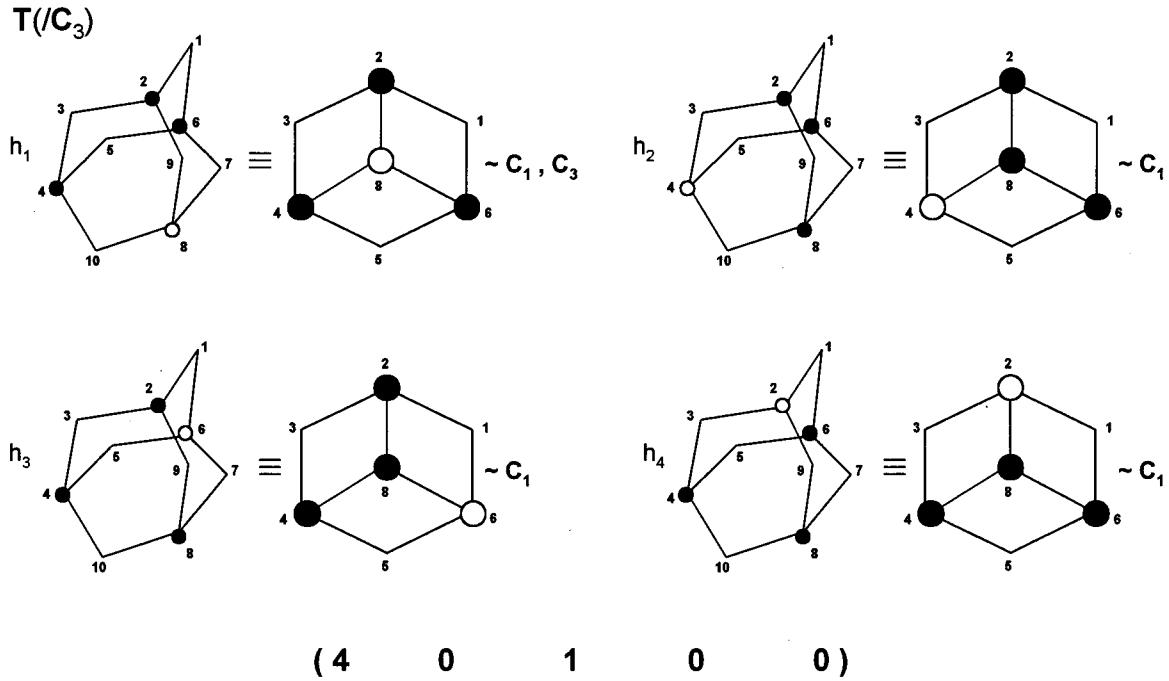


Figure 2. Coset representation of **T** point group modeled by the appropriate set of homomers along with the corresponding mark rows. In all cases the set of homomers that models $\mathbf{G}(/\mathbf{G}_i)$ remains fixed *only* under a symmetry element of $\mathbf{G}_i$.

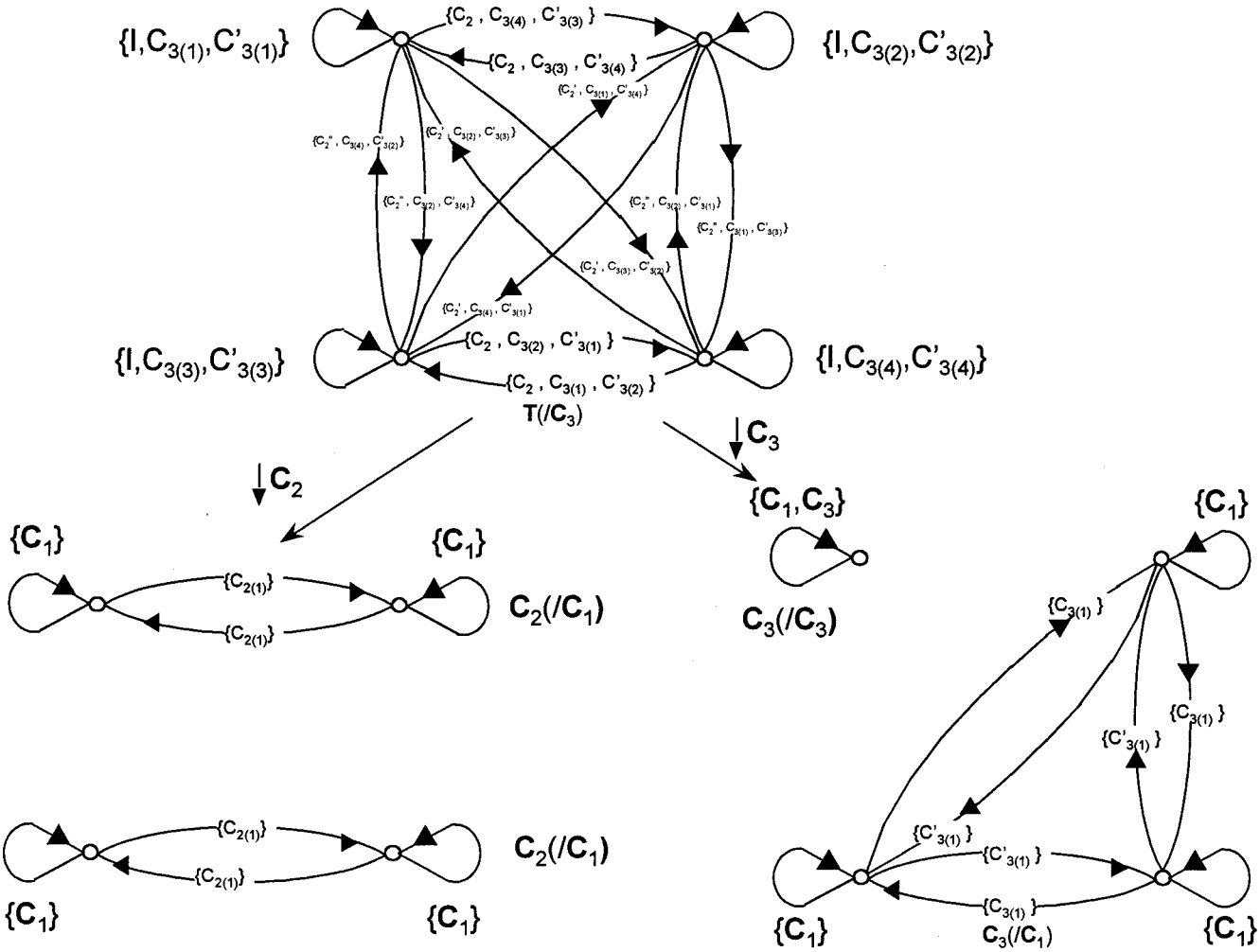


Figure 3. Graphical modeling of eq 3 illustrated for $\mathbf{T}(/\mathbf{C}_3) \downarrow \mathbf{C}_3$; $\mathbf{T}(/\mathbf{C}_3) \downarrow \mathbf{C}_2$ through the use of the Cayley color diagram[7] of $\mathbf{T}(/\mathbf{C}_3)$.

(b) If $\mathbf{M}[\mathbf{G}(/\mathbf{G}_i) \downarrow \mathbf{G}_j]$ is not already in block form, then apply to it the appropriate set of row/column operations[16] to transform it into block form. (The notation H_{ij} (K_{ij}) ≡ interchanging rows (columns) i and j.) A general form of

Chart 1

$$\begin{pmatrix} \{I,C_2\} & \{C_2',C_2''\} & \{C_{3(1)},C_{3(3)}\} & \{C_{3(2)},C_{3(4)}\} & \{C'_{3(2)},C'_{3(3)}\} & \{C'_{3(1)},C'_{3(4)}\} \\ \{C_2',C_2''\} & \{I,C_2\} & \{C_{3(2)},C_{3(4)}\} & \{C_{3(1)},C_{3(3)}\} & \{C'_{3(1)},C'_{3(4)}\} & \{C'_{3(2)},C'_{3(3)}\} \\ \{C'_{3(1)},C'_{3(3)}\} & \{C'_{3(2)},C'_{3(4)}\} & \{I,C_2'\} & \{C_2,C_2''\} & \{C_{3(3)},C_{3(4)}\} & \{C_{3(1)},C_{3(2)}\} \\ \{C'_{3(2)},C'_{3(4)}\} & \{C'_{3(1)},C'_{3(3)}\} & \{C_2,C_2''\} & \{I,C_2'\} & \{C_{3(1)},C_{3(2)}\} & \{C_{3(3)},C_{3(4)}\} \\ \{C_{3(2)},C_{3(3)}\} & \{C_{3(1)},C_{3(4)}\} & \{C'_{3(3)},C'_{3(4)}\} & \{C'_{3(1)},C'_{3(2)}\} & \{I,C_2''\} & \{C_2,C_2'\} \\ \{C_{3(1)},C_{3(4)}\} & \{C_{3(2)},C_{3(3)}\} & \{C'_{3(1)},C'_{3(2)}\} & \{C'_{3(3)},C'_{3(4)}\} & \{C_2,C_2'\} & \{I,C_2''\} \end{pmatrix}$$

$$\mathbf{M[T(/C_2)]}$$

$$\downarrow \quad \text{Keep only } g \in \mathbf{D}_2$$

$$\begin{pmatrix} \{I,C_2\} & \{C_2',C_2''\} & 0 & 0 & 0 & 0 \\ \{C_2',C_2''\} & \{I,C_2\} & 0 & 0 & 0 & 0 \\ 0 & 0 & \{I,C_2'\} & \{C_2,C_2''\} & 0 & 0 \\ 0 & 0 & \{C_2,C_2''\} & \{I,C_2'\} & 0 & 0 \\ 0 & 0 & 0 & 0 & \{I,C_2''\} & \{C_2,C_2'\} \\ 0 & 0 & 0 & 0 & \{C_2,C_2'\} & \{I,C_2''\} \end{pmatrix}$$

$$\mathbf{M}\,[\mathbf{T}(/\mathbf{C}_2) \downarrow \mathbf{D}_2]$$

$$\sim \begin{pmatrix} [\mathbf{D}_2(/\mathbf{C}_2)] & \mathbf{0}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & [\mathbf{D}_2(/\mathbf{C}'_2)] & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{0}_2 & [\mathbf{D}_2(/\mathbf{C}''_2)] \end{pmatrix}$$

$$\mathbf{M[T(/C_2)} \downarrow \mathbf{D_2]}$$

the matrix that results in this step is given by

$$\begin{pmatrix} [\mathbf{G}_j(/\mathbf{G}_k)] & 0 & 0 & \dots & 0 \\ 0 & [\mathbf{G}_j(/\mathbf{G}_l)] & 0 & \dots & 0 \\ . & . & . & & . \\ . & . & . & & . \\ . & . & . & & . \\ . & . & . & & . \\ 0 & 0 & 0 & \dots & [\mathbf{G}_j(/\mathbf{G}_m)] \end{pmatrix} \qquad (9)$$

where $\mathbf{G}_k$, $\mathbf{G}_l$, ..., $\mathbf{G}_m$ are subgroups of $\mathbf{G}_j$.

(c) The block matrix (eq 9) represents the disconnected Cayley-like color graphs:

$$\{G\,[\mathbf{G}_j(/\mathbf{G}_k)]\cdot G\,[\mathbf{G}_j(/\mathbf{G}_l)]\ \dots\ G\,[\mathbf{G}_j(/\mathbf{G}_m)]\} \qquad (11)$$

(d) Then the matrix given by eq 9 corresponds to the subduction expression given by eq 7.

Example 1

$$\mathbf{T}(/\mathbf{C}_2) \downarrow \mathbf{D}_2 = \mathbf{D}_2(/\mathbf{C}_2) + \mathbf{D}_2(/\mathbf{C}_2') + \mathbf{D}_2(/\mathbf{C}_2'') \quad (11)$$

We observe that $|G\,[\mathbf{T}(/\mathbf{C}_2)]| = 6$, and whence it is more convenient to work with matrix forms, steps a−d are illustrated in Chart 1 where $\mathbf{0}_2$ is a 2×2 null matrix.

In this example no row/column operations were necessary; i.e., the subduced matrix was already in block form. The following example represents a more general situation where one must apply a set of row/column operations to obtain the expression of the subduced representation (Chart 2).

An Application of the Model. Find the isomer-count matrix of the substituted trishomocubane graph shown in Figure 4. The orbit of substitution is controlled by $\mathbf{D}_3(/\mathbf{C}_1)$.

Trishomocubane is a caged compound that belongs to the $\mathbf{D}_3$ point group[17] (cf. Figure 1). The compound can be envisaged from the fusion of six equivalent cyclopentane rings (or three norbornanes). The parent (unsubstituted graph) of this molecule has three C_2 axes each passing through a methylene carbon and the center of an opposite edge. One C_2 axis passes through vertex 4 and edge-joining vertices 1 and 8. Another C_2 axis passes through vertex 7 and the bond joining vertices 3 and 10. Finally a third C_2 passes through vertex 11 and the bond between vertices 5 and 6. The molecule also has one C_3 axis, which passes through vertices 2 and 9. The resulting USCI's are outlined below together with the corresponding generating functions adopting the weights

$$w(\mathrm{C}) = x; \quad w(\mathrm{N}) = y \qquad (12)$$

$$\downarrow C_1 \rightarrow \mathrm{S}_1^6 \rightarrow (x+y)^6 \qquad (13)$$

$$\downarrow C_2 \rightarrow \mathrm{S}_2^3 \rightarrow (x^2+y^2)^3 \qquad (14)$$

$$\downarrow C_3 \rightarrow \mathrm{S}_3^2 \rightarrow (x^3+y^3)^2 \qquad (15)$$

$$\downarrow D_3 \rightarrow \mathrm{S}_6 \rightarrow (x^6+y^6) \qquad (16)$$

Chart 2

$$[\mathbf{T}(/\mathbf{C}_2)] \xrightarrow[g \in \mathbf{C}_3]{\text{Keep only}} \begin{pmatrix} \{I\} & 0 & \{C_{3(1)}\} & 0 & 0 & \{C'_{3(1)}\} \\ 0 & \{I\} & 0 & \{C_{3(1)}\} & \{C'_{3(1)}\} & 0 \\ \{C'_{3(1)}\} & O & \{I\} & 0 & 0 & \{C_{3(1)}\} \\ 0 & \{C'_{3(1)}\} & 0 & \{I\} & \{C_{3(1)}\} & 0 \\ 0 & \{C_{3(1)}\} & 0 & \{C'_{3(1)}\} & \{I\} & 0 \\ \{C_{3(1)}\} & 0 & \{C'_{3(1)}\} & 0 & 0 & \{I\} \end{pmatrix}$$

$$\xrightarrow[H_{23}\,,\,H_{36}]{K_{23}\,,\,K_{36}} \begin{pmatrix} [\mathbf{C}_3(/\mathbf{C}_1)] & \mathbf{0}_3 \\ \mathbf{0}_3 & [\mathbf{C}_3(/\mathbf{C}_1)] \end{pmatrix}$$

An Illustration of the Subduction $\mathbf{D}_3(/\mathbf{C}_1) \downarrow \mathbf{C}_2 = 3\mathbf{C}_2(/\mathbf{C}_1)$. The Cayley graph of the CR $\mathbf{D}_3(/\mathbf{C}_1)$ has six vertices that represent its six homomer models. This graph is too large to construct and then apply the pruning technique to expand the required subduction. In this and similar situations, the matrix representation of CR is a more convenient method. The homomers of $\mathbf{D}_3(/\mathbf{C}_1)$ transform to one another according to the following matrix:

$$\mathbf{M}[\mathbf{D}_3(/\mathbf{C}_1)] = \begin{array}{c} \\ h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \\ h_6 \end{array} \begin{array}{c} \begin{array}{cccccc} h_1 & h_2 & h_3 & h_4 & h_5 & h_6 \end{array} \\ \begin{pmatrix} \{I\} & \{C_2\} & \{C_2'\} & \{C_2''\} & \{C_3\} & \{C_3'\} \\ \{C_2\} & \{I\} & \{C_3'\} & \{C_3\} & \{C_2''\} & \{C_2'\} \\ \{C_2'\} & \{C_3\} & \{I\} & \{C_3'\} & \{C_2\} & \{C_2''\} \\ \{C_2''\} & \{C_3'\} & \{C_3\} & \{I\} & \{C_2'\} & \{C_2\} \\ \{C_3'\} & \{C_2''\} & \{C_2\} & \{C_2'\} & \{I\} & \{C_3\} \\ \{C_3\} & \{C_2'\} & \{C_2''\} & \{C_2\} & \{C_3'\} & \{I\} \end{pmatrix} \end{array} \quad (17)$$

To obtain the required expression for subduction (with $\mathbf{C}_2$), we keep only those elements of $\mathbf{C}_2$ (=$\{I, C_2\}$) in the above matrix and carry out the appropriate row/column operations as shown below

$$\begin{array}{c} \\ h_1 \\ h_2 \\ h_3 \\ h_4 \\ h_5 \\ h_6 \end{array} \begin{array}{c} \begin{array}{cccccc} h_1 & h_2 & h_3 & h_4 & h_5 & h_6 \end{array} \\ \begin{pmatrix} I & C_2 & 0 & 0 & 0 & 0 \\ C_2 & I & 0 & 0 & 0 & 0 \\ 0 & 0 & I & 0 & C_2 & 0 \\ 0 & 0 & 0 & I & 0 & C_2 \\ 0 & 0 & C_2 & 0 & I & 0 \\ 0 & 0 & 0 & C_2 & 0 & I \end{pmatrix} \end{array} = \mathbf{M}[\mathbf{D}_3(/\mathbf{C}_1) \downarrow \mathbf{C}_2] \quad (18)$$

$$\begin{array}{c} \xrightarrow[2.H_{35}]{1.K_{45}} \\ \begin{pmatrix} I & C_2 & 0 & 0 & 0 & 0 \\ C_2 & I & 0 & 0 & 0 & 0 \\ 0 & 0 & I & C_2 & 0 & 0 \\ 0 & 0 & C_2 & I & 0 & 0 \\ 0 & 0 & 0 & 0 & I & C_2 \\ 0 & 0 & 0 & 0 & C_2 & I \end{pmatrix} \end{array} \equiv \begin{pmatrix} \mathbf{C}_2(/\mathbf{C}_1) & \mathbf{0}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{C}_2(/\mathbf{C}_1) & \mathbf{0}_2 \\ \mathbf{0}_2 & \mathbf{0}_2 & \mathbf{C}_2(/\mathbf{C}_1) \end{pmatrix} \quad (19)$$

where K_{ij} represents the interchange between column i and column j while H_{ij} represents the interchange between row i and row j and $\mathbf{0}_2$ is a 2×2 null matrix. Equation 19 then corresponds to three $\mathbf{C}_2(/\mathbf{C}_1)$'s, which is what one obtains using conventional coset algebra which requires both permutation representations **and** mark tables of the subducing groups.

Table 1. Fixed-Point Matrix of the Trishomocubane Problem

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_3$
x^6	1	1	1	1
y^6	1	1	1	1
xy^5	6	0	0	0
x^5y	6	0	0	0
x^2y^4	15	3	0	0
x^4y^2	15	3	0	0
x^3y^3	20	0	2	0

Table 2. Isomer-Count Matrix of the Trishomocubane Graph[a]

	$\mathbf{C}_1$	$\mathbf{C}_2$	$\mathbf{C}_3$	$\mathbf{D}_3$
x^6				$*^1$
y^6				$*^2$
xy^5	$*^3$			
x^5y	$*^4$			
x^2y^4	$*^5$	$*^6$ $*^7$ $*^8$		
x^4y^2	$*^9$	$*^{10}$ $*^{11}$ $*^{12}$		
x^3y^3	$*^{13}$ $*^{14}$ $*^{15}$		$*^{16}$	

[a] Vacant positions correspond to zeros and stars to ones.

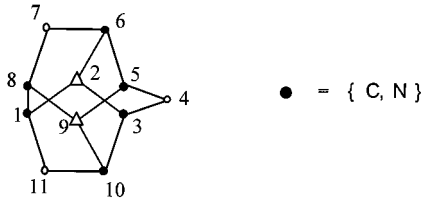


Figure 4. Trishomocubane graph studied in this work. There are three orbits colored as solid circles, open circles, and open triangles.

The resulting polynomials (eqs 12−16) when expanded generate the FP matrix in Table 1.

When Table 1 is multiplied by the inverse of the mark table of the $\mathbf{D}_3$ point group,[11] one obtains Table 2.

Observe that each star corresponds to a row from the mark table. The labelings of the stars correspond to the heterocycles derived from this caged molecule. These are drawn in Figure 5.

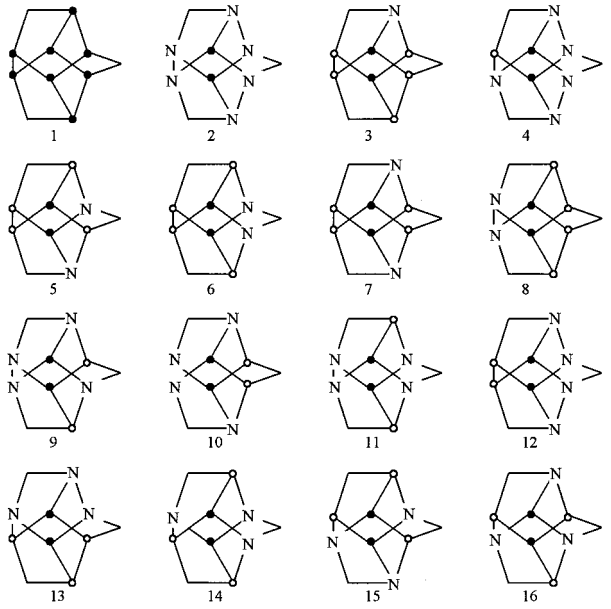


Figure 5. Heterocyclic derivatives derived from trishomocubane, which correspond to Table 2 (the isomer-count matrix).

4. MODELING ALGEBRAIC PROPERTIES OF MARK AND GROUP-SUBDUCTION TABLES

4.1. Properties of Marks. 4.1.1. The row of marks of $\mathbf{G}(/\mathbf{G}_1)$ has the general form[18]

$$(|\mathbf{G}| \quad 0 \quad 0 \quad \ldots \quad 0) \tag{20}$$

where the number of 0's is equal to |SSG| − 1. This is because every loop in $G\,[\mathbf{G}(/\mathbf{G}_1)]$ is colored with just one component, viz., $\mathbf{C}_1$, and recalling that $|\mathbf{G}(/\mathbf{G}_1)| = |\mathbf{G}| = |\mathbf{G}[\mathbf{G}(/\mathbf{G}_1)]|$, the general form of row of marks given by eq 20 results.

4.1.2. The row of marks of $\mathbf{G}(/\mathbf{G})$ has the general form[18]

$$(1 \quad 1 \quad \ldots \quad 1) \tag{21}$$

where the number of 1's = |SSG|. This property, which one observes at the bottoms of mark tables, results from the fact that $G\,[\mathbf{G}(/\mathbf{G})]$ has the general form of a single vertex whose loop is colored with every subgroup of **G**, i.e., takes the general form

$$\{\mathbf{C}_1, \mathbf{G}_2, \ldots, \mathbf{G}\}$$

4.1.3. The row of marks of a given $\mathbf{G}(/\mathbf{G}_i)$ has only two values, viz.

$$m_{ij} = \begin{Bmatrix} 0 \\ r \end{Bmatrix} \tag{23}$$

if all the loops of $G\,[\mathbf{G}(/\mathbf{G}_i)]$ are **identically** colored with the same subgroups.

4.2. Properties of Subduced Representations. 4.2.1. There are two dominant characters of the general sum given by eq 7, namely

(a) The number of homomers that represents (models) a given coset representation, $\mathbf{G}(/\mathbf{G}_i)$, is equal to the number of homomers that models a given subduced representation of $\mathbf{G}(/\mathbf{G}_i)$ by one of its subgroups, i.e.

$$|H\,[\mathbf{G}(/\mathbf{G}_i)]| = |H\,[\mathbf{G}(/\mathbf{G}_i)\downarrow \mathbf{G}_j]| \tag{24}$$

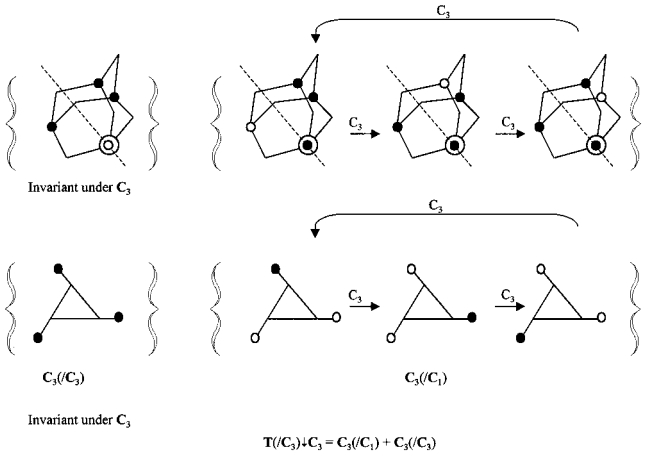


Figure 6. Modeling eq 24 for $\mathbf{G} = \mathrm{T}$, $\mathbf{G}_i = \mathbf{C}_3$. Observe that (a) $|H\,[\mathbf{T}(/\mathbf{C}_3)]| = 4$, cf. Figure 2, one homomer remains invariant under $\mathbf{C}_3$ while three homomers transform to each other as shown: (b) exactly the same transformation properties are displayed by the four homomers of $\mathbf{C}_3(/\mathbf{C}_3) + \mathbf{C}_3(/\mathbf{C}_1)$; whence one writes $\mathbf{T}(/\mathbf{C}_3)\downarrow \mathbf{C}_3 = \mathbf{C}_3(/\mathbf{C}_1) + \mathbf{C}_3(/\mathbf{C}_3)$.

(b) The two sets of homomers of eq 24 have identical transformation properties under all $g \in \mathbf{G}_j$, i.e., under all symmetry operations of the subducing groups.

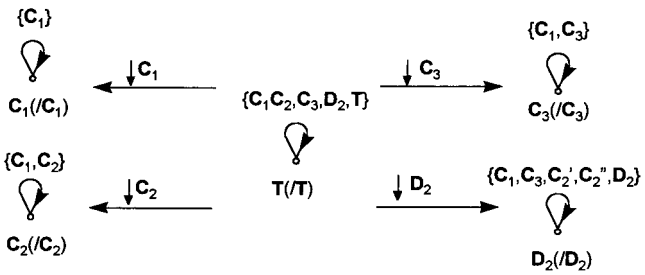
These two properties may be modeled by considering the example shown in Figure 6.

Property a is also understood using graphical subduction of the Cayley diagram since the total number of vertices in the fragmented graph is preserved.

4.2.2. Subduction of the identity representation of a group leads to the identity representation of the subducing group, i.e.

$$\mathbf{G}(/\mathbf{G})\downarrow \mathbf{G}_j = \mathbf{G}_j(/\mathbf{G}_j) \tag{25}$$

This result is understood from the general form of the Cayley diagram of $\mathbf{G}(/\mathbf{G})$, being a single vertex the loop of which is colored with all the subgroups of **G**. Then subduction by $\mathbf{G}_1$ leaves only the color component $\mathbf{G}_1$ to give $\mathbf{G}_1(/\mathbf{G}_1)$, while general subduction by $\mathbf{G}_i$ leads to a vertex whose loop is colored by all the subgroups of $\mathbf{G}_i$ that correspond to $\mathbf{G}_i(/\mathbf{G}_i)$ and so on. This property is modeled below for the identity representation of the **T** point group.



(26)

$$\mathbf{G}(/\mathbf{G}_1)\downarrow \mathbf{G}_j = r\mathbf{G}_j(/\mathbf{G}_1) \tag{27}$$

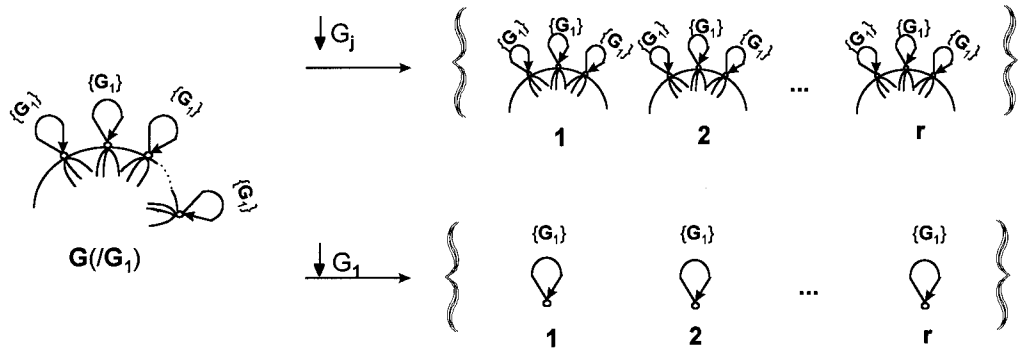


Figure 7. Modeling of eqs 27 and 28.

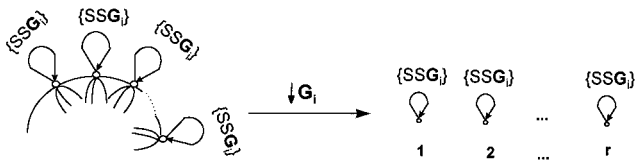


Figure 8. Modeling of eq 29.

4.2.3. Here the Cayley graph of $\mathbf{G}(/\mathbf{G}_1)$ possesses loops that are colored by $\mathbf{C}_1$ only, and because $\mathbf{C}_1$ is a common subgroup of all subgroups, the resulting subduced Cayley graphs will also have loops that are colored by $\mathbf{C}_1$ only and therefore they will be all identically regular representations of the subducing group, i.e., $\mathbf{G}_j(/\mathbf{G}_1)$. Because r is equal to $|\mathbf{G}|/|\mathbf{G}_j|$, there will be r such $G\,[\mathbf{G}_j(/\mathbf{G}_1)]$.

$$\mathbf{G}(/\mathbf{G}_1)\downarrow \mathbf{G}_1 = |\mathbf{G}|\mathbf{G}_1(/\mathbf{G}_1) \tag{28}$$

4.2.4. Equation 28 is understood from the fact that the Cayley graph $G\,[\mathbf{G}(/\mathbf{G}_1)]$ contains $|\mathbf{G}|$ vertices, each loop of which is colored with $\mathbf{G}_1$ while the arcs with $g \notin \mathbf{G}_1$. Then subduction by $\mathbf{G}_1$ fragments it into $|\mathbf{G}|$ vertices each of which is nothing but $\mathbf{G}_1(/\mathbf{G}_1)$. Equations 27 and 28 are modeled in Figure 7.

4.2.5. If all $h_i \in H\,[\mathbf{G}(/\mathbf{G}_i)]$ remain invariant under $\mathbf{G}_i$

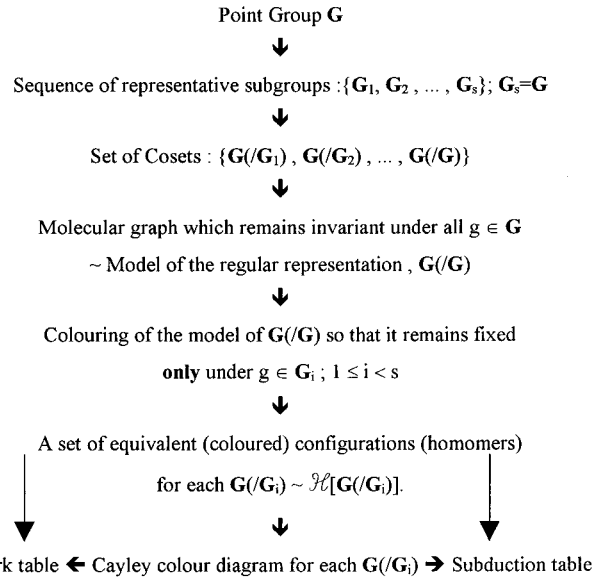
$$\mathbf{G}(/\mathbf{G}_i)\downarrow \mathbf{G}_i = r\,\mathbf{G}_i(/\mathbf{G}_i) \tag{29}$$

In this particular case the loops of the vertices of $G\,[\mathbf{G}(/\mathbf{G}_i)]$ are colored with all the subgroups of $\mathbf{G}_i$ (because by assumption all r homomers of $H\,[\mathbf{G}(/\mathbf{G}_i)]$ remain invariant under all $g \in \mathbf{G}_i$) and whence none of the arcs are colored with any $g \in \mathbf{G}_i$. Then subduction by $\mathbf{G}_i$ generates r lonely vertices whose loops are colored with all subgroups of $\mathbf{G}_i$, i.e., by $\{\mathrm{SS}\mathbf{G}_i\}$ which is nothing but r copies of the regular representation of $\mathbf{G}_i$. This case is modeled in Figure 8.

5. DISCUSSION AND CONCLUSIONS

Scheme 1 outlines the main feature of this work.

Scheme 1



Abstract description of a physical phenomenon remains a most precise and exact description, while a given model is always going to be approximate; cf., the three (popular) physical chemistry models of an ideal gas, ideal electrolyte, and ideal solution. However modeling usually carries both educational as well as theoretical endeavors. In the present work several group theoretical properties are rederived or became more easily seen through modeling, namely, eq 3, which defines subductions of a given CR and the concept of a mark. Figure 3 is a pictorial illustration of eq 3. We believe that the preparation of Cayley diagrams of CR's of the point groups of chemical interest is a worthy task and that such an appendix in a text that deals with enumeration of chemical structures is at least as important as appendices that contain mark tables, subduction tables, and their "predecessors": character tables!

In conclusion, the model presented here translates the three basic (and abstract) alphabets used in the "enumeration journey" of Fujita, viz., coset representation, mark, and subduction of a group into the language of graphs. The latter shall always remain the more appealing for chemists. Indeed the present work extends an invitation to organic chemists who would like to see organic chemistry from a theoretical (computational) vent but who are also repelled by the (sometimes) offensive algebra in their way. It may be convenient to end this paper by a parody of famous Greek myth (Warner, Rex. *Men and Gods*; Kenkyusha: Tokyo, 1959).[19]

"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 award and he was made King of the heaven!"

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