Prolegomenon on Theory and Applications
of Tables of Marks[*]

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The more popular type of physico-chemical applications of group theory is based on group-representation theory and **character tables**[1]. The strategy of this approach is to reduce a linear representation of a point-group into a set of irreducible representations which form the character table of the group.

This type of application uses **symmetry adapted functions** for molecular orbital theory and ligand field theory to analyze molecular orbitals and molecular vibrations of a molecule.

Such a scheme assumes a superposition of a set of wavefunctions to realize a molecule and thence implies only a **secondary** existence of the concepts of bonds and atoms. Most of the existing textbooks on group-theoretical applications consider this type of model.

The other branch of applied group theory[2] bears a direct relation to **combinatorial enumeration and stereochemistry** which is the topic of this special issue of Match, this latter area of applications requires a three-dimensional structural formula, i.e. a model which has a **discrete** nature and therefore a **primary** meaning of atoms and bonds.

Three main stages led to the development of a systematic study of (stereo) chemical isomer enumeration, viz.,

[*] Dedicated to Professor Milan Randic on the occasion of his 72 birthday.

(1) The Pólya –Redfield Theory[3] : (1935 and 1927)

The contemporary mathematician **George Pólya** developed a theory named after him which determines numbers of equivalence classes of chemical isomers, graphs and trees. Pólya's methods were discovered independently by **J. Howard Redfield**[4] and further developed by **Nicolas Govert de Bruijn**[5]. The Pólya–Redfield theorem uses a cycle index that is composed of terms associated with conjugacy classes. This task does not require knowledge of group–subgroup relationships but only the examination of the elements of symmetry of the particular point–group. The "mathematical origins" of **organic** stereochemistry, (namely, the **tetrahedral** geometry of the carbon atom) may be found in the Pólya–Redfield theory. Indeed **van't Hoff's** conclusion[6] that "**if the four valencies of the carbon atom are arranged tetrahedrally with the carbon atom at center, then all the cases of isomerism known are accounted for**" is in harmony with the **generating function, GF** ($\equiv$ pattern inventory $\equiv$ library) of a substituted methane. Namely, in a two-dimensional space (where **only rotations** are included in the regular tetrahedron – cycle index), the cycle index is given by[7]:

$$Z_2 (\text{tetrahedron}) = 12^{-1} [S_1^4 + 8S_1S_3 + 3S_2^2]$$

And, the GF which corresponds to the lactic acids, for example, is given by :

$$GF = Z [S_i^j \longrightarrow (a^i + b^i + c^i + d^i)^j]$$

where : $a = w(H)$; $b = w(CH_3)$; $c = w(COOH)$; $d = w(OH)$, $w(H)$ is the weight (number of) hydrogen atoms in a particular isomer and so on. Then the number of enantiomers of lactic acid is the **coefficent of abcd** in the GF (Z_2) which is calculated to be **2**, a result which is consistent with the experimental fact that there are indeed 2 lactic acids (now known as S- and R- lactic acids). This is one of the earliest striking relations between mathematics and a chemical observable! Indeed, if reflections are included as well, a 3-space cycle index results which looks like:

$$Z_3 (\text{tetrahedron}) = 24^{-1} [S_1^4 + 8S_1S_3 + 3S_2^2 + 6S_4 + 6S_1^2S_2]$$
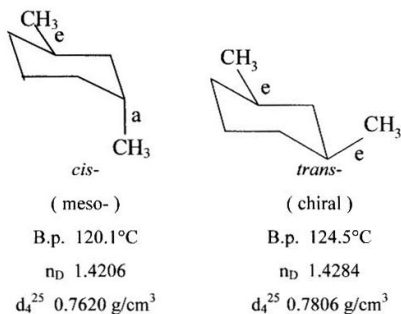
This time, the coefficient of abcd is 1 because a reflection plane "counts" 2 enantiomers as one. In other words: in the absence of reflections enantiomers are distinct and they become equivalent if reflections are included:
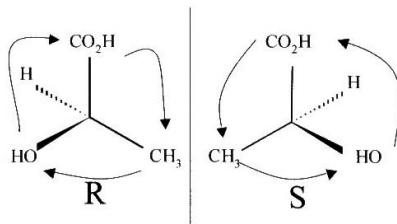
This case of simple enumeration is one of the earliest and clearest connections between (stereo) chemical enumeration and the Pólya–Redfield theory. But **surprisingly indeed van't Hoff[8] reached his conclusion in 1874, some 60 years before the publication of the Pólya–Redfield enumeration scheme!** (A reader might wish to take a look at I.L. Finar's book[6] where a simulation of van't Hoff's isomer–count based on various assumed geometries of the carbon atom is found.) At this stage of the introduction to the theory and applications of mark tables, it is remarkable to observe the "educational" aspects of the Pólya–Redfield formula in relation to organic chemistry[9]: many undergraduate students live under the impression that the tetrahedral nature of the carbon atom was discovered using experimental tools, being quite unaware of the mathematical origins cited here or, in fact, van't Hoff's work on isomer–count. (see : organic chemistry paradox, later). Another major success of the Pólya–Redfield enumeration scheme is understanding cyclohexane stereochemistry[10]: **Experimental** chemists observed two distinct substitution patterns, viz., axial and equatorial substitution patterns:
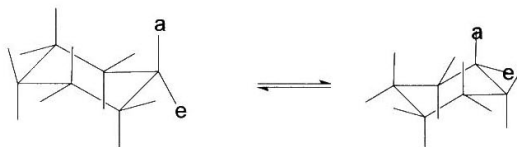
As an illustration we show below the most stable conformer of the *cis* – and the *trans*-1,3-dimethyl-cyclohexanes[11] and their boiling points, B.P.s; refractive indices, n_D; densities, d_4^{25}:

cis-	trans-
(meso-)	(chiral)
B.p. 120.1°C	B.p. 124.5°C
n_D 1.4206	n_D 1.4284
d_4^{25} 0.7620 g/cm^3	d_4^{25} 0.7806 g/cm^3

I.e., the above and other such pairs of diastereomers enjoy a real existence and this is what the symmetry told us: axial and equatorial bonds are distinct (not equivalent)!. Indeed a 3-space Z which assumes a D_{3d} point group of the chair conformation of cyclohexane looks like[10]:

$$Z_3 \text{ (chair)} = 12^{-1} [S_1^{12} + 4S_2^6 + 2S_3^4 + 2S_6^2 + 3S_1^4 S_2^4]$$

The above cycle index predicts **2** monochlorocyclohexanes (an axially substituted isomer and an equatorially substituted one), **10** dichlorocy-clohexanes and **24** trichloro isomers. The above count is consistent with only two types of bonds.

A beginning student of organic chemistry might have difficulties predicting the distinction between **a** and **e** bonds in cyclohexane until his teacher convinces him of the "steric differences" between the two situations. But symmetry is decisive here: the coefficient of xy^{11} [x = w(Cl), y = w(H)] is **2** in the corresponding GF.

The above is a situation where an observable (a set of diastereomers) might be predicted from a nonobservable (combinatorial theory of symmetry)! Many other situations may be found elsewhere.

(2) The "Application Era"

As stated earlier, **N.G. de Bruijn** extensively developed the Pólya–Redfield enumeration scheme. In addition many distinguished scientists contributed several applications along these lines. It is not our purpose here to count all contributions or even most of them. However, we will mention the names of "chemically –oriented" distinguished pioneers who contributed to this area. **In alphabetical order,** these scientists include: Balalan[12], Balasubramanian[13], Cyvin[14], Fowler[15], Haesselbarth[16], Harary[17], Kerber[18], Klein[19], Lloyd[20], Read[21] and Yeh[22].

The previous is **not** a complete list and the references cited represent illustrative example of authors' works rather than complete lists of their publications.

(3) The "Era of Fujita"[2,23]

During the last 20 years of the twentieth century, **Shinsaku Fujita** an ingenious prolific scientist of our times, revived interest in the (then neglected but already known) theory of marks of coset representations of a point-group. These numbers are usually listed in so-called **Tables of Marks** (or simply **Mark Tables)** of groups.

Fujita's enumeration scheme generates mark tables of a group by expressing its cosets as permutations. Such a scheme requires information of all group-subgroup relations which may not be trivial. Tables of marks were once discussed in **Burnside's** textbook[24] (1911) but were neglected for several decades and, in fact, omitted even from voluminous texts[1] on group theory except for a few[25]. Apparently Redfield[26] believed that he had invented the table of marks, (He had access to the first edition of Burnside's book which does not contain the concept of a mark. Redfield, did not have access to the second edition which does contain it).

In his development, Fujita integrated point-group and permutation group theories and used coset representations of a group to obtain mark tables. A coset representation is the mathematical term for what is considered in chemistry to be a set of equivalent ligands or atoms. Each set is regarded as an equivalence class (i.e. an orbit). While the Pólya-Redfield

formula leads to a gross count of the number of isomers, the scheme of Fujita classifies subsets of isomers according to their proper molecular symmetry group realized as a subgroup of that of the parent skeleton.

The algorithm of Fujita and inter-relations among all the steps is graphed in **Fig. 1**. The crucial step is the determination of the orbit which controls substitution, $G(/G_i)$, where G_i is a subgroup of the point-group G. The next step is to **subduce** this orbit by all subgroups of G and obtain what Fujita called **Unit Subduced Cycle Indices, USCI's**, for all subgroups. These functions are then incorporated in a Pólya type substitution to obtain Fujita's **Fixed-Point Matrix, FPM**. The latter matrix is then multiplied by the inverse of the corresponding table of markes to obtain the "long-promised" **Isomer Count Matrix, ICM** which lists the number of isomers in each of the subgroups with appropriate weight-power of substituents. For example, the **ICM** of all heterocycles derived from the molecular graph of bicyclobutadiene looks like[27]:

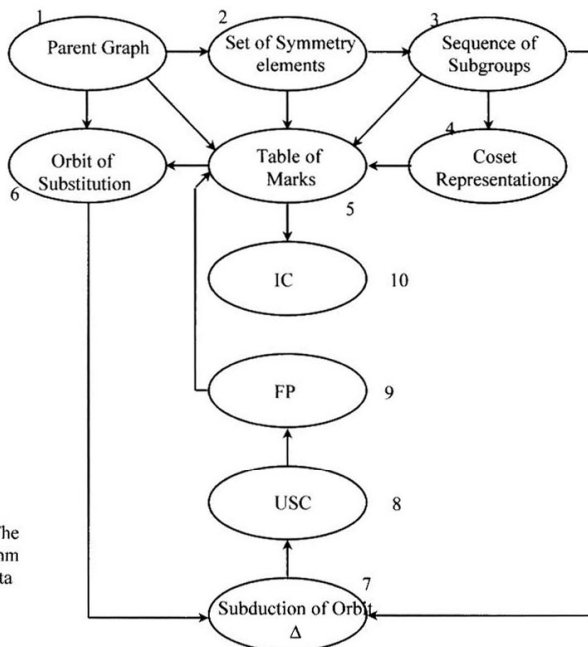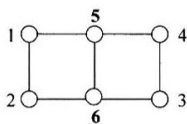|	C_1	C_2	C_s	C_s'	C_{2v}
1	.	.	.	.	1
x	2	.	.	.	.
y	.	.	3	.	.
y^2	.	.	.	.	4
x^2	.	5	6	7	.
$x\,y$	8,9	.	.	.	.
x^3	10	.	.	.	.
$x^2\,y$	11,12	.	13,14	.	.
$x\,y^2$	15	.	.	.	.
x^4	.	.	.	.	16
$x^3\,y$	17,18	.	.	.	.
$x^2\,y^2$	.	19	20	21	.
$x^4\,y$	.	.	22	.	.
$x^3\,y^2$	23	.	.	.	.
$x^4\,y^2$	.	.	.	.	24

Fig. 1 The Algorithm of Fujita

The bicyclobutadiene molecular graph has two orbits ($\equiv$ two cosets), as shown below:

$$\Delta_1 = \{1,2,3,4\} \sim \mathbf{C}_{2v}(/\mathbf{C}_1)$$
$$\Delta_2 = \{5,6\} \quad \sim \mathbf{C}_{2v}(/\mathbf{C}_s)$$

The following weights are adopted:

$w(C) = 1$ (for Δ_1 and Δ_2)

$w(N) = x$ (for Δ_1)

$w(N) = y$ (for Δ_2)

where N is the hetero-atom.

Now from the coefficient, $x^i y^j$, and the subgroup it is an "amusing task" to put down the structure E.g., two heterocycles labeled 17, 18 contain, each, 3 N atom $\in \Delta_1$ and 1 N atom $\in \Delta_2$ and they both belong to C_1 subgroup. I.e., each of these isomers remains invariant **only** under C_1. The only two structures consistent with with this "easy puzzle" would be:
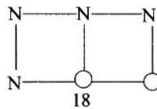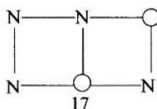
Other heterocycles can easily be drawn without too much effort and one obtains the full library. It is also possible to have more than one type of heteroatom.

Because of the "pleasing" appearance of the **ICM** designed at the "last stop" of the (relatively long) **enumeration journey** (of Fujita), it is tempting to call such a matrix: **The Heaven of Fujita**. To facilitate the computations Fujita appended his excellent book with many tables of marks, their inverses, group-subductions and USCI's (with and without chirality fittingness).

Recently Fujita directed his efforts to nonrigid molecules and compounds with rotatable ligands. Still a third aspect of Fujita's research involves merging character and mark tables together under the name markaracter tables[23].

An "Organic Chemistry Paradox"

A long-time organic chemistry teacher, myself, came across a copy of Fujita's book. Reading some parts of the book, and with his organic chemistry "culture" I soon realized the following paradox:

a)   Fujita's work (in result form) is very interesting particularly to organic (stereo-) chemists

b) Fujita's work requires appreciation and understanding of abstract (formal) formalism of coset algebra

c) Organic chemists are least exposed to mathematics

(A physical or inorganic chemist may need various aspects of group theory or other mathematics to understand his main field of study. This is usually not the case with organic chemistry).

Here a) and c) generate a paradox!

Indeed in C. Alden Mead's[*][28] comment on Fujita's book he said **"Although the book is in principle self-contained, containing some introductory chapters on fundamentals of group theory, it is really aimed at readers who already are acquainted at least with the basic concepts of group theory and who are willing to think mathematically"**.

This means that the important work of Fujita will be read **and** understood by theoretical chemists who may **not** be particularly interested in organic stereochemistry!

The formal concepts involved in Fujita's theory are pictorially illustrated in a recent book,[7] viz.,

i) A coset-representation is represented as a set of colored graphs.

ii) Numbers indicating marks are replaced by subsets of colored graphs. Members of each subset remain fixed under a particular subgroup of operations.

iii) Cayley (color) graphs are used to graphically generate marks and unit subduced cycle indices.

Certainly it is much simpler for an experimental chemist to do simple graph operations (such as graph-reflection, graph-rotation or pruning some edges out of a graph) and that is all that is required to reach the main ideas presented in Fujita's book.

As an illustration, a graphical form of the mark table of C_{3v} is shown in **Fig. 2**[29] where now the numbers that show up in columns of subgroups are replaced by (colored) graphs. Look, for example, at both the colored graphs under the C_3 subgroup which corresponds to C_{3v} (/C_3). It is not difficult to see now that either of these **two** graphs remains invariant under the

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[*] Incidentally, I was a student of some courses of quantum chemistry taught, then, by Professor C.A. Mead, at Univ. of Minnesota some 30 year ago!

symmetry operations of $C_3 = \{I, C_3, C_3'\}$ That is why the number **2** appears in the corresponding place in the usual forms of mark tables.

Tables 1 and 2[30] clarify the bijective ($\equiv$ one-to-one, onto) relation between coset algebra (table1) and (what might be called) "graph algebra", both generate the second row in the mark table, viz., (3 1 0 0). My book[7] contains many mark tables in their graphical forms.

In **Fig. 3** a Cayley graph of coset-representation is illustrated for two cases of the D_{2d} group.[31] A loop shows the subgroups which stabilize a given coset ($\equiv$ colored graph) while directed lines indicate how cosets (colored graphs) are transformed to one-another. Now the subduction operation is easy: simply prune out all edges except those which carry elements of symmetry of the subducing group. The resulting (pruned-out) graphs are to be identified as cosets. In El-Basil's book there is a collection of Cayley graphs representing cosets. It seems, then, that theory and applications of Tables of Marks are still open for chemical enumeration research. This special issue of MatCh is to explore and encourage the development of this promising tool.
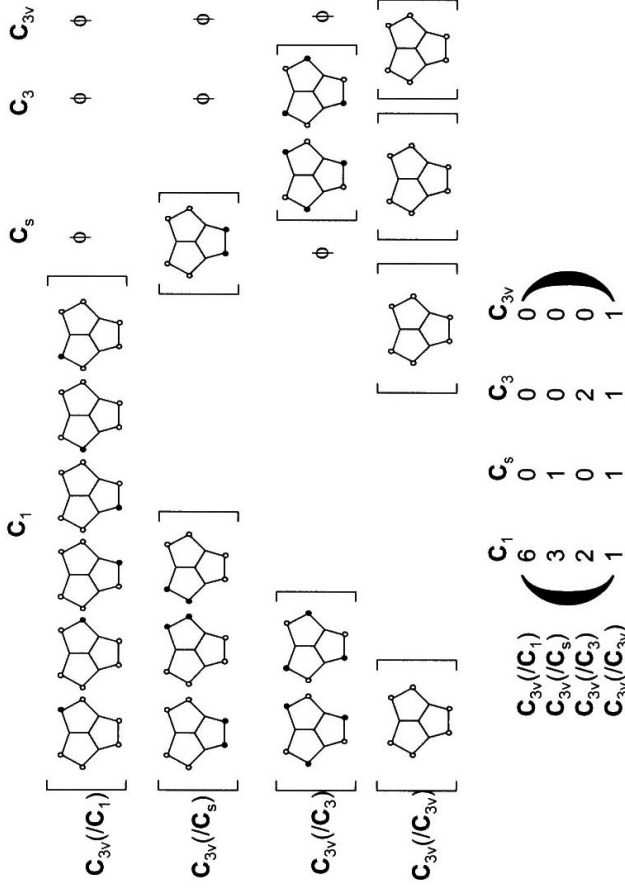
Fig 2 Graphic vs. Numerical forms of Mark Table of C_{3v}

	C_1	C_s	C_3	C_{3v}
$C_{3v}(/C_1)$	6	0	0	0
$C_{3v}(/C_s)$	3	1	0	0
$C_{3v}(/C_3)$	2	0	2	0
$C_{3v}(/C_{3v})$	1	1	1	1

$$\mathbf{D}_{2d}(/\mathbf{C}_2) \downarrow \mathbf{S}_4 = 2\mathbf{S}_4(/\mathbf{C}_2)$$

$$\mathbf{D}_{2d}(/\mathbf{C}_s) \downarrow \mathbf{C}_s = 2\mathbf{C}_s(/\mathbf{C}_s) + \mathbf{C}_s(/\mathbf{C}_1)$$
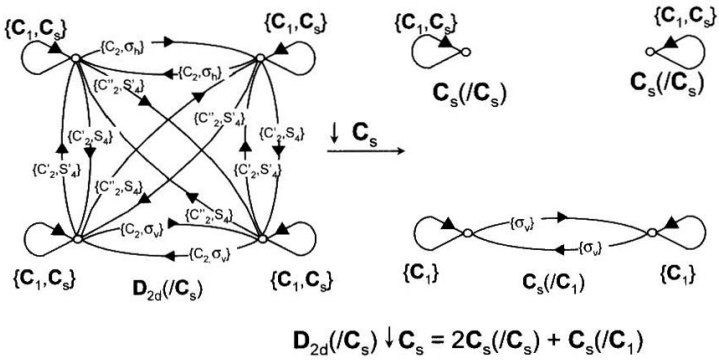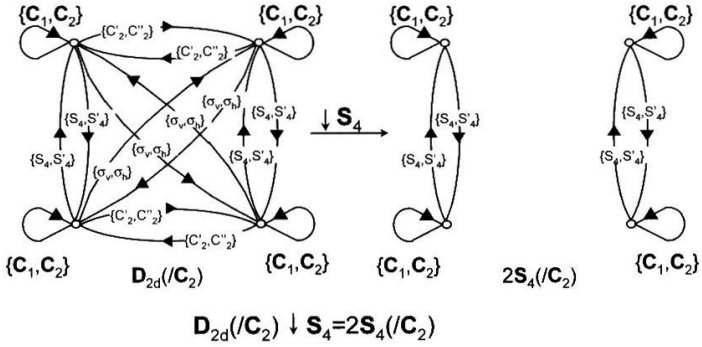
Fig 3 Graphical Subduction of Two CR's of $\mathbf{D}_{2d}$

Table 1

Permutations generated by the coset representation $C_{3v}(/C_s)$.(The coset - partitions of C_{3v} are labeled as 1,2 and 3)

$$C_{3v}(/C_s) \qquad = C_s + \ C_sC_{3'} + \ C_sC_3$$

$$\{1,\sigma_v\} \ \{C_{3'},\sigma_v''\} \ \{C_3, \sigma_v'\}$$

Symmetry Element	1	2	3	Permutation
I	1	2	3	(1)(2)(3)
C_3'	2	3	1	(123)
C_3	3	1	2	(132)
σ_v	1	3	2	(1)(23)
σ_v'	3	2	1	(2)(13)
σ_v''	2	1	3	(3)(12)

Table 2

Permutations generated from the set of colored graphs (homomers) which represent $C_{3v}(/C_s)$. (The homomers are labeled as 1,2 and 3)

$\mathcal{H}[C_{3v}(/C_s)]$	$\{h_1$	h_2	$h_3\}$	
Element of symmetry	1	2	3	Permutation
I	1	2	3	(1)(2)(3)
C_3'	2	3	1	(123)
C_3	3	1	2	(132)
σ_v	1	3	2	(1)(23)
σ_v'	3	2	1	(2)(13)
σ_v''	2	1	3	(3)(12)

Either tables 1 or 2 leads to the following row of marks:

		C_1	C_s	C_3	C_{3v}
I $\rightarrow$ (1)(2)(3)		✔	✔	✔	✔
$C_3' \rightarrow$ (123)				✔	✔
$C_3 \rightarrow$ (132)				✔	✔
$\sigma_v \rightarrow$ (1)(23)			✔		✔
$\sigma_v' \rightarrow$ (2)(13)					✔
$\sigma_v'' \rightarrow$ (3)(12)					✔
		(3	1	0	0)

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