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Vector Spaces of Permutomers and Symmetry Itemized Isomers Numbers for Substituted C_{2V}-Based Compounds. I

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Abstract

The mathematical properties of isomers numbers of substituted C_{2v}-based compounds presented in this paper includes : -(1) the formulation of 4-dimensional permutomers count vectors $PCV = (N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}})$ and 5-dimensional itemized isomers count vectors IICV=$a_{c_1}, a_{c_2}, a_{c_s}, a_{c'_s}, a_{c_{2v}}$ which satisfy the dot product PCV $= IICV \times W_{C_{2v}}$. (2)- The expansion of this equation to obtain the denumerants of type $N_{g_i \epsilon C_{2v}} = \sum_{g_i \epsilon C_{2v}} a_{G_j \epsilon C_{2v}} W_{G_j}, g_i$ mapping permutomers numbers as sum of symmetry itemized isomers numbers $a_{G_j \epsilon C_{2v}}$ scaled by W_{G_j}, g_i the markaracters of C_{2v}. (3)-The collection of 4 and 5 entries PCV_s and $IICV_s$ generating respectively, permutomers count matrices (PCM_s) and itemized isomers count matrices ($IICM_s$) that construct two associated vector spaces of isomers numbers for such series of molecules.

1 Introduction

The results of combinatorial enumeration procedures reported in the literature [1–10] are often presented in the form of extended lists of numerical data counting isomers of distinct series of compounds. The structure and

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properties of the linear space of these bulk figure inventories containing numerous integer sequences is a pending mathematical problem.

A vector space also called a linear space in mathematics is a set of objects called vectors which may be added together or multiplied(scaled) by numbers called scalars. The dimension of a vector space V is the cardinality i.e the number of vectors of the basis of V over its base field F. [11] In stereochemistry the vector space of permutational isomers numbers can be visualized as a set of vectors whose entries are numbers of arrangements of substituents derived from distinct classes of permutations induced by the symmetry operations of a point group G acting on a parent molecule M. The aim of this paper is to present the general structure and mathematical properties of the linear space of permutomers numbers and symmetry itemized isomers numbers for substituted C_{2v}-based derivatives.

2 Mathematical formulation

2.1 Permutations of n substitution sites of a parent C_{2v} hydrocarbon C_mH_n

Consider a parent hydrocarbon C_mH_n of C_{2v} symmetry with n substitution sites collected in a set $H_n = 1, 2, ..., i, ..., n$. The C_{2v} group action on H_n denoted $P^{C_{2v}}H_n$

$$P^{C_{2v}}H_n = P^E H_n, P^{C_2} H_n, P^{\sigma_{V1}} H_n, P^{\sigma_{v2}} H_n \tag{1}$$

is a set of permutations of n substitution sites induced by the symmetry operations $E, C_2, \sigma_{v1}, \sigma_{v2}$ of C_{2v}.These classes of permutations are expressed in cycle structure notation [12, 13] as follows:

$$P^E H_n = 1^n, P^{C_2} H_n = 2^{n/2}, P^{\sigma_{V1}} H_n = P^{\sigma_{v2}} H_n = \begin{cases} 2^{n/2} or \\ 1^{\alpha} 2^{(n-\alpha)/2} \end{cases} \tag{2}$$

The terms $1^n, 2^{n/2}, 1^{\alpha}2^{(n-\alpha)/2}$ correspond to n unitary cycles, $n/2$ transpositions, and a combination of α unitary cycles and $(n-\alpha)/2$ transpositions.

2.2 Permutomers numbers for homo and heteropolysubstituted C_{2v}-based hydrocarbons

Let us consider that permutomers of a homopolysubstituted C_{2v}-based hydrocarbon $C_mH_{n-q}X_q$ (or $C_mH_{q_0}X_{q_1}$) are obtained by putting in distinct ways qX achiral substituents of the same kind qX among n substitution sites submitted to 4 classes of permutations previously indicated. Similarly, permutomers of a heteropolysubstituted C_{2v}-based hydrocarbon $C_mH_{q_0}X_{q1}...Y_{q_i}...Z_{q_k}$ are obtained by putting in distinct ways $(q_0, q_1...q_i, ..., q_k)$ achiral substituents of distinct kinds $H, X, Y, \ldots, Z$ among n substitution sites submitted to 4 classes of permutations indicated in Eq. (2). We recall in table 1 some characteristics of the notation of a generic molecular formula $C_mH_{q_0}X_{q_1}...Y_{q_i}...Z_{q_k}$ where is the number of hydrogen atoms, indicate partial degrees of substitution or numbers of distinct kinds of achiral substituents $X, Y, \ldots, Z$. The sub-indices $1 \leq i \leq k$ are substitution orders i.e. numbers of distinct types of non hydrogen substituents in the series $MX = C_mH_{q_0}X_{q_1}, C_mH_{q_0}X_{q_1}Y_{q_2}, C_mH_{q_0}X_{q_1}Y_{q_2} \ldots Z_{q_i}, \ldots, C_mH_{q_0}X_{q_1}Y_{q_2}...Z_{q_k}$ where the indices $q_0, q_1...q_i, ..., q_k$ satisfy the restriction

$$\sum_{i=0}^{k} q_i = n \tag{3}$$

We put J_i as the number of representatives (molecular formulas with non congruent indices $(q_0, q_1...q_i, ..., q_k)$) obtained for each series having a substitution order i.

Permutational isomers numbers $N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}$ for a homopolysubstituted C_{2v}-based hydrocarbon issued from placements of qX substituents among n substitution sites submitted to the permutations $P^E H_n$, $P^{C_2} H_n, P^{\sigma_{V1}} H_n, P^{\sigma_{v2}} H_n$ are derived from Eqs. (4-6) as follows :

$$1^n \to N_E = \binom{n}{q} \tag{4}$$

$$2^{n/2} \to N_{c_2} = N_{\sigma_{v1}} = N_{\sigma_{v2}} = \begin{cases} \binom{n/2}{q/2} & q\ even \\ 0 & q\ odd \end{cases} \tag{5}$$

Table 1. Characteristics of the notation of generic molecular formulas of series of substituted C_{2v}-based hydrocarbons $C_mH_{q0}X_{q1}...Y_{q_i}...Z_{q_k}$: (a) sub-indices or substitutions orders $1 \leq i \leq k$, (b) sets of partial degrees of substitution satisfying the restriction (Eq. (3)) above mentioned, (c) number J_i of representatives (sets) obtained for each substitution order i.

Generic formulas of series of substituted C_{2v}-based hydrocarbons $MX = C_mH_{q_0}X_{q_1}...Y_{q_i}...Z_{q_k}$	Sub-indices or Substitution Orders $1 \leq i \leq k$	Sets of partial degrees of substitution $q_0,\ q_1,..q_i,...,q_k$	Numbers j_i of representatives for the substitution oder i
$C_mH_{q_0}X_{q_1} = C_mH_{n-q}X_q$	1	$(q_0,\ q_1)$	j_1
$C_mH_{q_0}X_{q_1}Y_{q_2}$	2	$(q_0,\ q_1,q_2)$	j_2
$C_mH_{q_0}X_{q_1}Y_{q_2}Z_{q_3}$	3	(q_0,q_1,q_2,q_3)	j_3
....	....	....	.....
$C_mH_{q_0}X_{q_1}Y_{q_2}...Z_{q_i}$	i	$(q_0,\ q_1,q_2,..,q_i)$	j_i
....	....	....	
$C_mH_{q_0}X_{q_1}Y_{q_2}...Z_{q_k}$	k	$(q_0,\ q_1,..q_i,...,q_k)$	j_k

$$1^{\alpha}2^{(n-\alpha)/2} \rightarrow N_{\sigma_{v1}} = N_{\sigma_{v2}} = \sum_{j=0}^{\alpha} \binom{\alpha}{\beta} \binom{(n-\alpha)/2}{(q-\beta)/2} \tag{6}$$

α is the number of invariant substitution positions submitted to the inversion σ_{v1} or σ_{v2} while $0 \leq \beta \leq \alpha$ indicates the number of achiral substituents located on these invariant positions. For a heteropolysubstituted C_{2v}-based hydrocarbon $C_mH_{q0}X_{q1}Y_{q2}...Z_{q_k}$:

$$1^n \rightarrow N_E = \binom{n}{q_0, q_1...q_i, ..., q_k} \tag{7}$$

$$2^{n/2} \rightarrow N_{c_2} = N_{\sigma_{v1}} = N_{\sigma_{v2}} = \begin{cases} \binom{n/2}{q_0/2, q_1/2, ..., q_i/2, ..., q_k/2} & if\ q_i\ even \\ 0 & if\ q_i\ odd \end{cases} \tag{8}$$

$$1^2 2^3 \to N_{\sigma_{v1}} = N_{\sigma_{v2}} = \begin{cases} \sum_\lambda \binom{\alpha}{p_0,\ldots,p_i,\ldots,p_k}\binom{(n-\alpha)/2}{q'_0,\ldots,q'_i,\ldots,q'_k} & if\ q'_i\ even \\ 0 & if\ (q_i - p_i)\ odd \end{cases} \tag{9}$$

with the restrictions

$$\sum_{i=0}^{k} p_i = \alpha, q'_i = \frac{(q_i - p_i)}{2}, \sum_{i=0}^{k} q'_i = \frac{(n-\alpha)}{2} \tag{10}$$

$p_0, ..., p_i, ..., p_k$ and $q'_0, ..., q'_i, ..., q'_k$ are numbers of unitary cycles and transpositions of H,X,Y,...,Z.

2.3 The vector space of permutomers numbers for C_{2v}-based compounds

Rule 1 : If Eqs. (4-10) are verified permutational isomers numbers N_E, $N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}$ for α homo- or a hetero polysubstituted C_{2v}-based compound MX can be collected to form a 4 entries row vector called permutomers count vector (PCV) expressed as follows:

$$PCV(MX) = (N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}) \tag{11}$$

Rule 2 : The collection of 4-dimensional PCVs given in Eq. (11) for a series of substituted C_{2v}-based hydrocarbons $MX = C_m H_{q_0} X_{q_1} ... Y_{q_i} ... Z_{q_k}$ possessing the same substitution order i and J_i representatives (molecular formulas) with non congruent set of indices$(q_0, q_1 ..., q_i ..., q_k)$ generates a $(J_i \times 4)$ - permutomers count matrix (PCM) denoted:

$$PCM(MX) = \overset{\text{PCVs ranking}}{\begin{pmatrix} \\ 1 \\ \cdots \\ s \\ \cdots \\ j_i \end{pmatrix}} \underbrace{\begin{pmatrix} E & c_2 & \sigma_{v_1} & \sigma_{v_2} \\ N_E^1 & N_{C_2}^1 & N_{\sigma_{v_1}}^1 & N_{\sigma_{v_2}}^1 \\ \cdots & \cdots & \cdots & \cdots \\ N_E^s & N_{C_2}^s & N_{\sigma_{v_1}}^s & N_{\sigma_{v_2}}^s \\ \cdots & \cdots & \cdots & \cdots \\ N_E^{j_i} & N_{C_2}^{j_i} & N_{\sigma_{v_1}}^{j_i} & N_{\sigma_{v_2}}^{j_i} \end{pmatrix}}_{j \times 4\ \textit{\textbf{entries}}} \tag{12}$$

Eq. (12) presents the general structure of the vector space V_4 which is a PCM possessing j_i 4-dimensional permutomers count vectors (PCV_s). To exemplify this rule let us consider the series $C_mH_{q_0}X_{q_1}Y_{q_2}$ possessing the substitution order i=2 and suppose that its set of indices (q_0, q_1, q_2) satisfy the restriction $\sum_{i=0}^{2} q_i = 8$. Non congruent (non permuted) set of indices verifying this condition are $(q_0, q_1, q_2) = (6, 1, 1), (5, 2, 1), (4, 3, 1), (4, 2, 2), (3, 3, 2)$. From this sequence of 3-tuples of indices we derive $j_i = 5$ representatives (molecular formulas) denoted : C_mH_6XY,$C_mH_5X_2Y$, $C_mH_4X_3Y$, $C_mH_4X_2Y_2$,$C_mH_3X_3Y_2$ which yield 5 distinct PCV_s. Therefore the PCM for the series ($C_mH_{q_0}X_{q_1}Y_{q_2}$) is a collection of j_i=5, 4-dimensional PCV_s identified by the ranking 1,2,3,4,5.

2.4 The vector space of symmetry adapted isomers numbers for C_{2v} based hydrocarbons

Let us consider the sequence of subgroups of C_{2v} given in Eq. (13):

$$SSG_{G_j \epsilon C_{2v}} = \{C_1, C_2, C_s, C_s', C_{2v}\} \tag{13}$$

and note that the parts resulting from the partitions of $N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}$ are itemized isomers numbers $a_{c_1}, a_{c_2}, a_{c_s}, a_{c_s'}, a_{c_{2v}}$ assign to the subgroups of C_{2v}. Such an integer sequence forms a 5-dimensional itemized isomers count vector (IICV) for substituted C_{2v}-based molecule MX expressed as:

$$IICV(MX) = (a_{c_1}, a_{c_2}, a_{c_s}, a_{c_s'}, a_{c_{2v}}) \tag{14}$$

Rule 3 : The collection of 5-dimensional $IICV_s$ for a series of substituted C_{2v}-based compounds MX possessing a substitution order i and j_i molecular formulas with non congruent sets of indices $q_0, q_1 ... q_i, ..., q_k$ satisfying the restriction $\sum_{i=0}^{k} q_i = n$ generates a $(j_i \times 5)$ itemized isomers count matrix (IICM) denoted:

$$IICM(MX) = \overset{\substack{IICVs\\ranking}}{\begin{pmatrix} 1 \\ \cdots \\ s \\ \cdots \\ j_i \end{pmatrix}} \underbrace{\overbrace{\begin{pmatrix} a^1_{C_1} & a^1_{C_2} & a^1_{C_s} & a^1_{C_s} & a^1_{C_{2v}} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a^s_{C_1} & a^s_{C_2} & a^s_{C_s} & a^s_{C_s} & a^s_{C_{2v}} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ a^{j_i}_{C_1} & a^{j_i}_{C_2} & a^{j_i}_{C_s} & a^{j_i}_{C_s} & a^{j_i}_{C_{2v}} \end{pmatrix}}^{IICVs}}_{(j_i \times 5)\ \boldsymbol{entries}} \tag{15}$$

Eq. (15) presents the general structure of the vector space V_5 which is an IICM possessing j_i 5-dimensional itemized isomers count vectors $(IICV_s)$.

2.5 The linear mapping of PCV_s and $IICV_s$ over the field of substituted C_{2v}-based isomers numbers

Let V_4 denote the vector space of 4-dimensional permutomers count vectors (PCV_s) and V_5 the vector space of 5-dimensional itemized isomers count vectors $(IICV_s)$ over the field $F_{C_{2v}}$ of C_{2v}-based isomers numbers.

Rule 4 : A 4-dimensional permutomers count vector (PCV) and a 5-dimensional itemized isomers count vector (IICV) of the same rank $1 \leq s \leq j_i$ in the vector spaces V_4 and V_5 over the field $F_{C_{2v}}$ of C_{2v}-based isomers numbers are two associated vectors which satisfy the dot product (scalar product) [14]:

$$PCV(MX) = IICV(MX) \times W_{C_{2v}} \tag{16}$$

This equation is a linear mapping [15] between V_4 and V_5 spaces (that is, every vector from the second space is associated with one of the first) over the field $F_{C_{2v}}$ of C_{2v}-based isomers numbers. Eq.16 is explicitly written as:

$$\overbrace{\left[N_E, N_{C_2}, N_{\sigma_{v1}}, N_{\sigma_{v2}}\right]}^{PCV(MX)} = \overbrace{\left(a_{C_1}, a_{C_2}, a_{C_s}, a_{C_s'}, a_{C_{2v}}\right)}^{IICV(MX)} \overbrace{\begin{pmatrix} \overbrace{\begin{matrix} \mathbf{E} & \mathbf{C_2} & \sigma_{v_1} & \sigma_{v_2} \end{matrix}} \\ \begin{matrix} w_{C_1,E} & w_{C_1,c_2} & w_{C_1,\sigma_{v_1}} & w_{C_1,\sigma_{v_2}} \\ w_{C_2,E} & w_{C_2,c_2} & w_{C_2,\sigma_{v_1}} & w_{C_2,\sigma_{v_2}} \\ w_{C_s,E} & w_{C_s,c_2} & w_{C_s,\sigma_{v_1}} & w_{C_s,\sigma_{v_2}} \\ w_{C_s',E} & w_{C_s',c_2} & w_{C_s',\sigma_{v_1}} & w_{C_s',\sigma_{v_2}} \\ w_{C_{2v},E} & w_{C_{2v},c_2} & w_{C_{2v},\sigma_{v_1}} & w_{C_{2v},\sigma_{v_2}} \end{matrix} \end{pmatrix}}^{W_{C_{2v}}} \quad (17)$$

$W_{C_{2v}}$ is the matrix of the weights of the subgroups of C_{2v} and its entries are derived from Eq. (18).

$$w_{G_j,g_i} = \begin{cases} \dfrac{\mu_{g_i \in G_j}}{\mu_{g_i \in C_{2v}}} \times \dfrac{|C_{2v}|}{|G_j|} & \text{for } g_i \in G_j \\ 0 & \text{for } g_i \notin G_j \end{cases} \quad (18)$$

The terms $\mid G_j \mid = \mid C_1 \mid, \mid C_2 \mid, \mid C_s \mid, \mid C_s' \mid, \mid C_{2v} \mid$ =1,2,2,2,4 are the cardinalities of the subgroups of C_{2v} and $\mu_{g_i \epsilon G_j}$ represents the multiplicities given in table 2 of the symmetry operations $E, C_2, \sigma_{v_1}, \sigma_{v_2}$.

Table 2. Multiplicities $\mu_{g_i \epsilon G_j}$ of C_{2v} the symmetry operations for the subgroups.

$SSG_{G_j \in C_{2v}}$	μ_E	μ_{c_2}	$\mu_{\sigma_{v1}}$	$\mu_{\sigma_{v2}}$
C_1	1	0	0	0
C_2	1	1	0	0
C_s	1	0	1	0
C_s'	1	0	0	1
C_{2v}	1	1	1	1

By introducing these data in Eq. (16) $W_{C_{2v}}$ becomes a (5×4)-matrix given in Eq. (19) which is equivalent to the matrix character table of coset representations of C_{2v} of Fujita. [16]

$$W_{C_{2v}} = \begin{pmatrix} E & C_2 & \sigma_{v_1} & \sigma_{v_2} \\ \frac{\mu_{E\in C_1}}{\mu_{E\in C_{2v}}}\times\frac{|C_{2v}|}{|C_1|} & 0 & 0 & 0 \\ \frac{\mu_{E\in C_2}}{\mu_{E\in C_{2v}}}\times\frac{|C_{2v}|}{|C_2|} & \frac{\mu_{c_2\in C_2}}{\mu_{c_2\in C_{2v}}}\times\frac{|C_{2v}|}{|C_2|} & 0 & 0 \\ \frac{\mu_{E\in C_s}}{\mu_{E\in C_{2v}}}\times\frac{|C_{2v}|}{|C_s|} & 0 & \frac{\mu_{\sigma_{v_1}\in C_s}}{\mu_{\sigma_{v_1}\in C_{2v}}}\times\frac{|C_{2v}|}{|C_s|} & 0 \\ \frac{\mu_{E\in C'_s}}{\mu_{E\in C_{2v}}}\times\frac{|C_{2v}|}{|C'_s|} & 0 & 0 & \frac{\mu_{\sigma_{v_1}\in C_s}}{\mu_{\sigma_{v_1}\in C_{2v}}}\times\frac{|C_{2v}|}{|C'_s|} \\ \frac{\mu_{E\in C_2}}{\mu_{E\in C_{2v}}}\times\frac{|C_{2v}|}{|C_{2v}|} & \frac{\mu_{c_2\in C_{2v}}}{\mu_{c_2\in C_{2v}}}\times\frac{|C_{2v}|}{|C_{2v}|} & \frac{\mu_{\sigma_{v_1}\in C_{2v}}}{\mu_{\sigma_{v_1}\in C_{2v}}}\times\frac{|C_{2v}|}{|C_{2v}|} & \frac{\mu_{\sigma_{v_2}\in C_2}}{\mu_{\sigma_{v_1 2}\in C_{2v}}}\times\frac{|C_{2v}|}{|C_{2v}|} \end{pmatrix} == \begin{pmatrix} SSG_{C_{2v}} \\ C_1 \\ C_1 \\ C_s \\ C'_s \\ C_{2v} \end{pmatrix} \begin{pmatrix} E & C_2 & \sigma_{v_1} & \sigma_{v2} \\ 4 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 \\ 2 & 0 & 2 & 0 \\ 2 & 0 & 0 & 2 \\ 1 & 1 & 1 & 1 \end{pmatrix} \quad (19)$$

The expansion of Eq. (16) gives rise to 4 associated partition Eqs. (20-23) decomposing permutomers numbers as a sum of symmetry adapted isomers numbers scaled by the markaracters of C_{2v}.

$$N_E = a_{C_1}w_{C_1,E} + a_{C_2}w_{C_2,E} + a_{C_s}w_{C_s,E} + a_{C'_s}w_{C_s,E} + a_{C_{2v}}w_{C_{2v},E} \quad (20)$$

$$N_{C_2} = a_{C_1}w_{C_1,C_2}+a_{C_2}w_{C_2,C_2}+a_{C_s}w_{C_s,C_2}+a_{C'_s}w_{C_s,C_2}+a_{C_{2v}}w_{C_{2v},C_2} \quad (21)$$

$$N_{\sigma_{v_1}} = a_{C_1}w_{C_1,\sigma_{v_1}} + a_{C_2}w_{C_2,\sigma_{v_1}} + a_{C_s}w_{C_s,\sigma_{v_1}} + a_{C'_s}w_{C_s,\sigma_{v_1}} + a_{C_{2v}}w_{C_{2v},\sigma_{v_1}} \quad (22)$$

$$N_{\sigma_{v_2}} = a_{C_1}w_{C_1,\sigma_{v_2}} + a_{C_2}w_{C_2,\sigma_{v_2}} + a_{C_s}w_{C_s,\sigma_{v_2}} + a_{C'_s}w_{C_s,\sigma_{v_2}} + a_{C_{2v}}w_{C_{2v},\sigma_{v_2}} \quad (23)$$

With regards to numerical values of the entries of $w_{C_{2v}}$ given in Eq. (19) Eqs. (20-23) become:

$$N_E = 4a_{c_1} + 2a_{c_2} + 2a_{c_s} + 2a_{c'_s} + a_{c_{2v}} \quad (24)$$

$$N_{C_2} = 2a_{c_2} + a_{c_{2v}} \quad (25)$$

$$N_{\sigma_{v_1}} = 2a_{c_s} + a_{c_{2v}} \quad (26)$$

$$N_{\sigma_{v_2}} = 2a_{c'_s} + a_{c_{2v}} \quad (27)$$

Eqs. (24-27) called Sylvester's denumerants [17,18] of C_{2v}-group are linear mappings between PCV and IICV entries over the field $F_{C_{2v}}$ of isomers numbers of substituted C_{2v}-based derivatives. Such partition equations are used for the determination of symmetry itemized isomers numbers $a_{c_1}, a_{c_2}, a_{c_s}, a_{c'_s}, a_{c_{2v}}$ for series of substituted C_{2v}-based compounds MX. Fig. 1 depicts the mapping between a PCV and an IICV entries and shows for the sake of comparison their connexions with A_c chiral, Aac achiral isomers numbers derived from bipartite enumeration method [19] and Polya isomers numbers (Np) computed from cycle indices.

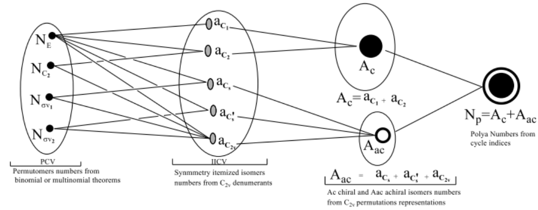

Figure 1. Illustration of the linear mapping between a PCV and an IICV and their connexions to A_c chiral, A_{ac} achiral and Polya C_{2v}-based isomers numbers.

2.6 The linear mapping between the PCM and the IICM over the field of C_{2v}-based isomers numbers

Rule 5 : $A-(J_i \times 4)$ and a $(J_i \times 5)$ - IICM for a series of substituted C_{2v}-based compounds MX having a substitution order i and j_i representatives with non congruent sets of substitution indices $(q_0, q_1 ... q_i, ..., q_k)$ satisfying the restriction $\sum_{i=0}^{k} q_i = n$ are two associated matrices whose entries satisfy the matrix dot product:

$$\underbrace{\begin{pmatrix} 1 \\ 2 \\ \cdots \\ s \\ \\ j_i \end{pmatrix}}_{\text{IICVs ranking}} \underbrace{\begin{pmatrix} a^1_{C_1} & a^1_{C_2} & a^1_{C_s} & a^1_{C_s} & a^1_{C_{2v}} \\ a^2_{C_1} & a^2_{C_2} & a^2_{C_s} & a^2_{C_s} & a^2_{C_{2v}} \\ \cdots & & & & \\ a^s_{C_1} & a^s_{C_2} & a^s_{C_s} & a^s_{C_s} & a^s_{C_{2v}} \\ \cdots & & & & \\ a^{j_i}_{C_1} & a^{j_i}_{C_2} & a^{j_i}_{C_s} & a^{j_i}_{C_s} & a^{j_i}_{C_{2v}} \end{pmatrix}}_{\text{IICM, } (j_i \times 5) \text{ entries}} \underbrace{\begin{pmatrix} E & c_2 & \sigma_{v_1} & \sigma_{v2} \\ 4 & 0 & 0 & 0 \\ 2 & 2 & 0 & 0 \\ 2 & 0 & 2 & 0 \\ 2 & 0 & 0 & 2 \\ 1 & 1 & 1 & 1 \end{pmatrix}}_{W_{C_{2v}}, \ (5\times 4) \text{ entries}} = \underbrace{\begin{pmatrix} 1 \\ 2 \\ \cdots \\ s \\ \\ j_i \end{pmatrix}}_{\text{PCVs ranking}} \underbrace{\begin{pmatrix} N^1_E & N^1_{C_2} & N^1_{\sigma_{v1}} & N^1_{\sigma_{v2}} \\ N^2_E & N^2_{C_2} & N^2_{\sigma_{v1}} & N^2_{\sigma_{v2}} \\ \cdots & & & \\ N^s_E & N^s_{C_2} & N^s_{\sigma_{v1}} & N^s_{\sigma_{v2}} \\ \cdots & & & \\ N^{j_i}_E & N^{j_i}_{C_2} & N^{j_i}_{\sigma_{v1}} & N^{j_i}_{\sigma_{v2}} \end{pmatrix}}_{\text{PCM, } j_i \times 4 \text{ entries}} \qquad (28)$$

In Eq. (28) the integer sequence 1,2,3,...,s,...,j_i indicates the ranking of 5-dimensional $IICV_s$ and 4-dimensional PCV_s collected to form a $(j_i \times 5)$-$IICM$ and a $(j_i \times 4)$-PCM respectively.

2.7 The structure of the vector space of C_{2v}-based isomers numbers

Rule 6 : The vector spaces V_4 of permutomers and V_5 of symmetry itemized isomers numbers for various series of C_{2v}-substituted derivatives $C_mH_{q_0}X_{q_1}...Y_{q_2}...Z_{q_k}$ with different substitution orders$1 \leq i \leq k$ generating j_i distinct molecular formulas where the indices $(q_0, q_1, ..., q_i, ..., q_k)$ satisfy the restriction $\sum_{i=0}^{k} q_i = n$ possess k PCM_s and k $IICM_s$, respectively. The illustration is given in table 3 where each row shows distinct kinds of PCM_s and $IICM_s$that may be derived for a series having a substitution order i, and j_i sets of indices $q_0, .., q_i, , \ldots, q_k$.

Table 3. The V_4 and V_5 vector spaces of isomers numbers of C_{2v}-substituted derivatives $C_mH_{q_0}X_{q_1}...Y_{q_2}...Z_{q_k}$ include one PCM= j_i PCV_s and one $IICM$ = j_i $IICV_s$ in each series having a substitution order $1 \leq i \leq k$.

$1\leq i\leq k$	j_i	$q_0,..,q_i,....,q_k$	Series of C_{2v}-substituted derivatives	PCMs of V_4	IICMs of V_5
1	j_1	q_0,q_1	$C_mH_{q_0}X_{q_1}$	$PCM(q_0,q_1)$	$IICM(q_0,q_1)$
2	J_2	q_0,q_1,q_2	$C_mH_{q_0}X_{q_1}Y_{q_2}$	$PCM(q_0,q_1,q_2)$	$IICM(q_0,q_1,q_2)$
3	J_3	q_0,q_1,q_2,q_3	$C_mH_{q_0}X_{q_1}Y_{q_2}Z_{q_3}$	$PCM(q_0,q_1,q_2,q_3)$	$IICM(q_0,q_1,q_2,q_3)$
……	….	…………….	…………….	…………….	…………….
i	J_i	$q_0,q_1,q_2,q_3,...,q_i$	$C_mH_{q_0}X_{q_1}Y_{q_2}...Z_{q_i}$	$PCM(q_0,q_1,q_2,q_3,...,q_i)$	$IICM(q_0,q_1,q_2,q_3,...,q_i)$
……	….	…………….	…………….	…………….	…………….
……	….	…………….	…………….	…………….	…………….
k	J_k	$q_0,q_1,q_2,q_3,...,q_i$	$C_mH_{q_0}X_{q_1}...Y_{q_i}...Z_{q_k}$	$PCM(q_0,q_1,q_2,...q_i,...,q_k)$	$IICM(q_0,q_1,q_2,...q_i,...,q_k)$

3 Concluding remarks

Permutomers numbers $N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}$ and symmetry itemized isomers numbers $a_{c_1}, a_{c_2}, a_{c_s}, a_{c'_s}, a_{c_{2v}}$ obtained for a substituted C_{2v}-based derivative are collected to form a 4-dimensional permutomers count vectors PCV=$(N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}})$ and a 5-dimensional itemized isomers count vectors IICV =$(a_{c_1}, a_{c_2}, a_{c_s}, a_{c'_s}, a_{c_{2v}})$ respectively. These vectors are associated to each other by the dot product $PCV = IICV \times W_{C_{2v}}$ where $W_{C_{2v}}$ is the markaracter table of C_{2v}. This equation is the linear mapping between a and over the field F_{C_2} of isomers numbers of substituted C_{2v}-based derivatives. Its expansion gives rise to the denumerants of type $N_{g_i \epsilon C_{2v}} = \sum_{G_i} a_{G_j} W_{G_j}, g_i$ which decompose permutomers numbers $N_E, N_{C_2}, N_{\sigma_{v_1}}, N_{\sigma_{v_2}}$ as sum of symmetry itemized isomers numbers a_{G_j} scaled by w_{G_j,g_i} the markaracters of C_{2v}. The vector spaces V_4 of permutomers numbers and V_5 of symmetry itemized isomers numbers are obtained by collecting 4-entries PCV_s and 5-entries $IICV_s$ to form the PCM and the IICM for a series of substituted C_{2v}-based compounds $C_m H_{q_0} X_{q_1} ... Y_{q_2} ... Z_{q_k}$ with distinct sets of indices $(q_0, q_1 ... q_i, ..., q_k)$ satisfying the restriction $\sum_{i=0}^{k} q_i = n$. These properties of the linear space of isomers numbers of C_{2v}-based derivatives may open new perspectives of research and teaching in stereochemistry. The applications are given in part II.

References

[1] G. Polya, R. C. Read, *Combinatorial Enumeration of Groups, Graphs and Chemical Compounds*, Springer, Berlin, 1987.

[2] A. Tucker, Polya's enumeration by example, *Math Magazine* **47** (1974) 248–256.

[3] D. H. Rouvray, Isomers enumeration method, *Chem. Soc. Rev.* **3** (1974) 355–372.

[4] F. Harary, E. M. Palmer, *Graphical Enumeration*, Acad. Press, New York, 1973.

[5] S. Fujita, *Symmetry and Combinatorial Enumeration in Chemistry*, Springer, Berlin, 1991.

[6] K. Balasubramanian, Enumeration of stable stereo and position isomers of polyalcohols, *Ann. New York Acad. Sci.* **379** (1979) 33–36.

[7] R. M. Nemba, A. T. Balaban, Algorithm for direct Enumeration of chiral and achiral skeletons of homosubstituted derivatives of a monocyclic cycloalkane with a large ring size, *J. Chem. Inf. Comput. Sci.* **38** (1998) 1145–1150.

[8] R. M. Nemba, A. T. Balaban, Enumeration of chiral and achiral isomers of an n-membered ring with m homomorphic alkyl groups, *MATCH Commun. Math. Comput. Chem.* **46** (2002) 235–250.

[9] R. M. Nemba, F. Ngouhouo, On the Enumeration of Chiral and achiral skeletons of stereo and position isomers of homosubstituted monocyclic cycloalkanes with a ring size odd or even, *Tetrahedron* **50** (1994) 6663–6670.

[10] R. M. Nemba, M. Fah, Application of the sieve method to the enumeration of stable stereo and position isomers of deoxycyclitols, *J. Chem. Inf. Comput. Sci.* **17** (1997) 723–725.

[11] D. C. Lay, *Linear Algebra and Its Applications*, Addison Wesley, Boston, 2005.

[12] J. Riordan, *An Introduction to Combinatorial Analysis*, Wiley, New York, 1958.

[13] C. Berge, *Principle of Combinatorics*, Acad. Press, New York, 1971.

[14] C. M. Fiduccia, E. R. Scheinerman, A. Trenk, J. S. Zito, Dot product representations of graphs, *Discr. Math.* **181** (1998) 113–138.

[15] S. Lipschutz, M. Lipson, *Linear Algebra*, Mc Graw Hill, New York, 2009.

[16] S. Fujita, Subduction of coset representations, an application to systematic enumeration of chemical structures with achiral and chiral ligands, *J. Math. Chem.* **5** (1990) 121–156.

[17] J. J. Sylvester, On a discovery in the partition of numbers, *Quarterly J. Math.* **I** (1857) 81–84.

[18] P. Lisonek, Denumerants and their approximations, *J. Comb. Math. Comb. Comput.* **18** (1995) 225–232.

[19] R. M. Nemba, T. Makon, E. J. Ndobo, Bipartite enumeration of chiral and achiral skeletons of substituted cubane derivatives and heteroanalogues. I, *MATCH Commn. Math. Comput. Chem.* **84** (2020) 429–448.