Acta Chimica & Pharmaceutica Indica

Acta Chim. Pharm. Indica: 2(3), 2012, 119-131

ISSN 2277-288X

APPLICATION OF THE YOUNG'S PARTITION METHOD FOR COMBINATORIAL ENUMERATION OF GEM POSITION ISOMERS OF HOMO POLYSUBSTITUTED LINEAR N-ALKANES (PART II: N EVEN)

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(*Received : 30.03.2012; Revised : 09.04.2012; Accepted : 10.04.2012*)

ABSTRACT

A generalized combinatorial enumeration method is proposed for counting gem position isomers (GPIs) of any homopolysubstituted linear n-alkanes (HPSNA) with the empirical formula $C_nH_{2n+2-m}X_m$ where the chain length n_+ is even and where the degree of substitution $m_\pm$ (odd or even) satisfies the Young's partition models $m_- = 32^{k_\pm}$, $m_+ = 3^2\,2^{k_\pm}$ or $2^{k_\pm}$ with the restrictions $m_\pm \geq 2$ and $k_\pm \geq 0$.

Key words: Gem position isomer, Disubstitution, Trisubstitution, Homopolysubstituted linear n-alkane, Young's partition, Combinatorial enumeration.

INTRODUCTION

The different organic compounds possessing cumulative gem di and tri substitutions currently reported in the literature are perfluoro hydrocarbons used as fluorosurfactants, anaesthetics or thermo plastic fluoropolymers [1-3] and polychlorinated n-alkanes(PCAs) [4-7] consisting of C_{10} to C_{30} n-alkanes with chlorine content from 30 to 70 by mass PCAs used as high temperature lubricants, plasticizers, flame retardants, and additives in adhesives, paints, rubber and sealants[8-9].

The organo-chemists dealing with such molecules are often faced to the mathematical problem of enumerating with exactness all possible isomeric structures of straight chain polyhalogenated compounds. Such theoretical studies are scarce[10-12] and this second part of the study presents a method for direct combinatorial enumeration of gem position isomers (GPIs) of the series of homopolysubstituted linear n-alkanes (HPSNA) having the empirical formula $C_nH_{2n+2-m}X_m$ where the linear chain length n_+ is even and where the degree of substitution $m_\pm$ is odd or even.

Mathematical formulation and computational method

Let us note the system $C_nH_{2n+2-m}X_m = (n_+, m_\pm)$ when n_+ is even and $m_\pm$ (odd or even) and consider that all germinal substitutions performed which the obligatory respect of the tetra valence of primary and secondary carbon atoms satisfy three Young's partition[13] models given in Eqs. 1-2(a,b) hereafter:

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$$m_{-} = 3 2^{k_{\pm}} \quad if\, m_{-} \geq 3 \;\; and\; k_{\pm} = \frac{m-3}{2} \qquad ...(1)$$

$$m_{+} = 3^{2}\, 2^{k_{\pm}} \quad if\, m_{+} \geq 6 \; and\; k_{\pm} = \frac{m-6}{2} \qquad ...(2a)$$

$$m_{+} = 2^{k_{\pm}}\, if \quad m_{+} \geq 2 \; and\; k_{\pm} = \frac{m}{2} \qquad ...(2b)$$

In these previous equations the integer numbers 3 and 3^2 are one part or two parts of cardinality 3 which correspond to one gem or two gem trisubstitutions or formation of the $–CX_3$ group on one or two extreme primary carbon atoms while the number $2^{k_{\pm}}$ refers to $k_{\pm}$ parts 2 representing $k_{\pm}$ gem disubstitutions or formation of $k_{\pm}$ ($–CX_2$-) groups among n_+-2 internal secondary carbon atoms of the chain. Throughout this paper the subscripts + and – refer to even and odd integer numbers, respectively.

Let $G_0(n)$ shown in Figure 1 denote the linear graph which is defined as a finite non empty set of n_+ white vertices indicated by numerical labels 1,…,i,…,n_+ together which a set of n_+-1 edges (dotted lines) connecting adjacent vertices i-1 and i. These white vertices and these edges represent the positions of carbon atoms and C-C bonds, respectively.

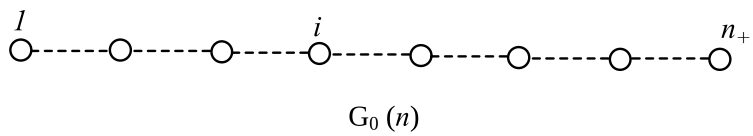


Fig. 1: Linear graph of an n-alkane

Molecular Graphs for GPIs of HPSNA

Let us represent in Fig. 2(a) shown below, a gem homo disubstitution as an operation which consists to attach two ligands of the same type X on a secondary or a primary carbon atom in order to generate the chemical group -CX_{2-} . Similarly a gem homo tri substitution represented in Fig. 2(b) is an operation consisting to attach three substituents of the same type X on a primary carbon atom located at the extremity of the linear chain in order to generate the chemical group -CX_3.

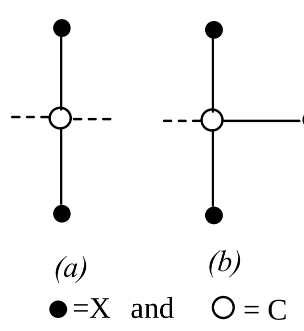
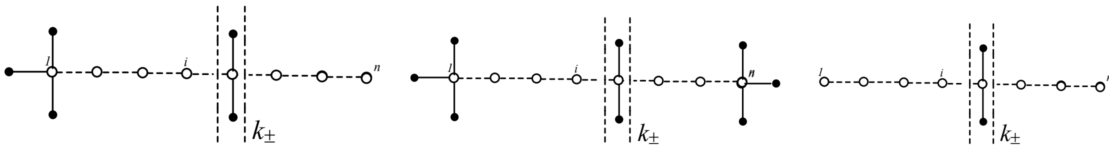


Fig. 2: Subgraphs representing -CX_{2-} and –CX_3 groups

The formation of geminal groups -CX_{2-} and -CX_3 are Young's partition of $m_{\pm}$ substituents into parts 2 and 3 while the locations of these groups among n_+ positions of $G_0(n)$ are combinations of distinct placements which generate numerous gem position isomers (GPIs) that may be classified in accordance with Eq. 1-2 into the following three categories of configurations: ${}^{32^{k_{\pm}}}G(n_+, m_-)$, ${}^{3^2 2^{k_{\pm}}}G(n_+, m_+)$, and ${}^{2^{k_{\pm}}}G(n_+, m_+)$ depicted by the generic molecular graphs given in Fig. 3 (*a, b, c*) hereafter:



$(3a)$ $^{32^{k_\pm}}G(n_+,m_-)$ $(3b)$ $^{3^2 2^{k_\pm}}G(n_+,m_+)$ $(3c)$ $^{2^{k_\pm}}G(n_+,m_+)$

Fig. 3 (a,b, c): Generic molecular graphs of the three categories of gem homopolysubstituted linear n_{+-}alkanes

Combinatorial enumeration of GPIs for HPSNA having the configuration $^{32^{k_\pm}}G(n_+,m_-)$

The partition model given in Eq. 1, suitable for odd positive integer numbers m_- allows the formation of GPIs with the configuration $^{32^{k_\pm}}G(n_+,m_-)$ which results from the placement of one $-CX_3$ on one extreme position of the graph $G_0(n)$ and the distribution of $k_\pm$ ($-CX_{2-}$) among the n_+*-1* remaining positions.

Proposition 1: By virtue of Eq. 1, the number of GPIs with the configuration $^{32^{k_\pm}}G(n_+,m_-)$ or number of distinct ways of putting one $-CX_3$ on one extreme position and $k_\pm$ ($-CX_2-$) on the remaining n_+*-1* positions of a linear chain $G_0(n)$ with a length n_+, denoted $^{32^{k_\pm}}I(n_+,m_-)$ is derived from Eq. 4:

$$^{32^{k_\pm}}I_{GPI}(n_+,m_-) = \binom{n_+ - 1}{\frac{m_- - 3}{2}} \qquad \text{...(4)}$$

Combinatorial enumeration of GPIs for HPSNA having the configuration $^{3^2 2^{k_\pm}}G(n_+,m_+)$

The partition model given in Eq. 2(a) allows the formation of GPIs with the configuration $^{3^2 2^{k_\pm}}G(n_+,m_+)$ which results from the placement of $k_\pm$ ($-CX_2$-) groups (k_- for m_+ doubly even and k_+ for m_+ singly even) on n_+-2 internal positions and 2 ($-CX_3$) groups on the two extreme positions of $G_0(n)$.

Proposition 2*:* The number $^{3^2 2^{k_\pm}}I(n_+,m_+)$ of configurations of type $^{3^2 2^{k_\pm}}G(n_+,m_+)$ or number of distinct ways of putting two $-CX_3$ on two extreme positions and $k_\pm$ ($-CX_2$-) on the remaining n_+-2 internal positions of G_0 (n), is the binomial coefficient derived from Eq. 5 hereafter:

$$^{3^2 2^{k_\pm}}I(n_+,m_+) = \binom{n_+ - 2}{\frac{m_+ - 6}{2}} \qquad \text{...(5)}$$

It is to be noticed that $^{3^2 2^{k_\pm}}I(n_+,m_+)$ is the sum given in Eq. 6 of the number $^{3^2 2^{k_\pm}}I_s(n_+,m_+)$ of meso symmetrical configurations and the double of the number $^{3^2 2^{k_\pm}}I_u(n_+,m_+)$ of pairs of redundant unsymmetrical configurations:

$$^{3^2 2^{k_\pm}}I(n_+,m_+) = {}^{3^2 2^{k_\pm}}I_s(n_+,m_+) + 2\left[{}^{3^2 2^{k_\pm}}I_u(n_+,m_+)\right] \qquad \text{...(6)}$$

The number ${}^{3^2 2^{k_\pm}}I_s\left(n_+,m_+\right)$ is derived according to the parities of the integers m_+ and $k_\pm$ from Eqs. 7 and 8. If m_+ is singly even one obtains an even integer number $k_+ = \frac{m_+ - 6}{2}$ then:

$$ {}^{3^2 2^{k_+}}I_s\left(n_+,m_+\right) = \begin{pmatrix} \frac{n_+\text{-}2}{2} \\ \frac{k_+}{2} \end{pmatrix} = \begin{pmatrix} \frac{n_+\text{-}2}{2} \\ \frac{m_+\text{-}6}{4} \end{pmatrix} \quad \ldots(7) $$

If m_+ is doubly even one obtains an odd integer number $k_- = \frac{m_+ - 6}{2}$ then:

$$ {}^{3^2 2^{k_-}}I_s\left(n_+,m_+\right) = 0 \quad \ldots(8) $$

Determination of the number ${}^{3^2 2^{k_\pm}}I_u\left(n_+,m_+\right)$ of unsymmetrical gem position isomers

The number of chemically distinct unsymmetrical GPIs or number of pairs of redundant unsymmetrical configurations, noted ${}^{3^2 2^{k_\pm}}I_u\left(n_+,m_+\right)$ is obtained from Eq. 9 hereafter:

$$ {}^{3^2 2^{k_\pm}}I_u\left(n_+,m_+\right) = \frac{1}{2}\left[{}^{3^2 2^{k_\pm}}I\left(n_+,m_+\right) - {}^{3^2 2^{k_\pm}}I_s\left(n_+,m_+\right)\right] \quad \ldots(9) $$

If one considers the parity of $k_\pm$, therefore Eq. 9 becomes Eq. 10 if m_+ is doubly even:

$$ {}^{3^2 2^{k_-}}I_u\left(n_+,m_+\right) == \frac{1}{2}\left[\begin{pmatrix} n_+ - 2 \\ k_+ \end{pmatrix}\right] = \frac{1}{2}\left[\begin{pmatrix} n_+ - 2 \\ \frac{m_+ - 6}{2} \end{pmatrix}\right] \quad \ldots(10) $$

or Eq. 9 becomes Eq. 11 if m_+ is singly even:

$$ {}^{3^2 2^{k_+}}I_u\left(n_+,m_+\right) = \frac{1}{2}\left[\begin{pmatrix} n_+ - 2 \\ k_+ \end{pmatrix} - \begin{pmatrix} \frac{n_+ - 2}{2} \\ \frac{k_+}{2} \end{pmatrix}\right] = \frac{1}{2}\left[\begin{pmatrix} n_+ - 2 \\ \frac{m_+ - 6}{2} \end{pmatrix} - \begin{pmatrix} \frac{n_+ - 2}{2} \\ \frac{m_+ - 6}{4} \end{pmatrix}\right] \quad \ldots(11) $$

Proposition 3: The number of chemically distinct gem position isomers ${}^{3^2 2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ obtained by putting 2 $-CX_3$ on two extreme positions of the chain having a length n_+ and permuting $k_\pm$ ($-CX_2$) among the remaining n_+-2 internal positions of $G_0(n)$ is derived from Eq. 12 :

$$ {}^{3^2 2^{k_\pm}}I_{GPI}\left(n_+,m_+\right) = {}^{3^2 2^{k_\pm}}I_s\left(n_+,m_+\right) + {}^{3^2 2^{k_\pm}}I_u\left(n_+,m_+\right) \quad \ldots(12) $$

By replacing the right hand side terms of Eq. 12 by their equivalent given in Eqs. 7-8 and 10-11 one obtains, for m_+ doubly even and k_- :

$$ {}^{3^2 2^{k_-}}I_{GPI}\left(n_+,m_+\right) = \frac{1}{2}\left[\begin{pmatrix} n_+ - 2 \\ k_- \end{pmatrix}\right] = \frac{1}{2}\left[\begin{pmatrix} n_+\text{-}2 \\ \frac{m_+\text{-}6}{2} \end{pmatrix}\right] \quad \ldots(13) $$

and for m_+ singly even and k_+ :

$$ {}^{3^2\,2^{k_+}} I_{GPI}\left(n_+,m_+\right) = \frac{1}{2}\left[\binom{n_+-2}{k_+} + \binom{\frac{n_+-2}{2}}{\frac{k_+}{2}}\right] = \frac{1}{2}\left[\binom{n_+\text{-}2}{\frac{m_+\text{-}6}{2}} + \binom{\frac{n_+-2}{2}}{\frac{m_+-6}{4}}\right] \quad ...(14) $$

Combinatorial enumeration of GPIs for HPSNA having the configuration ${}^{2^{k_\pm}}G\left(n_+,m_+\right)$

Let ${}^{2^{k_\pm}}I\left(n_+,m_+\right)$ denote the total number of configurations of type ${}^{2^{k_\pm}}G\left(n_+,m_+\right)$ issued from the given in Eq. 2b which allows $k_\pm = \frac{m_+}{2}$ gem disubstitutions distributed among n_+ sites. Hence:

$$ {}^{2^{k_\pm}}I\left(n_+,m_+\right) = \binom{n_+}{k_\pm} = \binom{n_+}{\frac{m_+}{2}} \quad ...(15) $$

As previously defined, ${}^{2^{k_\pm}}I\left(n_+,m_+\right)$ is a sum of two components given in the right hand side of Eq. 16:

$$ {}^{2^{k_\pm}}I\left(n_+,m_+\right) = {}^{2^{k_\pm}}I_s\left(n_+,m_+\right) + 2\left[{}^{2^{k_\pm}}I_u\left(n_+,m_+\right)\right] \quad ...(16) $$

The components ${}^{2^{k_\pm}}I_s\left(n_+,m_+\right)$ and ${}^{2^{k_\pm}}I_u\left(n_+,m_+\right)$ are respectively the numbers of symmetrical and redundant unsymmetrical configurations ${}^{2^{k_\pm}}G\left(n_+,m_+\right)$ derived from Eqs. 17-18 according to the parities of the integers m_+ and $k_\pm = \frac{m_+}{2}$:

$$ {}^{2^{k_-}}I_s\left(n_+,m_+\right) = 0 $$

for m_+ singly even k_- (odd) ...(17)

or

$$ {}^{2^{k_+}}I_s\left(n_+,m_+\right) = \binom{\frac{n_+}{2}}{\frac{k_+}{2}} = \binom{\frac{n_+}{2}}{\frac{m_+}{4}} \quad ...(18) $$

for m_+ doubly even k_+ (even)

The numbers of chemically distinct unsymmetrical configurations ${}^{2^{k_\pm}}G\left(n_+,m_+\right)$ is derived from Eq. 19:

$$ {}^{2^{k_\pm}}I_u\left(n_+,m_+\right) = \frac{1}{2}\left[{}^{2^{k_\pm}}I\left(n_+,m_+\right) - {}^{2^{k_\pm}}I_s\left(n_+,m_+\right)\right] \quad ...(19) $$

which becomes Eq. 20 for m_+ singly even and k_- :

$$ {}^{2^{k_-}}I_u\left(n_+,m_+\right) = \frac{1}{2}\left[\binom{n_+}{k_-}\right] = \frac{1}{2}\left[\binom{n_+}{\frac{m_+}{2}}\right] \quad ...(20) $$

or for m_+ doubly even and k_+ :

$$ {}^{2^{k_+}}I_u\left(n_+,m_+\right) = \frac{1}{2}\left[\binom{n_+}{k_+} - \binom{\frac{n_+}{2}}{\frac{k_+}{2}}\right] = \frac{1}{2}\left[\binom{n_+}{\frac{m_+}{2}} - \binom{\frac{n_+}{2}}{\frac{m_+}{4}}\right] \quad ...(21) $$

Proposition 4: The number ${}^{2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ of chemically distinct GPIs obtained by putting in distinct ways $k_\pm$ (–CX_2-) groups among n_+ positions of a linear chain $G_0(n)$ is derived from Eq. 22:

$$ {}^{2^{k_\pm}}I_{GPI}\left(n_+,m_+\right) = {}^{2^{k_\pm}}I_s\left(n_+,m_+\right) + {}^{2^{k_\pm}}I_u\left(n_+,m_+\right) \quad ...(22) $$

By replacing the right hand side terms of Eq. 22 by their equivalent given in Eqs. 17-21 one obtains for m_+ singly even and k_-:

$$ {}^{2^{k_-}}I_{GPI}\left(n_+,m_+\right) = \frac{1}{2}\left[\binom{n_-}{k_-}\right] = \frac{1}{2}\left[\binom{n_+}{\frac{m_+}{2}}\right] \quad ...(23) $$

and for m_+ doubly even and k_+:

$$ {}^{2^{k_+}}I_{GPI}\left(n_+,m_+\right) = \frac{1}{2}\left[\binom{n_+}{k_+} + \binom{\frac{n_+}{2}}{\frac{k_+}{2}}\right] = \frac{1}{2}\left[\binom{n_+}{\frac{m_+}{2}} + \binom{\frac{n_+}{2}}{\frac{m_+}{4}}\right] \quad ...(24) $$

By virtue of Eqs. 2(a) and 2(b), the occurrence of two simultaneous modes of partition for the degree of substitution m_+ suggests the following assertion:

Proposition 5 : When the degree of substitution m_+ is doubly or singly even the total number of constitutionally distinct GPIs in the series $C_nH_{2n+2-m}X_m$, noted $I_{GPI}\left(n_+,m_+\right)$, is the sum of the numbers ${}^{3^2 2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ and ${}^{2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ for HPSNA having the configurations ${}^{3^2 2^{k_\pm}}G\left(n_+,m_+\right)$ and ${}^{2^{k_\pm}}G\left(n_+,m_+\right)$ respectively. Hence:

$$ I_{GPI}\left(n_+,m_+\right) = {}^{3^2 2^{k_\pm}}I_{GPI}\left(n_+,m_+\right) + {}^{2^{k_\pm}}I_{GPI}\left(n_+,m_+\right) \quad ...(25) $$

By splitting the right hand terms ${}^{3^2 2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ and ${}^{2^{k_\pm}}I_{GPI}\left(n_+,m_+\right)$ into their respective components given in Eqs. 12 and 22, one obtains Eq. 26:

$$ I_{GPI}\left(n_+,m_+\right) = {}^{3^2 2^{k_\pm}}I_s\left(n_+,m_+\right) + {}^{3^2 2^{k_\pm}}I_u\left(n_+,m_+\right) + {}^{2^{k_\pm}}I_s\left(n_+,m_+\right) + {}^{2^{k_\pm}}I_u\left(n_+,m_+\right) \quad ...(26) $$

If the right hand side terms of Eq. 26 are replaced by their explicit formula given in Eqs. 13-14 and 23 - 24, one obtains the generalized Eq. 27 and 28 for combinatorial enumeration of GPIs for any HPSNA having a singly or doubly even integer number m_+ of cumulative gem homo substitutions. Hence, for m_+ doubly even:

$$I_{GPI}\left(n_+,m_+\right)=\frac{1}{2}\left[\begin{pmatrix} n_+ \\ \frac{m_+}{2} \end{pmatrix}+\begin{pmatrix} \frac{n_+}{2} \\ \frac{m_+}{4} \end{pmatrix}+\begin{pmatrix} n_- \text{-} 2 \\ \frac{m_+ \text{-} 6}{2} \end{pmatrix}\right] \quad ...(27)$$

and for m_+ singly even:

$$I_{GPI}\left(n_+,m_+\right)=\frac{1}{2}\left[\begin{pmatrix} n_+ \\ \frac{m_+}{2} \end{pmatrix}+\begin{pmatrix} n_+ \text{-} 2 \\ \frac{m_+ \text{-} 6}{2} \end{pmatrix}+\begin{pmatrix} \frac{n_+ \text{-} 2}{2} \\ \frac{m_+ \text{-} 6}{4} \end{pmatrix}\right] \quad ...(28)$$

RESULTS AND DISCUSSION

Applications

Example 1: To illustrate the application of Eq. 4 let us consider the molecular system $C_4H_5X_5$, where $n_+ = 4$, $m_- = 5$ and $k_- = 1$. Therefore the number of configurations ${}^{321^1}G(4,5)$ is ${}^{321^1}I_{GPI}(4,5)=\begin{pmatrix} 3 \\ 1 \end{pmatrix}=3$. The chemical graphs representing the two GPIs of a penta homosubstituted n-butane are depicted in Fig. 4 hereafter:

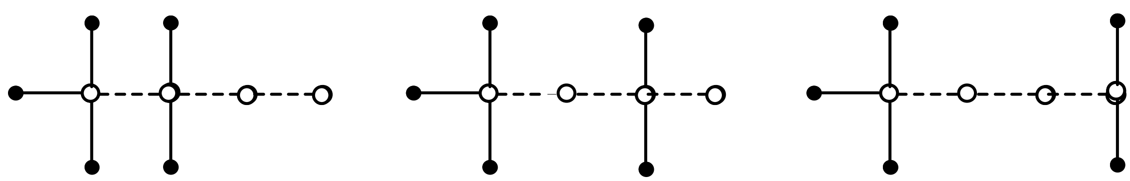


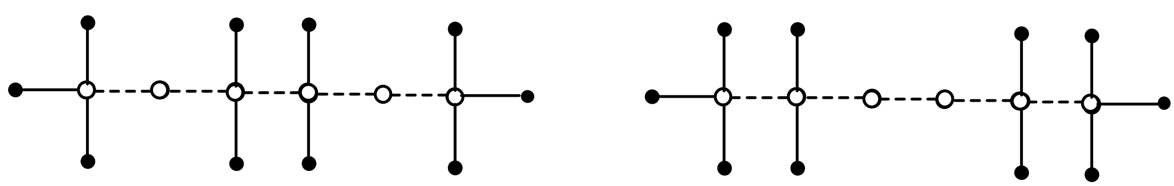
Fig. 4: Molecular graphs of the two GPIs of a penta homosubstituted n-butane.

The figure inventories of GPIs for HPSNAs having the configuratio ${}^{32^{k_\pm}}G\left(n_+,m_-\right)$ where $2 \le n_+ \le 12$, $3 \le m_\pm \le 25$ and $0 \le k_\pm \le 11$, are given in Table 1 hereafter:

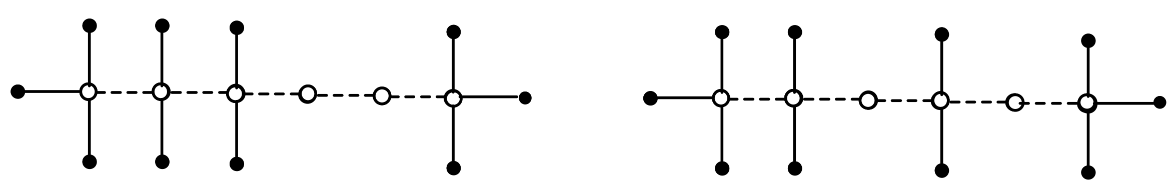
Example 2: Let us consider the molecular system $C_6H_4X_{10}$ with the configuration ${}^{3^22^2}G(6,10)$ having $n_+ = 6$, $m_+ = 10$ and $k_+ = 2$. Two ($-CX_2-$) are to be placed among $n_+ - 2 = 4$ internal positions while 2 ($-CX_3$) are located at the two extreme positions of $G_0(n)$. The application of Eqs. 7 and 11 gives respectively ${}^{3^2 2^2}I_s(6,10)=\begin{bmatrix} 2 \\ 1 \end{bmatrix}=2$ meso forms and ${}^{3^2 2^2}I_u(6,10)=\frac{1}{2}\left[\begin{pmatrix} 4 \\ 2 \end{pmatrix} - \begin{pmatrix} 2 \\ 1 \end{pmatrix}\right]=2$ unsymmetrical GPIs while Eq. 14 predicts ${}^{3^22^2}I_{GPI}(6,10)=\frac{1}{2}\left[\begin{pmatrix} 4 \\ 2 \end{pmatrix}+\begin{pmatrix} 2 \\ 1 \end{pmatrix}\right]=4$ GPIs. These results indicate that the total number of GPIs having the configuration ${}^{3^22^2}G(6,10)$ for a gem homo decasubstituted linear n-hexane is 4, subdivided into 2 meso and 2 unsymmetrical forms which are represented by molecular graphs shown in Fig. 5 hereafter :

Table 1: Figure inventories of GPIs for HPSNA having the configuration $^{32^k}G(n_+,m_-)$

n_+	m_-	$k_\pm$	$^{32^{k_\pm}}I(n_+,m_-)$	n_+	m_-	$k_\pm$	$^{32^{k_\pm}}I(n_+,m_-)$	n_+	m_-	$k_\pm$	$^{32^{k_\pm}}I(n_+,m_-)$
2	3	0	1	4	3	0	1	6	3	0	1
	5	1	1		5	1	3		5	1	5
					7	2	3		7	2	10
					9	3	1		9	3	10
										4	5
										5	1
8	3	0	1	10	3	0	1	12	3	0	1
	5	1	7		5	1	9		5	1	11
	7	2	21		7	2	36		7	2	55
	9	3	35		9	3	84		9	3	165
	11	4	35		11	4	126		11	4	330
	13	5	21		13	5	126		13	5	462
	15	6	7		15	6	84		15	6	462
	17	7	1		17	7	36		17	7	330
					19	8	9		19	8	165
					21	9	1		21	9	55
									23	10	11
									25	11	1



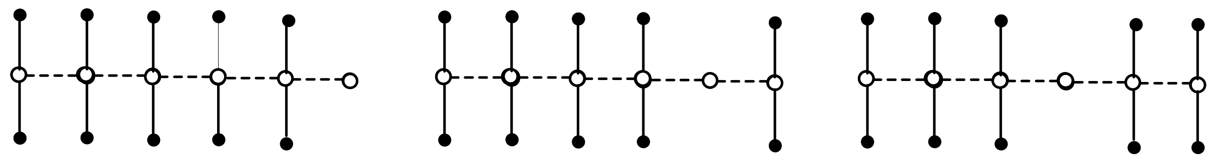
$^{3^2 2^2}I_s(6,10)=2$



$^{3^2 2^2}I_u(6,10)=2$

Fig. 5: Molecular graphs of the 4 GPIs having the configuration $^{3^2 2^2}G(6,10)$ **for a homo deca substituted n-hexane**

Let us consider the configuration ${}^{2^5}G(6,10)$ where k = 5. From Eqs. 17, 20 and 23 one deduce respectively: ${}^{2^5}I_s(6,10)=0$, ${}^{2^5}I_u(6,10)=\frac{1}{2}\left[\binom{6}{5}\right]=3$ and ${}^{2^5}I_{GPI}(7,10)=\frac{1}{2}\left[\binom{6}{5}\right]=3$ unsymmetrical GPIs depicted in Fig. 6 hereafter:



${}^{2^5}I_u(6,10)=3$

Fig. 6: Molecular graphs of the 3 GPIs having the configuration ${}^{2^5}G(6,10)$ for a homo decasubstituted n-hexane

The total number of GPIs for a homo decasubstituted n-hexane is:

$$I_{GPI}(6,10)={}^{2^5}I_s(6,10)+{}^{2^5}I_u(6,10)+{}^{3^22^2}I_u(6,10)+{}^{3^22^2}I_s(6,10)=0+3+2+2=7$$

This figure inventory match up with the result obtained from the direct application of Eq. 28 hereafter :

$$I_{GPI}(6,10)=\frac{1}{2}\left[\binom{6}{5}+\binom{4}{2}+\binom{2}{1}\right]=7$$

Example 3: For the series $C_6H_6X_8$ having n_+= 6, m_+ = 8 and k_- =1 the generic configuration ${}^{3^22^1}G(6,8)$ includes 2(-CX_3) at two extreme positions of $G_0(n)$ and 1(-CX_2-) groups to be placed among 4 internal positions. From Eqs. 8, 10 and 13 one obtains respectively:

$${}^{3^22^1}I_s(6,8)=0,\ {}^{3^22^1}I_u(6,8)=\frac{1}{2}\left[\binom{4}{1}\right]=2 \text{ and } {}^{3^22^1}I_{GPI}(6,8)=\frac{1}{2}\left[\binom{4}{1}\right]=2 \text{ forms shown in Fig. 7.}$$

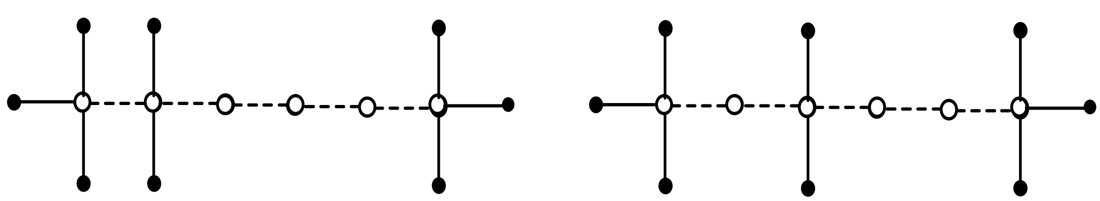
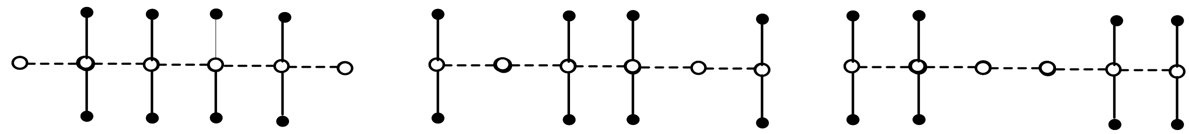


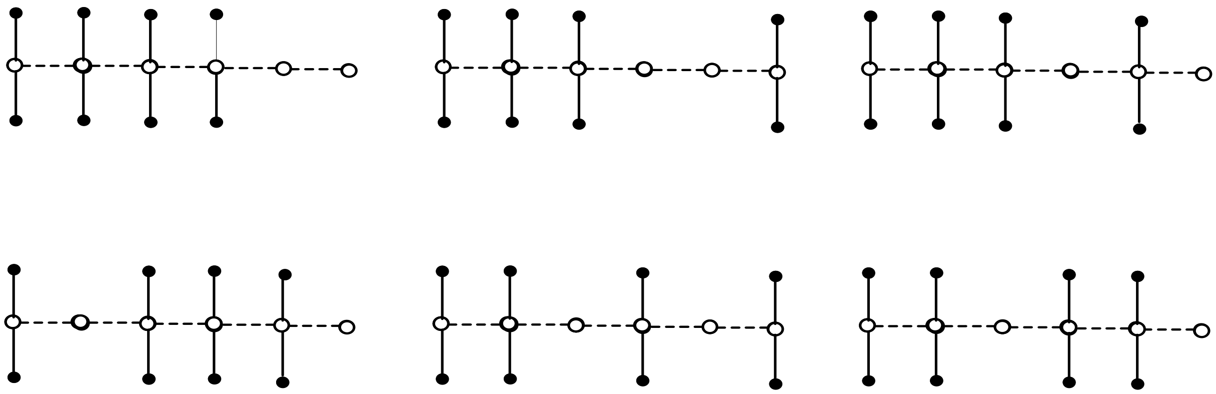
Fig. 7: Molecular graphs of the 2 unsymmetrical GPIs having the configuration ${}^{3^22^1}G(6,8)$ for a homo octasubstituted n-hexane.

For the configuration ${}^{2^4}G(6,8)$ where k_+ = 4, Eqs. 18, 21 and 24 give respectively:

$${}^{2^4}I_s(6,8)=\binom{3}{2}=3\ ,\ {}^{2^4}I_u(6,8)=\frac{1}{2}\left[\binom{6}{4}-\binom{3}{2}\right]=6 \text{ and } {}^{2^6}I_{GPI}(6,8)=\frac{1}{2}\left[\binom{6}{4}+\binom{3}{2}\right]=9$$ depicted in Fig. 8 hereafter:



$^{2^4}I_s(6,8)=3$



$^{2^4}I_u(6,8)=6$

Fig. 8: Molecular graphs of 3 meso and 6 unsymmetrical GPIs having the configuration $^{2^4}G(6,8)$ for a homo octasubstituted n-hexane.

This enumeration process indicates that the total number of GPIs for a homo octasubstituted n-hexane is: $I_{GPI}(6,8) = {}^{2^4}I_s(6,8) + {}^{2^4}I_u(6,8) + {}^{3^2 2^1}I_u(6,8) + {}^{3^2 2^1}I_s(6,8) = 0+2+3+6=11$

This figure inventory match up with the result obtained from the direct application of Eq. 27 hereafter:

$$I_{GPI}(6,8) = \frac{1}{2}\left[\binom{6}{4} + \binom{3}{2} + \binom{4}{1}\right] = 11$$

The results of the extensive application of such calculations are reported in Table 2 for HPSNA having $2 \le m_+ \le 20$ and $2 \le n_+ \le 10$. It is to be noticed that for m_+=2 and 4 only Eqs. 23 and 24 are applicable respectively. The 3 examples given in this study illustrate the direct and general application of this pattern inventory of GPIs for the systems $C_nH_{2n+2-m}X_m$ having the configurations $^{32^{k_\pm}}G(n_+, m_-)$, $^{3^2 2^{k_\pm}}G(n_+, m_+)$ and $^{2^{k_\pm}}G(n_+, m_+)$ and the accuracy of our theoretical results is testified by the method of drawing and counting molecular graphs of systems with smaller chain length.

CONCLUSION

In linear homopolysubstituted n-alkanes (HPSNAs) with the empirical formula $C_nH_{2n+2-m}X_m$, the gemination of $m_\pm$ substituents among the n_+ positions of the straight carbon chain is a perfect Young's partition process which allows to identify three classes of constitutionally distinct GPIs as follows -

The GPIs $^{32^{k_\pm}}G(n_+, m_-)$ having one –CX_3 located on one extreme position and $k_\pm$ (–CX_2) distributed among n_+ - *1* positions.

Table 2: Figures inventories of GPIs for HPSNA having a degree of substitution m_+ even and the configurations $^{3^2 2^{k\pm}}G(n_+,m_+)$ and $^{2^{k\pm}}G(n_+,m_+)$

$^{3^2 2^{k\pm}}G(n_+,m_+)$						$^{2^{k\pm}}G(n_+,m_+)$				$I_{GPI}(n_-,m_+)$
n_+	m_+	$k_\pm$	$^{3^2 2^{k\pm}}I_s$	$^{3^2 2^{k\pm}}I_u$	$^{3^2 2^{k\pm}}I_{GPI}$	$k_\pm$	$^{2^{k\pm}}I_s$	$^{2^{k\pm}}I_u$	$^{2^{k\pm}}I_{GPI}$	
2	2	-	-	-	-	1	0	1	**1**	**1**
	4	-	-	-	-	2	1	0	**1**	**1**
	6	0	1	0	**1**	3	-	-	**1**	**1**
4	2	-	-	-	-	1	0	2	**2**	**2**
	4	-	-	-	-	2	2	2	**4**	**4**
	6	0	1	0	**1**	3	0	2	**2**	**3**
	8	1	0	1	**1**	4	1	0	**1**	**2**
	10	2	1	0	**1**	-	-	-	-	**1**
6	2	-	-	-	-	1	0	3	**3**	**3**
	4	-	-	-	-	2	3	6	**9**	**9**
	6	0	1	0	**1**	3	0	10	**10**	**11**
	8	1	0	2	**2**	4	3	6	**9**	**11**
	10	2	2	2	**4**	5	0	3	**3**	**7**
	12	3	0	2	**2**	6	1	0	**1**	**3**
	14	4	1	0	**1**	-	-	-	-	**1**
8	2	-	-	-	-	1	0	4	**4**	**4**
	4	-	-	-	-	2	4	12	**16**	**16**
	6	0	1	0	**1**	3	0	28	**28**	**29**
	8	1	0	3	**3**	4	6	32	**38**	**41**
	10	2	3	6	**9**	5	0	28	**28**	**37**
	12	3	**0**	10	**10**	6	4	12	**16**	**26**
	14	4	**3**	6	**9**	7	0	4	**4**	**13**
	16	5	**0**	3	**3**	8	1	0	**1**	**4**
	18	6	**1**	0	**1**	9	-	-	-	**1**
10	2	-				1	0	5	**5**	**5**
	4	-				2	5	20	**25**	**25**
	6	0	**1**	0	**1**	3	0	60	**60**	**61**
	8	1	**0**	4	**4**	4	10	100	**110**	**114**
	10	2	**4**	12	**16**	5	0	126	**126**	**142**

Cont…

$^{3^2 2^{k_\pm}}G(n_+,m_+)$						$^{2^{k_\pm}}G(n_+,m_+)$				$I_{GPI}(n_-,m_+)$
n_+	m_+	$k_\pm$	$^{3^2 2^{k_\pm}}I_s$	$^{3^2 2^{k_\pm}}I_u$	$^{3^2 2^{k_\pm}}I_{GPI}$	$k_\pm$	$^{2^{k_\pm}}I_s$	$^{2^{k_\pm}}I_u$	$^{2^{k_\pm}}I_{GPI}$	
	12	3	**0**	28	**28**	6	10	100	**110**	**138**
	14	4	**6**	32	**38**	7	0	60	**60**	**98**
	16	5	**0**	28	**28**	8	5	20	**25**	**53**
	18	6	**4**	12	**16**	9	0	5	**5**	**21**
	20	7	**0**	4	**4**	10	1	0	**1**	**5**
	22	8	**1**	0	**1**	11	-	-	-	**1**

- the GPIs $^{2^{k_\pm}}G(n_+,m_+)$ exhibiting $k_\pm$ ($–CX_2$-) among n_+ positions of the chain and,
- the GPIs $^{3^2 2^{k_\pm}}G(n_+,m_+)$ having $k_\pm$ ($–CX_2$-) distributed among $n_+ - 2$ positions and 2 ($–CX_3$) groups located on the two extreme positions of the chain

The figures inventories of GPIs for these 3 categories of molecular systems are derived from the direct calculations of the number of distinct ways of putting a set of $k_\pm$ ($–CX_2$-) and one or two $-CX_3$ groups among n_+ positions of the linear chain. This combinatorial enumeration method is a useful tool for stereo chemical analyses and molecular design of these series of chemical compounds.

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