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COMBINATORIAL ENUMERATION OF HOMO AND HETERO-POLYSUBTITUTED [4.2]-PARACYCLOPHANE DERIVATIVES

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ABSTRACT

A combinatorial enumeration using the unit-subduced-cycle index approach with symmetry chararacterisation is carried out for homo- and hetero-polysubstituted [4.2]-paracyclophane derivatives symbolized respectively by the empirical formulas $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ and $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$ where X and Y are a non-isomerisable ligands and where the greek symbol φ represents the hydrogen depleted benzene ring.

Key words: Homo and hetero-disubtutited [4.2] paracyclophane, Unit-subduced-cycle index, Coset representation, Subduction, Isomer count vector, Combinatorial enumeration.

INTRODUCTION

During the last four decades, some satisfactorily routes for the preparation of [*m.n*] paracyclophanes among which the [4.2] paracyclophane ([4.2] PCP) as well as several derivatives of these compound has been described[1-8].

Hammond and Longone[9] for instance reported that the direct synthesis of this hydrocarbon is achieved via the cross dimerization of vinyl-p-xylylene with other xylylene type intermediates. Another route for its preparation is the thermal cleavage of the benzyl-benzyl bond of the [2.2] paracyclophane, which at 200°C leads to a diradical. This latter species collapse to regenerate starting materials and undergoes a cycloaddition reaction which gives [4.2] paracyclophane derivatives. It is to be noticed that the [4.2] PCP belongs to the [*m.n*] paracyclophanes series, which two carbon bridges of unequal length. Such compounds undergo electrophylic aromatic substitution (halogenation or Friedel Crafts acylation) under very mild conditions as long as one bridge contains less than four carbon atoms.

The emphasis in this study is to present a combinatorial enumeration detailing the symmetries of stereo and position isomers of homo-polysubstituted-[4.2]-paracyclophane (Ho[4.2] PCP and hetero-polysubstituted-[4.2]-paracyclophane (He-[4.2] PCP) derivatives symbolized by the empirical formula $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ and $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$, where the subscripts q_0, q_1 and q_2 are respectively the numbers of unsubstituted hydrogen atoms and the degrees of substitution with non isomerisable ligands of distinct types X and Y.

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Mathematical formulation and computational method

Let us now consider the parent [4.2]-PCP as a three dimensional object represented by the stereograph G having a C_{2V} global symmetry as shown in Fig. 1.

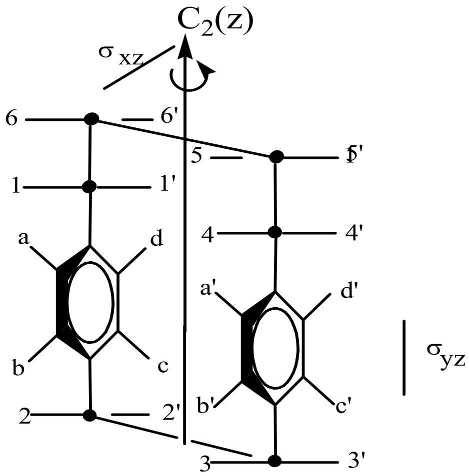


Fig. 1: Stereograph of [4.2]-PCP

The four symmetry operations of this abelian group listed in Eq. 1 hereafter :

$$C_{2v} = \{E, C_{2(z)}, \sigma_{(xz)}, \sigma_{(yz)}\} \quad ...(1)$$

are partitioned into four equivalence classes given in eq. 2 as follows:

$$\{I\} ;\{C_{2(z)}\}; \{\sigma_{(xz)}\}; \{\sigma_{(yz)}\} \quad ...(2)$$

These latter generate 5 subgroups comprising the 2 chiral subgroups C_1 and C_2 and the 3 achiral subgroups C_s, C'_s and C_{2V} D_{2h} reported in Table 1 with their respective symmetry operations.

Table 1: The subgroups of C_{2v}

Subgroup	Symmetry operations	Chirality
C_1	$\{I\}$	Chiral
C_2	$\{I, C_{2(z)}\}$	Chiral
C_s	$\{I, \sigma_{(xz)}\}$	Achiral
C'_s	$\{I, \sigma_{(yz)}\}$	Achiral
C_{2v}	$\{I, C_{2(z)}, \sigma_{(xz)}, \sigma_{(yz)}\}$	Achiral

These 5 subgroups construct a non redundant set of subgroups[10] for C_{2v} denoted SSG_{D2h} SSG_{C2v} given in Eq. 3:

$$SSG_{C2v} = \{C_1, C_2, C_s, C'_s, C_{2V}\} \quad ...(3)$$

The complete set of coset representations (CR) forC_{2v} denoted $SCR_{C_{2v}}$ listed in Eq. 4 hereafter SCR_{D2h}:

$$SCR_{C2v} = \{C_{2v}(/\mathrm{C}_1),\ C_{2v}(/\mathrm{C}_2),\ C_{2v}(/\mathrm{C}_s),\ C_{2v}(/\mathrm{C}'_s),\ C_{2v}(/C_{2v})\} \qquad ...(4)$$

is in a univoque correspondence with the SSG_{C2v}. The term designating each coset representation (CR) includes the global symmetry C_{2v} followed by a subgroup $\mathrm{G}_i\,\mathrm{G}_i \in SSG_{C2v}$. The explicit forms of these CRs are given in Eqs. 5-9 as follows:

$$C_{2v}\ (/\mathrm{C}_1) = \mathrm{C}_1 I + \mathrm{C}_1\, C_{2(z)} + \mathrm{C}_1\, \sigma_n + \mathrm{C}_1\, \sigma_{(xz)} + \mathrm{C}_1\, \sigma_{(yz)} \qquad ...(5)$$

$$C_{2v}\ (/\mathrm{C}_2) = \mathrm{C}_2 I + \mathrm{C}_2\, \sigma_{(xz)} \qquad ...(6)$$

$$C_{2v}\ (/\mathrm{C}_s) = \mathrm{C}_s I + \mathrm{C}_S\, \mathrm{C}_{2(z)} \qquad ...(7)$$

$$C_{2v}\ (/\mathrm{C}'_s) = \mathrm{C}'_s I + \mathrm{C}'_s\, C_{2(z)} \qquad ...(8)$$

$$C_{2v}\ (/\mathrm{C}_{2v}) = \mathrm{C}_{2v} I \qquad ...(9)$$

$$\mathrm{D}_{2h}\ (/\mathrm{C}'_{2v}) = \mathrm{C}'_{2v}\,\mathrm{I} + \mathrm{C}'_{2v}\, \mathrm{C}_{2(z)}$$

$\mathrm{D}_{2h}\ (/\mathrm{D}_{2h}) = \mathrm{D}_{2h}\,\mathrm{I}$ By multiplying the right hand side terms of Eqs. 5-9 by each symmetry operation of C_{2v}, we permute the elements of each CR. Then we obtain a row vector of marks assign to each CR by counting invariant elements related to each subgroup. The five row vectors of marks generated by these operations form the Table of mark for C_{2v} denoted $\mathrm{M}_{\mathrm{C2v}}\,\mathrm{M}_{\mathrm{D2h}}$ which is given hereafter:

$$\mathrm{M}_{\mathrm{C2v}} = \begin{array}{r|ccccc} & \mathrm{C}_1 & \mathrm{C}_2 & \mathrm{C}_S & \mathrm{C}'_S & \mathrm{C}_{2v} \\ \mathbf{C}_{2v}(/\mathbf{C}_1) & 4 & 0 & 0 & 0 & 0 \\ \mathbf{C}_{2v}(/\mathbf{C}_2) & 2 & 2 & 0 & 0 & 0 \\ \mathbf{C}_{2v}(/\mathbf{C}_s) & 2 & 0 & 2 & 0 & 0 \\ \mathbf{C}_{2v}(/\mathbf{C}'_s) & 2 & 0 & 0 & 2 & 0 \\ \mathbf{C}_{2v}(/\mathbf{C}_{2v}) & 1 & 1 & 1 & 1 & 1 \end{array}$$

The corresponding inverse of this mark table denoted $\mathrm{M}^{-1}_{\mathrm{C}2v}$ is obtained from Eq. 10:

$$\mathrm{M}_{\mathrm{C}2v}\, \mathrm{M}^{-1}_{\mathrm{C}2v} = \mathrm{I} \qquad \ldots(10)$$

where I represents the 5 x 5 identity matrix.

$$M^{-1}_{c_{2v}} = \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix}$$

The 20 hydrogen atoms of the parent [4.2]-PCP depicted in Fig. 1 by alphabetical and numerical labels constitute 5 distinct sets of equivalent atoms or orbits Δ_1, Δ_2, Δ_3, Δ_4, and Δ_5 given hereafter:

$\Delta_1 = \{1,4,\ 1',4'\}$, $\Delta_2 = \{2,3,\ 2',3'\}$, $\Delta_3 = \{5,6,\ 5',6'\}$, $\Delta_4 = \{a,d,\ a',d'\}$ and $\Delta_5 = \{b,c,\ b',c'\}$

To assign an appropriate CR to each orbit, we find the largest subgroup that keeps each orbit invariant. The subgroup C_1 keeps all the elements of Δ_1, Δ_2, Δ_3, Δ_4, and Δ_5 unchanged. Therefore the coset representation governing the 20 substitution sites located on the two benzene rings and the eight others located on the two carbon bridges isdenoted D_{2h} (/C_1).

RESULTS AND DISCUSSION

The Fujita mathematical procedure of subduction[11-13] of the coset representation C_{2v} (/D_{2h} (/C_s), D_{2h} (/D_2), D_{2h} (/C_{2v}), D_{2h} (C'_{2v}), D_{2h} (/C_{2v})) by all subgroups of C_{2v} has been derived from Eq. 11 hereafter :

$$D_{2h}(/C_1) \downarrow G_i \; \mathrm{G_i} = \beta_i \; \beta_i \; \mathrm{G_i} (/C_1 \; D_{2h} (/C_1) \qquad \dots(11)$$

Where G_i $\mathrm{G_i} \in SSG_{D_{2h}}\, SSG_{C_{2v}}$ and β_i β_i is a positive integer number. The results obtained are given in column 2 of Table 2.

Table 2: Subductions of the coset representation D_{2h} (/D_{2h} (/C_s), D_{2h} (/D_2), D_{2h} (/C_{2v}), D_{2h} (/C'_{2v}), D_{2h} (/C_{2v})) and resulting USCIs

	Subduction	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5	ICR Total
C_{2v} (/C_1) ↓ C_1	4 (C_1/C_1)	S_1^4	S_1^4	S_1^4	S_1^4	S_1^4	S_1^{20}
C_{2v} (/C_1) ↓ C_2	2 (C_2/C_1)	S_2^2	S_2^2	S_2^2	S_2^2	S_2^2	S_2^{10}
C_{2v} (/C_1) ↓ C_s	2 (C_s/C_1)	S_2^2	S_2^2	S_2^2	S_2^2	S_2^2	S_2^{10}
C_{2v} (/C_1) ↓ C'_s	2 (C'_s/C_1)	S_2^2	S_2^2	S_2^2	S_2^2	S_2^2	S_2^{10}
C_{2v} (/C_1) ↓ C_{2v}	(C_{2v}/C_1)	S_4	S_4	S_4	S_4	S_4	S_4^5

Then the right hand side term of Eq. 11 is transformed as given in Eq. 12, into aunit-subduced-cycle-index (USCI)[14] noted $s_{d_i}^{\beta_i}$ and where $d_i = \frac{|G_i|}{|C_1|}$.

$$\beta_i \; \beta_i \; \mathrm{G_i} \; (/C_1 \; D_{2h} \; (/C_1) \rightarrow \mathrm{s}_{\mathrm{d_i}}^{\beta_i} \, s_{d_i}^{\beta_i} \qquad \dots(12)$$

These USCIs are reported in column 3, 4, 5, 6 and 7 of Table 2 for the orbits Δ_1, Δ_2, Δ_3, Δ_4, and Δ_5, respectively. In each row the product of unit subduced cycle indices for the orbits Δ_1, Δ_2, Δ_3, Δ_4, and Δ_5 gives rise to $s_{d_i}^{5\beta_i}$ which is the global USCI for the subgroup considered. For example the global USCI for the sub symmetry C_1 results from the $\left(s_1^{4\times5}\right) = s_1^{20}$. Each global USCI $s_{d_i}^{5\beta_i}$ belonging to the sub symmetry $\mathrm{G}_i \in SSG_{C_{2v}}$ is transformed into a generating function $F(x) = \sum_j a_j x^j$ as given in Eqs. 13 and 14 for homo- and hetero-polysubstitution, respectively**.**

$$G_i \rightarrow s_{d_i}^{5\beta_i} \rightarrow F(x) = \left(1 + x^{d_i}\right)^{5\beta_i} = \sum_{q_1} A_{q_1} x^{q_1} \text{ where } 0 \le q_1 \le 5\beta_i d_i \text{ and} \qquad \dots(13)$$

$$G_i \to s_{d_i}^{5\beta_i} \to F(x,y) = \left(1 + x^{d_i} + y^{d_i}\right)^{5\beta_i} = \sum_{q_1,q_2} A_{q_1,q_2} x^{q_1} y^{q_2} \text{ where } 0 \le q_1 + q_2 \le 5\beta_i d_i \qquad ...(14)$$

and in both Eqs. $5\beta_i d_i = 20$.

- **Case of homopolysubstitution $C_1 \to S^{20} \to (1 + x)^{20} =$**

The application of Eq. 13 to the different subsymmetries for the series of homopoly substituted [4.2] PCPs yields the following polynomials:

$C_1 \to S^{20} \to (1 + x)^{20} = x^{20} + 20x^{19} + 190x^{18} + 1140x^{17} + 4845x^{16} + 15504x^{15}$

$+ 38760x^{14} + 77520x^{13} + 125970x^{12} + 167960x^{11} + 184756x^{10}$

$+ 38760x^{14} + 77520x^{13} + 125970x^{12} + 167960x^{11} + 184756x^{10}$

$+ 167960x^{9} + 125970x^{8} + 77520x^{7} + 38760x^{6} + 15504x^{5} + 4845x^{4}$

$+ 1140x^{3} + 190x^{2} + 1$

Similarly

$S_2^{10} \to (1 + x^2)^{10} + x^{20} + 10x^{18} + 45x^{16} + 120x^{14} + 210x^{12} + 252x^{10} + 210x^{8} + 120x^{6}$

$+ 45x^{4} + 10x^{2} + 1$

for the sub symmetries $C_2, C_s, C_s^{'}$

and $S_2^5 \to (1 + x^4)^5 = x^{20} + 5x^{16} + 10x^{12} + 10x^{8} + 5x^{4} + 1$ for C_{2v}

- **Case of heteropolysubstitution**

Similarly, the application of Eq. 14 to the different subsymmetries for the series of heteropolysubstituted [4.2] PCPs yields the following polynomials:

$C_1 \to S_1^{20} \to (1 + x + y)^{20} \to 380xy + 3420x^2y + 19380x^3y + 29070x^2y^2 + 77520x^4y$

$+ 155040x^3y^2 + 232560x^5y + 581400x^4y^2 + 775200x^4y^3$

$+ 542640x^6y + 1627920x^5y^2 + 2713200x^4y^3 + 1007760x^7y$

$+ 3527160x^6y^2 + 7054320x^5x^3 + 8817900x^4x^4 + 1511640x^8y$

$+ 60446560x^7y^2 + 14108640x^6y^3 + 21162960x^5y^4 \ldots,$

Similarly

$C_2, C_s, C'_s \to S_2^{20} \to (1 + x^2 + y^2)^{10} \to 1 + \ldots + 90x^2y^2 + 360x^4y^2 + 1260x^4y + 840x^6y^2 + \ldots.,$

and $C_{2v} \to S_4^5 \to (1 + x^4 + y^4)^5 \to 1 + \ldots + 20x^4y4 + \ldots x^{20}y^{20}$

The different coefficients x^2 in the above mentioned polynomials are collected together to form the fixed point matrices *FPM* (x^q) and *FPM* ($x^{q1} y^{q2}$) given below:

$$\mathrm{FPM}\left(x^{q}\right)=\begin{array}{c|ccccc}
 & C_1 & C_2 & C_s & C'_s & C_{2v}\\
1 & 1 & 1 & 1 & 1 & 1\\
x & 20 & 0 & 0 & 0 & 0\\
x^{2} & 190 & 10 & 10 & 10 & 0\\
x^{3} & 1140 & 0 & 0 & 0 & 0\\
x^{4} & 4845 & 45 & 45 & 45 & 5\\
x^{5} & 15504 & 0 & 0 & 0 & 0\\
x^{6} & 38760 & 120 & 120 & 120 & 0\\
x^{7} & 77520 & 0 & 0 & 0 & 0\\
x^{8} & 125970 & 210 & 210 & 210 & 10\\
x^{9} & 167960 & 0 & 0 & 0 & 0\\
x^{10} & 184756 & 252 & 252 & 252 & 0\\
x^{11} & 167960 & 0 & 0 & 0 & 0\\
x^{12} & 125970 & 210 & 210 & 210 & 10\\
x^{13} & 77520 & 0 & 0 & 0 & 0\\
x^{14} & 38760 & 120 & 120 & 120 & 0\\
x^{15} & 15504 & 0 & 0 & 0 & 0\\
x^{16} & 4845 & 45 & 45 & 45 & 5\\
x^{17} & 1140 & 0 & 0 & 0 & 0\\
x^{18} & 190 & 10 & 10 & 10 & 0\\
x^{19} & 20 & 0 & 0 & 0 & 0\\
x^{20} & 1 & 1 & 1 & 1 & 1
\end{array}
\qquad
\mathrm{FPM}\left(x^{q_1}y^{q_2}\right)=\begin{array}{c|ccccc}
 & C_1 & C_2 & C_s & C'_s & C_{2v}\\
xy & 380 & 0 & 0 & 0 & 0\\
x^{2}y & 3420 & 0 & 0 & 0 & 0\\
x^{3}y & 19380 & 0 & 0 & 0 & 0\\
x^{2}y^{2} & 29070 & 90 & 90 & 90 & 0\\
x^{4}y & 77520 & 0 & 0 & 0 & 0\\
x^{3}y^{2} & 155040 & 0 & 0 & 0 & 0\\
x^{5}y & 232560 & 0 & 0 & 0 & 0\\
x^{4}y^{2} & 581400 & 360 & 360 & 360 & 0\\
x^{3}y^{3} & 775200 & 0 & 0 & 0 & 0\\
x^{6}y & 542640 & 0 & 0 & 0 & 0\\
x^{5}y^{2} & 1627920 & 0 & 0 & 0 & 0\\
x^{4}y^{3} & 2713200 & 0 & 0 & 0 & 0\\
x^{7}y & 1007760 & 0 & 0 & 0 & 0\\
x^{6}y^{2} & 3527160 & 840 & 840 & 840 & 0\\
x^{5}y^{3} & 7054320 & 0 & 0 & 0 & 0\\
x^{4}y^{4} & 8817900 & 1260 & 1260 & 1260 & 20\\
x^{8}y & 1511640 & 0 & 0 & 0 & 0\\
x^{7}y^{2} & 60446560 & 0 & 0 & 0 & 0\\
x^{6}y^{3} & 14108640 & 0 & 0 & 0 & 0\\
x^{5}y^{4} & 211662960 & 0 & 0 & 0 & 0
\end{array}$$

The corresponding isomer count matrices *ICM* (x^{q}) and *ICM* ($x^{q1}\,y^{q2}$) are derived from Eq. 15

$$ICM = FPM.\,M_{C_{2v}}^{-1} \qquad ...(15)$$

where $M_{C_{2v}}^{-1}$ represents the inverse of the mark table aforementioned. The result obtained are the two rectangular matrices of isomers numbers given hereafter with respect to each sub symmetry of C_{2v} for different values of q_1 in the system $\varphi_2\, C_6\, H_{q0}\, X_{q1}$ and of (q_1, q_2) in the series $\varphi_2\, C_6\, H_{q0}\, X_{q1}\, Y_{q2}$.

$$\mathrm{ICM}\left(x^{q}\right)=\begin{array}{c|ccccc}
 & C_1 & C_2 & C_s & C'_s & C_{2v}\\
1 & 0 & 0 & 0 & 0 & 1\\
x & 5 & 0 & 0 & 0 & 0\\
x^{2} & 40 & 5 & 5 & 5 & 0\\
x^{3} & 285 & 0 & 0 & 0 & 0\\
x^{4} & 1180 & 20 & 20 & 20 & 5\\
x^{5} & 3876 & 0 & 0 & 0 & 0\\
x^{6} & 9600 & 60 & 60 & 60 & 0\\
x^{7} & 19380 & 0 & 0 & 0 & 0\\
x^{8} & 31340 & 100 & 100 & 100 & 10\\
x^{9} & 41990 & 0 & 0 & 0 & 0\\
x^{10} & 46000 & 126 & 126 & 126 & 0\\
x^{11} & 41990 & 0 & 0 & 0 & 0\\
x^{12} & 31340 & 100 & 100 & 100 & 10\\
x^{13} & 19380 & 0 & 0 & 0 & 0\\
x^{14} & 9600 & 60 & 60 & 60 & 0\\
x^{15} & 3876 & 0 & 0 & 0 & 0\\
x^{16} & 1180 & 20 & 20 & 20 & 5\\
x^{17} & 285 & 0 & 0 & 0 & 0\\
x^{18} & 40 & 5 & 5 & 5 & 0\\
x^{19} & 5 & 0 & 0 & 0 & 0\\
x^{20} & 0 & 0 & 0 & 0 & 1
\end{array}
\qquad
\mathrm{ICM}\left(x^{q_1}y^{q_2}\right)=\begin{array}{c|ccccc}
 & C_1 & C_2 & C_s & C'_s & C_{2v}\\
xy & 95 & 0 & 0 & 0 & 0\\
x^{2}y & 855 & 0 & 0 & 0 & 0\\
x^{3}y & 4845 & 0 & 0 & 0 & 0\\
x^{2}y^{2} & 7200 & 45 & 45 & 45 & 0\\
x^{4}y & 19380 & 0 & 0 & 0 & 0\\
x^{3}y^{2} & 38760 & 0 & 0 & 0 & 0\\
x^{5}y & 58140 & 0 & 0 & 0 & 0\\
x^{4}y^{2} & 145080 & 180 & 180 & 180 & 0\\
x^{3}y^{3} & 193800 & 0 & 0 & 0 & 0\\
x^{6}y & 135660 & 0 & 0 & 0 & 0\\
x^{5}y^{2} & 406980 & 0 & 0 & 0 & 0\\
x^{4}y^{3} & 678300 & 0 & 0 & 0 & 0\\
x^{7}y & 251940 & 0 & 0 & 0 & 0\\
x^{6}y^{2} & 881160 & 420 & 420 & 420 & 0\\
x^{5}y^{3} & 1763580 & 0 & 0 & 0 & 0\\
x^{4}y^{4} & 2203540 & 620 & 620 & 620 & 20\\
x^{8}y & 377910 & 0 & 0 & 0 & 0\\
x^{7}y^{2} & 15111640 & 0 & 0 & 0 & 0\\
x^{6}y^{3} & 3527160 & 0 & 0 & 0 & 0\\
x^{5}y^{4} & 52915740 & 0 & 0 & 0 & 0
\end{array}$$

Symmetry characterization of enumerated Ho(4.2)PCPs and He(4,2)PCPs

The chirality fittingness of $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ and $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$ is governed by the parity of their respective degrees of homopoly substitution q_1 and of heteropoly substitution q_1 and q_2 according to the following rules :

(a) The formation of chiral isomers with C_1 symmetry only is allowed if the degree of homopoly substitution q_1 is odd in the system $\varphi_2\ C_6\ H_{q0}\ X_{q1}$, or if the degrees of heteropoly substitution q_1 and q_2 are simultaneously odd or both odd and even in the system $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$.

This assumption is verified by the results given in the rows of the *ICM* (x^{q1}) and *ICM* $(x^{q1}\,y^{q2})$ where one can see that for any value q_1 odd in the system $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ $A_{q1} \neq 0$ only for the C_1 chiral symmetry and $A_{q1} = 0$ for the symmetries C_2 , C_s , C'_s and C_{2v}; for q_1 and q_2 simultaneously odd or both odd and even in the system $\varphi_2 C_6 H_{q_0} X_{q_1} Y_{q_2}$, $A_{q_1 q_2} \neq 0$ only for the C_1 chiral symmetry and $A_{q_1 q_2} = 0$ for the symmetries C_2 , C_s , C'_s andC_{2v}.

(b) The simultaneous occurrence of chiral C_1 and C_2 isomers together with achiral C_s and C_{2v} isomersis allowed if the degree of homopoly substitution q_1 is even in the system $\varphi_2\ C_6\ H_{q0}\ X_{q1}$,or if the degrees of heteropoly substitution q_1 and q_2 are both even in the system $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$.

The inspection of the coefficients of x^2 in the third row of the *ICM* (x^{q1}) for the system $\varphi_2\ C_6\ H_{18}\ X_2$ reveals that there are 55 homodisubstituted (4.2) paracyclophane derivatives and 40 of these belong to C_1, 5 to C_2, 5 to both C_s and C'_s. The molecular graphs of these isomers are illustrated in Fig. 2 (a,b,c,d) where one can easily depict that inter annular substitutions yields *2* pseudo gem (**48, 49**), *2* pseudo meta (**43,44**), *1* pseudo para (**37**), *1* pseudo ortho (**35**) isomers. Similarly the coefficients of x^2y^2 at the fourth row of the *ICM* $(x^{q1}\ y^{q2})$ predictthat $A_{2,2}$= 7200C_1, 45C_2, 45C_s and 45C'_s isomers for the system $C_6\ H_{16}\ X_2\ Y_2$.

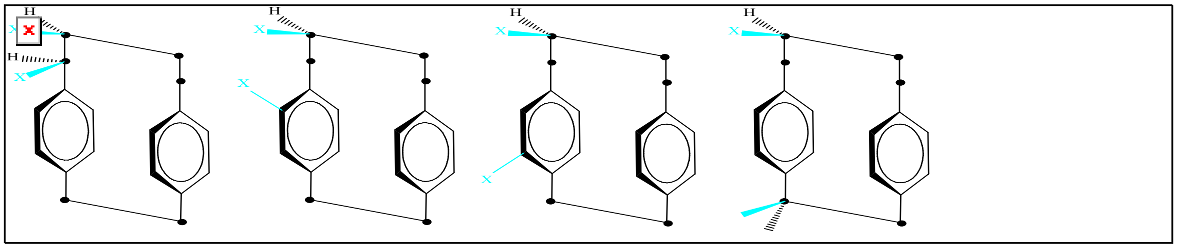
Finally these results also indicates that:-1)-Any $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ or $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$ series with even degrees of substitution $q_i.(i=1,2)$ exhibit the same number of isomer having C_2, C_s and C'_s symmetry, respectively. Hence:

$A_{q1}\,(C_2) = A_{q1}\,(C_s) = A_{q1}\,(C'_s)$ for $\varphi_2\ C_6\ H_{q0}\ X_{q1}$

and

$A_{q1,\,q2}\,(C_2) = A_{q1,q2}\,(C_s) = A_{q1,\,q2}\,(C'_s)$ for $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$

2) C_{2v}-achiral isomers are formed in $\varphi_2\ C_6\ H_{q0}\ X_{q1}$ and $\varphi_2\ C_6\ H_{q0}\ X_{q1}\ Y_{q2}$ series only if their respective degrees of substitution are even and satisfy the restriction: $q_i.(i=1,2)= 4N$ modulo 0.



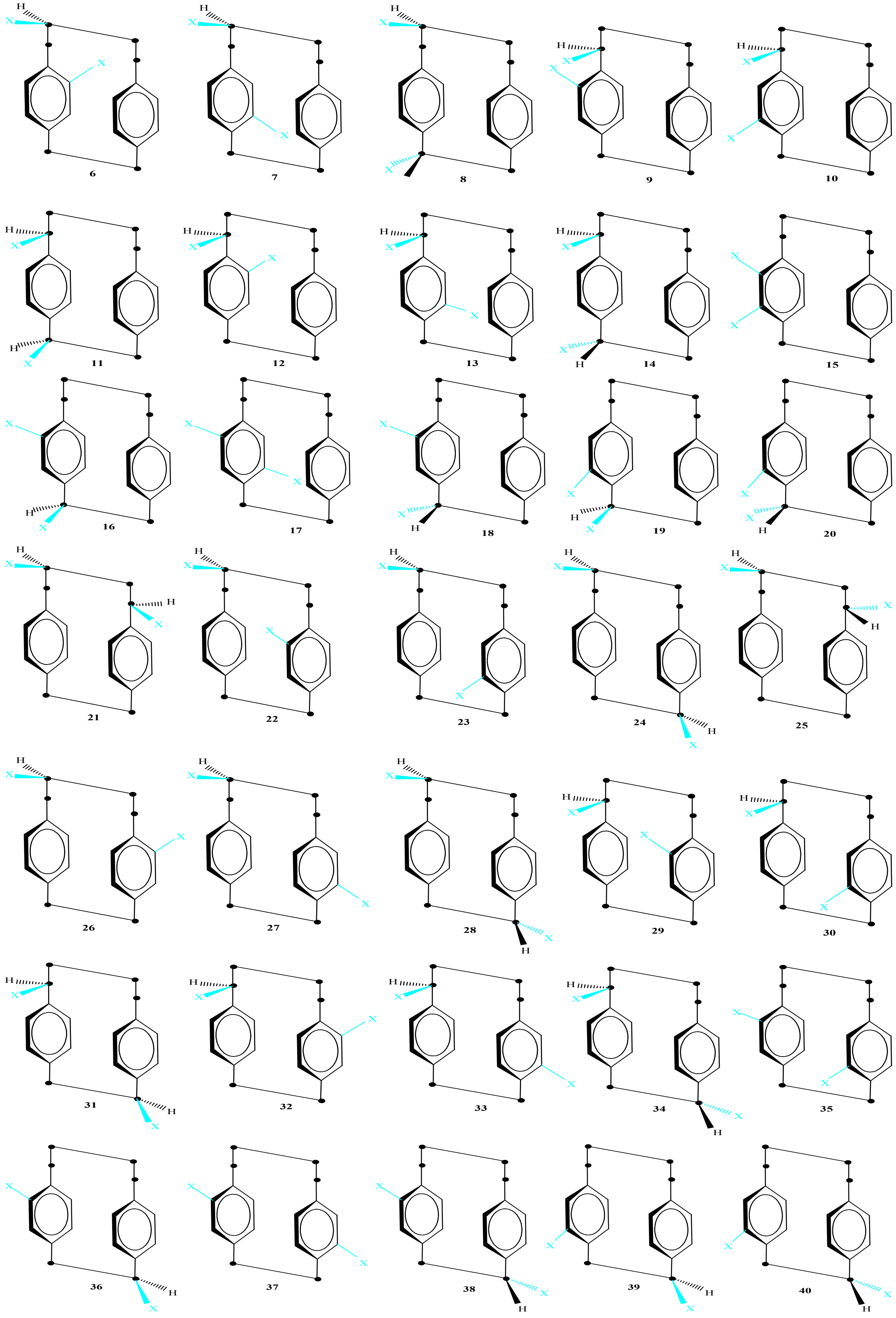


Fig. 2a: 40 C_1 chiral molecular graphs

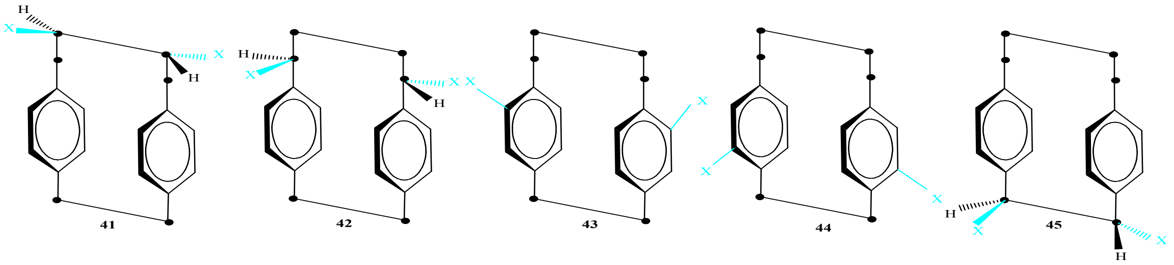


Fig. 2b: 5 C_2 chiral molecular graphs

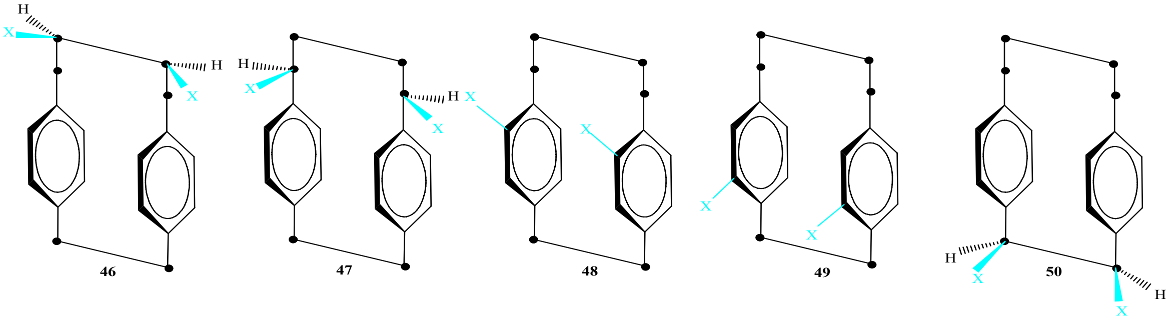


Fig. 2c: 5 C_s achiral molecular graphs

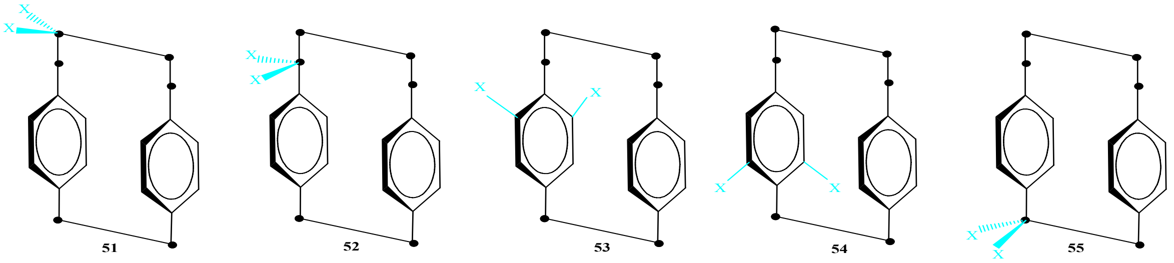


Fig. 2d: 5 C'_s achiral molecular graphs

CONCLUSION

The enumeration with symmetry characterization of stereo and position isomers of Ho[4.2]PCPs and He[4.2]PCPs derivatives have shown that the chirality of these series of polycyclic hydrocarbons having two benzene deck rings tethered at para position to two carbon chains, is controlled by the parity of the degrees of substitution as follows;

(i) Odd degrees of homo- or hetero –polysubstitution yield only C_1-chiral isomers,

(ii) Even degrees of homo- or hetero –polysubstitution yield a dominant class of C_1-chiral isomers together with three degenerate classes having respectively the C_2, C_s and C'_s symmetries and the same isomer number.

(iii) C_{2v} achiral isomers resulting from higher degrees of homo or hetero poly substitution satisfying the restriction $q_i = 4N$ modulo 0.

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