Acta Chimica & Pharmaceutica Indica

Acta Chim. Pharm. Indica: 3(3), 2013, 201-211
ISSN 2277-288X

COMBINATORIAL ENUMERATION AND SYMMETRY CHARACTERIZATION OF HOMO POLYSUBTITUTED[3.3]-PARACYCLOPHANE DERIVATIVES

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(*Received : 22.07.2013; Revised : 27.07.2013; Accepted : 29.07.2013*)

ABSTRACT

A combinatorial enumeration using the unit-subduced-cycle index approach with symmetry chararacterisation is carried out for homopolysubstituted [3.3]-paracyclophane derivatives having the empirical formula $\phi_2C_6H_{q_0}X_{q_1}$ where X is a non isomerisable ligand and where the greek ϕ symbol represents the hydrogen depleted benzene ring.

Key words: Homopolysubstitution, [3.3]-paracyclophane, Unit-subduced-cycle index, Coset representation, Subduction, Isomer count matrix, Degenerate subsymmetry.

INTRODUCTION

The [3.3] PCP is is a polycyclic hydrocarbon considered as a pivotal structure, which is intermediate in ring size between [2.2] PCP, where ring strain and transannular effects are pronounced and [4.4] PCP where these effects are reduced[1]. The satisfactory routes for its preparation use the acyloin ring closure[2,3] or the solvolytic ring expansion from [2.2] PCP[4] and its chemical and physical properties have been reported in the literature[5,6].

The focus of this study is to present a combinatorial enumeration detailing the symmetries of stereo and position isomers of homopolysubstituted-[3.3]-paracyclophane (Ho[3.3]PCP) derivatives symbolized by the empirical formula $\phi_2 C_6H_{q_0}X_{q_1}$, where ϕ represents the hydrogen depleted benzene ring and the subscripts q_0 and q_1 are respectively the numbers of unsubstituted hydrogen atoms and the degree of homopoly-substitution with non isomerisable ligands of type X.

Mathematical formulation of the combinatorial method

Let us consider Fig. 1 as the tridimensional graph or stereograph of the parent [3.3] PCP, which has been oriented according to the convention used by Ron and Schnepp[7].

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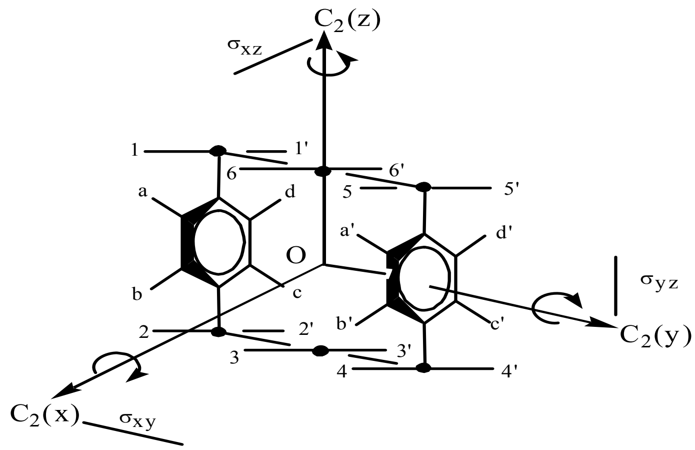

Fig. 1: Stereograph of [3.3]-PCP

In accordance with the results of previous structural studies[8], we assign to this representation the symmetry point group D_{2h}. This abelian group[9] consists of 8 symmetry operations listed in Eq. 1:

$$D_{2h} = \{I, C_2(z), C_{2(y)}, C_{2(x)}, \sigma_{(xy)}, i, \sigma_{(yz)}, \sigma_{(xz)}\} \qquad \ldots(1)$$

and partitioned into 8 equivalence classes given in Eq. 2:

$$\{E\};\ \{C_{2(z)}\};\ \{C_{2(y)}\};\ \{C_{2(x)}\};\ \{C_{2(xy)}\};\ \{i\};\ \{\sigma_{(yz)}\};\ \{\sigma_{(xz)}\} \qquad \ldots(2)$$

These latter generate a set of 5 chiral subgroups comprising $C_1, C_2, C'_2, C''_2,$ and D_2 and a second set of 11 achiral subgroups which are $C_s, C'_s, C''_s, C_i, C_{2v}, C'_{2v}, C''_{2v}, C_{2h}, C'_{2h}, C'_{2h}$ and D_{2h} given in Table 1 with their respective symmetry operations.

Table 1: Subgroups of D_{2h}

Subgroups	Symmetries opérations	Chirality
C_1	$\{I\}$	Chiral
C_2	$\{I, C_{2(x)}\}$ $\{I, C_{2(y)}\}$ $\{I, C_{2(x)}\}$	Chiral
C'_s	$\{I, C_{2(x)}\}$	Chiral
C''_2	$\{I, C_{2(x)}\}$	Chiral
C_s	$\{I, \sigma_{(xy)}\}$	Achiral
C'_s	$\{I, \sigma_{(xy)}\}$	Achiral
C''_s	$\{I, \sigma_{(yz)}\}$	Achiral
C_i	$\{I, i\}$	Achiral
D_2	$\{I, C_{2(z)}, C_{2(y)}, C_{2(x)}\}$	Chiral
C_{2v}	$\{I, C_{2(z)}, \sigma_{(yz)}, \sigma_{(xz)}\}$	Achiral
C'_{2v}	$\{I, C_{2(y)}, \sigma_{(xy)}, \sigma_{(yz)}\}$	Achiral
C''_{2v}	$\{I, C_{2(x)}, \sigma_{(xy)}, \sigma_{(xz)}\}$	Achiral
C_{2h}	$\{I, C_{2(z)}, \sigma_{(xy)}, i\}$	Achiral

Cont…

Subgroups	Symmetries opérations	Chirality
C'_{2h}	$\{I, C_{2(y)}, \sigma_{(xz)}, i\}$	Achiral
C''_{2h}	$\{I, C_{2(x)}, \sigma_{(yz)}, i\}$	Achiral
D_{2h}	$\{I, C_{2(z)}, C_{2(y)}, C_{2(x)}, \sigma_{(xy)}, i, \sigma_{(yz)}, \sigma_{(xz)}\}$	Achiral

These 16 subgroups construct a non redundant set of subgroups[10,11] for D_{2h} denoted $SSG_{D_{2h}}$, which is given in Eq. 3:

$$SSG_{D_{2h}} = \{C_1, C_2, C'_2, C''_2, C_s, C'_s, C''_s, C_i, D_2, C_{2v}, C'_{2v}, C''_{2v}, C_{2h}, C'_{2h}, C''_{2h}, D_{2h}\} \quad \ldots(3)$$

The elements of the complete set of coset representations for D_{2h} denoted $SCR_{D_{2h}}$, which are in a univoque correspondence with the elements of $SSG_{D_{2h}}$ are listed in Eq. 4:

$$SCR_{D_{2h}} = \left\{\begin{array}{l} D_{2h}(/C_1), D_{2h}(/C_2), D_{2h}(/C'_2), D_{2h}(/C''_2), D_{2h}(/C_s), D_{2h}(/C'_s), D_{2h}(/C''_s), \\ D_{2h}(/C_i), D_{2h}(/D_2), D_{2h}(/C_{2v}), D_{2h}(/C'_{2v}), D_{2h}(/C''_{2v}), D_{2h}(/C_{2h}), D_{2h}(/C'_{2h}), \\ D_{2h}(/C''_{2h}), D_{2h}(/D_{2h}) \end{array}\right\} \quad \ldots(4)$$

The term designating each coset representation includes the global symmetry D_{2h} followed by a subgroup $G_i \in SCR_{D_{2h}}$. The explicit forms of these coset representations are given as follows:

$$D_{2h}(/C_1) = C_1\, I + C_1C_{2(x)} + C_1C_{2(y)} + C_1C_{2(x)} + C_1\sigma_{(xy)} + C_1\, i + C_1\sigma_{(yz)} + C_1\sigma_{(xz)} \quad \ldots(5)$$

$$D_{2h}(/C_2) = C_2\, I + C_2C_{2(y)} + C_2\sigma_{(xy)} + C_2\sigma_{(yz)} \quad \ldots(6)$$

$$D_{2h}(/C'_2) = C'_2\, I + C'_2C_{2(z)} + C'_2\sigma_{(xy)} + C'_2 i \quad \ldots(7)$$

$$D_{2h}(/C''_2) = C''_2\, I + C''_2C_{2(z)} + C''_2\sigma_{(xy)} + C''_2 i \quad \ldots(8)$$

$$D_{2h}(/C_s) = C_s\, I + C_sC_{2(z)} + C_sC_{2(y)} + C_sC_{2(x)} \quad \ldots(9)$$

$$D_{2h}(/C'_s) = C'_s\, I + C'_sC_{2(z)} + C'_sC_{2(y)} + C'_sC_{2(x)} \quad \ldots(10)$$

$$D_{2h}(/C''_s) = C''_s\, I + C''_sC_{2(z)} + C''_sC_{2(y)} + C''_sC_{2(x)} \quad \ldots(11)$$

$$D_{2h}(/C_i) = C_i\, I + C_iC_{2(z)} + C_iC_{2(y)} + C_iC_{2(x)} \quad \ldots(12)$$

$$D_{2h}(/C_{2v}) = C_{2v}\, I + C_{2v}C_{2(y)} \quad \ldots(13)$$

$$D_{2h}(/C'_{2v}) = C'_{2v}\, I + C'_{2v}C_{2(z)} \quad \ldots(14)$$

$$D_{2h}(/C''_{2v}) = C''_{2v}\, I + C''_{2v}C_{2(z)} \quad \ldots(15)$$

$$D_{2h}(/C_{2h}) = C_{2h}\, I + C_{2h}C_{2(y)} \quad \ldots(16)$$

$$D_{2h}(/C'_{2h}) = C'_{2h}\, I + C'_{2h}C_{2(z)} \quad \ldots(17)$$

$$D_{2h}(/C''_{2h}) = C''_{2h}\, I + C''_{2h}C_{2(z)} \quad \ldots(18)$$

$$D_{2h}(/D_2) = D_2\ I + D_2\sigma_{(xy)} \qquad \ldots(19)$$

$$D_{2h}(/D_{2h}) = D_{2h}\ I \qquad \ldots(20)$$

By multiplying the right hand side terms of Eqs. 5-20 by each symmetry operation of D_{2h}, we permute the elements of each CR. Then, we obtain a row vector of marks assign to a CR by counting invariant elements related to each subgroup. The sixteen row vectors of marks generated by these operations form the Table of marks for D_{2h} denoted $M_{D_{2h}}$, which is given hereafter:

$$M_{D_{2h}} = \begin{pmatrix}
8&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
4&4&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
4&0&4&0&0&0&0&0&0&0&0&0&0&0&0&0\\
4&0&0&4&0&0&0&0&0&0&0&0&0&0&0&0\\
4&0&0&0&4&0&0&0&0&0&0&0&0&0&0&0\\
4&0&0&0&0&4&0&0&0&0&0&0&0&0&0&0\\
4&0&0&0&0&0&4&0&0&0&0&0&0&0&0&0\\
4&0&0&0&0&0&0&4&0&0&0&0&0&0&0&0\\
2&2&2&2&0&0&0&0&2&0&0&0&0&0&0&0\\
2&2&0&0&0&2&2&0&0&2&0&0&0&0&0&0\\
2&0&2&0&2&2&0&0&0&0&2&0&0&0&0&0\\
2&0&0&2&2&0&2&0&0&0&0&2&0&0&0&0\\
2&2&0&0&0&0&0&2&0&0&0&0&2&0&0&0\\
2&0&2&0&0&0&2&2&0&0&0&0&0&2&0&0\\
2&0&0&2&0&2&0&2&0&0&0&0&0&0&2&0\\
1&1&1&1&1&1&1&1&1&1&1&1&1&1&1&1
\end{pmatrix}$$

The corresponding inverse of this mark table denoted M^{-1}_{D2h} is obtained from Eq. 21 :

$$M_{D2h}\ M^{-1}_{D2h} = I \qquad \ldots(21)$$

where I represents the 16 x 16 identity matrix.

$$M^{-1}_{D_{2h}} = \begin{pmatrix}
1/8&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
-1/8&1/4&0&0&0&0&0&0&0&0&0&0&0&0&0&0\\
-1/8&0&1/4&0&0&0&0&0&0&0&0&0&0&0&0&0\\
-1/8&0&0&1/4&0&0&0&0&0&0&0&0&0&0&0&0\\
-1/8&0&0&0&1/4&0&0&0&0&0&0&0&0&0&0&0\\
-1/8&0&0&0&0&1/4&0&0&0&0&0&0&0&0&0&0\\
-1/8&0&0&0&0&0&1/4&0&0&0&0&0&0&0&0&0\\
-1/8&0&0&0&0&0&0&1/4&0&0&0&0&0&0&0&0\\
1/4&-1/4&-1/4&-1/4&0&0&0&0&1/2&0&0&0&0&0&0&0\\
1/4&-1/4&0&0&0&-1/4&-1/4&0&0&1/2&0&0&0&0&0&0\\
1/4&0&-1/4&0&-1/4&-1/4&0&0&0&0&1/2&0&0&0&0&0\\
1/4&0&0&-1/4&-1/4&0&-1/4&0&0&0&0&1/2&0&0&0&0\\
1/4&-1/4&0&0&0&0&0&-1/4&0&0&0&0&1/2&0&0&0\\
1/4&0&-1/4&0&0&0&-1/4&-1/4&0&0&0&0&0&1/2&0&0\\
1/4&0&0&-1/4&0&2&0&-1/4&0&0&0&0&0&0&1/2&0\\
-1&1/2&1/2&1/2&1/2&1/2&1/2&1/2&-1/2&-1/2&-1/2&-1/2&-1/2&-1/2&-1/2&1
\end{pmatrix}$$

The 20 hydrogen atoms of the parent [3.3]-PCP depicted in Figure 1 by alphabetical and numerical labels constitute 3 distinct sets of equivalent atoms or orbits Δ_1, Δ_2 and Δ_3 given hereafter:

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

To assign an appropriate CR to Δ_1, Δ_2 and Δ_3, we find the largest subgroup that keeps each orbit invariant. The subgroup C1 keeps all the elements of Δ_1 and Δ_3 unchanged. Therefore, the coset representation governing Δ_1 and Δ_3 is denoted D_{2h} $(/C_1)$ and that one governing Δ_2 is denoted $D_{2h}(/C_s^{''})$.

RESULTS AND DISCUSSION

The subduction of coset representation is a mathematical proce dure largely discussed by Fujita[12,13]. In this paper, we have operated the subductions of the coset representation $D_{2h}(/C_1)$ and $D_{2h}(/C_s^{''})$ by all subgroups of D_{2h}. These operations of subduction are symbolized by Eq. 22 and 23:

$$D_{2h}(/C_1)\downarrow G_i=\beta_i G_i(/C_1) \quad \ldots(22)$$

$$D_{2h}(/C_s^{''})\downarrow G_i=\gamma_i G_i(/C_j) \quad \ldots(23)$$

where β_i and γ_i are positive integer numbers and $G_i \in SSG_{D_{2h}}$. The results obtained are given in column 1 and 2 of Table 2. Then we use Eq. 24 and 25 to transform the term in the right hand side of Eq. 22 and 23, respectively as follows:

$$\beta_i G_i(/C_1)\rightarrow S_{d_i}^{\beta_i} \quad \ldots(24)$$

$$\gamma_i G_i(/G_j)\rightarrow S_{k_i}^{\gamma_i} \quad \ldots(25)$$

In these expressions $S_{d_i}^{\beta_i}$ and $S_{k_i}^{\gamma_i}$ are respectively unit-subduced-cycle-index (USCI) having the superscripts β_i and γ_i previously defined, the subscripts $d_i=\frac{|G_i|}{|C_1|}$ and $k_i=\frac{|G_i|}{|G_j|}$. The notations $|G_i|$, $|G_j|$ and $|\mathbf{C}_1|$ are the cardinalities of these respective subgroups. The USCIs obtained are reported in columns 3, 4 and 5 of Table 2 for Δ_1, Δ_2 and Δ_3, respectively. The product $S_{d_i}^{\beta_i}.S_{d_i}^{\beta_i}.S_{k_i}^{\gamma_i}$ of different USCIs in each row gives rise to the term $S_{d_i}^{2\beta_i+\gamma_i}$ (if $d_i = k_i$) or $S_{d_i}^{2\beta_i}.S_{k_i}^{\gamma_i}$ (if $d_i \neq k_i$) which is the global USCI for the subgroup considered. For example the global USCI for the subsymmetry C_1 is: $s_1^8\times s_1^4\times s_1^8=s_1^{20}$.

Table 2: Subductions of $D_{2h}(/C_1)$ and $D_{2h}(/C_s^{''})$ and resulting USCIs

Subductions		Δ_1	Δ_2	Δ_3	Global USCI
$D_{2h}(/C_1)\downarrow C_1=8C_1(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_1=4C_1(/C_1)$	S_1^8	S_1^4	S_1^8	S_1^{20}
$D_{2h}(/C_1)\downarrow C_2=4C_2(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_2=2C_2(/C_1)$	S_2^4	S_2^2	S_2^4	S_2^{10}

Cont…

Subductions		Δ_1	Δ_2	Δ_3	**Global USCI**
$D_{2h}(/C_1)\downarrow C_2^{'} = 4C_2^{'}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_2^{'} = 2C_2^{'}(/C_1)$	S_2^4	S_2^2	S_2^4	S_2^{10}
$D_{2h}(/C_1)\downarrow C_2^{''} = 4C_2^{''}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_2^{''} = 2C_2^{''}(/C_s^{''})$	S_2^4	S_2^2	S_2^4	S_2^{10}
$D_{2h}(/C_1)\downarrow C_s = 4C_s(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_s = 2C_s(/C_1)$	S_2^4	S_2^2	S_2^4	S_2^{10}
$D_{2h}(/C_1)\downarrow C_s^{'} = 4C_s^{'}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_s^{'} = 2C_s^{'}(/C_1)$	S_2^4	S_2^2	S_2^4	S_2^{10}
$D_{2h}(/C_1)\downarrow C_s^{''} = 4C_s^{''}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_s^{''} = 2C_s^{''}(/C_s^{''})$	S_2^4	S_1^4	S_2^4	$S_2^8\,S_1^4$
$D_{2h}(/C_1)\downarrow C_i = 4C_i(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_i = 2C_i(/C_1)$	S_2^4	S_2^2	S_2^4	S_2^{10}
$D_{2h}(/C_1)\downarrow D_2 = 2D_2(/C_1)$	$D_{2h}(/C_s^{''})\downarrow D_2 = D_2(/C_1)$	S_4^2	S_4^1	S_4^2	S_4^5
$D_{2h}(/C_1)\downarrow C_{2v} = 2C_{2v}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2v} = C_{2v}(/C_s^{''})$	S_4^2	S_2^2	S_4^2	$S_4^4\,S_2^2$
$D_{2h}(/C_1)\downarrow C_{2v}^{'} = 4C_{2v}^{'}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2v}^{'} = C_{2v}^{'}(/C_1)$	S_4^2	S_4^1	S_4^2	S_4^5
$D_{2h}(/C_1)\downarrow C_{2v}^{''} = 2C_{2v}^{''}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2v}^{''} = C_{2v}^{''}(/C_s^{''})$	S_4^2	S_2^2	S_4^2	$S_4^4\,S_2^2$
$D_{2h}(/C_1)\downarrow C_{2h} = 2C_{2h}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2h} = C_{2h}(/C_1)$	S_4^2	S_4^1	S_4^2	S_4^5
$D_{2h}(/C_1)\downarrow C_{2h}^{'} = 2C_{2h}^{'}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2h}^{'} = C_{2h}^{'}(/C_s^{''})$	S_4^2	S_2^2	S_4^2	$S_4^4\,S_2^2$
$D_{2h}(/C_1)\downarrow C_{2h}^{''} = 2C_{2h}^{''}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2h}^{''} = C_{2h}^{''}(/C_1)$	S_4^2	S_4^1	S_4^2	S_4^5
$D_{2h}(/C_1)\downarrow C_{2h} = D_{2h}(/C_1)$	$D_{2h}(/C_s^{''})\downarrow C_{2h} = C_{2h}(/C_s^{''})$	S_8^1	S_4^1	S_8^1	$S_4^2\,S_4^1$

To obtain the generating function $F(X^{q_1}) = \sum_{q_1=0}^{20} A_{q_1} X^{q_1}$ from the USCI approach, we have made the following transformations given in Eqs. 26-27 for each subsymmetry $G_i \in D_{2h}$:

$$G_i \rightarrow s_{d_i}^{2\beta_i} \times s_{k_i}^{\gamma_i} = (1+x^{d_i})^{2\beta_i}(1+x^{k_i})^{\gamma_i} = \sum_{q_1=0}^{20} A_{q_1} X^{q_1} = F(X^{q_1}) \qquad \ldots(26)$$

where $0 \le q_1 \le 2\beta_i d_i + \lambda_i k_i$ and $2\beta_i d_i + \lambda_i k_i = 20$

or

$$G_i \rightarrow s_{d_i}^{2\beta_i} \times s_{k_i}^{\gamma_i} = (1+x^{d_i})^{2\beta_i+\gamma_i} = \sum_{q=0}^{20} A^{q_1} X^{q_1} = F(X^{q_1}) \qquad \ldots(27)$$

where $0 \le q_1 \le 2\beta_i d_i + \lambda_i d_i$ and $2\beta_i d_i + \lambda_i d_i = 20$

The following generating functions have been obtained:

$$\begin{aligned} C_1 \rightarrow s_1^{20}(1+x)^{20} = {} & x^{20} + 20x^{19} + 190x^{18} + 1140x^{17} + 4845x^{16} + 15504x^{15} + 38760x^{14} + 77520x^{13} \\ & + 125970x^{12} + 167960x^{11} + 184756x^{10} + 167960x^{9} + 125970x^{8} + 77520x^{7} \\ & + 38760x^{6} + 15504x^{5} + 4845x^{4} + 1140x^{3} + 190x^{2} + 20x + 1 \end{aligned}$$

$$C_2, C_2^{'}, C_2^{''}, C_s, C_s^{'}, C_i \rightarrow s_2^{10} \rightarrow (1+x^2)^{10} = x^{20} + 10x^{18} + 45x^{16} + 120x^{14} + 210x^{12} + 252x^{10} + 210x^8 + 120x^6 + 45x^4 + 10x^2 + 1$$

$$s_s^{''} \rightarrow s_2^8 s^4 \rightarrow (1+x^2)^8 (1+x)^4 = x^{20} + 4x^{19} + 14x^{18} + 36x^{17} + 77x^{16} + 144x^{15} + 232x^{14} + 336x^{13} + 434x^{12} + 504x^{11} + 532x^{10} + 504x^9 + 434x^8 + 336x^7 + 232x^6 + 144x^5 + 77x^4 + 36x^3 + 14x^2 + 4x + 1$$

$$D_2, C_{2v}^{'}, C_{2h}, C_{2h}^{''} \rightarrow s_4^5 \rightarrow (1+x^4)^5 = x^{20} + 5x^{16} + 10x^{12} + 10x^8 + 5x^4 + 1$$

$$D_{2v}, C_{2v}^{''}, C_{2h}^{'} \rightarrow s_4^4 s_2^2 \rightarrow (1+x^4)^4 (1+x^2)^2 = x^{20} + 2x^{18} + 5x^{16} + 8x^{14} + 10x^{12} + 12x^{10} + 10x^8 + 8x^6 + 5x^4 + 2x^2 + 1$$

and similarly $D_{2h} \rightarrow s_8^2 s_4^1 \rightarrow (1+x^8)^2 (1+x^4) = x^{20} + x^{16} + 2x^{12} + 2x^8 + x^4 + 1$

The coefficients of the aforementioned polynomials are collected together to form the fixed point matrix FPM (X^{q_1}) given hereafter :

FPM : (x^{q_1}) =

	C_1	C_2	$C_2^{'}$	$C_2^{''}$	C_s	$C_s^{'}$	$C_s^{''}$	C_i	D_2	C_{2v}	$C_{2v}^{'}$	$C_{2v}^{''}$	C_{2h}	$C_{2h}^{'}$	$C_{2h}^{''}$	D_{2h}
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
x	20	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0
x^2	190	10	10	10	10	10	14	10	0	2	0	2	0	2	0	0
x^3	1140	0	0	0	0	0	36	0	0	0	0	0	0	0	0	0
x^4	4845	45	45	45	45	45	77	45	5	5	5	5	5	5	5	1
x^5	15504	0	0	0	0	0	144	0	0	0	0	0	0	0	0	0
x^6	38760	120	120	120	120	120	232	120	0	8	0	8	0	8	0	0
x^7	77520	0	0	0	0	0	336	0	0	0	0	0	0	0	0	0
x^8	125970	210	210	210	210	210	434	210	10	10	10	10	10	10	10	2
x^9	167960	0	0	0	0	0	504	0	0	0	0	0	0	0	0	0
x^{10}	184756	252	252	252	252	252	532	252	0	12	0	12	0	12	0	0
x^{11}	167960	0	0	0	0	0	504	0	0	0	0	0	0	0	0	0
x^{12}	125970	210	210	210	210	210	434	210	10	10	10	10	10	10	10	2
x^{13}	77520	0	0	0	0	0	336	0	0	0	0	0	0	0	0	0
x^{14}	38760	120	120	120	120	120	232	120	0	8	0	8	0	8	0	0
x^{15}	15504	0	0	0	0	0	144	0	0	0	0	0	0	0	0	0
x^{16}	4845	45	45	45	45	45	77	45	5	5	5	5	5	5	5	1
x^{17}	1140	0	0	0	0	0	36	0	0	0	0	0	0	0	0	0
x^{18}	190	10	10	10	10	10	14	10	0	2	0	2	0	2	0	0
x^{19}	20	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0
x^{20}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

The corresponding isomer count matrix ICM (X^{q_1}) is derived from Eq. 26:

$$ICM\ (X^{q_1}) = FPM\ (X^{q_1}) . M_{D_{2h}}^{-1} \qquad \text{...(28)}$$

where $M_{D_{2h}}^{-1}$ represent the inverse of the mark table aforementioned. The result obtained is a rectangular matrix of itemized isomers numbers given hereafter with respect to each sub symmetry of D_{2h}.

$ICM(x^{q_i}) =$

	C_1	C_2	$C_2^{'}$	$C_2^{''}$	C_s	$C_s^{'}$	$C_s^{''}$	C_i	D_2	C_{2v}	$C_{2v}^{'}$	$C_{2v}^{''}$	C_{2h}	$C_{2h}^{'}$	$C_{2h}^{''}$	D_{2h}
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
x	2	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
x^2	16	2	2	2	2	2	2	2	0	2	0	2	0	2	0	0
x^3	138	0	0	0	0	0	9	0	0	0	0	0	0	0	0	0
x^4	570	8	8	8	8	8	16	8	2	2	2	2	2	2	2	1
x^5	1920	0	0	0	0	0	36	0	0	0	0	0	0	0	0	0
x^6	4732	28	28	28	28	28	52	28	0	4	0	4	0	4	0	0
x^7	9648	0	0	0	0	0	84	0	0	0	0	0	0	0	0	0
x^8	15550	46	46	46	46	46	102	46	4	4	4	4	4	4	4	2
x^9	20932	0	0	0	0	0	126	0	0	0	0	0	0	0	0	0
x^{10}	22848	60	60	60	60	60	124	60	0	6	0	6	0	6	0	0
x^{11}	20932	0	0	0	0	0	126	0	0	0	0	0	0	0	0	0
x^{12}	15550	46	46	46	46	46	102	46	4	4	4	4	4	4	4	2
x^{13}	9648	0	0	0	0	0	84	0	0	0	0	0	0	0	0	0
x^{14}	4732	28	28	28	28	28	52	28	0	4	0	4	0	4	0	0
x^{15}	1920	0	0	0	0	0	36	0	0	0	0	0	0	0	0	0
x^{16}	570	8	8	8	8	8	16	8	2	2	2	2	2	2	2	1
x^{17}	138	0	0	0	0	0	9	0	0	0	0	0	0	0	0	0
x^{18}	16	2	2	2	2	2	2	2	0	2	0	2	0	2	0	0
x^{19}	2	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
x^{20}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

Symmetry characterization of enumerated Ho(3.3) PCPs.

The chirality fittingness of Ho(3.3) PCPs is governed by the parity of the degree of homopoly-substitution q_1 according to the following rules :

q_1 Odd: For q_1 odd only C_1-chiral isomers and $C_s^{''}$-achiral isomers are formed for the system $\phi_2C_6H_{q_0}X_{q_1}$.

q_1 Singly even: If the degree of homopolysubstitution q_1 is singly even in the system $\phi_2C_6H_{q_0}X_{q_1}$ the occurrence of chiral isomers is allowed for the subsymmetries $C_1, C_2, C_2^{'}, C_2^{''}$ where C_1 is the dominantclass and $C_2, C_2^{'}, C_2^{''}$ is a triply degenerate second class. In this case $A_{q1}(C_1) = A_{q1}(C_2) = A_{q1}(C_2^{'}) = A_{q1}(C_2^{''})$.

When $q_1 > 2$, is singly even the occurrence of achiral isomers is allowed for the subsymmetries $C_s, C_s^{'}, C_s^{''}, C_i, C_{2v}, C_{2v}^{''}, C_{2h}^{'}$, where $C_s^{''}$ is the dominant and where $C_s, C_s^{'}, C_i$ and $C_{2v}, C_{2v}^{''}, C_{2v}^{'}$ are respectively the first and the second triply degenerate classes of subsymmetries.

Hence, $A_{q1}(C_s^{''}) = A_{q1}(C_s) = A_{q1}(C_s^{'}) = A_{q1}(C_i) = A_{q1}(C_{2v}) = A_{q1}(C_{2v}^{''}) = A_{q1}(C_{2h}^{''})$.

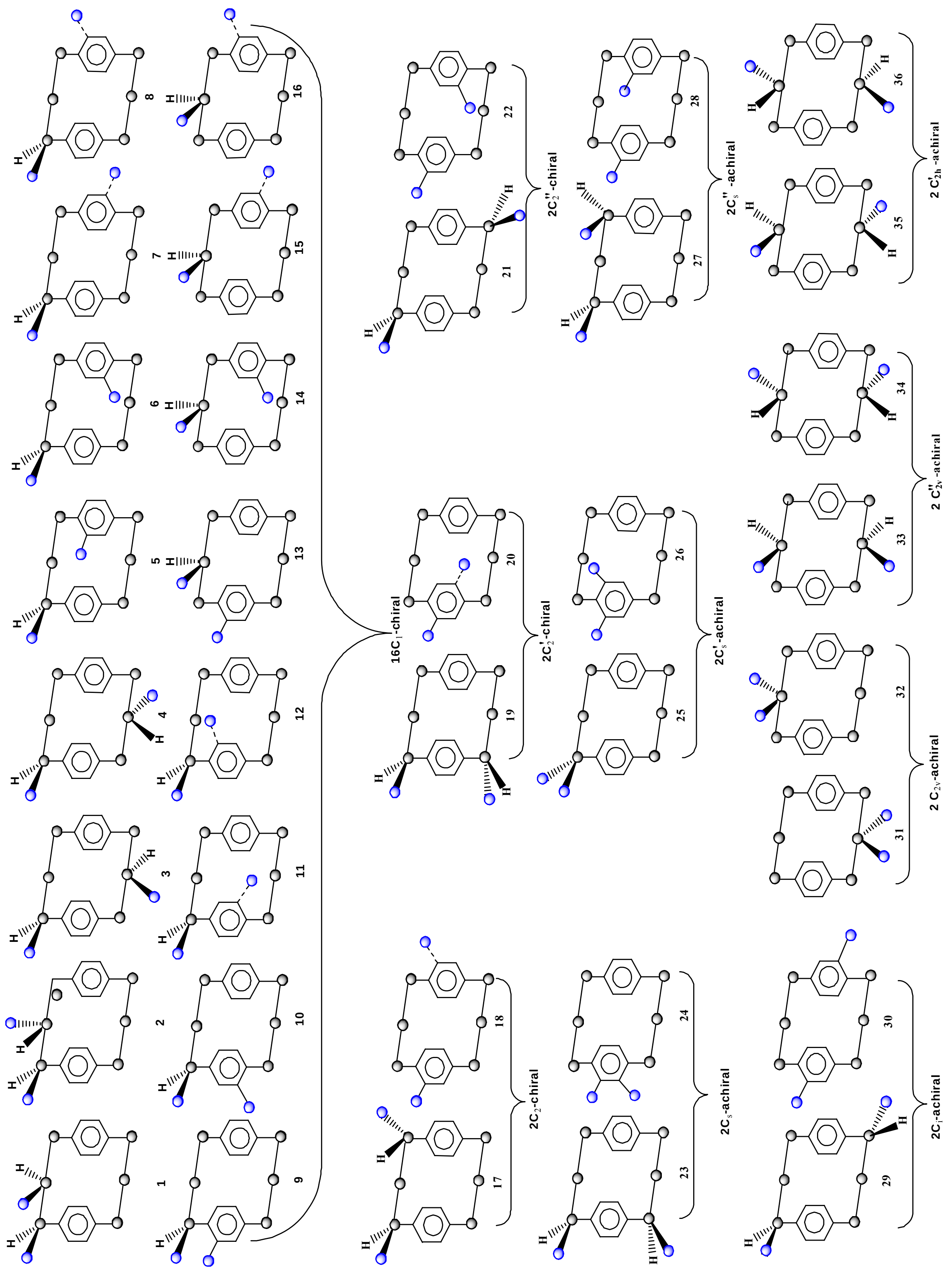

Fig. 2: Molecular graphs presenting 22 chiral and 14 achiral graphs of homodisubstituted [3.3] PCPs

q_1 Doubly even: If the degree of homopolysubstitution q_1 is doubly even in the system $\phi_2C_6H_{q_0}X_{q_1}$ the occurrence of chiral isomers is allowed for the subsymmetries C_1, C_2, C_2', C_2'' and D_2. The C_1-chiral isomers are dominant over C_2, C_2', C_2'' which constitute a triply degenerate second class and D_2 the third class. In this case $A_{q1}(C_1) = A_{q1}(C_2) = A_{q1}(C_2') = A_{q1}(C_2'') = A_{q1}(D_2)$.

The occurrence of achiral isomers is allowed for the following 11 subsymmetries: C_s, C_s', $C_s'', C_i, C_{2v}, C_{2v}', C_{2v}'', C_{2h}, C_{2h}', C_{2h}'', D_{2h}$, which may be classified in accordance with the magnitude of the integer value A_{q1} into 4 distinct equivalent classes as follows: $\{C_s''\}, \{C_s, C_s', C_i\}$, $\{C_{2v}, C_{2v}', C_{2v}'', C_{2h}, C_{2h}', C_{2h}''\}$ and $\{D_{2h}\}$. The results given in the rows of ICM (X^{q1}) show that the abundance of stereo and position isomers for $\phi_2C_6H_{q0}X_{q1}$ decrease in the following order: $A_{q1}(C_s'') = A_{q1}\{C_s, C_s', C_i\} = A_{q1}$ $\{C_{2v}$, $\{C_{2v}', C_{2v}'', C_{2h}, C_{2h}', C_{2h}''\} = A_{q1}(D_{2h})$.

These assumptions are verified by the results given in the rows of the ICM (X^{q_1}) for any q_1 odd or even in the system $\phi_2C_6H_{q_0}X_{q_1}$. It is to be noticed that for $q_1 = 2$ the coefficients of X^2 in the third row of the ICM (X^{q_1}) reveals that the system $\phi_2C_6H_{18}X_2$ exhibits 36 homodisubstituted [3.3] paracyclophane derivatives and 16 of them belong to C_1 while only 2 are assigned to each subsymmetry classified in the following 3 degenerate classes $\{C_2, C_2', C_2''\}$, $\{C_s, C_s', C_s'', C_i\}$, $\{C_{2v}, C_{2v}'', C_{2h}'\}$. The molecular graphs for these stereoisomers are given in Fig. 2, where one can depict that inter annular homodisubstitution yields derivatives having their 2 ligands in position pseudo-meta (**18**), pseudo ortho (**22**), pseudo gem (**28**) and pseudo para (**30**).

CONCLUSION

The enumeration of Ho(3.3) PCPs derivatives have shown that the chirality of this polycyclic hydrocarbon is controlled by the parity of the degree of homopolysubstitution as follows :

- An odd degree of homopolysubstitution yields only C_1-chiral isomers and C_s'' achiral isomers.

- A singly even degree of homopolysubstitution yields:

(i) A dominant class of C_1-chiral isomers together with 3 degenerate subsymmetries C_2, C_2', C_2'' having respectively the same number of chiral isomers.

(ii) A dominant class of C_s'' achiral isomers together with 3 degenerate subsymmetries C_s, C_s', C_i with equivalent number of achiral isomers.

(iii) A doubly even degree of homopolysubstitution yields:

(iv) A dominant class of C_1-chiral isomers together with 3 degenerate classes C_2, C_2', C_2'' - and 1 class of D_2 chiral isomers.

(v) A dominant class of C_s'' -achiral isomers together with 3 degenerate classes $\{C_s, C_s', C_i\}$ followed by 6 degenerate classes $\{C_{2v}, C_{2v}', C_{2v}'', C_{2h}, C_{2h}', C_{2h}''\}$ and a single $\{D_{2h}\}$ class of achiral isomers.

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