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COMBINATORIAL ENUMERATION AND SYMMETRY CHARACTERIZATION OF HOMODISUBTITUTED [2,2] PARACYCLOPHANE DERIVATIVES

ROBERT M. NEMBA*, PATOUOSSA ISSOFA and A. EMADAK

Faculty of Sciences, Laboratory of Physical and Theoretical Chemistry, University of Yaoundé I, P.O. Box – 812, YAOUNDE I, CAMEROON

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ABSTRACT

A method of combinatorial enumeration of stereo and position isomers of homodisubstituted [2,2] paracyclophane derivatives having the empirical formula $\varphi_2C_4H_{14}X_2$ where X is a non isomerisable substituent and the symbol φ represents the hydrogen depleted benzene ring is presented. The 16 substitution sites of the [2,2]-PCP are regarded as an orbit assigned to the coset representation $D_{2h}(/C_1)$. The subductions of this coset representation by all subgroups of D_{2h} are calculated and the combinatorial enumeration with symmetry chararacterization performed by virtue of the unit-subduced-cycle-index (USCI) approach.

Key words: Homodisubstituted paracyclophane, Coset representation, Subduction, Unit-subduced-cycle-index isomer count vector, Combinatorial enumeration.

INTRODUCTION

In 1949, Brown and Farthing[1] had obtained the [2,2] paracyclophane ([2,2]-PCP), which is the first member of the series of [n-m]-paracyclophanes, accidentally as a product of the pyrolytic polymerization of xylene into poly-para-xylene. Since this date, the syntheses and characterization of homo or hetero polysubstituted [2,2]-PCP derivatives has become very attractive.

Recent studies[2,3] have reported that such molecules are interesting because they exhibit structural, optical and electronic properties substantially different from their more common one of two dimension counterparts. These properties have led [2,2]-PCP derivatives to be employed in a wide range of disciplines including polymer, material, electronic and coordination chemistry[4-11].

The enumeration of stereo and position isomers of these series of chemical compounds is useful for molecular design leading to the extension of the library of such molecules. The emphasis in this study is to present a combinatorial enumeration detailing the symmetries of homodisubstuted [2,2]-PCP derivatives. In so doing, we use the unit-subduced-cycle-index approach largely developed by Fujita[12].

Mathematical formulation and computational method

Let us symbolize the homodisubstituted [2,2]-PCP derivatives by the empirical formula $\varphi_2C_4H_{14}X_2$,

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Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: robertmartinnemba@yahoo.com

where X is a non isomerisable substituent and where the symbol φ represents the hydrogen depleted benzene ring. Let us now consider the parent [2,2]-PCP as a three dimensional object represented by the stereograph G shown in Fig. 1.

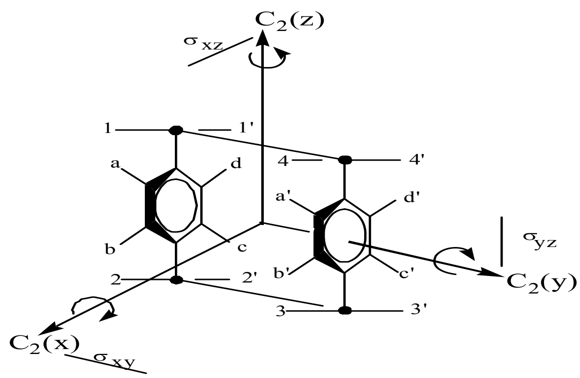

Fig. 1: Stereograph of [2,2]-PCP

In accordance with the results of previous structural studies[13] we assign to this molecule the symmetry point group:

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

which is an Abelian group [14] with the cardinality $|\mathbf{D_{2h}}| = 8$. The eight symmetry operations listed in eq. (1) are partitioned into the 8 equivalence classes as given in eq. (2):

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

These latter generate 5 chiral subgroups $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_2^{/}}$, $\mathbf{C_2^{//}}$ and $\mathbf{D_2}$ and 11 achiral subgroups $\mathbf{C_s}, \mathbf{C_s^{/}}, \mathbf{C_s^{//}}, \mathbf{C_i}$, $\mathbf{C_{2v}}, \mathbf{C_{2v}^{/}}, \mathbf{C_{2v}^{//}}, \mathbf{C_{2h}}$, $\mathbf{C_{2h}^{/}}, \mathbf{C_{2h}^{//}}$ and $\mathbf{D_{2h}}$, which are reported in Table 1 with their respective symmetry operations. Throughout this paper, all subgroups (or subsymmetries) are indicated in bold letters.

Table 1: Subgroups of D_{2h}

Subgroup	Symmetry operations	Chirality
C_1	{I}	Chiral
C_2	{I, $C_{2(z)}$}	Chiral
$\mathbf{C_2^{/}}$	{I, $C_{2(y)}$}	Chiral
$\mathbf{C_2^{//}}$	{I, $C_{2(x)}$}	Chiral
C_s	{I, σ_h}	Achiral
$\mathbf{C_s^{/}}$	{I, $\sigma_{(yz)}$}	Achiral
$\mathbf{C_s^{//}}$	{I, $\sigma_{(xz)}$}	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

Cont…

Subgroup	Symmetry operations	Chirality
$\mathbf{C}'_{\mathbf{2v}}$	$\{I, C_{2(y)}, \sigma_{(xy)}, \sigma_{(yz)}\}$	Achiral
$\mathbf{C}''_{\mathbf{2v}}$	$\{I, C_{2(y)}, \sigma_{(xy)}, \sigma_{(xz)}\}$	Achiral
C_{2h}	$\{I, C_{2(z)}, i, \sigma_{(xy)}\}$	Achiral
$\mathbf{C}'_{\mathbf{2h}}$	$\{I, C_{2(y)}, i, \sigma_{(xz)}\}$	Achiral
$\mathbf{C}''_{\mathbf{2h}}$	$\{I, C_{2(x)}, i, \sigma_{(yz)}\}$	Achiral
D_{2h}	$\{I, C_{2(z)}, C_{2(y)}, C_{2(x)}, i, \sigma_{(xy)}, \sigma_{(yz)}, \sigma_{(xz)}\}$	Achiral

These 16 subgroups construct a non redundant set of subgroups[15,16] for D_{2h} denoted by $SSG_{D_{2h}}$ which is given in eq. (3):

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

The complete set of coset representations (CR) for D_{2h} denoted by $SCR_{D_{2h}}$ which are in a univoque correspondence with the $SSG_{D_{2h}}$ are listed in eq. (4):

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

The term designating each coset representation (CR) comprises the global symmetry $\mathbf{D_{2h}}$ followed by a subgroup $\mathbf{G_i} \in SSG_{D_{2h}}$. The explicit forms of these CRs are given as follows:

$$\mathbf{D_{2h}}(/\mathbf{C_1}) = \mathbf{C_1}I + \mathbf{C_1}C_{2(z)} + \mathbf{C_1}C_{2(y)} + \mathbf{C_1}C_{2(x)} + \mathbf{C_1}\sigma_{(xy)} + \mathbf{C_1}I + \mathbf{C_1}\sigma_{(yz)} + \mathbf{C_1}\sigma_{(xz)} \quad \ldots(5)$$

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

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

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

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

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

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

$$\mathbf{D_{2h}}(/\mathbf{C_i}) = \mathbf{C_i}I + \mathbf{C''_s}C_{2(z)} + \mathbf{C_i}C_{2(x)} \quad \ldots(12)$$

$$\mathbf{D_{2h}}(/\mathbf{D_2}) = \mathbf{D_2}I + \mathbf{D_2}\sigma_{(xy)} \quad \ldots(13)$$

$$\mathbf{D_{2h}}(/\mathbf{C_{2v}}) = \mathbf{C_{2v}}I + \mathbf{C_{2v}}C_{2(y)} \quad \ldots(14)$$

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

$$\mathbf{D_{2h}}(/\mathbf{C''_{2v}}) = \mathbf{C''_{2v}}I + \mathbf{C''_{2v}}C_{2(z)} \quad \ldots(16)$$

$$\mathbf{D_{2h}}\ (/\mathbf{C_{2h}}) = \mathbf{C_{2h}}\mathrm{I}\ + \mathbf{C_{2h}}\, C_{2(y)} \qquad \ldots(17)$$

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

$$\mathbf{D_{2h}}\,(/\mathbf{C}''_{\mathbf{2h}}) = \mathbf{C}''_{\mathbf{2h}}\,\mathrm{I}\ + \mathbf{C}''_{\mathbf{2h}}\, C_{2(z)} \qquad \ldots(19)$$

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

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 mark for D_{2h} denoted by $M_{D_{2h}}$ which is given hereafter:

$$\boldsymbol{M}_{D_{2h}} = \begin{array}{c|cccccccccccccccc}
 & C_1 & C_2 & C_2' & C_2'' & C_s & C_s' & C_s'' & C_i & D_2 & C_{2v} & C_{2v}' & C_{2v}'' & C_{2h} & C_{2h}' & C_{2h}'' & D_{2h} \\
\hline
D_{2h}(/C_1) & 8 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_2) & 4 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_2') & 4 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_2'') & 4 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_s) & 4 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_s') & 4 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_s'') & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_i) & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/D_2) & 2 & 2 & 2 & 2 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_{2v}) & 2 & 2 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_{2v}') & 2 & 0 & 2 & 0 & 2 & 2 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_{2v}'') & 2 & 0 & 0 & 2 & 2 & 0 & 2 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 \\
D_{2h}(/C_{2h}) & 2 & 2 & 0 & 0 & 2 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 \\
D_{2h}(/C_{2h}') & 2 & 0 & 2 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 \\
D_{2h}(/C_{2h}'') & 2 & 0 & 0 & 2 & 0 & 2 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 \\
D_{2h}(/D_{2h}) & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1
\end{array}$$

The corresponding inverse of this mark table denoted by $M^{-1}_{D_{2h}}$ is obtained from eq. (21):

$$M_{D_{2h}}\, M^{-1}_{D_{2h}} = \mathrm{I} \qquad \ldots(21)$$

Where **I** represents the 16 x 16 identity matrix.

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

The 16 hydrogen atoms of the parent [2.2]-PCP depicted in Fig. 1 by alphabetical and numerical labels constitute 2 distinct sets of equivalent atoms or orbits Δ_1 and Δ_2 are given hereafter:

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

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

RESULTS AND DISCUSSION

The subduction of a coset representation is a mathematical process largely presented by Fujita[17-18]. In this paper, we have calculated the subductions of the coset representation $\mathbf{D_{2h}}(/\mathbf{C_1})$ by all subgroups of D_{2h}**.** These operations of subduction are symbolized by eq. (22):

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

where $G_i \in SSG_{D_{2h}}$ and β_i is a positive integer number**.** The results obtained are given in column 2 of Table 2. Then we use eq. (23) to transform the term in the right hand side of eq. (22) as follows:

$$\beta_i \; G_i(/\mathbf{C_1}) \rightarrow s_{d_i}^{\beta_i} \qquad \ldots(23)$$

where $s_{d_i}^{\beta_i}$ is a unit-subduced-cycle-index (USCI)[19], $d_i = \dfrac{|G_i|}{|C_1|}$ and $|G_i|$ and $|C_1|$ are the cardinalities of the respective subgroup**.** These USCIs are reported in column 3 and 4 of Table 2 for the orbits Δ_1 and Δ_2 respectively. In each row the product $s_{d_i}^{\beta_i} . s_{d_i}^{\beta_i}$ of unit subduced cycle indices for the orbits Δ_1 and Δ_2 gives rise to $s_{d_i}^{2\beta_i}$ which is the global USCI for the subgroup considered.

Table 2: Subductions of the coset representation $\mathbf{D_{2h}}(/\mathbf{C_1})$ and resulting USCIs.

$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow G_i$	$\beta_i \; G_i(/\mathbf{C_1})$	Δ_1	Δ_2	Global USCI
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_1}$	$8\ \mathbf{C_1}(/\mathbf{C_1})$	s_1^8	s_1^8	s_1^{16}
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_2}$	$4\ \mathbf{C_2}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_2'}$	$4\ \mathbf{C_2'}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_2''}$	$4\ \mathbf{C_2''}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_s}$	$4\ \mathbf{C_s}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_s'}$	$4\ \mathbf{C_s'}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_s''}$	$4\ \mathbf{C_s''}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_i}$	$4\ \mathbf{C_i}(/\mathbf{C_1})$	s_2^4	s_2^4	s_2^8
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{D_2}$	$2\ \mathbf{D_2}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4

Cont…

$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2v}}$	$2\ \mathbf{C_{2v}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2v}^{/}}$	$2\ \mathbf{C_{2v}^{/}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2v}^{//}}$	$2\ \mathbf{C_{2v}^{//}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2h}}$	$2\ \mathbf{C_{2h}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2h}^{/}}$	$2\ \mathbf{C_{2h}^{/}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{C_{2h}^{//}}$	$2\ \mathbf{C_{2h}^{//}}(/\mathbf{C_1})$	s_4^2	s_4^2	s_4^4
$\mathbf{D_{2h}}(/\mathbf{C_1}) \downarrow \mathbf{D_{2h}}$	$\mathbf{D_{2h}}(/\mathbf{C_1})$	s_8	s_8	s_8^2

For example the global USCI for the sub symmetry $\mathbf{C_1}$ results from the combination $\{ s_1^8 \times s_1^8 = s_1^{16} \}$. We obtain from the substitution given in eq. (24) a generating function $F(x) = \sum_j a_j x^j$ for each global USCI belonging to the sub symmetry $\mathbf{G}_i \in \mathbf{D_{2h}}$:

$$G_i \to s_{d_i}^{2\beta_i} \to F(x) = \left(1 + x^{d_i}\right)^{2\beta_i} = \sum_j A_j x^j$$

Where $0 \le j \le 2\beta_i d_i$ and $2\beta_i d_i = 16$ …(24)

Hence:

$$\mathbf{C_1} \to s_1^{16} \to (1+x)^{16} = 1 + 16x + 120x^2 + 560x^3 + 1820x^4 + 4368x^5 + 8008x^6 + 11440x^7 + 12870x^8 + 11440x^9 + 8008x^{10} + 4368x^{11} + 1820x^{12} + 560x^{13} + 120x^{14} + 16x^{15} + x^{16}$$

Similarly $s_2^8 \to \left(1 + x^2\right)^8 = 1 + 8x^2 + 28x^4 + 56x^6 + 70x^8 + 56x^{10} + 28x^{12} + 8x^{14} + x^{16}$

for the sub symmetries $\mathbf{C_2, C_2^{'}, C_2^{''}, C_s, C_s^{'}, C_s^{''}, C_i}$;

$s_4^4 \to \left(1 + x^4\right)^4 = 1 + 4x^4 + 6x^8 + 4x^{12} + x^{16}$ for $\mathbf{D_2, C_{2v}, C_{2v}^{'}, C_{2v}^{''}, C_{2h}, C_{2h}^{'}, C_{2h}^{''}}$ and

$s_8^2 \to \left(1 + x^8\right)^2 = 1 + 2x^8 + x^{16}$ for $\mathbf{D_{2h}}$.

The coefficients of x^2 in the above polynomials are collected together to form the fixed point vector $\mathbf{FPV}\left(\mathbf{x^2}\right)$ given below:

	$\mathbf{C_1}$	$\mathbf{C_2}$	$\mathbf{C_2^{'}}$	$\mathbf{C_2^{''}}$	$\mathbf{C_s}$	$\mathbf{C_s^{'}}$	$\mathbf{C_s^{''}}$	$\mathbf{C_i}$	$\mathbf{D_2}$	$\mathbf{C_{2v}}$	$\mathbf{C_{2v}^{'}}$	$\mathbf{C_{2v}^{''}}$	$\mathbf{C_{2h}}$	$\mathbf{C_{2h}^{'}}$	$\mathbf{C_{2h}^{''}}$	$\mathbf{D_{2h}}$
$\mathbf{FPV(x^2)}$	**120**	**8**	**8**	**8**	**8**	**8**	**8**	**8**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

Then we derive the isomer count vector ($\text{ICV}(x^2)$) from eq. (25):

$$\mathbf{ICV(x^2)} = \mathbf{FPV(x^2)}.\ M_{D_{2h}}^{-1} \quad \text{…(25)}$$

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

	$\mathbf{C_1}$	$\mathbf{C_2}$	$\mathbf{C_2^{'}}$	$\mathbf{C_2^{''}}$	$\mathbf{C_s}$	$\mathbf{C_s^{'}}$	$\mathbf{C_s^{''}}$	$\mathbf{C_i}$	$\mathbf{D_2}$	$\mathbf{C_{2v}}$	$\mathbf{C_{2v}^{'}}$	$\mathbf{C_{2v}^{''}}$	$\mathbf{C_{2h}}$	$\mathbf{C_{2h}^{'}}$	$\mathbf{C_{2h}^{''}}$	$\mathbf{D_{2h}}$
$\mathbf{ICV(x^2)}$	**8**	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

By summing up all these positive integer numbers we deduce that the molecular system $\varphi_2C_4H_{14}X_2$ exhibits a total of 22 stereo and position isomers which are depicted by molecular graphs shown in Figure 2. The partition of these isomer numbers in accordance with the chirality/achirality character of the molecular system reveals that the pattern of substitution of two non isomerisable X among the 16 positions of the skeleton of the parent [2-2]PCP generates simultaneously: $\mathbf{8+2+2+2=14}$ enantiomeric pairs or chiral forms, which consist of 8 $\mathbf{C_1}$ and 6 $\mathbf{C_2}$ representatives (graphs 1-8 and 9-14) respectively and $\mathbf{2+2+2+2=8}$ achiral stereo isomers which include 6$\mathbf{C_s}$ and 2$\mathbf{C_i}$ representatives (graphs 15-20 and 21-22). It is to be noticed for the sake of comparison that the 22 stereo and position isomers of $\varphi_2C_4H_{14}X_2$ systems deduced from this pattern inventory is the same number predicted by applying the Pólya's topological enumeration method.[20]

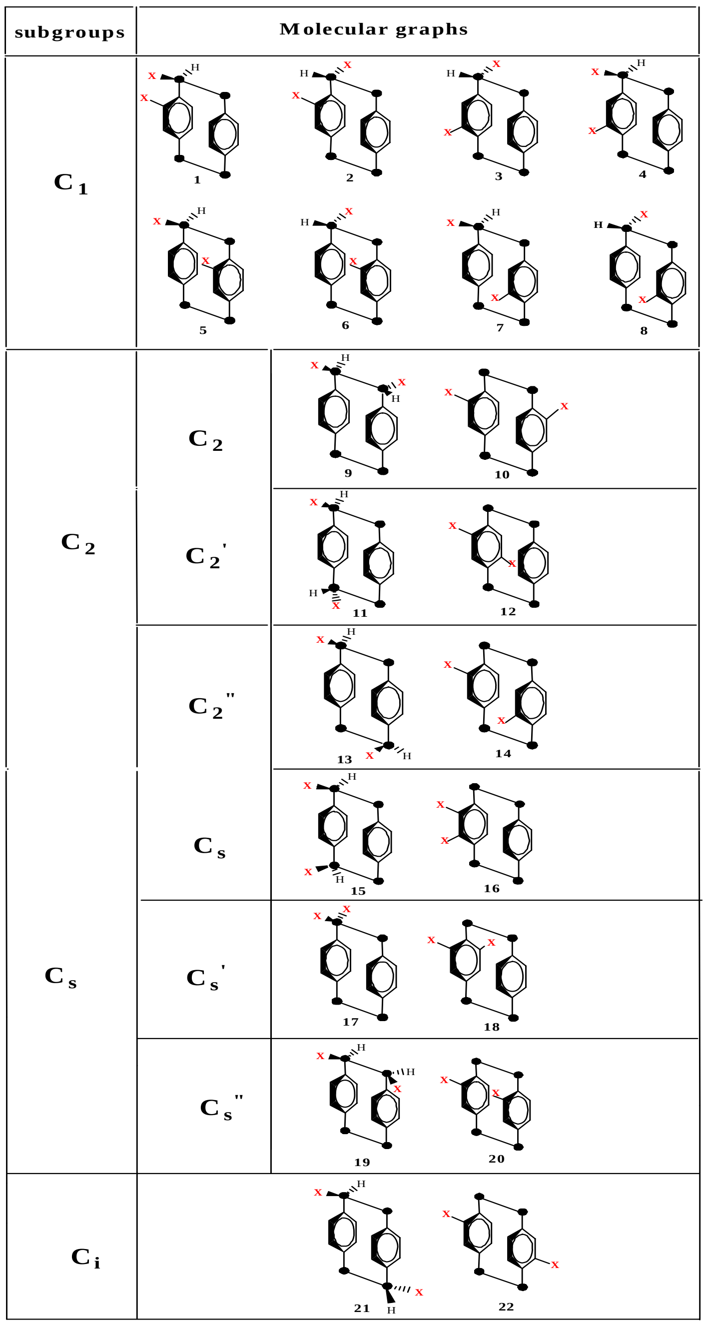

Fig. 2: Molecular graphs of homodisubstituted [2.2]PCP derivatives

CONCLUSION

The enumeration of stereo and position isomers of homodisubstituted [2.2]PCP derivatives symbolized by the empirical formula $\varphi_2 C_4 H_{14} X_2$ is a combinatorial problem in which two non isomerisable substituents of the same kind X are placed in distinct ways among the 16 substitution sites of the parent molecular skeleton. In order to obtain the solution to this enumerative problem we have derived from the global symmetry D_{2h} of the [2.2]PCP the coset representation $\mathbf{D_{2h}}(/\mathbf{C_1})$ governing the two orbits of substitution. Then the subductions of this coset representation by all subgroups of D_{2h} are calculated and the combinatorial enumeration performed by the unit-subduced-cycle-index (USCI) approach. The emphasis of this work is to obtain the row vector of itemized isomers numbers given with respect to the different sub symmetries of $\mathbf{D_{2h}}$. This detailed enumeration of chiral and achiral graphs of distinct position isomers of homodisubstituted [2.2]PCP derivatives is a useful tool for stereochemical analyses and molecular design of this category of chemical compounds.

REFERENCES

1. C. J. Brown and A. C. Farthing, Nature, **164**, 915-916 (1949).
2. R. Gleiter and H. Hopf, Modern Cyclophane Chemistry, Wiley-VCH, Weinheim, Germany (2004).
3. F. Vögtle, Cyclophane Chemistry, Wiley, Chichester, U.K (1993).
4. S. Amthor and C. Lambert, J. Phys. Chem. A, **110**, 3495-3504 (2006).
5. P. J. Ball, T. R. Shtoyko, J. A. Krause Bauer, W. J. Oldham and W. B. Connick, Inorg. Chem., **43**, 622-632 (2004).
6. G. C. Bazan, J. Org. Chem., **72**, 8615-8635 (2007).
7. Y. Morisaki and Y. Chujo, Angew. Chem. Int. Ed., **45**, 6430-6437 (2006).
8. L. Valentini, F. Mengoni, A. Taticchi, A. Marrocchi and J. M. Kenny, J. Mater. Chem., **16**, 1622-1625 (2006).
9. L. Valentini, F. Mengoni, A. Taticchi, A. Marrocchi, S. Landi, L. Minuti and J. M. Kenny, New J. Chem., **30**, 939-943 (2006).
10. K. M. El-Shaieb, A. F. E Mourad and H. Hopf, ARKIVOC, **2**, 193-200 (2006).
11. D. J. Cram and N. L. Allinger, J. Am. Chem. Soc., **77**, 6289-6294 (1955);
12. D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter and E. Heilbronner, J. Am. Chem. Soc., **81**, 5977-5983 (1959).
13. S. Fujita, Systematic Enumeration of Nonrigid Isomers with Given Ligand Symmetries, J. Chem. Inf. Comput. Sci., **40**, 135-146 (2000).
14. S. Fujita, Benzene Derivatives with Chiral and Achiral Substituent, J. Chem. Inf. Comput. Sci., **39**, 151-163 (1999).
15. H. Hope, J. Brenstein and K. N. Trueblood, Acta Cryst., **28**, 1733-1742 (1972).
16. L. B. Norman, Discrete Mathematics, Oxford Univ. Press, 5th Ed., New-York (1989) p. 276.
17. S. Fujita, Symmetry and Combinatorial Enumeration in Chemistry, Springer-Verlag, Berlin-Heidelberg (1991) pp. 40-48.
18. S. El-Basil, Combinatorial Organic Chemistry: An Education Approach, Nova Science Publishers, Inc., Huntington, New York (2000) p. 50.

19. S. Fujita, Subduction of Coset Representations, Theor. Chim. Acta, **76**, 247-268 (1989).

20. S. Fujita, Subduction of Dominant Representations, Theor. Chim. Acta, **91**, 315-332 (1995).

21. S. Fujita, Symmetry and Combinatorial Enumeration in Chemistry, Springer-Verlag, Berlin-Heidelberg, (1991).

22. G. Polya, Kombinatorische Anzahlbestimmungen Für Gruppen, Graphen and Chemische Verbindungen, Acta Math., **68**, 145-254 (1937).