On the Generalized Combinatorial Enumeration of Stereo and Position Isomers of Homopolysubstituted Derivatives of [m.n] Paracyclophanes (Part II: m≠n)

Robert M. Nemba[*a], A. Emadak[a], C. E. Nemba[a]

[a]Faculty of sciences, Laboratory of Physical and Theoretical Chemistry,

University of Yaounde I, P.O.Box 812 Yaounde, Cameroon

Email: robertmartinnemba@yahoo.com.

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Abstract: A general combinatorial method is given for direct enumeration of stereo and position isomers of any homopolysubstituted [m.n] paracyclophanes with the empirical formula $\varphi_2 C_j H_{2j+8-q} X_q$ where X is a non isomerisable ligand, q is the degree of substitution and j=m+n is the number of methylene units of the two carbon bridges. The integer sequences of enantiomer pairs $A_c(j, q_{\pm})$ and achiral skeletons $A_{ac}(j, q_{\pm})$ are given for substituted derivatives of [2.3]-, [2.4]-, [2.5]-, [2.6]-, [3.4]-, [3.5] paracyclophanes with the degrees of substitution $1\leq q \leq 2j+8$.

1 Intoduction

The [m.n] paracyclophanes ([m.n]PCP) are a family of polycyclic hydrocarbons which exhibit stereo and position isomerism due to their particular constitution consisting of two eclipsing arene moieties tethered by two carbon bridges located at the para position and comprising variable numbers m and n of methylene groups.

Previous studies [1-2] have shown the existence in such molecular systems, of strong electronic and structural interactions between the two rings and the substituents appended to each layer. For instance according to Jones et al[2] the intraannular distance in [2.2]PCP is approximately 3.1Å and hence is shorter than the separation of the layers in graphite (3.4 Å) and the molecular skeletons of the [2.3] PCP, [3.3] PCP and [4.4] PCP show a gradation of

structural distorsions notably the steric effects of forced bridgehead proximity becoming less as the bridges become longer. For bridges of equal length, the rings are parallel but slightly rotated with respect to each other[3].

This unusual geometrical and electronic feature giving rise to new chemical compounds with interesting optical and stereochemical properties has lead to the development of paracyclophanes chemistry. During the last two decades the focus of research in this topic includes syntheses of various derivatives[4-7] and their applications to a wide range of disciplines such as polymer material[8], electronic chemistry[9], organometallic chemistry[10]. Such studies have to be complemented by the enumeration of families of paracyclophanes derivatives. This task has not yet been achieved and our aim in this work has been to propose a combinatorial method for direct enumeration of stereo and position isomers of any homopolysubstituted [m.n]paracyclophane (Ho[m.n]PCP) derivative having m≠n.

2 Mathematical formulation

Let us symbolize a parent Ho[m.n]PCP by the empirical formula $\varphi_2 C_j H_{2j+8-q} X_q$ where the positive integers $j = m_\pm + n_\pm$, $q_\pm$ and $2j+8-q$ represent respectively the total number of methylene units of the two carbon bridges, the number of non isomerisable substituents of the same kind X and the number of unsubstituted hydrogen atoms while the greek symbol φ represents the hydrogen depleted benzene ring. The parity of the integer numbers m and n suggests to classify [m.n]PCP into 3 categories as follows: (a)- the $[m_+.n_+]PCP$, (b) the $[m_-.n_+]PCP$ and (c) the $[m_-.n_-]PCP$. Throughout this paper the subscripts (+) and (-) are indicating even and odd positive integer numbers respectively. The suitable representations of such molecular systems submitted to skeletal distortions induced by two unequal carbon bridge lengths m≠n and the eclipsing position of the two benzene rings are tridimensional graphs or stereographs in C_{2v} symmetry which are G_{m,n_+} , $G_{m_-n_+}$ and $G_{m_-n_-}$ shown in figure 1.
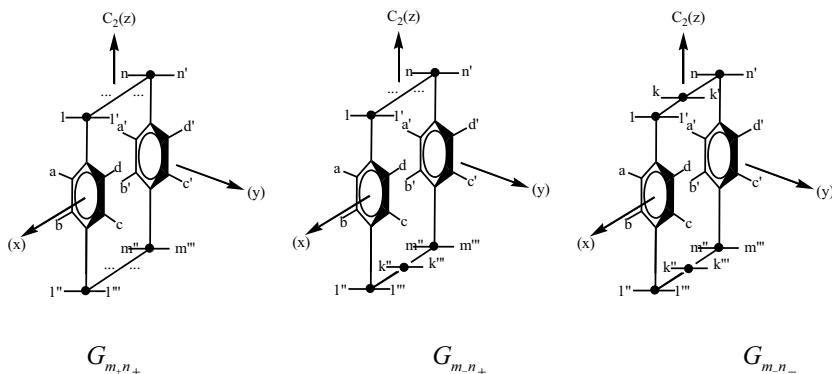
Figure 1: Stereographs of parent $[m_+.n_+]$-, $[m_-.n_+]$-, $[m_-.n_-]$- PCP.

2.1 Average weight of permutations controlling the chirality/achirality fittingness

Each stereograph contains $2j+8$ substitution sites labeled $1,…,n$; $1',…,n'$; $1'',…,m''$; $1''',…,m'''$. The permutations of these $2j+8$ substitution sites induced by the 4 symmetry operations of $C_{2v}= \{E, C_2(x), \sigma(xz), \sigma(yz) \}$ are reported in Table 1 for the three series of parent [m.n]paracyclophanes. In each stereograph depicted in Figure 1 the symmetry operation E fixes all hydrogen atoms and gives rise to $2j+8$ one-cycle permutations (permutations of length $l_1 =1$) which are symbolized in partition notation by the term 1^{2j+8}. In the case of $G_{m_+n_+}$, each one of the following symmetry operations $C_2(z)$, $\sigma(xz)$, $\sigma(yz)$ induces $j+4$ permutation cycles of length $l_2 = 2$ (transpositions) represented by the term 2^{j+4}. In the case of $G_{m_n_+}$ and $G_{m_n_-}$ the symmetry operations $C_2(z)$ and $\sigma(xz)$ induce transpositions as previously indicated but the symmetry plane $\sigma(yz)$ simultaneously generates two one-cycle permutations and $j+3$ transpositions represented by the term $1^2 2^{j+3}$ for $G_{m_n_+}$ and induces in the case of $G_{m_n_-}$ four one-cycles permutations and $j+2$ transpositions symbolized by the term $1^4 2^{j+2}$.

Table 1: **Permutations of 2j+8 substitution sites of parent** $[m_+.n_+]$-, $[m_-.n_+]$-, $[m_-.n_-]$- **PCP induced by** C_{2v} **symmetry operations**.

C_{2v} Symmetry operations	Permutations cyles of substitution sites	Partition notation		
		$G_{m_+n_+}$	$G_{m_-n_+}$	$G_{m_-n_-}$
E	(1)…(n)(1')…(n')(1'')…(n'')(1''')…(n''')(a)(b)(c)(d)(a') (b')(c')(d')	1^{2j+8}	1^{2j+8}	1^{2j+8}
C₂(xz)	(1,n')…(1',n)(1'',m''')…(1''',m'')(a,d')(d,a')(b,c')(c,b')	2^{j+4}	2^{j+4}	2^{j+4}
σ(xz)	(1,1')…(n,n')(1'',1''')…(m'',m''')(a,d)(b,c)(a',d')(b',c')	2^{j+4}	2^{j+4}	2^{j+4}
σ(yz)	(1,n)…(1',n')(1'',m'')…(1''',m''')(a,a')(b,b')(c,c')(d,d')	2^{j+4}	-	-
	(k'')(k''')(1,n)…(1',n')(1'',m'')…(1''',m''')(a,a')(b,b')(c,c')(d,d')…	-	$1^2 2^{j+3}$	-
	(k)(k')(k'')(k''')(1,n)…(1',n')(1'',m'')…(1''',m''')(a,a')(b,b')(c, c')(d,d')	-	-	$1^4 2^{j+2}$

Now let P denote in eqs.1-3 and according to the parities of m and n the set which contains all the permutations generated by the four symmetry operations of C_{2v} acting on the 2j+8 substitution sites of the parent [m.n] PCP:

$$P = \left\{ \left[1^{2j+8} \right], \ 3\left[2^{j+4} \right] \right\} \quad \text{for } (m_+n_+) \tag{1}$$

$$P = \left\{ \left[1^{2j+8} \right], \ 2\left[2^{j+4} \right], \left[1^4 2^{j+2} \right] \right\} \quad \text{for } (m.n_-) \tag{2}$$

$$P = \left\{ \left[1^{2j+8} \right], \ 2\left[2^{j+4} \right], \left[1^2 2^{j+3} \right] \right\} \quad \text{for } (m_+n_-) \tag{3}$$

By eliminating in P the permutations induced by the two reflections) σ(xz) and σ(yz), one derive the set P' given in eq.4:

$$P' = \left\{ [1^{2j+8}], \quad [2^{j+4}] \right\} \text{ for } (m_+n_+), (m_-n_-) \text{ or } (m_-n_+). \tag{4}$$

Let us consider $\overline{P}$ and $\overline{P'}$ in eqs.5-6, as the averaged sum of permutations collected in P and P':

$$\overline{P} = \frac{1}{4} \begin{cases} \left(\left[1^{2j+8} \right] + 3 \left[2^{j+4} \right] \right) & \text{for } m_+n_+ \\ \left(\left[1^{2j+8} \right] + 2 \left[2^{j+4} \right] + \left[1^2 2^{j+3} \right] \right) & \text{for } m_-n_+ \\ \left(\left[1^{2j+8} \right] + 2 \left[2^{j+4} \right] + \left[1^4 2^{j+2} \right] \right) & \text{for } m_-n_- \end{cases} \tag{5}$$

$$\overline{P'} = \frac{1}{2} \left(\left[1^{2j+8} \right] + \left[2^{j+4} \right] \right) \quad \text{for} \quad m_+n_+, m_-n_+ \text{ or } m_-n_- \tag{6}$$

and derive the differences $\Delta_c = \overline{P'} - \overline{P}$ given in eq.7

$$\Delta_c = \frac{1}{4} \begin{cases} \left(\left[1^{2j+8} \right] - \left[2^{j+4} \right] \right) & \text{for } m_+n_+ \\ \left(\left[1^{2j+8} \right] - \left[1^2 2^{j+3} \right] \right) & \text{for } m_-n_+ \\ \left(\left[1^{2j+8} \right] - \left[1^4 2^{j+2} \right] \right) & \text{for } m_-n_- \end{cases} \tag{7}$$

and

$$\Delta_a = 2\overline{P} - \overline{P'} \quad \text{in eq.8 :}$$

$$\Delta_a = \frac{1}{2} \begin{cases} \left(2 \left[2^{j+4} \right] \right) & \text{for } m_+n_+ \\ \left(\left[2^{j+4} \right] + \left[1^2 2^{j+3} \right] \right) & \text{for } m_-n_+ \\ \left(\left[2^{j+4} \right] + \left[1^4 2^{j+2} \right] \right) & \text{for } m_-n_- \end{cases} \tag{8}$$

Δ_c and Δ_a are respectively the averaged weight of permutations controlling the chirality and the achirality fittingness of the 2j+8 substitution sites of the parent [m.n] PCP. It is to be noticed that the concept of chirality/achirality fittingness of orbits that consist of a set of atoms, bonds, substitution sites, substituents or ligands in organic molecules has been widely presented by Fujita. [11-14]

2.2 Generalized equations for counting enantiomer pairs
and achiral skeletons of Ho[m.n]PCP

The numbers of distinct placements of q substituents among 2j+8 positions induced by the permutations of types 1^{2j+8}, 2^{j+4}, $1^2 2^{j+3}$, $1^4 2^{j+2}$ are obtained from expressions 9-12 given in column 2 of Table 2 where each term $T(a,b) = \begin{pmatrix} a \\ b \end{pmatrix}$ refers to a binomial coefficient.

Table 2: Number of distinct placements of q substituents among 2j+8 substitution sites induced by permutations of types 1^{2j+8}, 2^{j+4}, $1^2 2^{j+3}$, $1^4 2^{j+2}$.

Types of Permutations	Number of distinct placements of q substituents among 2j+8 substitution sites
$\left[1^{2j+8}\right]$	$T(2j+8, q)$ (9)
$\left[2^{j+4}\right]$	$T\left(j+4, \dfrac{q}{2}\right)$ (10)
$\left[1^2 2^{j+3}\right]$	$\displaystyle\sum_{\alpha_1=0}^{2} T(2,\alpha_1) T\left(j+3, \dfrac{q-\alpha_1}{2}\right)$ (11)
$\left[1^4 2^{j+2}\right]$	$\displaystyle\sum_{\alpha_1=0}^{4} T(4,\alpha_1) T\left(j+2, \dfrac{q-\alpha_1}{2}\right)$ (12)

By replacing the right hand side terms of eqs.7-8 with their equivalent algebraic expressions given in eqs.9-12, we convert Δ_c and Δ_a into generalized formulas $A_c(j, q_\pm)$ and $A_{ac}(j, q_\pm)$ for counting enantiomer pairs and achiral skeletons for molecules of the series Ho[m$_+$.n$_+$]PCP, Ho[m$_-$.n$_+$]PCP or Ho[m$_-$.n$_-$]PCP. These generalized counting formulas are declined in accordance with the parity of the variable q$_-$ (odd) or q$_+$ (even) as follows:

2.2a The number $A_c(j, q_\pm)$ of enantiomer pairs and the number

$A_{ac}(j, q_\pm)$ of achiral skeletons for Ho[m+.n+]PCP .

In the series Ho[m+.n+]PCP consisting of $j = m_+ + n_+$ methylene units and a degree of substitution $q_\pm$ the number of enantiomer pairs $A_c(j, q_\pm)$ is obtained from the generalized counting formula given in eq.13:

$$A_c(j, q_\pm) = \frac{1}{4}\left[\binom{2j+8}{q} - \binom{j+4}{\frac{q}{2}}\right]$$

(13)

which splits into eqs.14-15 in accordance with the variables q_+ or q_- :

$$A_c(j, q_+) = \frac{1}{4}\left[\binom{2j+8}{q} - \binom{j+4}{\frac{q}{2}}\right]$$

(14)

$$A_c(j, q_-) = \frac{1}{4}\left[\binom{2j+8}{q}\right]$$

(15)

The associate number $A_{ac}(j, q_\pm)$ of achiral skeletons of Ho[m+.n+]PCP with a degree of substitution $q_\pm$ is obtained from eq-16 :

$$A_{ac}(j, q_\pm) = \left[\binom{j+4}{\frac{q}{2}}\right]$$

(16)

which becomes eqs.17-18 in accordance with the variables q_+ or q_- :

$$A_{ac}(j, q_+) = \left[\binom{j+4}{\frac{q}{2}}\right]$$

(17)

$$A_{ac}(j, q_-) = 0$$

(18)

Eqs.17 and 18 suggests according to the parity of the positive integers j and q the following:

Remark: *Any* Ho[m+.n+]PCP *consisting of* $j_+ = m_+ + n_+$ *methylene units and a degree of substitution* q_- *is exclusively a chiral structure.*

Conversely the occurrence of achiral structure is prohibited in the series of molecular systems
$\varphi_2 C_j H_{2j+8-q} X_q$ *having* $j_+ = m_+ + n_+$ *methylene units and a degree of substitution* q_-.

2.2b The number $A_c(j, q_\pm)$ **of enantiomer pairs and the number**

$A_{ac}(j, q_\pm)$ **of achiral skeletons for Ho[m₋n₊]PCP**

In the series Ho[m₋n₊]PCP comprising $j = m_+ + n_+$ methylene units and a degree of substitution $q_\pm$ the number of enantiomer pairs $A_c(j, q_\pm)$ is obtained from the generalized counting formula given in eq.19:

$$A_c(j, q_\pm) = \frac{1}{4} \left[\binom{2j+8}{q} - \sum_{p_1=0}^{2} \binom{2}{p_1} \binom{\frac{j+3}{q-p_1}}{2} \right] \tag{19}$$

which becomes eqs.20-21 in accordance with the variables q_+ or q_-:

$$A_c(j, q_+) = \frac{1}{4} \left[\binom{2j+8}{q} - \binom{\frac{j+3}{q}}{2} - \binom{\frac{j+3}{q-2}}{2} \right] \tag{20}$$

$$A_c(j, q_-) = \frac{1}{4} \left[\binom{2j+8}{q} - 2\binom{\frac{j+3}{q-1}}{2} \right] \tag{21}$$

The associate number $A_{ac}(j, q_\pm)$ of achiral skeletons of Ho[m₋n₊]PCP with a degree of substitution q is obtained from eq-22 :

$$A_{ac}(j, q_\pm) = \frac{1}{2} \left[\binom{\frac{j+4}{q}}{2} + \sum_{p_1=0}^{2} \binom{2}{p_1} \binom{\frac{j+3}{q-p_1}}{2} \right] \tag{22}$$

which becomes in accordance with the variables q_+ or q_- eqs.23 and 24 :

$$A_{ac}(j, q_+) = \frac{1}{2} \left[\binom{\frac{j+4}{q}}{2} + \binom{\frac{j+3}{q}}{2} + \binom{\frac{j+3}{q-2}}{2} \right] \tag{23}$$

$$A_{ac}(j, q_-) = \binom{\frac{j+3}{q-1}}{2} \tag{24}$$

2.2c The number $A_c(j, q_\pm)$ of enantiomer pairs and the number $A_{ac}(j, q_\pm)$ of achiral skeletons for Ho[m‥n‥]PCP.

In the series Ho[m‥n‥]PCP comprising $j = m_- + n_-$ methylene units and a degree of substitution $q_\pm$ the number of enantiomer pairs $A_c(j, q_\pm)$ is obtained from the generalized counting formula given in eq.25 :

$$A_c(j,q_\pm) = \frac{1}{4}\left[\binom{2j+8}{q} - \sum_{p_1=0}^{4} \binom{4}{p_1}\binom{j+2}{\frac{q-p_1}{2}} \right] \tag{25}$$

which becomes eqs.26 and 27 for q_+ and q_- respectively.

$$A_c(j,q_+) = \frac{1}{4}\left[\binom{2j+8}{q} - \binom{j+2}{\frac{q}{2}} - 6\binom{j+2}{\frac{q-2}{2}} - \binom{j+2}{\frac{q-4}{2}} \right] \tag{26}$$

$$A_c(j,q_-) = \frac{1}{4}\left[\binom{2j+8}{q} - 4\binom{j+2}{\frac{q-1}{2}} - 4\binom{j+2}{\frac{q-3}{2}} \right] \tag{27}$$

The associate number $A_{ac}(j, q_\pm)$ of achiral skeletons of Ho[m‥n‥]PCP with a degree of substitution $q_\pm$ is obtained from eq.28 :

$$A_{ac}(j,q_\pm) = \frac{1}{2}\left[\binom{j+4}{\frac{q}{2}} + \sum_{p_1=0}^{4} \binom{4}{p_1}\binom{j+2}{\frac{q-p_1}{2}} \right] \tag{28}$$

which becomes eqs.29 and 30 for q_+ and q_- respectively.

$$A_{ac}(j,q_+) = \frac{1}{2}\left[\binom{j+4}{\frac{q}{2}} + \binom{j+2}{\frac{q}{2}} + 6\binom{j+2}{\frac{q-2}{2}} + \binom{j+2}{\frac{q-4}{2}} \right] \tag{29}$$

$$A_{ac}(j,q_-) = 2\left[\binom{j+2}{\frac{q-1}{2}} + \binom{j+2}{\frac{q-3}{2}} \right] \tag{30}$$

3 Application to direct combinatorial enumeration

To examplify the application of the present pattern inventory, let us attribute numerical values to the positive integers numbers j and $q_{\pm}$ in the molecular formula $\varphi_2 C_j H_{2j+8-q} X_q$ of a given Ho[m.n] PCP in order to compute its numbers $A_c(j, q_{\pm})$ of enantiomer pairs and $A_{ac}(j, q_{\pm})$ of achiral skeletons.

Example 1: Let $m_+ = 4$, $n_+ = 2$ and $j = m_+ + n_+ = 6$ and consider the generalized molecular formula $\varphi_2 C_6 H_{20-q} X_q$ of the series of Ho-[4.2] PCP where $1 \le q_{\pm} \le 20$. From eqs.1 and 4 we derive the sets of permutations $P = \left\{ [1^{20}], \ 3[2^{10}] \right\}$ and $P' = \left\{ [1^{20}], \ [2^{10}] \right\}$ and from eqs.5-6 we deduce the average sum of permutations $\overline{P} = \frac{1}{4}\left\{ [1^{20}] + 3[2^{10}] \right\}$ and $\overline{P'} = \frac{1}{2}\left\{ [1^{20}] + [2^{10}] \right\}$. The averaged weight of permutations controlling the chirality fittingness of 20 substitution sites of the [4.2] PCP determined from eqs.7 is $\Delta_c = \frac{1}{4}\left([1^{20}] - [2^{10}] \right)$. The numbers $A_c(6; q_{\pm})$ of enantiomers pairs are calculated by means of eqs 14 and 15. For instance if $q_- = 1$ and $q_+ = 2$, hence:

$$A_c(6;1) = \frac{1}{4}\left[\binom{20}{1} \right] = 5 \ \ and \ \ A_c(6;2) = \frac{1}{4}\left[\binom{20}{2} - \binom{10}{1} \right] = 45$$

Conversely, from eq.10, we deduce the averaged weight of permutations controlling the achirality fittingness of 20 substitution sites of [4.2] PCP by the difference $\Delta_a = 2^{10}$. We compute from eq.23 and 24 the numbers of achiral skeletons for $q_- = 1$ and $q_+ = 2$ as follows:

$$A_{ac}(6 ; 1) = 0 \ \ and \ \ A_{ac}(6 ; 2) = \left[\binom{10}{1} \right] = 10$$

Example 2: Let $m_- = 3$, $n_+ = 2$ and $j = m_- + n_+ = 5$ and consider the generalized molecular formula $\varphi_2 C_5 H_{18-q} X_q$ of the series of Ho [3.2] PCP where $1 \le q_{\pm} \le 18$. From eqs 2 and 4 we derive the sets of permutations $P = \left\{ [1^{18}], \ 2[2^9], [1^2 2^8] \right\}$ and $P' = \left\{ [1^{18}], \ [2^9] \right\}$ and from eqs.5-6 we deduce the average sum of permutations $\overline{P} = \frac{1}{4}\left\{ [1^{18}] + 2[2^9] + [1^2 2^8] \right\}$ and $\overline{P'} = \frac{1}{2}\left\{ [1^{18}] + [2^9] \right\}$. The averaged weight of permutations controlling the chirality fittingness of 18 substitution sites of the [3.2]PCP is

$\Delta_c = \overline{P'} - \overline{P} = \frac{1}{4} \left(\left[1^{18} \right] - \left[1^2 2^8 \right] \right)$. The numbers $A_c \left(5; q_\pm \right)$ of enantiomer pairs are calculated by means of eqs 20 and 21. For instance if $q_- = 1$ and $q_+ = 2$, hence:

$$A_c (5;1) = \frac{1}{4} \left[\binom{18}{1} - 2 \binom{8}{0} \right] = 4$$

$$A_c (5;2) = \frac{1}{4} \left[\binom{18}{2} - \binom{8}{1} - \binom{8}{0} \right] = 36$$

Conversely, from eq.10, we deduce the averaged weight of permutations controlling the achirality fittingness of 18 substitution sites of [3.2]PCP by the difference $\Delta_a = 2\overline{P} - \overline{P'} = \frac{1}{2} \left(\left[2^9 \right] + \left[1^2 2^8 \right] \right)$. We compute from eq.23 and 24 the numbers of achiral skeletons for $q_- = 1$ and $q_+ = 2$, as follows:

$$A_{ac} (5 ; 1) = \binom{8}{0} = 1 \text{ and } A_{ac} (5 ; 2) = \frac{1}{2} \left[\binom{9}{1} + \binom{8}{1} + \binom{8}{0} \right] = 9$$

Example 3: Let $m_- = 5$, $n_- = 3$ and $j = m_- + n_- = 8$ and consider the generalized molecular formula $\varphi_2 C_8 H_{24-q} X_q$ of the series of Ho [5.3] PCP where $1 \le q_\pm \le 24$. From eqs 3 and 4 we derive the sets of permutations $P = \left\{ \left[1^{24} \right], 2 \left[2^{12} \right], \left[1^4 2^{10} \right] \right\}$ and $P' = \left\{ \left[1^{24} \right], \left[2^{12} \right] \right\}$ and from eqs.5-6 we deduce the average sum of permutations $\overline{P} = \frac{1}{4} \left\{ \left[1^{20} \right] + 2 \left[2^{12} \right] + \left[1^4 2^{10} \right] \right\}$ and $\overline{P'} = \frac{1}{2} \left\{ \left[1^{24} \right] + \left[2^{12} \right] \right\}$. The averaged weight of permutations controlling the chirality fittingness of 24 substitution sites of the [5.3]PCP is $\Delta_c = \overline{P'} - \overline{P} = \frac{1}{4} \left(\left[1^{24} \right] - \left[1^4 2^{10} \right] \right)$. The numbers $A_c \left(8; q_\pm \right)$ of enantiomer pairs are calculated by means of eqs 26 and 27. For instance if $q_- = 1$ and $q_+ = 2$, hence :

$$A_c (8;1) = \frac{1}{4} \left[\binom{24}{1} - 4 \binom{10}{0} \right] = 5$$

$$A_c (8;2) = \frac{1}{4} \left[\binom{24}{2} - \binom{10}{1} - 6 \binom{10}{0} \right] = 65$$

Conversely, from eq.10, we deduce the averaged weight of permutations controlling the achirality fittingness of 24 substitution sites of [5.3]PCP by the difference

$\Delta_a = 2\overline{P} - \overline{P}' = \frac{1}{2}\left(\left[2^{12}\right] + \left[1^4 2^{10}\right]\right)$. We compute from eq.29 and 30 the numbers of achiral skeletons for $q_- = 1$ and $q_+ = 2$, as follows:

$$A_{ac}(8;1) = 2\binom{10}{0} = 2 \text{ and } A_{ac}(8;2) = \frac{1}{2}\left[\binom{12}{1} + \binom{10}{1} + 6\binom{10}{0}\right] = 14$$

These 3 examples and the integer sequences $A_c(j,q_\pm)$ and $A_{ac}(j,q_\pm)$ reported in Table 3 for Ho[m.n]PCP symbolized with the empirical formula $\varphi_2 C_j H_{2j+8-q} X_q$ where (m,n)= (3.2), (4.2), (5.2), (6.2), (4.3) ,(5.3) , j = m + n = (5, 6, 7, 8) and the degrees of substitution $1 \le q \le 2j+8$, illustrate the selectivity and the general application of our pattern inventory. It should also be noticed that $A_c(j,q_\pm)$ and $A_{ac}(j,q_\pm)$ obtained from this direct combinatorial enumeration method satisfies the following relations:

$$A_c(j,q_\pm) + A_{ac}(j,q_\pm) = C_T(j,q_\pm) \tag{31}$$

and

$$2A_c(j,q_\pm) + A_{ac}(j,q_\pm) = C_E(j,q_\pm) \tag{32}$$

where $C_T(j,q_\pm)$ and $C_E(j,q_\pm)$ are the coefficients of topological and enantiomeric generating functions $f_T(x,q_\pm) = \sum_{q_\pm} C_T(j,q_\pm).x^{q_\pm}$ and $f_E(x,q_\pm) = \sum_{q_\pm} C_E(j,q_\pm).x^{q_\pm}$ derived through Pólya's counting method[15]. For the sake of comparison if one considers for instance the series of homopolysubstituted derivatives of [3.2] PCP represented by the empirical formula $\varphi_2 C_5 H_{18-q} X_q$ where $1 \le q \le 18$, our results reported in Table 3 match up according eqs 31-32 with the coefficients of Pólya's topological and enantiomeric counting polynomials given in eqs.33-34.

$F_T(x, q) = 1 + 5x + 45x^2 + 208x^3 + 792x^4 + 2156x^5 + 4704x^6 + 7984x^7 + 11034x^8 + 12190x^9 + 11034x^{10} + 7984x^{11} + 4704x^{12} + 2156x^{13} + 792x^{14} + 208x^{15} + 45x^{16} + 5x^{17} + x^{18}$ $\qquad$ (33)

$F_E(x, q) = 1 + 9x + 81x^2 + 408x^3 + 1548x^4 + 4284x^5 + 9324x^6 + 15912x^7 + 21942x^8 + 24310x^9 + 21942x^{10} + 15912x^{11} + 9324x^{12} + 4284x^{13} + 1548x^{14} + 408x^{15} + 81x^{16} + 9x^{17} + x^{18}$ $\qquad$ (34)

Finally the accuracy of our theoretical results is also testified by the method of drawing and counting graphs. An illustration given in figures 2a and 2b depict the molecular

graphs of the homo disubstituted derivatives of the [3.2 PCP] which consist of $A_{ac}(5,2)=9$ achiral skeletons including $(8C_s+1C_{2v})$ symmetries and $A_c(5,2)=36$ enantiomer pairs including $(4\ C_2 + 32\ C_1)$ symmetries.

Table 3 : Sequences of Integers Numbers $A_c(j,q_\pm)$ and $A_{ac}(j,q_\pm)$ computed for the first members of Ho[m.n]PCP symbolized with the empirical formula $\varphi_2 C_j H_{2j+8-q} X_q$ where $(m,n) = (3.2), (4.2), (5.2), (6.2),$ $(4.3),(5.3)$, $j = m + n = (5, 6, 7, 8)$ and the degrees of substitution $1 \le q \le 2j+8$.
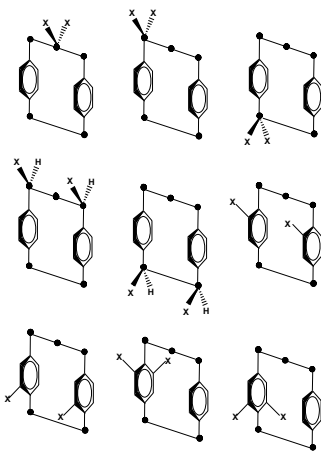
$q_\pm$	[3-2]-PCP			[4-2]-PCP		
	$A_c(j,q_\pm)$	$A_{ac}(j,q_\pm)$	$C_E(j,q_\pm)$	$A_c(j,q_\pm)$	$A_{ac}(j,q_\pm)$	$C_E(j,q_\pm)$
1	4	1	9	5	0	10
2	36	9	81	45	10	100
3	200	8	408	285	0	570
4	756	36	1548	1200	45	2445
5	2128	28	4284	3876	0	7752
6	4620	84	9324	9660	120	19440
7	7928	56	15912	19380	0	38760
8	10908	126	21942	31440	210	63090
9	12120	70	24310	41990	0	83980
10	10908	126	21942	46126	252	92504
11	7928	56	15912	41990	0	83980
12	4620	84	9324	31440	210	63090
13	2128	28	4284	19380	0	38760
14	756	36	1548	9660	120	19440
15	200	8	408	3876	0	7752
16	36	9	81	1200	45	2445
17	4	1	9	285	0	570
18	0	1	1	45	10	100
19				5	0	10
20				0	1	1

Table 3 (continued)

$q_{\pm}$	[5-2]-PCP			[4-3]-PCP		
	$A_c(j,q_{\pm})$	$A_{ac}(j,q_{\pm})$	$C_E(j,q_{\pm})$	$A_c(j,q_{\pm})$	$A_{ac}(j,q_{\pm})$	$C_E(j,q_{\pm})$
1	5	1	11	5	1	11
2	55	11	121	55	11	121
3	380	10	770	380	10	770
4	1815	55	3685	1815	55	3685
5	6561	45	13167	6561	45	13167
6	18612	165	37389	18612	165	37389
7	42576	120	85272	42576	120	85272
8	79860	330	160050	79860	330	160050
9	124250	210	248710	124250	210	248710
10	161546	462	323554	161546	462	323554
11	176232	252	352716	176232	252	352716
12	161546	462	323554	161546	462	323554
13	124250	210	248710	124250	210	248710
14	79860	330	160050	79860	330	160050
15	42576	120	85272	42576	120	85272
16	18612	165	37389	18612	165	37389
17	6561	45	13167	6561	45	13167
18	1815	55	3685	1815	55	3685
19	380	10	770	380	10	770
20	55	11	121	55	11	121
21	5	1	11	5	1	11
22	0	1	1	0	1	1

Table 3 (continued)

$q_\pm$	[6-2]-PCP			[5-3]-PCP		
	$A_c(j,q_\pm)$	$A_{ac}(j,q_\pm)$	$C_E(j,q_\pm)$	$A_c(j,q_\pm)$	$A_{ac}(j,q_\pm)$	$C_E(j,q_\pm)$
1	6	0	12	5	2	12
2	66	12	144	65	14	144
3	506	0	1012	495	22	1012
4	2640	66	5346	2630	86	5346
5	10626	0	21252	10571	110	21252
6	33594	220	67408	33549	310	67408
7	86526	0	173052	86361	330	173052
8	183744	495	367983	183624	735	367983
9	326876	0	653752	326546	660	653752
10	490116	792	981024	489906	1212	981024
11	624036	0	1248072	623574	924	1248072
12	675808	924	1352540	675556	1428	1352540
13	624036	0	1248072	623574	924	1248072
14	490116	792	981024	489906	1212	981024
15	326876	0	653752	326546	660	653752
16	183744	495	367983	183624	735	367983
17	86526	0	173052	86361	330	173052
18	33594	220	67408	33549	310	67408
19	10626	0	21252	10571	110	21252
20	2640	66	5346	2630	86	5346
21	506	0	1012	495	22	1012
22	66	12	144	65	14	144
23	6	0	12	5	2	12
24	0	1	1	0	1	1

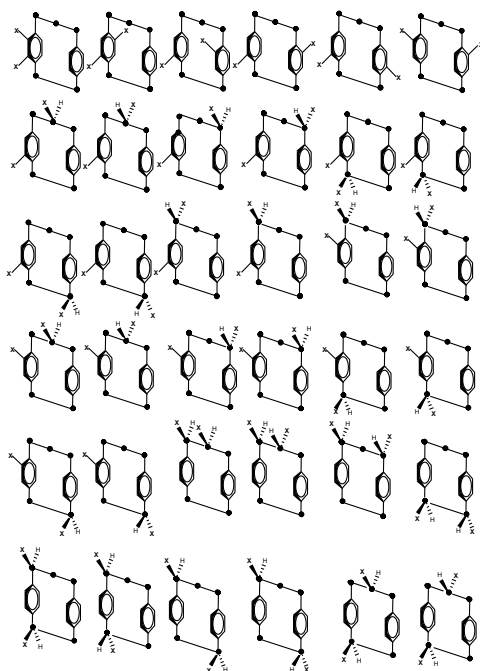$A_{ac}(5,2) = 9$ achiral skeletons including ($1C_{2v} + 8C_s$) symmetries.

Figure 2a : Achiral skeletons of homo disubstituted derivatives of [3.2] Paracyclophane.

4 Conclusion

This combinatorial method for enumerating enantiomer pairs and achiral skeletons of Ho[m.n] PCP symbolized by the empirical formulae $\varphi_2 C_j H_{2j+8-q} X_q$ is applicable to general cases of these series with $m \neq n$ and $1 \leq q_\pm \leq 2j+8$. It includes from the determination of permutations of substitution sites induced by the symmetry point group of the parent hydrocarbon:

1°)-the derivation of the averaged weight controlling the chirality and achirality fittingness of substitution sites;

2°)-the transformation of these averaged contributions into generalized counting formulas which allow the direct computation of the numbers $A_c(j,q_\pm)$ of enantiomer pairs and $A_{ac}(j,q_\pm)$ of achiral skeletons. This procedure has already been applied with success by Nemba and Balaban[16] and its advantage is to circumvent the Pólya's counting method which is largely presented by Pólya, Tarjan and Woods [17], Harary, Palmer, Robinson and Read [18], Tucker[19] and Rouvray[20] and requires first to derive the cycle index in accordance with the symmetry point group of the molecular system and second

$A_c(5,2) = 36$ Chiral skeletons including $4C_2 + 32C_1$ symmetries.

Figure 2b : Chiral skeletons of homo disubstituted derivatives of [3.2] Paracyclophane.

the transformation of the cycle index into a generating function of order 2j+8 (in the case of [m.n] PCP) the coefficients of which are solution of the enumeration problem. Finally it should also be mentioned that the application of this enumerative method to symmetric [n.n] PCP homosubstituted derivatives has been examined in another paper.

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