

ENUMERATION OF CHIRAL AND ACHIRAL ISOMERS OF AN n -MEMBERED RING WITH n HOMOMORPHIC ALKYL GROUPS.

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Abstract : The number of chiral and achiral skeletons resulting from homomorphic polyalkylations of any degree m of a monocyclic cycloalkane with a ring size n are derived from combinatorial formulae. Furthermore this theoretical study shows the composite character of the chirality and achirality of n -membered rings substituted by alkyl groups.

Introduction

Among numerous articles devoted to the enumeration of isomers of polysubstituted organic molecules one may retain the original contribution of Robinson et al¹ who have provided a method to derive explicit recurrence formulae useful for counting chiral and achiral alkanes and monosubstituted alkanes. More recently Balaban et al² have presented an algorithm for

the determination of the number of alkanes having n carbons and a longest chain length d . The mathematical modelling generally encountered in these papers and many others deals with Polya's counting theorem³ particularly in the series of acyclic organic compounds. Despite the abundant chemical literature on this topic one may notice that the final goal of Polya's model is to obtain a counting polynomial of the form $f(x) = \sum_i c_i x^i$ where the coefficients c_i represent the bulk results of the enumeration of chemical isomers or stereoisomers of any series of organic molecules with a degree of substitution i . Furthermore this enumerative procedure is not selective for a defined polysubstituted organic compound and its main disadvantages is the unwieldiness to expand the power series $\sum_i c_i x^i$ which increases exponentially for higher integer values i in the case of large polysubstituted organic molecules. The applications of Polya's counting method are scarce owing to these reasons, in the series of monocyclic and polycyclic organic compounds^{4,6} with coexisting constitutional position and stereoisomerisms. Our purpose in this paper is to circumvent the limitations of Polya's method and develop a direct and selective combinatorial procedure for counting chiral and achiral skeletons of an n -membered ring connected to m homomorphic alkyl groups. Throughout this paper we use some graph theory concepts by reference to the corresponding chemical terms and give some definitions and preliminaries.

Definitions and mathematical formulation

Let HPMCA denote any homomorphically polyalkylated derivative of a monocyclic cycloalkane (i.e an n -membered ring system substituted by m homomorphic alkyl groups) with the empirical formula $C_n H_{2n-m} (C_k H_{2k+1})_m$. The m alkyl groups $(C_k H_{2k+1})$ are homomorphic (from Greek *homos* meaning same and *morphe* meaning form)⁷ if they are structurally and stereochemically identical when they are detached from the ring system. Thus single homomorphic alkyl groups exhibit the same geometrical structure and the same steric configuration. The molecular stereograph G_k of HPMCA shown in figure 1 consists of m subgraphs T_k called *steric trees* representing alkyl groups $(C_k H_{2k+1})$ and one subgraph G_0 which is a stereograph of the parent monocyclic hydrocarbon $C_n H_{2n}$ with a ring size n . The stereograph G_0 contains n labelled vertices corresponding to tetravalent carbons which are

linked to unlabeled vertices representing a total of $2n$ hydrogen atoms or substitution sites. We claim that the composite molecular graph G_k can be constructed by attaching the roots of m homomorphic rooted steric trees T_k of order k to m unlabeled vertices.

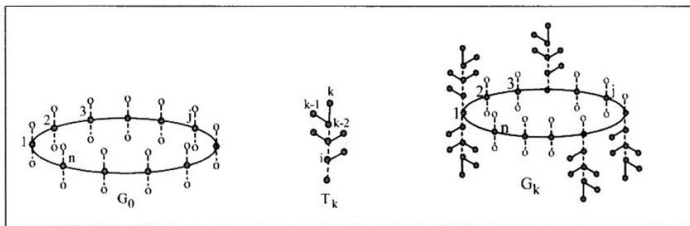


Figure 1 : Molecular graphs G_0 , T_k and G_k representing respectively a monocycloalkane C_nH_{2n} , an alkyl group (C_kH_{2k+1}) and a branched monocyclic cycloalkane $C_nH_{2n-m}(C_kH_{2k+1})_m$.

Let the system $C_nH_{2n-m}(C_kH_{2k+1})_m$ be denoted by $(n, 2n, m, k)$. These four positive integers denote respectively the ring size, the number of available substitution sites, the degree of substitution, and the order of the alkyl group. In the parlance of graph theory any alkyl group (C_kH_{2k+1}) is equivalent to a rooted steric tree which may have one or several structural isomers and several stereoisomers including chiral and achiral forms. Let s_k and p_k denote respectively the total number and the number of achiral rooted steric trees of order k . It may be recalled that the generating functions containing these numbers have been derived by Robinson et al¹ in the polynomials: $s_k(x) = \sum_k s_k x^k$, and $p_k(x) = \sum_k p_k x^k$ for $0 \leq k \leq 14$.

In table 1 hereafter we present the values of s_k , p_k and $s_k - p_k$ that we have extended to the level $k \leq 18$.

Table 1: Values of s_k , p_k and $s_k - p_k$ representing respectively the total number and the numbers of achiral and chiral rooted steric trees of order $k \leq 18$.

k	s_k	p_k	$s_k - p_k$
0	1	1	0
1	1	1	0
2	1	1	0
3	2	2	0
4	5	3	2
5	11	5	6
6	28	8	20
7	74	14	60
8	199	23	176
9	551	41	510
10	1533	69	1464
11	4436	122	4314
12	12832	208	12624
13	37496	370	37126
14	110500	636	109864
15	327420	1134	326286
16	979819	1963	977856
17	2944873	3505	2941368
18	8896315	6099	8890416

All the graphical representations of $(C_k H_{2k-1})$ by rooted steric trees can be collected into three sets of elements equivalent to sterically distinct stereoisomers. Let E_{a+c} , E_a and E_c denote these sets with the cardinality s_k , p_k , and $(s_k - p_k)$, respectively. The elements of E_{a+c} include the enantiomer pairs and achiral skeletons while those of E_a and E_c are exclusively achiral and chiral skeletons. We adopt the convention to designate each sterically distinct stereoisomer by a letter of the alphabet and each enantiomer pair by a couple of identical letters differentiated by a prime symbol (see figure 2 and table 2 the notations of type B , B' and so on). Therefore E_{a+c} , E_a , and E_c are transformed into sets of alphabetical letters and some examples are given for $1 \leq k \leq 5$ in table 2.

$C_k H_{2k+1}$	Rooted steric trees
$C_3 H_7$	
$C_4 H_9$	
$C_5 H_{11}$	

Figure 2: Graphical representations of distinct rooted steric trees identified by letters of the alphabet.

Table 2: Collection in the sets E_{a+c} , E_a , and E_c of alphabetical letters as alternative designations of distinct rooted steric trees.

$C_k H_{2k+1}$	E_{a+c}	E_a	E_c
CH_3	$\{A\}$	$\{A\}$	$\{\emptyset\}$
$C_2 H_5$	$\{A\}$	$\{A\}$	$\{\emptyset\}$
$C_3 H_7$	$\{A, B\}$	$\{A, B\}$	$\{\emptyset\}$
$C_4 H_9$	$\{A, B, B', C, D\}$	$\{A, C, D\}$	$\{B, B'\}$
$C_5 H_{11}$	$\{A, B, B', C, C', D, E, F, F', G, H\}$	$\{A, D, E, G, H\}$	$\{B, B', C, C', F, F'\}$

The substitutions of m hydrogen atoms by m homomorphic alkyl groups or rooted steric trees is equivalent in combinatorics to the placement of m objects of one kind into m boxes. A homomorphism between rooted steric trees is then a structural and sterical homomorphism in which the structures and configurations of substituents are preserved. If the rooted steric trees may be symbolized by an alphabet collected in the sets E_{a+c} , E_a and E_c , the first problem to solve is the determination of the number of homomorphic m -tuples of letters one may obtain

from these sets i.e. how many words of length m and of type $w_m=aa\dots a$ one may form with one kind of letter chosen among the elements of the sets E_{a+c} , E_a and E_c .

Let $N(s_k, r)$, $N(s_k - p_k, r)$ and $N(p_k, r)$ be the numbers of distinct words of length m formed with r kinds of distinct letters collected in the sets E_{a+c} , E_a and E_c , respectively.

The relation between these three associated sets and their cardinalities are as given in equations (1) and (2), respectively:

$$E_{a+c} = E_c \cup E_a \tag{1}$$

$$|E_{a+c}| = s_k, |E_a| = p_k, |E_c| = s_k - p_k \tag{2}$$

Therefore one obtains:

$$N(s_k, r) = \binom{s_k}{r}, N(s_k - p_k, r) = \binom{s_k - p_k}{r} \text{ and } N(p_k, r) = \binom{p_k}{r} \tag{3}$$

In the case of homomorphic words of length m , $r = 1$, then $N(s_k, 1) = s_k$, $N(s_k - p_k, 1) = s_k - p_k$ and $N(p_k, r) = p_k$. Note that $N(s_k, 1) = N(s_k - p_k, 1) + N(p_k, 1)$. With this result one may easily deduce that the numbers $N(s_k, 1)$, $N(s_k - p_k, 1)$ and $N(p_k, 1)$ of distinct homomorphic words written up by using a unique letter of an alphabet are independent of their length m . To exemplify this situation we consider the set E_{a+c} , for rooted steric trees T_k where $3 \leq k \leq 5$. If we let $r = 1$ the complete list of distinct homomorphic words of length $m = 4$, noted by w_j , are given in table 3.

Table 3: Homomorphic words of length $m = 4$ symbolizing distinct types of homomorphic polyalkylations for a given integer number k .

$C_k H_{2k+1}$	s_k	p_k	E_{a+c}	$w_4 (r = 1)$
$C_3 H_7$	2	2	$\{A, B\}$	AAAA, BBBB
$C_4 H_9$	5	3	$\{A, B, B', C, D\}$	AAAA, BBBB, B' B' B' B', CCCC, DDDD
$C_5 H_{11}$	11	5	$\{A, B, B', C, C', D, E, F, F', G, H\}$	AAAA, BBBB, B' B' B' B', CCCC, C' C' C' C', DDDD, EEEE, FFFF, F' F' F' F', GGGG, HHHH

From the above notations one may retain that the alphabet of s_k distinct letters generates $N(s_k, 1) = s_k$ distinct homomorphic words w_m and this result is the number of homomorphic polyalkylations. Then the number $N(s_k, 1)$ includes $N(s_k - p_k, 1) = s_k - p_k$ homomorphic polyalkylations generated from $(s_k - p_k)$ chiral rooted trees and $N(p_k, 1) = p_k$ homomorphic

polyalkylations generated from p_k achiral rooted trees. For fixed values $s_k = 11$ and $p_k = 5$ given in our example one may obtain $N(s_k, 1) = 11$ types of homomorphic polyalkylations using the alkyl group C_5H_{11} . This result includes $N(s_k - p_k, 1) = 6$ homomorphic polyalkylations noted : $\{BBBB, B'B'B'B', CCCC, C'C'C'C', FFFF, F'F'F'F'\}$ which are issued from chiral configurations and $N(p_k, 1) = 5$ other homomorphic polyalkylations noted $\{AAAA, DDDD, EEEE, GGGG, HHHH\}$ which come from achiral rooted trees of C_5H_{11} . In conclusion to this part it appears that a polyalkylated monocyclic cycloalkane with an empirical formula $C_nH_{2n-m}(C_kH_{2k+1})_m$ gives rise to $N(s_k - p_k, 1)$ skeletons with chiral homomorphic alkyl groups and $N(p_k, 1)$ skeletons with achiral homomorphic alkyl groups. Therefore the problem of counting chiral and achiral skeletons for an n -membered ring substituted by homomorphic rooted steric trees is split into :

1°)- the enumeration of chiral and achiral skeletons of stereo and positions isomers resulting from homopolyalkylations of order m with chiral rooted trees of order k ; there are $N(s_k - p_k, 1)$ such possibilities.

2°)- the enumeration of chiral and achiral skeletons of stereo and positions isomers resulting from homopolyalkylations of order m with achiral rooted trees of order k ; there are $N(p_k, 1)$ such occurrences.

The subgraph G_0 of an n -membered ring belongs to the symmetry point group D_{nh} which includes $4n$ symmetry operations and contains $2n$ unlabeled vertices or substitution sites which are permutable under the action of these $4n$ symmetry operations. According to this consideration we must carry out $4n$ permutation operations among the $2n$ substitution sites for each homomorphic substitution of degree m (i.e we have to proceed each time to the placement of m homomorphic rooted steric trees of one kind among the $2n$ substitution sites).

These $4n$ permutations are collected in partition notation in the set P given by eqs (4) and (5) :

$$P = \left\{ a_i \left[2^n \right], (n+1) \left[2^n \right], \dots, a_d \left[d^{\frac{2n}{d}} \right], \dots, a_n \left[n^2 \right], a_{2n} \left[2n \right], n \left[2^{n-1} \right] \right\} \text{ for } n \text{ odd} \quad (4)$$

$$P = \left\{ a_i \left[2^n \right], \frac{3}{2} (n+2) \left[2^n \right], \dots, a_d \left[d^{\frac{2n}{d}} \right], \dots, a_n \left[n^2 \right], \frac{n}{2} \left[4 \cdot 2^{n-2} \right] \right\} \text{ for } n \text{ even} \quad (5)$$

By eliminating in P the contributions of reflections and roto-reflections one may derive in relations (6)-(7) the set P' of $2n$ permutations induced by rotation symmetries only.

$$P' = \left\{ a'_i [i^{2n}], n [2^n], \dots, a'_d \left[d^{\frac{2n}{d}} \right], \dots, a'_n [n^2] \right\} \text{ for } n \text{ odd} \quad (6)$$

$$P' = \left\{ a'_i [i^{2n}], (n+1) \cdot [2^n], \dots, a'_d \left[d^{\frac{2n}{d}} \right], \dots, a'_n [n^2] \right\} \text{ for } n \text{ even} \quad (7)$$

The notation $[i^j]$ in expressions (4)-(7) refers to j permutation cycles with length i , and the coefficients a_d and a'_d are determined from equations (8)-(12) where $\varphi(d)_{rp} = \varphi(d)_{ri}$ and $\varphi(\mu)_{ri}$ correspond to the

$$a_d = \varphi(d)_{rp} \quad d(\text{odd}) \quad (8)$$

$$a_{2d} = \varphi(d)_{ri} \quad d(\text{odd}) \quad (9)$$

$$a_d = \varphi(d)_{rp} + \varphi(d)_{ri} \quad d(\text{even}) \neq 2\mu \quad (\mu \text{ odd}) \quad (10)$$

$$a_d = \varphi(d)_{rp} + \varphi(d)_{ri} + \varphi(\mu)_{ri} \quad d(\text{even}) = 2\mu \quad (\mu \text{ odd}) \quad (11)$$

$$a'_d = \varphi(d)_{rp} \quad \text{si } d \text{ odd or even} \quad (12)$$

Euler totient function⁸ for the integer numbers d or μ which are the order of proper or improper rotation axes (see indices rp or ri respectively).

The $4n$ permutations occur for each type of rooted steric tree T_k . The number of such occurrences is equal to $N(s_k - p_k, 1)$ and $N(p_k, 1)$ for chiral and achiral rooted steric trees of order k , respectively. Finally the determination of chiral and achiral skeletons of stereo and position isomers of a monocycloalkane polyalkylated with a single type of homomorphic rooted steric tree of order k is equivalent to the problem of counting chiral and achiral skeletons of the system $C_n H_{2n-2m} X_m$. The solution to this problem presented in our previous studies⁵⁻⁶ is summarized in eqs (13)-(20). Let the system $C_n H_{2n-2m} X_m$ be denoted $(n, 2n, m)$ and let us define for n odd and m odd or even, the sets $D_{2n} = \{1, 2, \dots, d, \dots, n, 2n\}$ and $D_{m\pm} = \{1, \dots, d', \dots, m\}$ containing the divisors of $2n$ and m . Throughout this paper the notations n_-, m_- and n_+, m_+ are assigned to the integer numbers n odd m odd, and n even, m even, respectively. We extract from the sets aforementioned the subsets $D_{2n_-} \cap D_{m_-}$ and $D_{2n_+} \cap D_{m_+}$ which contain the common divisors $\{d_c\}$ of the integer numbers $(2n, m)$. Then the enantiomer pairs and achiral skeletons inventories are given by eqs (13)-(16).

If $d_c \neq 2 \in D_{2n} \cap D_m$ and $\mu' = \frac{m-1}{2}$, then

$$A_+(n, m) = \frac{1}{4n} \left[\sum_{d, v^2} (2a'_d - a_d) \cdot \left(\frac{2n}{d_c} \right) - 2n \binom{n-1}{\mu'} \right] \quad (13)$$

$$A_-(n, m) = \frac{1}{2n} \left[\sum_{d, v^2} (a_d - a'_d) \cdot \left(\frac{d_c}{m} \right) + 2n \binom{n-1}{\mu'} \right] \quad (14)$$

If $d \neq 2 \in D_{2n} \cap D_m$, then :

$$A_+(n, m) = \frac{1}{4n} \left[\sum_{d, v^2} (2a'_d - a_d) \cdot \left(\frac{2n}{d} \right) - 2n \binom{\frac{n}{m}}{\frac{m}{2}} \right] \quad (15)$$

$$A_-(n, m) = \frac{1}{2n} \left[\sum_{d, v^2} (a_d - a'_d) \cdot \left(\frac{d}{m} \right) + (n+1) \binom{\frac{n}{m}}{\frac{m}{2}} \right] \quad (16)$$

But if n even and m odd or even, we define this time the sets $D_{n_{\pm}} = \{1, 2, \dots, d, \dots, n\}$ and $D_{m_{\pm}} = \{1, \dots, d', \dots, m\}$ containing the divisors of n and m . We extract from these sets the subsets $D_{n_{\pm}} \cap D_{m_{\pm}}$ or $D_{n_{\pm}} \cap D_{m_{\pm}}$ which contain the common divisors $\{d_c\}$ of the integer numbers (n, m) . Then the enantiomer pairs and achiral skeletons inventories are given by eqs (17)-(20).

If $d_c \neq 2 \in D_{n_c} \cap D_{m_c}$ and $\mu' = \frac{m-1}{2}$, then

$$A_{ac}(n_c, m_c) = \frac{1}{4n} \left[\sum_{d_c \neq 2} (2a_{d_c}' - a_{d_c}) \cdot \left(\frac{2n}{d_c} \cdot \frac{d_c}{m} \right) - 2n \binom{n-1}{\mu'} \right] \quad (17)$$

$$A_{ac}(n_c, m_c) = \frac{1}{2n} \left[\sum_{d_c \neq 2} (a_{d_c} - a_{d_c}') \cdot \left(\frac{2n}{d_c} \cdot \frac{d_c}{m} \right) + 2n \binom{n-1}{\mu'} \right] \quad (18)$$

If $d_c \neq 2 \in D_{n_c} \cap D_{m_c}$, then :

$$A_s(n_c, m_c) = \frac{1}{4n} \left[\sum_{d_c \neq 2} (2a_{d_c}' - a_{d_c}) \cdot \left(\frac{2n}{d_c} \cdot \frac{d_c}{m} \right) + \frac{1}{n-1} \left(\frac{m^2 - n(m+1) + 1}{2} \right) \binom{n}{\frac{m}{2}} \right] \quad (19)$$

$$A_{ac}(n_c, m_c) = \frac{1}{2n} \left[\sum_{d_c \neq 2} (a_{d_c} - a_{d_c}') \cdot \left(\frac{2n}{d_c} \cdot \frac{d_c}{m} \right) + \frac{1}{n-1} \left(n^2 + n(m+1) - \frac{m^2}{2} - 2 \right) \binom{n}{\frac{m}{2}} \right] \quad (20)$$

The terms $A_c(n_c, m_c)$ and $A_{ac}(n_c, m_c)$ denote respectively the numbers of chiral and achiral skeletons of stereo and position isomers of a homopolysubstituted monocyclic cycloalkane (HPMCA) $C_n H_{2n-m} X_m$ where X is a singular and structurally non isomerizable substituent. Some of these numbers summarized in table 4 have been presented in our previous studies.⁵⁻⁶

Table 4: Number of enantiomer pairs and achiral skeletons of a homopolysubstituted cycloalkane $C_nH_{2n-m}X_m$ where $3 \leq n \leq 8$ and $1 \leq m \leq n$.

n	m	$A_e(n, m)$	$A_{ac}(n, m)$
3	1	0	1
	2	1	2
	3	1	2
4	1	0	1
	2	1	4
	3	2	3
	4	3	7
5	1	0	1
	2	2	3
	3	4	4
	4	10	6
	5	10	6
6	1	0	1
	2	2	5
	3	7	5
	4	18	14
	5	28	10
	6	35	20
7	1	0	1
	2	3	4
	3	10	6
	4	35	12
	5	64	15
	6	106	20
	7	113	20
8	1	0	1
	2	3	6
	3	14	7
	4	53	24
	5	126	21
	6	241	50
	7	340	35
	8	390	65

On the other hand, the molecules of the series $C_nH_{2n-m}C_kH_{2k+1}_m$ where the m alkyl groups are homomorphic give rise to a wide range of stereo and position isomers due to distinct placements of the m alkyl groups C_kH_{2k+1} among $2n$ substitution sites of the n -membered ring. The second characteristic of these compounds is related to distinct steric configurations exhibited by these alkyl groups which may be chiral or achiral. With regard to this double

stereospecificity we claim that the chirality or achirality of HPMCA results from crossed composition of the chiral or achiral placements of m homomorphic alkyl groups on the ring (stereoisomerism issued from the positioning of m groups) and the intrinsic chiral or achiral character of each alkyl group. Such a composition is summarized in table 5 hereafter.

Table 5: Composition of the chirality and achirality of HPMCA.

Chirality or achirality of HPMCA	Chiral alkyl groups	Achiral alkyl groups
Chiral placement	chiral alkyl groups-chiral placement (A_c^c)	achiral alkyl groups-chiral placement (A_c^a)
Achiral placement	chiral alkyl groups-achiral placement (A_a^c)	achiral alkyl groups-achiral placement (A_a^a)

Now according to table 5, let $A_c^c(n_{\pm}, m_{\pm}, k)$, $A_a^c(n_{\pm}, m_{\pm}, k)$, $A_c^a(n_{\pm}, m_{\pm}, k)$, $A_a^a(n_{\pm}, m_{\pm}, k)$ denote the numbers of skeletons of HPMCA with : (a) chiral alkyl groups-chiral placement, (b) chiral alkyl groups-achiral placement, (c) achiral alkyl groups-chiral placement, (d) achiral alkyl groups-achiral placement, respectively. In table 5 the superscripts (c) or (a) refer to chiral or achiral alkyl groups while the underscripts (c) or (a) are assigned to the chiral or achiral placement or positioning of the m alkyl groups on the carbon ring. To derive these numbers which are the solution of our enumeration problem, we apply the following rule:

The number of chiral or achiral skeletons of HPMCA is directly obtained from the product of the number of occurrences $N(s_k - p_k, 1)$ and $N(p_k, 1)$ for chiral and achiral rooted steric trees T_k of order k and the number of chiral or achiral placements $A_c(n_{\pm}, m_{\pm})$ and $A_a(n_{\pm}, m_{\pm})$ of these rooted steric trees on the n -membered ring.

Hence:

$$A_c^c(n, m, k) = N(s_k - p_k, 1) [A_c(n_{\pm}, m_{\pm})] = (s_k - p_k) A_c(n, m) \quad (21)$$

$$A_c^a(n, m, k) = N(s_k - p_k, 1) [A_a(n_{\pm}, m_{\pm})] = (s_k - p_k) A_a(n, m) \quad (22)$$

$$A_a^c(n_{\pm}, m_{\pm}, k) = N(p_k, 1) [A_c(n_{\pm}, m_{\pm})] = (p_k) A_c(n, m)$$

(23)

$$A_a^a(n, m, k) = N(p_k, 1) [A_a(n_{\pm}, m_{\pm})] = (p_k) A_a(n, m) \quad (24)$$

The total number of enantiomer pairs of HPMCA is obtained by summing up three parameters

$A_c^c(n, m, k)$, $A_c^a(n, m, k)$ and $A_a^c(n, m, k)$. Then :

$$A_c(n_{\pm}, m_{\pm}, k) = A_c^c(n_{\pm}, m_{\pm}, k) + A_c^a(n_{\pm}, m_{\pm}, k) + A_a^c(n_{\pm}, m_{\pm}, k) \quad (25)$$

while the total number of achiral skeletons of HPMCA is:

$$A_{ac}(n, m, k) = A_a^a(n, m, k) \quad (26)$$

We illustrate our counting procedure by two examples of calculations given hereafter in the series of molecules $C_3H_{6-m}(C_4H_9)_m$.

Example 1: Enantiomer pairs and achiral skeletons of $C_3H_4(C_4H_9)_2$.

Let $n=3$, $m=2$, $k=4$, $s_4=5$, $p_4=3$, $s_4 - p_4 = 2$, $A_c(3,2)=1$, $A_{ac}(3,2) = 2$, then according to equations (21)-(26) $A_c^c(3,2,4)=(s_4 - p_4) \cdot A_c(3,2)=2 \times 1=2$ and $A_a^c(3,2,4)=(s_4 - p_4) \cdot A_{ac}(3,2)=2 \times 2=4$; these species exhibit the absolute configurations RR or SS, see figure 3), $A_c^a(3,2,4)=p_4 \cdot A_c(3,2)=3 \times 1=3$, $A_a^a(3,2,4)=p_4 \cdot A_{ac}(3,2)=3 \times 2=6$ (these species are meso forms). Finally the total number of enantiomer pairs and achiral skeletons of this system are respectively:

$$A_c(3,2,4) = A_c^c(3,2,4) + A_a^c(3,2,4) + A_c^a(3,2,4) = 2 + 4 + 3 = 9 \text{ and } A_{ac}(3,2,4) = A_a^a(3,2,4) = 6.$$

Example 2: Enantiomer pairs and achiral skeletons of $C_3H_3(C_4H_9)_3$.

Let $n=3$, $m=3$, $k=4$, $s_4=5$, $p_4=3$, $s_4 - p_4 = 2$, $A_c(3,3)=1$ and $A_{ac}(3,3) = 2$, then according to equations (21)-(26): $A_c^c(3,3,4)=(s_4 - p_4) \cdot A_c(3,3)=2 \times 1=2$ and $A_a^c(3,3,4)=(s_4 - p_4) \cdot A_{ac}(3,3)=2 \times 2=4$; these species exhibit the absolute configurations RR or SS, see figure 3), $A_c^a(3,3,4)=p_4 \cdot A_c(3,3)=3 \times 1=3$, $A_a^a(3,3,4)=p_4 \cdot A_{ac}(3,3)=3 \times 2=6$. Finally the total number of enantiomer pairs and achiral skeletons of this system are respectively:

$$A_c(3,3,4) = A_c^c(3,3,4) + A_a^c(3,3,4) + A_c^a(3,3,4) = 2 + 4 + 3 = 9 \text{ and } A_{ac}(3,3,4) = A_a^a(3,3,4) = 6.$$

The figure inventories obtained from this counting procedure are given in table 5 for ring sizes $3 \leq n \leq 6$, the degrees of substitution $m \leq n$, and the order $3 \leq k \leq 8$.

Table 6 : Numbers of enantiomer pairs and achiral skeletons for monocyclic systems with a ring size $3 \leq n \leq 6$ the degrees of substitution $m \leq n$ and the order $3 \leq k \leq 8$.

k	$N \rightarrow$	3				4				5				6			
		m	A_c^c	A_a^c	A_c^a	A_a^a	A_c^c	A_a^c	A_c^a	A_a^a	A_c^c	A_a^c	A_c^a	A_a^a	A_c^c	A_a^c	A_c^a
3	1	0	0	0	2	0	0	0	2	0	0	0	2	0	0	0	2
	2	0	0	2	4	0	0	2	8	0	0	4	6	0	0	4	10
	3	0	0	2	4	0	0	4	6	0	0	8	8	0	0	14	10
	4					0	0	6	14	0	0	20	12	0	0	36	28
	5									0	0	20	12	0	0	56	20
	6													0	0	70	40
4	1	0	2	0	3	0	2	0	3	0	2	0	3	0	2	0	3
	2	2	4	3	6	2	8	3	12	4	6	6	9	4	10	6	15
	3	2	4	3	6	4	6	6	9	8	8	12	12	14	10	21	15
	4					6	14	9	21	20	12	30	18	36	28	54	42
	5									20	12	30	18	56	20	84	30
	6													70	40	105	60
5	1	0	6	0	5	0	6	0	5	0	6	0	5	0	6	0	5
	2	6	12	5	10	6	24	5	20	12	18	10	15	12	30	10	25
	3	6	12	5	10	12	18	10	15	24	24	20	20	42	30	35	25
	4					18	42	15	35	60	36	50	30	108	84	90	70
	5									60	36	50	30	168	60	140	50
	6													210	120	175	100
6	1	0	20	0	8	0	20	0	8	0	20	0	8	0	20	0	8
	2	20	40	8	16	20	80	8	32	40	60	16	24	40	100	16	40
	3	20	40	8	16	40	60	16	24	80	80	32	32	140	100	56	40
	4					60	140	24	56	200	120	80	48	360	280	144	112
	5									200	120	80	48	560	200	224	80
	6													700	400	280	160
7	1	0	60	0	14	0	60	0	14	0	60	0	14	0	60	0	14
	2	60	120	14	28	60	240	14	56	120	180	28	42	120	300	28	70
	3	60	120	14	28	120	180	28	42	240	240	56	56	420	300	98	70
	4					180	420	42	98	600	360	140	84	1080	840	252	196
	5									600	360	140	84	1680	600	392	140
	6													2100	1200	490	280
8	1	0	176	0	23	0	176	0	23	0	176	0	23	0	176	0	23
	2	176	352	23	46	176	704	23	92	352	528	46	69	352	880	46	115
	3	176	352	23	46	352	528	46	69	704	704	92	92	1232	880	161	115
	4					528	1232	69	161	1760	1056	230	138	3168	2464	414	322
	5									1760	1056	230	138	4928	1760	644	230
	6													6160	3520	805	460

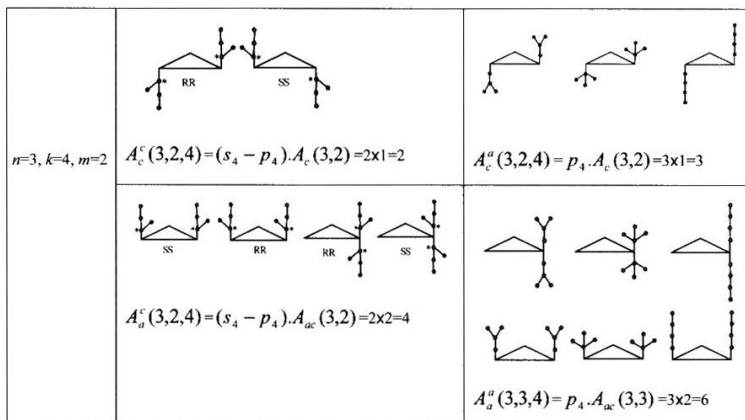


Figure 3: Representation of chiral and achiral skeletons of $C_3H_4(C_4H_9)_2$ with homomorphic C_4H_9 groups.

CONCLUSION.

This theoretical study gives a good insight to the composite chirality of branched cycloalkanes. In the series of HPMCA the molecular chirality results from the cross composition of the steric character of alkyl branches and the stereoisomerism due to the placements of these groups on the carbon ring. Furthermore the preceding developments give evidence of the stereospecificity of polyalkylation reactions in cyclic systems. In a future paper, the problem of pseudoachirality will be discussed arising when substituents of the same order may have opposite chirality; also, all general problems will be analyzed arising when the condition of homomorphic substitution will be suppressed i.e when alkyl substituents may have different orders or different chiralities.

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