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APPLICATION OF PÓLYA'S THEOREM TO CATAMANTANES

Alexandru T. Balaban [a] and Viorica Baciu [b]

[a] The Polytechnic, Organic Chemistry Departament, Bucharest

[b] Geological Prospecting Enterprise, Bucharest, Roumania

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Abstract

The numbers of substituted derivatives of diamantane, triamantane, and of the three possible tetramantanes are calculated using Pólya's theorem. Calculations are effected for C-labelled and H-labelled catamantanes for three cases : (i) including stereoisomerism ; (ii) excluding enantiomerism ; and (iii) excluding entirely stereoisomerism, i.e. calculating only the numbers of constitutional isomers.

Introduction

In analogous fashion to the derivation of the bidimensional benzenoid polycyclic hydrocarbons (polyhexes) from benzene, one can imagine the tridimentional diamond hydrocarbons (or diamondoid hydrocarbons) to be derived from adamantane. The polyhexes are classified into catafusenes and perifusenes, according to whether their dualist graphs (resulted

by joining the centres of condensed benzenoid rings) are acyclic or cyclic, respectively.[2-4]

A detailed discussion of the classification and nomenclature of diamond hydrocarbons is to be found in a recent paper by Balaban and Schleyer;[5] that paper[5] also contains an enumeration of polymantanes up to seven condensed adamantane units (cf. also ref.[6]).

In the present report we shall only indicate that the diamond hydrocarbons contain at least one adamantane unit and are wholly or largely superimposable on the diamond lattice.The group of diamondoid hydrocarbons whose carbon atoms all belong in complete adam. units(are face-fused, i.e. have six common carbon atoms for each pair of condensed adam. units) is termed the group of polymantanes. The polymantanes are classified into catamantanes and perimantanes, according to whether the dualist graphs of polymantanes (formed by joining the centres of the n condensed adam. units) is acyclic or cyclic respectively. The catamantanes are called regular if they have formula $C_{4n+6}H_{4n+12}$ and irregular otherwise(the smallest irregular catamantane is [1231] pentamantane and the smallest perimantane is [12312] hexamantane). All dualist graphs of catamantanes are staggered C-rotamers of alkanes which were enumerated previously[7], but some C-rotamers cannot be dualist graphs of catamantanes[5,6].For the nomenclature of catamantanes the dualist graphs may be coded by the sequences of four digits (1,2,3,4), as well be shown below for the tetramantanes. These digits indicate the four directions of valencies in a tetrahedral carbon atom and the sequence codes

the coiling of the dualist graph.

So far from the possible catamantanes, only four hydrocarbons are known (fig.1): n=1, adamantane,[8,9] I; n=2, diamantane,[10] II; n=3, triamantane,[11] III; and for n=4 there are three isomeric tetramantanes, namely [121]tetramantane,[12] IV, [123]tetramantane, V, having a non-branched dualist graph and [1(2)3]tetramantane, VI, whose dualist graph is branched.

All known catamantanes were obtained synthetically by $AlCl_3$-catalyzed isomerization of isomeric saturated bridged polycyclic hydrocarbons.

The numbers of substituted derivatives of adamantane were discussed earlier[13-15]. In the present paper we develop the preceding treatment[14], adapting it for counting the numbers of substituted isomers of di-,tri-,and tetramantanes. In the previous paper[14], after counting (i) all stereoisomers by applying Pólya's theorem to the adamantane molecule, <u>different graphs</u> were employed in order to count (ii) only diastereoisomers, omitting enantiomers or (iii) only constitutional isomers, omitting entirely srereoisomerism. A similar approach was used subsequently for enumerating substituted derivatives of cycloalkanes[16].

In the present paper, we shall make use of Pólya's theorem as in preceding paper[14] and as shown for a variety of organic stereoisomeric systems by Davidson[15].

We shall denote by <u>C-labelled</u> system a derivative where one (or more) carbon atom(s) was replaced by an isotopic carbon or by a heteroatom; the valence of the heteroatom must be 2 to 4 if a secondary carbon atom is substituted, or 3 to 4 if a

tertiary carbon atom is substituted. Analogously, a H-labelled system is a molecule where one or more hydrogen atom(s) have been replaced by univalent substituents.

An important step for the application of Pólya's theorem is the finding of the cycle index Z(A) of graph A which expresses the symmetry operations on this graph by

$$Z(A) = \frac{1}{|A|} \sum_{\alpha \in A} \prod_{k=1} y_k^{j_k(\alpha)} \qquad (1)$$

The order $|A|$ of the symmetry group is the sum of coefficients embraced by $\sum$.

In order to obtain the numbers of all stereoisomers including enantiomers the molecule is considered as a geometric object and only the proper rotation axes are taken into account. For obtaining diastereoisomers only, i.e. excluding enantiomers one has to take into account all proper and improper rotation axes, as well as symmetry planes. For obtaining only constitutional isomers, i.e. excluding entirely stereoisomers one has to include still more symmetry operations by considering all relevant permutations under the symmetric group S_2 combined with the cycle index for the U-labelled diastereoisomers; the variable associated with secondary carbon atoms is substituted by the symmetric group S_2.
It should be mentioned that the same procedure can be applied for obtaining the numbers of constitutional isomers of substituted cycloalkanes[16].

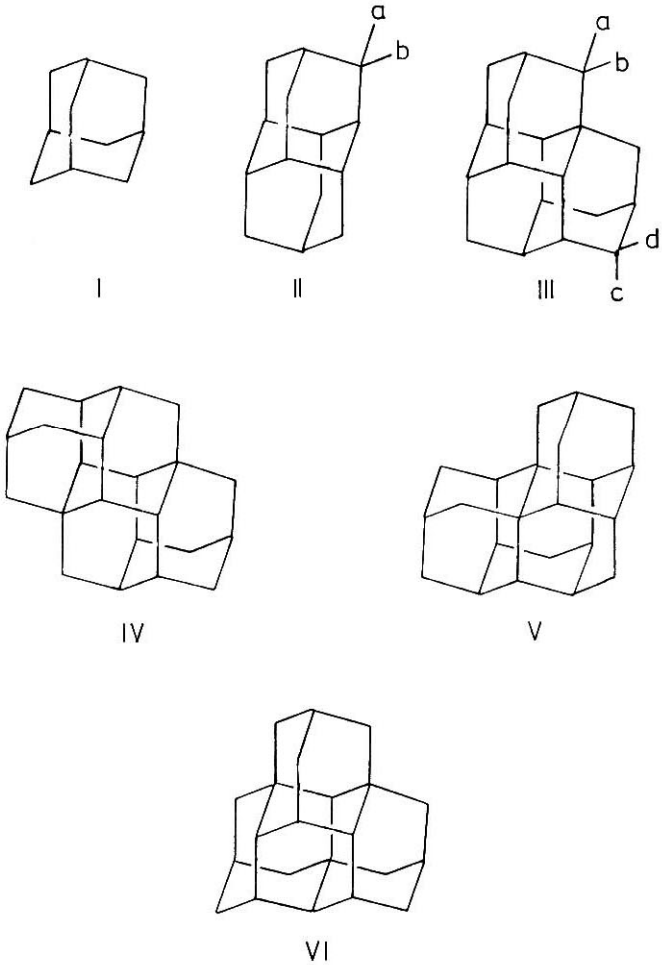

FIG. 1

Diamantane $(CH)_8(CH_2)_6$

For diamantane, $C_{14}H_{20}$, II, we discriminate in Fig.2 the two kinds of vertices according to their degrees*: black (closed) circles indicate tertiary carbon atoms (CH-type) or hydrogens bonded to them and the variable associated with these vertices will be denoted by t; white (open) circles indicate secondary carbon atoms (CH_2-type) with associated variable s, or pairs of hydrogens bonded to them (associated variable u).

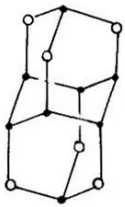

FIG. 2

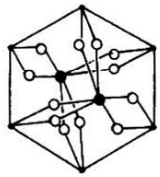

FIG. 3

Table 1 contains the symmetry operations displayed by diamantane (point group $\underline{D}_3$).

Considering only the proper rotation axes, the cycle index contains $|A| = 6$ symmetry operations, leading to all ste-

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* The degree of a vertex in a graph is the number of adjacent vertices, i.e. the number of its nearest neighbouring vertices.

Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	Permutation	Term in cycle index
1	2	3	4	5	6	7	8	9	10	11	12	13	14	(1)(2)(3)....	y_1^{14}
1	6	5	8	9	7	2	10	3	4	11	14	12	13	(1)(11)(2,6,7)(3,5,9)(4,8,10)(12,14,13)	$y_1^2 y_3^4$
1	7	9	10	3	2	6	4	5	8	11	13	14	12	(1)(11)(2,7,6)(3,9,5)(4,10,8)(12,13,14)	$y_1^2 y_3^4$
11	14	10	9	8	12	13	5	4	3	1	6	7	2	(1,11)(2,14)(3,10)(4,9)(5,8)(6,12)(7,13)	y_2^7
11	13	4	3	10	14	12	9	8	5	1	7	2	6	(1,11)(2,13)(3,4)(5,10)(6,14)(7,12)(8,9)	y_2^7
11	12	8	5	4	13	14	3	10	9	1	2	6	7	(1,11)(2,12)(3,8)(4,5)(6,13)(7,14)(9,10)	y_2^7
1	6	5	4	3	2	7	10	9	8	11	14	13	12	(1)(4)(7)(9)(11)(13)(2,6)(3,5)(8,10)(12,14)	$y_1^6 y_2^4$
1	7	9	8	5	6	2	4	3	10	11	13	12	14	(1)(5)(6)(10)(11)(14)(2,7)(3,9)(4,8)(13,12)	$y_1^6 y_2^4$
1	2	3	10	8	7	6	9	5	4	11	12	14	13	(1)(2)(3)(8)(11)(12)(6,7)(5,9)(4,10)(13,14)	$y_1^6 y_2^4$
11	12	8	9	10	14	13	3	4	5	1	2	7	6	(1,11)(2,12)(3,8)(4,9)(5,10)(6,14)(7,13)	y_2^7
11	13	4	5	8	12	14	9	10	3	1	7	6	2	(1,11)(3,4,5,8,9,10)(2,13,6,12,7,14)	$y_2 y_6^2$
11	14	10	3	4	13	12	5	8	9	1	6	2	7	(1,11)(3,10,9,8,5,4)(2,14,7,12,6,13)	$y_2 y_6^2$

reoisomers:

$$Z_S\ (\underline{D}_3,t,s) = \frac{1}{6}\ (t_1^8 s_1^6 + 2t_1^2 t_3^2 s_3^2 + 3t_2^4 s_2^3\ ) \qquad (2)$$

for C-labelled diamantanes.

$$Z_S\ (\underline{D}_3,t,u) = \frac{1}{6}\ (t_1^8 u_1^{12} + 2t_1^2 t_3^2 u_3^4 + 3t_2^4 u_2^6\ ) \qquad (3)$$

for H-labelled diamantanes.

Including all symmetry operations from Table 1, i.e. also the improper rotation axes and the reflexion planes, the cycle index for diastereoisomers is obtained (excluding enantiomers) :

$$Z_{S'}(\underline{D}_3,t,s) = \frac{1}{12}\Big[(t_1^8 s_1^6 + 2t_1^2 t_3^2 s_3^2 + 3t_2^4 s_2^3) + 3t_1^4 t_2^2 + t_2^4 s_2^3 + 2t_2 t_6 s_6\Big] \qquad (4)$$

for C-labelled diamantanes. This cycle index leads to the numbers of constitutional isomers of C-labelled system.

$$Z_{S'}(\underline{D}_3,t,u) = \frac{1}{12}\Big[(t_1^8 u_1^{12} + 2t_1^2 t_3^2 u_3^4 + 3t_2^4 u_2^6) + 3t_1^4 t_2^2 u_2^6 + t_2^4 u_2^6 + 2t_2 t_6 u_6^2\Big] \qquad (5)$$

for H-labelled diamantanes.

For neglecting all geometrical informations on the H-labelled diamantane molecule one has to find the cycle index of the graph presented in Fig.3 where all the pairs of hydrogens bonded to secondary carbon atoms are topologically equivalent under the symmetric permutation group S_2, with cycle index :

$$Z(S_2) = (s_1^2 + s_2)/2$$

Composition of the point group $\underline{D}_3$ with the symmetric permutation group S_2 leads to the desired cycle index on replacing s_k by:

$$s_k = \frac{1}{2}(u_k^2 + u_{2k}) \tag{6}$$

Thus we obtain from (4) and (6):

$$Z(\underline{D}_{3d};t,s \ \ Z\ S_2,u\ ) = \frac{1}{12}\Big\{t_1^8\Big[\frac{1}{2}(u_1^2 + u_2)\Big]^6 +$$

$$+ 2t_1^2t_3^2\Big[\frac{1}{2}(u_3^2 + u_6)\Big]^2 + 3t_2^4\Big[\frac{1}{2}(u_2^2 + u_4)\Big]^3 +$$

$$+ 3t_1^4t_2^2\Big[\frac{1}{2}(u_1^2 + u_2)\Big]^2\Big[\frac{1}{2}(u_2^2 + u_4)\Big]^2 + t_2^4\Big[\frac{1}{2}(u_2^2 + u_4)\Big]^3 +$$

$$+ 2t_2t_6\Big[\frac{1}{2}(u_6^2 + u_{12})\Big]\Big\} \tag{7}$$

Replacing in (2)-(5) and (7) s_k, t_k, u_k by y_k and effecting all algebraic transformations we obtain the cycle indices. For n-labelled diamantane excluding stereoisomerism we obtain:

$$Z = \frac{1}{768}(y_1^{20} + 6y_1^{18}y_2 + 15y_1^{16}y_2^2 + 20y_1^{14}y_2^3 + 15y_1^{12}y_2^4 +$$

$$+ 6y_1^{10}y_2^5 + y_1^8y_2^6 + 12y_1^8y_2^6 + 32y_1^2y_3^6 + 64y_1^2y_3^4y_6 +$$

$$+ 32y_1^2y_3^2y_6^2 + 32y_2^{10} + 96y_2^8y_4 + 96y_2^6y_4^2 + 32y_2^4y_4^3 + 24y_1^6y_2^7$$

$$+ 12y_1^4y_2^8 + 24y_1^8y_2^4y_4 + 48y_1^6y_2^5y_4 + 24y_1^4y_2^6y_4 + 12y_1^8y_2^2y_4^2 +$$

$$+ 24y_1^6y_2^3y_4^2 + 12y_1^4y_2^4y_4^2 + 64y_2y_6^3 + 64y_2y_6y_{12}) \tag{8}$$

In the previous cycle indices according to Pólya's theorem one has to introduce the figure counting series, by

the substitution,

$$y_k(s_k,t_k,u_k) = 1+ x^k \qquad (9)$$

for one type of substituent other than hydrogen.
For more complicated substitution patterns, other figure-counting series can be employed,[17] e.g. $y_k = 1+x^k+v^k$ for two types of substituents other than hydrogen.

The coefficient of term x^n which is obtained by this final substitution then gives the number of diamantanes with n substituents of the same type. The results of these calculations are presented in Table 2, where the heading x^n indicates the number n of substituents of the same type (other than hydrogen).

Triamantane $C(CH)_{10}(CH_2)_7$

The molecule of triamantane $C_{18}H_{24}$ (III), is presented in Fig.4.

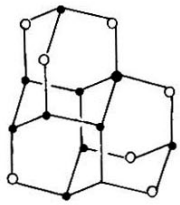

FIG.4

Table 2

Numbers of isomers for diamantane (substituted)

	Relation	x^{14}	x^{13}	x^{12}	x^{11}	x^{10}	x^{9}	x^{8}	x^{7}
C-labelled diamantane including stereoisomerism	(2)	1	3	19	62	180	335	520	576
C-labelled diamantane excluding stereoisomerism	(4)	1	3	15	42	112	198	302	330

	Relation	x^{20}	x^{19}	x^{18}	x^{17}	x^{16}	x^{15}	x^{14}	x^{13}	x^{12}	x^{11}	x^{10}
H -labelled diamantane includind stereoisomerism	(3)	1	4	37	192	834	2586	6520	12920	21105	28100	30932
H-labelled diamantane excluding enantiomerism but including diastereoisomerism	(5)	1	3	23	105	440	1329	3329	6544	10679	14126	15620
H-labelled diamantane excluding stereoisomerism	(7)	1	3	16	51	161	375	788	1332	1983	2457	2684

There are three types of vertices, according to their degrees symbolized as follows: the large closed circle represents the quaternary carbon atom (correspoding variable z) the small closed circles denote the tertiary carbon atoms or the hydrogen bonded to them (corresponding variable t) and the open circles represent the secondary carbon atoms or the pairs of hydrogens bonded to them (corresponding variable s). The code[7] of its dualist graph is 12 ; this dualist graph is the carbon skeleton of propane. The point group is $\underline{C}_2$. There are four symmetry operations: two proper rotation axes, C_1,C_2 and two reflexion planes σ and σ'. For C-labelled systems the corresponding terms in the cycle index are respectively, y_1^{18}, $y_1^2y_2^8$, $y_1^4y_2^7$ and $y_1^8y_2^5$. In these terms the exponent of y_1 terms indicates the number of carbon atoms on the symmetry element, while the exponent of y_2 terms indicates the number of pairs of carbon atoms which are interchanged by the symmetry operations.

Analogously to the previous section, we present in the following the cycle indices for substituted triamantanes including stereoisomerism, by considering only the proper rotatios:

$$Z_S(\underline{C}_2,z,t,s) = \frac{1}{2}(t_1^{10}s_1^7z + t_2^5s_1s_2^3z) \qquad (10)$$

for C-labelled triamantane.

$$Z_S(\underline{C}_2,t,s) = \frac{1}{2}(t_1^{10}s_1^{14} + t_2^5s_2^7) \qquad (11)$$

for H-labelled triamantane.

On including also the reflexions, the cycle indices for triamantanes excluding enantiomerism are obtained:

$$Z_{S'}(\underline{C}_2,z,t,s) = \frac{1}{4}\left[(t_1^{10}s_1^7z + t_2^5s_1s_2^6z) + t_1^2t_2^4s_1s_2^3z + \right.$$
$$\left. + t_1^4t_2^3s_1^3s_2^2z\right] \qquad (12)$$

for C- labelled triamantanes , which allows one to calculate the numbers of constitutional isomers.

$$Z_{S'}(\underline{C}_2,t,s) = \frac{1}{4}\left[(t_1^{10}s_1^{14} + t_2^5s_2^7) + t_1^2t_2^4s_1^4s_2^5 + t_1^4t_2^3s_2^7\right] \qquad (13)$$

for H-labelled triamantanes.

In order to find the cycle index for constitutional isomers of H-labelled triamantanes, we have to express the equivalence of the pairs of hydrogens bonded to the same secondary carbon atoms by the symmetric permutation group S_2 (6) introduced into (13):

$$Z[\underline{C}_2,t,s \rightarrow Z(S_2,u)] = \frac{1}{4}\left\{t_1^{10}\left[\frac{1}{2}(u_1^2 + u_2)\right]^7 + \right.$$
$$+ t_2^5\left[\frac{1}{2}(u_1^2 + u_2)\right]\left[\frac{1}{2}(u_2^2 + u_4)\right]^3 +$$
$$+ t_1^2t_2^4\left[\frac{1}{2}(u_1^2 + u_2)\right]\left[\frac{1}{2}(u_2^2 + u_4)\right] +$$
$$\left. + t_1^4t_2^3\left[\frac{1}{2}(u_1^2 + u_2)\right]^3\left[\frac{1}{2}(u_2^2 + u_4)\right]^2\right\} \qquad (14)$$

Then on replacing in (10)-(14) s_k,t_k and u_k by y_k we obtain

the corresponding cycle indices wherefrom on introducing the figure-counting series (9) the numbers of isomers are obtained. In particular, on replacing t_k and u_k by y_k in (14), the cycle index for constitutional isomers of H-labelled triamantanes is obtained:

$$
\begin{aligned}
Z = \frac{1}{512}(&y_1^{24} + 7y_1^{22}y_2 + 21y_1^{20}y_2^2 + 35y_1^{18}y_2^3 + 35y_1^{16}y_2^4 + \\
&+ 21y_1^{14}y_2^5 + 7y_1^{12}y_2^6 + y_1^{10}y_2^7 + 8y_1^2y_2^{11} + 24y_1^2y_2^9y_4 + \\
&+ 24y_1^2y_2^7y_4^2 + 8y_1^2y_2^5y_4^3 + 8y_2^{12} + 24y_2^{10}y_4 + 24y_2^8y_4^2 + \\
&+ 8y_2^6y_4^3 + 8y_1^4y_2^{10} + 24y_1^4y_2^8y_4 + 24y_1^4y_2^6y_4^2 + 8y_1^4y_2^4y_4^3 + \\
&+ 8y_1^2y_2^{11} + 24y_1^2y_2^9y_4 + 24y_1^2y_2^7y_4^2 + 8y_1^2y_2^5y_4^3 + 4y_1^{10}y_2^7 + \\
&+ 8y_1^{10}y_2^5y_4 + 4y_1^{10}y_2^3y_4^2 + 12y_1^8y_2^8 + 24y_1^8y_2^6y_4 + \\
&+ 12y_1^8y_2^4y_4^2 + 12y_1^6y_2^9 + 24y_1^6y_2^7y_4 + 12y_1^6y_2^5y_4^2 + 4y_1^4y_2^{10} + \\
&+ 8y_1^4y_2^8y_4 + 4y_1^4y_2^6y_4^2 \qquad (15)
\end{aligned}
$$

The numbers of isomers of substituted triamantanes are displayed in Table 3.

[121] Tetramantane $C_2(CH)_{12}(CH_2)_8$

As mentioned earlier, there are three possible isomeric tetramantanes (IV-VI) $C_{22}H_{28}$. They will be discussed in this order. The first two are valence-isomers, i.e. have the same partition of their vertex degrees, expressed by formula

Table 3

Numbers of isomers for triamantane (substituted)

	Relation	x^{18}	x^{17}	x^{16}	x^{15}	x^{14}	x^{13}
C-labelled triamantane including stereoisomerism	(10)	1	10	81	416	1528	4212
C-labelled triamantane excluding stereoisomerism	(12)	1	8	52	240	845	2288
	Relation	**x^{24}**	**x^{23}**	**x^{22}**	**x^{21}**	**x^{20}**	**x^{19}**
H-labelled triamantane including stereoisomerism	(11)	1	12	144	1052	5346	21252
H-labelled triamantane excluding enantiomerism but including diastereoisomerism	(13)	1	8	80	528	2726	10726
H-labelled triamantane excluding stereoisomerism	(14)	1	7	48	228	887	2748

$C_2(CH)_{12}(CH_2)_8$, while the third has a different partition expressed by the formula $C_3(CH)_{10}(CH_2)_9$.

[121]Tetramantane (IV) has point group $\underline{C}_{2h}$ and is presented in Fig.5 with the same conventions as in Fig.3. It is known.[12]

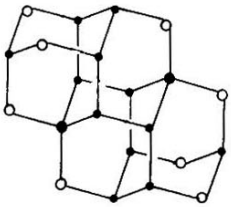

FIG. 5

In 5a, letters a-h, j, k, l indicate hydrogen atoms which are symmetrical under C_2 rotation and letter i indicates the inversion centre. The dualist graph is the carbon skeleton of n-butane in the staggered <u>trans</u>-conformation. There are four symmetry elements: two proper rotation axes C_1 and C_2, one reflexion plane σ and one inversion centre i equivalent to one binary improper rotation axis S_2. In order to sa e space, we shall present together the cycle indices Z_S and $Z_{S'}$: Z_S is the first part, in round brackets of the expression, and $Z_{S'}$ is in square brackets.

For C-labelled [121]tetramantanes,

$$Z_{S,S'}(\underline{C}_{2h},z,t,s) = \frac{1}{2}\left[\left(\frac{z_1^2t_1^{12}s_1^8 + z_2t_2^6s_2^4}{2}\right) +\right.$$

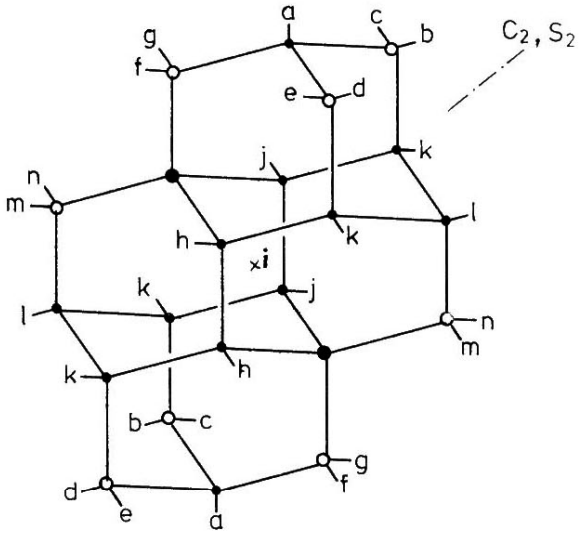
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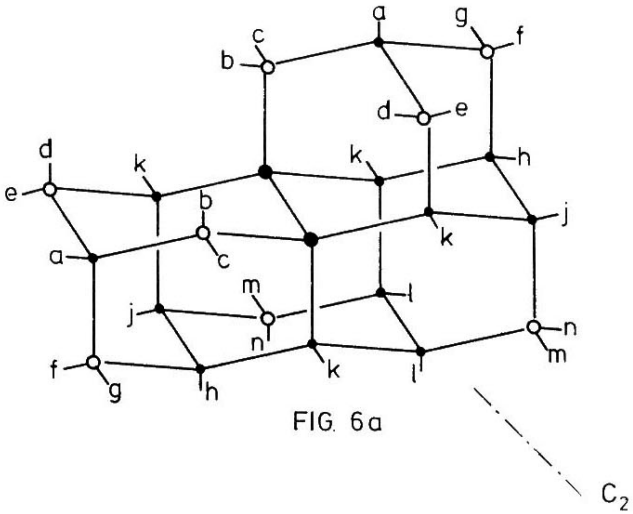
FIG. 5a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C_2

FIG. 6a

$$+ \frac{z_1^2 t_1^4 t_2^4 s_1^4 s_2^2 + z_2 t_2^6 t_2^4}{2} \Bigg] \qquad (16)$$

For H-labelled [121] tetramantanes,

$$Z_{S,S'}(\underline{G}_{2h},t,u) = \frac{1}{2}\Big[\Big(\frac{t_1^{12}u_1^{16} + t_2^6 u_2^8}{2} \Big) + \frac{t_1^4 t_2^4 u_2^8 + t_2^6 u_2^8}{2}\Big] \qquad (17)$$

For constitutional isomers of H-labelled [121] tetramantanes,

$$Z(\underline{G}_{2h},t,s \rightarrow Z[S_2,u]) = \frac{1}{4}\Big\{t_1^{12}\Big[\frac{1}{2}(u_1^2 + u_2)\Big]^8 +$$

$$+ 2t_2^6\Big[\frac{1}{2}(u_2^2 + u_4)\Big]^4 + t_1^4 t_2^4\Big[\frac{1}{2}(u_1^2 + u_2)\Big]^4 \Big[\frac{1}{2}(u_2^2 + u_4)\Big]^2\Big\} \qquad (18)$$

wherefrom on replacing u_k and t_k by y_k we obtain :

$$Z = \frac{1}{1024}(y_1^{28} + 8y_1^{26}y_2 + 28y_1^{24}y_2^2 + 56y_1^{22}y_2^3 + 70y_1^{20}y_2^4 +$$

$$+ 56y_1^{18}y_2^5 + 28y_1^{16}y_2^6 + 8y_1^{14}y_2^7 + y_1^{12}y_2^8 + 32y_2^{14} + 128y_2^{12}y_4$$

$$+ 192y_2^{10}y_4^2 + 128y_2^8y_4^3 + 32y_2^6y_4^4 + 4y_1^{12}y_2^8 + 8y_1^{12}y_2^6y_4 +$$

$$+ 4y_1^{12}y_2^4y_4^2 + 16y_1^{10}y_2^9 + 32y_1^{10}y_2^7y_4 + 16y_1^{10}y_2^5y_4^2 + 24y_1^8y_2^{10}$$

$$+ 48y_1^8y_2^8y_4 + 24y_1^8y_2^6y_4^2 + 16y_1^6y_2^{11} + 32y_1^6y_2^9y_4 + 16y_1^6y_2^7y_4^2 +$$

$$+ 4y_1^4y_2^{12} + 8y_1^4y_2^{10}y_4 + 4y_1^4y_2^8y_4^2 \qquad (19)$$

Results are displayed in Table 4.

Table 4

Numbers of isomers for [121]tetramantane (substituted)

	Relation	x^{22}	x^{21}	x^{20}	x^{19}	x^{18}	x^{17}
C-labelled [121]tetramantane including stereoisomerism	(16)	1	11	121	770	3685	13167
C-labelled [121]tetramantane excluding stereoisomerism	(16)	1	8	76	430	1975	6864
	Relation	x^{28}	x^{27}	x^{26}	x^{25}	x^{24}	x^{23}
H-labelled [121]tetramantane including stereoisomerism	(17)	1	14	196	1638	10283	49140
H-labelled [121]tetramantane excluding enantiomerism but including diastereoisomerism	(17)	1	8	106	832	5199	24648
H-labelled [121]tetramantane excluding stereoisomerism	(18)	1	7	64	356	1677	6158

[123] Tetramantane $C_2(CH)_{12}(CH_2)_8$ (V)

With the same conventions and corresponding variables as for Figures 3 and 5, the molecule of [123] tetramantane is presented in Fig.6. Its dualist graph is the carbon skeleleton of n-butane in the staggered gauche conformation. The point group is the lowest of tetramantanes, namely $\underline{C}_2$ and has as symmetry elements only two proper axes C_1 and C_2. Since the unsubstituted molecule itself, as well as its dualist graph, are chiral, (actually, [123] tetramantane is the smallest chiral polymantane) the numbers of isomers including enantiomers will be exactly twice the numbers obtained on disregarding enantiomerism. The cycle indices,however, will be identical for Z_S and $Z_{S'}$. Fig. 6a is analogous to Fig. 5a.

$$Z_S = S'(\underline{C}_2;z,t,s) = \frac{1}{2}(z_1^2 t_1^{12} s_1^8 + z_2 t_2^6 s_2^4) \qquad (20)$$

for C-labelled.

$$Z_S = S'(\underline{C}_2;t,u) = \frac{1}{2}(t_1^{12} u_1^{16} + t_2^6 u_2^8) \qquad (21)$$

for H-labelled.

By substituting (6) into (20) wherever s_k appears, we obtain:

$$Z(\underline{C}_2;t,s \rightarrow Z[S_2,u]) = \frac{1}{2}\left\{t_1^{12}\left[\frac{1}{2}(u_1^2 + u_2)\right]^8 + \right.$$

$$\left. + t_2^6\left[\frac{1}{2}(u_2^2 + u_4)\right]^4\right\} \qquad (22)$$

Table 5

Numbers of isomers for [123] tetramantane (substituted)

	Relation	x^{22}	x^{21}	x^{20}	x^{19}	x^{18}	x^{17}
C-labelled [123]tetramantane including stereoisomerism	(20)	2	22	242	1540	7360	26334
C-labelled [123]tetramantane excluding stereoisomerism	(20)	1	11	121	770	3685	13167

	Relation	x^{28}	x^{27}	x^{26}	x^{25}	x^{24}	x^{23}
H-labelled [123]tetramantane including stereoisomerism	(21)	2	28	392	3276	32566	38280
H-labelled [123]tetramantane excluding enantiomerism but including diastereoisomerism	(21)	1	14	196	1638	10283	49280
H-labelled [123]tetramantane excluding stereoisomerism	(23)	1	10	104	646	3145	11880

and finally we replce s_k, t_k, u_k by y_k in all above indices. In particular, (22) is converted into:

$$Z = \frac{1}{512}(y_1^{28} + 8y_1^{26}y_2 + 28y_1^{24}y_2^2 + 56y_1^{22}y_2^3 + 70y_1^{20}y_2^4 +$$

$$+ 56y_1^{18}y_2^5 + 28y_1^{16}y_2^6 + 8y_1^{14}y_2^7 + y_1^{12}y_2^8 + 16y_2^{14} +$$

$$+ 64y_2^{12}y_4 + 96y_2^{10}y_4^2 + 64y_2^8y_4^3 + 16y_2^6y_4^4) \qquad (23)$$

Results are presented in Table 5.

[1(2)3] Tetramantane $C_3(CH)_{10}(CH_2)_9$ (VI)

The molecule is presented in Fig. 7 with the same conventions as in Fig. 3. The dualist graph is the carbon skeleton of isobutane. The point group is $\underline{C}_3$ with three proper rotation axes (C_1, C_3, C_3^2) and three reflexion planes $(\sigma, \sigma', \sigma'')$. As in the section before last, we have for C-labelled systems:

$$Z_{S,S'}(\underline{C}_3; z, t, s) = \frac{1}{6}\left[(z_1^3 t_1^{10} s_1^9 + 2z_3 t_1 t_3^3 s_3^3) +\right.$$

$$\left. + 3z_1 z_2 t_1^4 t_2^3 s_1 s_2^4\right] \qquad (24)$$

and for H-labelled systems:

$$Z_{S,S'}(\underline{C}_3; t, u) = \frac{1}{6}\left[(t_1^{10} u_1^{18} + 2t_1 t_3^3 u_3^6) + 3t_1^4 t_2^3 u_2^9\right] \qquad (25)$$

For constitutional isomers, we have:

$$Z(\underline{C}_3\ ;t,s \to Z[S_2,u]) = \frac{1}{6}\Big\{t_1^{10}\Big[\frac{1}{2}(u_1^2 + u_2)\Big]^9 +$$

$$+ 2t_1t_3^3\Big[\frac{1}{2}(u_3^2 + u_6)\Big]^3 + 3t_1^4t_2^3\Big[\frac{1}{2}(u_1^2 + u_2)\Big]\ \Big[\frac{1}{2}(u_2^2 + u_4)\Big]^4\Big\} \tag{26}$$

In all the three expressions we replace z_k, t_k, s_k and u_k by y_k. In particular, (26) yields the cycle index for constitutional isomers:

$$Z = \frac{1}{3072}\,(y_1^{28} + 9y_1^{26}y_2 + 36y_1^{24}y_2^2 + 84y_1^{22}y_2^3 + 126y_1^{20}y_2^4 +$$

$$+ 126y_1^{18}y_2^5 + 84y_1^{16}y_2^6 + 36y_1^{14}y_2^7 + 9y_1^{12}y_2^8 + y_1^{10}y_2^9 +$$

$$+ 128y_1y_3^9 + 384y_1y_3^7y_6 + 384y_1y_3^5y_6^2 + 128y_1y_3^3y_6^3 +$$

$$+ 48y_1^6y_2^{11} + 192y_1^6y_2^9y_4 + 288y_1^6y_2^7y_4^2 + 192y_1^6y_2^5y_4^3 +$$

$$+ 48y_1^6y_2^3y_4^4 + 48y_1^4y_2^{12} + 192y_1^4y_2^{10}y_4 + 288y_1^4y_2^8y_4^2 +$$

$$+ 192y_1^4y_2^6y_4^3 + 48y_1^4y_2^4y_4^4\ ) \tag{27}$$

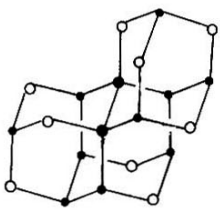

FIG. 6

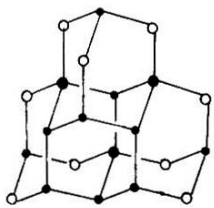

FIG. 7

Results are presented in Table 6.

Table 6

Numbers of isomers for [1(2)3] tetramantane (substituted)

	Relation	x^{22}	x^{21}	x^{20}	x^{19}	x^{18}	x^{17}
C-labelled [1(2)3]tetramantane including stereoisomerism	(24)	1	8	77	518	2443	8778
C-labelled [1(2)3]tetramantane excluding stereoisomerism	(24)	1	7	50	293	1306	4556

	Relation	x^{28}	x^{27}	x^{26}	x^{25}	x^{24}	x^{23}
H-labelled [1(2)3]tetramantane including stereoisomerism	(25)	1	10	126	1098	6831	32760
H-labelled [1(2)3]tetramantane excluding enantiomerism but including diastereoisomerism	(25)	1	7	72	575	3485	16536
H-labelled [1(2)3]tetramantane excluding stereoisomerism	(27)	1	6	39	215	940	3378

Conclusion

Table 7 presents a comparison between the numbers of mono and disubstituted isomers of catamantanes with n=1 to 4.* The data for n=1 are from a previous paper,[14] those for the remaining catamantanes are from Tables 2-6 of the present paper.

Conclusion on monosubstituted systems

On comparing the data from Table 7, it is apparent that monosubstituted adamantanes are achiral, and that starting with diamantanes, chiral monosubstituted catamantanes exist; their number is obtained as the difference between columns (3) and (4). For example, positions labelled a and b in II and III give rise to chiral monosubstituted isomers.

Starting with triamantane, monosubstituted catamantanes yield more than one diastereomer : e.g. in III positions labelled c and d give rise to diastereomers: the difference between columns (4) and (5) gives the numbers of diastereomers.

Also starting with triamantane, mono-C-labelled systems (e.g. with heteroatoms) may be chiral became of the lower symmetries: for $n \geqslant 3$ there exist carbon atoms which do not lie on a plane of symmetry. The numbers of such enantiomeric pairs result as differences between columns (1) and (2).

*It is assumed that substituents are not chiral.

Table 7

Numbers of mono- and disubstituted isomers of catamantanes with n = 1 to 4

n	Catamantane and its point group	Substi-tution	C-labelled		H-labelled		
			Stereo-isomers	Constitut. isomers	Stereo-isomers	Diastereo-isomers	Constitut. isomers
	Column		(1)	(2)	(3)	(4)	(5)
1	Adamantane	Mono	2	2	2	2	2
	$\underline{\underline{T}}_d$	Di	5	5	12	9	6
2	Diamantane	Mono	3	3	4	3	3
	$\underline{\underline{D}}_{3d}$	Di	19	15	37	23	16
3	Triamantane	Mono	10	8	12	8	7
	$\underline{\underline{C}}_{2d}$	Di	81	52	144	80	48
4	[121] Tetramantane	Mono	11	8	14	8	7
	$\underline{\underline{C}}_{2h}$	Di	121	76	196	106	64
4	[123] Tetramantane	Mono	22	11	28	14	10
	$\underline{\underline{C}}_2$	Di	242	121	392	196	104
4	[1(2)3] Tetramantane	Mono	8	7	10	7	6
	$\underline{\underline{C}}_{3d}$	Di	77	50	126	72	39

Conclusions on disubstituted systems

Since the numbers of enantiomeric pairs result as differences between columns (1) and (2) for C-labelled systems, and between columns (3) and (4) for H-labelled systems, it is apparent that even adamantane gives disubstituted chiral systems, and also diastereomeric systems. However, for di-C-labelled systems, chirality is observed only starting with diamantane.

It may be observed that in a few cases, the numbers of disubstituted systems are equal to the squares of monosubstitited ones: for H-labelled stereoisomers of tri- and [121]-tetramantanes and for C-labelled stereoisomers of [121]-tetramantane. It is also interesting to note that the numbers in columns (1) and (3) for [121]tetramantane are equal to those in columns (2) and (4) respectively, for [123] tetramantane. This is better apparent on comparing Tables 4 and 5.

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