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SYSTEMATIC CLASSIFICATION AND NOMENCLATURE OF DIAMOND HYDROCARBONS—I

GRAPH-THEORETICAL ENUMERATION OF POLYMANTANES

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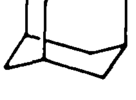
Abstract—Diamond hydrocarbons are defined as hydrocarbons containing at least one adamantane unit wholly or largely superimposable on the diamond lattice. When two or more adamantane units are present, diamond hydrocarbons can be further classified according to the number of C atoms common to each pair of such units. Face-fused systems (polymantanes, e.g. diamantane (18), triamantane (19), etc) have six common carbons between each pair of adamantane units. The character of the dualist graphs connecting the centers of each adamantane unit divides polymantanes into *catamantanes* (tree-like dualist graphs) or *perimantanes* (cyclic graphs). These graphs are identical to the carbon skeletons of alkanes or cycloalkanes in ideal staggered conformations ("C-rotamers"). Polymantanes with n adamantane units are termed "regular" if their empirical formula is $C_{4n+6}H_{4n+12}$, and "irregular" otherwise. All perimantanes and some catamantanes are irregular. A notation system based on the four possible relative orientations of the edges of the dualist graphs provides a code not only designating each polymantane uniquely, but also allowing their enumeration. Three tetramantanes, seven pentamantanes, 24 hexamantanes (one of these a perimantane) and 88 heptamantanes (two perimantanes) are possible (not taking enantiomers into account). The codes provide a convenient nomenclature and reveal by patterns of repeating digits whether irregular catamantanes or perimantanes are involved. The smallest chiral polymantane is [123]tetramantane (21), the smallest irregular catamantane is [1231]pentamantane (45), and the smallest perimantane is [12312]hexamantane (35).

The chemistry of adamantane (1) and of related hydrocarbons has developed considerably[1] since the discovery[2] that strong Lewis acid catalysts like aluminium chloride isomerize saturated polycyclic hydrocarbons to diamondoid hydrocarbons. Being almost strain-free (they have tetrahedral angles and no eclipsed bonds, but they possess an excess of repulsive over attractive nonbonded interactions in comparison with noncage hydrocarbons),[3] such diamond hydrocarbons typically are the "stabilomers";[4d] i.e., they have the lowest strain energy among other isomeric possibilities and therefore are expected to be the final products of thermodynamically-controlled isomerization.[1,4] Such reactions occur via multiple 1,2-shifts of carbenium ions,[1,2,4] and the elucidation of their mechanism requires a detailed graph-theoretical and computer-assisted analysis.[4] The exceptional stability of the adamantane skeleton is also apparent in heteroanalogs,[1c,d] which are often formed from simple precursors; e.g. hexamethylenetetramine was known long before adamantane.

The present paper applies a graph-theoretical approach to a hitherto neglected aspect, namely the systematic classification, nomenclature and enumeration of a subset of diamond hydrocarbons known as "polymantanes". The first four members of this class are already known.

Definition and classification of diamondoid hydrocarbons

The term "diamond hydrocarbons" implies hydrocarbons whose arrangement of C atoms are totally or largely superimposable on the diamond lattice. However, this is true for many hydrocarbons not normally considered "diamondoid"; cyclohexane, decalin, and the simple alkanes (even methane!) are examples. We consider the ten-carbon tricyclic adamantane unit (1) to be necessary for "diamond character" even though this restriction arbitrarily excludes cyclodecane (2)[5a] and other cyclic hydrocarbons possessing diamondoid conformations,[5b] as well as close relatives like bicyclo[3.3.1]nonane (3). In contrast, molecules like the adamantane dimer 4[6] are considered to be "diamondoid" even though the diamond lattice will not accomodate both adamantane units simultaneously. We thus define "diamond hydrocarbons" as hydrocarbons possessing at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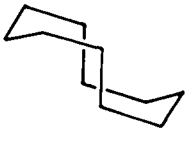
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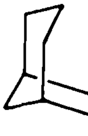
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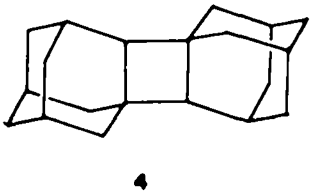
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least one adamantane unit which are totally or largely superimposable on the diamond lattice.

Diamond hydrocarbons may be classified as follows:

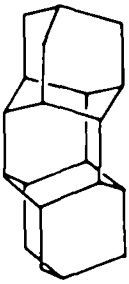
I. Diamond hydrocarbons which are only partly superimposable on the diamond lattice (e.g. **5**, and "bastardane", **6**,[7] an isomer of the tetramantanes).

II. Diamond hydrocarbons which are totally superimposable on the diamond lattice (at least in certain conformations). (1) Those with some C atoms not belonging in complete adamantane units (e.g., alkyladamantanes, polyadamantyl-alkanes, or structures such as **7**[8] and **8–9**. (2) Those with all C atoms belonging in complete adamantane units. (a) Isolated adamantane units (e.g. the biamantanes, 1,1'-, 1,2'- or the most stable[9] 2,2'-isomer **10**; **11** and **12** are different types). (b) Spiro-fused systems (with one common C atom for each pair of adamantane units, e.g. **13**[10]). (c) Edge-fused systems (with two adjacent common C atoms for each pair of adamantane units, e.g. **14**[11]). (d) Composite-fused systems (with three, e.g. **15**; four, e.g. **16**; or five, e.g. **17** C atoms common to two or more adamantane units). (In formulas **13–17** the common atoms and edges are indicated). (e) Face-fused or polymantanes (with six common C atoms for each pair of adamantane units).

The present paper discusses only the polymantanes. A subsequent paper will examine the other systems.

Polymantanes

Adamantane ($C_{10}H_{16}$, **1**), first isolated from petroleum,[12] is now readily available by isomerization of tetrahydrodicyclopentadiene.[2,13] Some of its derivatives have pharmaceutical applications.[14] The next homologue,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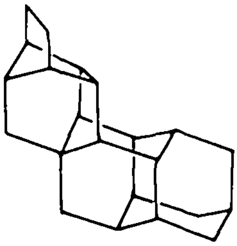
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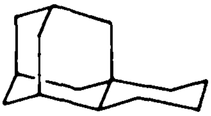
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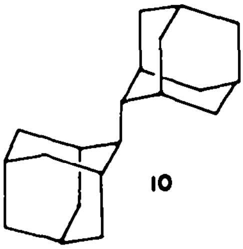
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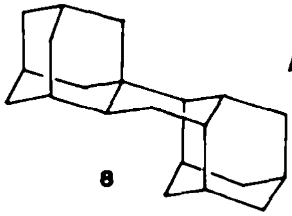
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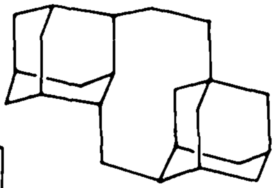
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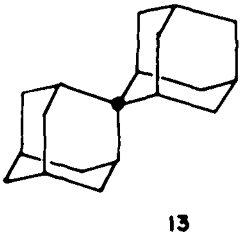
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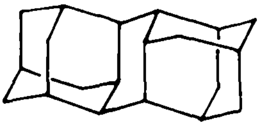
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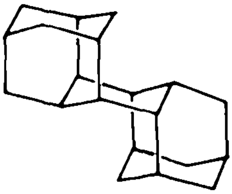
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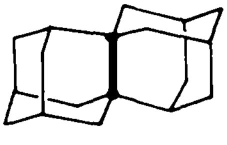
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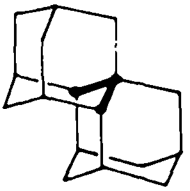
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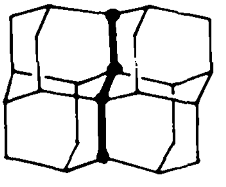
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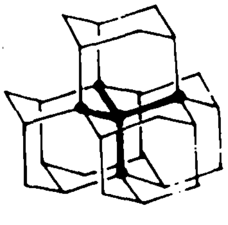
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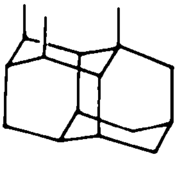

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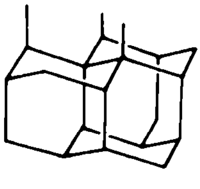

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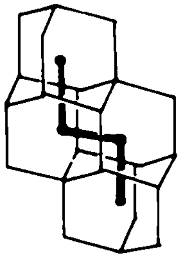

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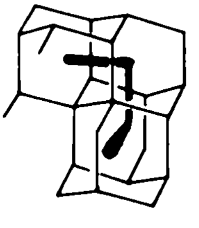

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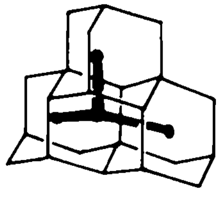

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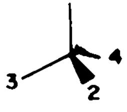
$C_{14}H_{20}$ (18), initially named "Congressane" and renamed diamantane,[14,15] has been prepared by isomerization of norbornene dimers or their relatives.[8,15] Triamantane, $C_{18}H_{24}$ (19), the third homologue, is also obtained by rearrangement of polycyclic isomers.[16] There are three possible tetramantanes, $C_{22}H_{28}$ (20–22);[1,16] the "anti" isomer 20 with C_{2h} symmetry was prepared recently with a catalyst permitting the use of olefinic precursors.[17] To date, these are the only known polymantanes.

The number of possible isomers increases rapidly for the higher polymantanes, so that means of designating them are necessary. The systematic von Baeyer names are very cumbersome: adamantane is tricyclo$[3.3.1.1^{3,7}]$decane, diamantane is pentacyclo$[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]$tetradecane, triamantane is heptacyclo$[7.7.1.1^{3,15}.0^{1,12}.0^{2,7}.0^{4,13}.0^{6,11}]$octadecane, etc. The present paper enumerates and codifies systematically the structures of polymantanes in anticipation of their eventual preparation. A rational nomenclature is proposed to avoid proliferation of trivial names which would probably be coined in order to distinguish isomeric polymantanes. Such proliferation has occured in the field of valenes (valence isomers of annulenes),[18,19] but proposals for a graph-theoretical nomenclature have been made there, too.[19,20]

Polymantanes are tridimensional analogues of the bidimensional benzenoid condensed polycyclic hydrocarbons (polyhexes); the former represent fragments of the diamond lattice, while the latter are portions of the graphite lattice. For the polyhexes, a graph-theoretical approach using the dualist graph ("characteristic graph")† formed by joining the centers of condensed rings, allowed the enumeration and codification of *cata*-condensed benzenoid systems (either linear[21] or branched[22]); peri-condensed benzenoid systems (cyclic)[21] could not be enumerated by algebraic or recurrence formulas, but only by a computer-implemented algorithm.[23] The enumeration of polyhexes or "hexagonal-cell animals" is an unsolved graph-theoretical problem similar to the square-cell and triangular-cell problems.[24]

While the C–C bonds in graphite may only have three orientations,[25] four orientations are possible in the diamond lattice. Saunders[26] used digits 1–4 as symbols for these four orientations when investigating conformations of large-ring cycloalkanes superimposable on the diamond lattice. We adopt the same convention (23, or its permutations) to code the relative orientations of adamantane units comprizing a polyamantane. For each orientation there are two alternative directions. Since one direction corresponds to odd positions (first, third, etc.) of the digit in the sequence of the code,[a] and the opposite direction to even positions, no confusion arises and no special sign for these two directions is necessary. This will become apparent when examples are considered.

If the centers of fused adamantane units in polymantanes are joined, the resulting *dualist graph* is again superimposable on the diamond lattice, i.e. the diamond lattice is "self-dualist" like the graphite and the cubic lattices. We may thus symbolize a polymantane by means of its dualist graph, i.e. 1 by a point, 18 by an edge, and 19 by two adjacent edges at an angle of 109°28'. This is the basic idea of the present paper; it has been expressed or implied previously.[1,6,7,16,26,27] The relationship between these dualist graphs and the carbon skeletons of paraffin hydrocarbons is obvious.



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A coding of such dualist graphs is possible using 23 (or its permutations) and certain conventions. The orientations are enumerated starting from one endpoint of the longest chain of the dualist graph. The code to be adopted from among all possibilities has the smallest number formed from the digits indicating the orientations of edges. Thus, diamantane 18 has code 1 because the single

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†Unlike the usual (geometric) dual graphs, where lengths and angles are arbitrary, in dualist graphs lengths and angles are fixed and the vertex corresponding to the outer region is missing. Vertices of a dualist graph may be centers of tridimensional arrays, as in the present case, and not only of planar regions as for dual graphs.

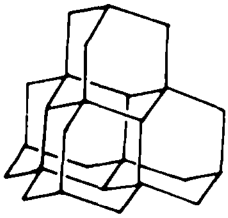
edge of its dualist graph may be symbolized by digits 1, 2, 3, or 4, but 1 is the smallest number. Of the twelve possible symbols, 12, 13, 14, 21, 23, 24, 31, 32, 34, 41, 42, 43, the smallest number is 12; this is the code for triamantane (19).

The following conclusions, observations and further conventiohns apply to this coding system:

(i) The system codes dualist graphs of polymantanes as well as idealized staggered conformations of alkane or cycloalkane skeletons ("C-rotamers"[26]) when hydrocarbons are superimposable on the diamond lattice. Since each digit codes an orientation of one edge in the graph, a sequence of $n-1$ digits corresponds to a polymantane having n fused adamantane units. Thus, the code for a pentamantane will have four digits, e.g. [1212]pentamantane.

(ii) Any digit must always be followed by a different digit since any sequence of three face-fused adamantane units must involve a change in orientation (*cf* 20–22). The smallest number rule insures that the first two digits of all codes be 12; only the next digit conveys topological information. For this reason, no codes need be used for adamantane, diamantane, or triamantane. The first three digits of all codes must be either 121 or 123. Codes [121] and [123] designate "anti" (20) and "syn", "gauche" or "skew" (21) tetramantane, respectively. Their dualist graphs are identical with the two conformational minima of butane.

(iii) Since any given adamantane unit can be fused with up to four other adamantane units, a digit may be followed not just by one digit (unbranched case), but by two or three additional digits (branched cases). These extra digits are placed in parentheses and are separated by commas as required. Code [1(2)3] designates 22, formerly called "iso" tetramantane because of the similarity of its dualist graph to isobutane. [1(2,3)4]Pentamantane (24) is the neopentane of the world of diamond hydrocarbons.



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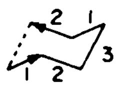
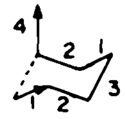
(iv) The coding of edge orientations of the dualist graphs starts from the endpoint of the longest chain, and involves, if possible, the longest zig-zag path (coded 1212...). When the dualist graph is a ring system, or when owing to branching an acyclic dualist graph has two or more equally long chains, the criterion of the minimal number decides the starting point. No special designation is necessary to indicate ring closure. In 25, such ring closure is shown by a dashed line (see below). In the case of cyclic dualist graphs with side-chains, the longest path should include the side-chain(s); this provision decreases the number of branches. For example, for a dualist graph formed by a chair-shaped cyclohexane with an axial methyl-like side-chain, code 123124 (26) is to be preferred to 1231(2)4 (27). However, this provision sometimes runs contrary to the minimal number rule; e.g. in the isomeric case when the one unit Me-like side-chain is equatorial, code 121321 (28) is to be preferred to 12(1)312 (29) even though the latter corresponds to the smaller number (ignoring the brackets). (In 25–29 the orientations are coded according to 30 and the longest path and starting units are indicated by arrows).



12312

25



123124

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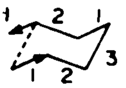
1231(2)4

27



123121

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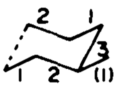
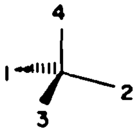


12(1)312

29



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Illustrations of sequences which are not allowed by the above rules include:

...11...	(repeating digit)
...1(1	(repeating digit)
...1(2)1...	(repeating digit, before and after the parentheses)
...1(2,3)1...	(repeating digit, before and after the parentheses)
...1(2,3)2	(repeating digit 2 within and after the parentheses; only a 4 can follow the parentheses in this instance)
...1)	(the last digit of a code in parentheses cannot be 1)
124...	(lowest number rule; the last digit should be 3)
1214...	(lowest number rule; the last digit should be 3)

(vi) When there are two or more codes for a dualist graph designated by the same sequence of digits, but differing only in the position of the parentheses, the preferred code has the parentheses as far to the *right* as possible. Examples 31–32 and 33 = 34 (the orientations are coded above each formula and the starting points indicated by arrows) show that by this convention the preferred codes are those of 32 and 34.†

Classification of polymantanes

The dualist graphs of polymantanes may be acyclic (tree-like) or cyclic; by analogy with polyhexes[26,27] we propose the term *catamantanes* for polymantanes with acyclic dualist graphs and the term *perimantanes* for

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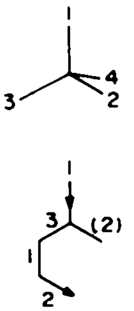
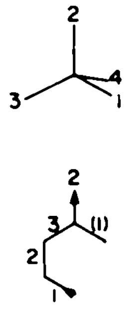
†In the enumeration and codification of C-rotamers,[26,27] along with the 4-digit code just described, a three-digit code, identical to that employed for *cata*-condensed benzenoid systems, could be applied to C-rotamers without quaternary carbons (i.e. to systems without geminal branching). Owing to this restriction and to the slightly more complicated rules for obtaining such three-digit codes, we only consider 4-digit codes for polymantanes.



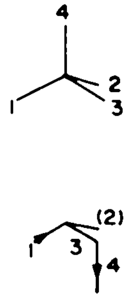
1(2)312

31



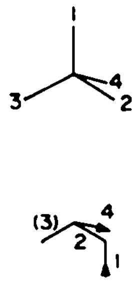
123(1)2

32



1(2)34

33



12(3)4

34

those polymantanes whose dualist graphs contain cycle(s). For indicating the number n of adamantane units one may use prefixes, e.g. *tetra*catamantane or *hexa*perimantane.

On fusing an additional adamantane unit onto an n-catamantane, two kinds of n + 1-catamantanes may result. Some, like **18–22**, have type formula $C_{4n+6}H_{4n+12}$ and are derived by an annulation process consisting in replacing three axial hydrogen atoms bonded to the same chair-shaped cyclohexane ring (*cf* the three short lines in **18**) by a trimethylenemethane group; the net result is the addition of C_4H_4. We call such catamantanes *regular*; all regular n-catamantanes with the same n are isomeric. The second kind of catamantanes, called "irregular", are derived by an annulation step which involves the addition of C_xH_y where x, y < 4. Irregular and regular catamantanes with the same n are not isomeric. This problem is encountered for the first time when annulation of [123]tetramantane (**21**) in orientation 1 is attempted. As indicated by the short lines in formula **21**, there are only two axial hydrogens to be replaced; a carbon already occupies the third point of attachment. The smallest irregular catamantane, [1231]pentamantane ($C_{25}H_{30}$), which results from further annulation will be discussed in a later section (see **45**).

The necessary and sufficient conditions for a catamantane to be irregular is to have a code with at least two identical digits separated by any two other digits (excluding branches, i.e. parentheses with their contents). For example, sequences a**1**bc**1**d..., ...**2**ab**2**c..., ab**3**(b)cd**3**..., ...abc**4**(a)b(d)a**4**d..., and ...ab**1**(a)bc(**1**)d... code irregular catamantanes; note the repeating boldface digit (letters a–d stand for any digit 1–4). This convention of indicating irregularity by boldface digits will be employed for emphasis in the following discussion, though it does not form part of the formal rules.

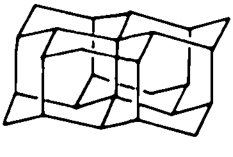
One pair of identical digits separated by any two other digits leads to an irregular catamantane with formula $C_{4n+5}H_{4n+10}$; two such pairs not in succession lead to an irregular catamantane with formula $C_{4n+4}H_{4n+8}$. When at least two such pairs occur in succession, a perimantane with a dualist graph containing at least one ring results. All perimantanes are irregular: with only two pairs in succession the formula is $C_{4n+2}H_{4n+4}$. A few examples follow: **12312** (**35**, the dualist graph (**25**) is a 6-membered ring), **1231432** (**36**, an 8-membered ring), **121231212** (**37**, the envelope of *trans*-decalin), **121321413** (**38**, the envelope of *cis*-decalin).

In more complicated cases, the ring closure of the dualist graph is less readily apparent. For instance, the code of the dualist graph of the third 10-membered ring on the diamond lattice (**39**) 121341213 does not have two pairs in succession. The code of the dualist graph of the tricyclic adamantane skeleton (**40**), 1231241(2)3, does not reveal special complexity; the corresponding decaperimantane ($C_{35}H_{36}$), shown in **41**, is an adamantane of adamantanes! In **37–40** the broken lines are those whose notation does not appear explicitly in the code. Dualist graph **42** is another example. In all these cases arrows mark the longest acyclic chain. Unlike the situation with the n-helicenes which may exist even for n > 6 with some steric distortion, or with the alkane C-rotamers discussed earlier,[26] when two vertices in the dualist graph of a polymantane are at a distance of one edge, these two vertices *must* be linked, and the dualist graph *must* be cyclic. Stated otherwise, although the link(s) closing the cycle(s) do not appear in the codes, these links must be imagined; the corresponding polymantanes are perimantanes.

Enumeration of polymantanes

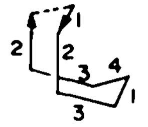
Table 1 compares the number of alkane C-rotamers with n = 1–7 carbon atoms,[26] and the polymantanes with n = 1–7 adamantane units. Starting with n = 6, the total number of polymantanes is smaller than that of C-rotamers. Two causes are responsible. Some C-rotamers cannot be dualist graphs of polymantanes. For example, no heptamantane is possible for the dualist graph with code 123123. Secondly, several dualist graphs may code the same perimantane, e.g. the acyclic C-rotamer 12312 (see **25**) and the chair-shaped cyclohexane both correspond to the same hexaperimantane **35**; each of the two heptaperimantanes corresponds to three different acyclic C-rotamers and to one cyclic C-rotamer. Closing the cycle is required in the polyamantane but not in the corresponding C-rotamer (if one allows reasonable distortions). In this way, the differences between the figures in the last columns for C-rotamers and polymantanes can be accounted for.

On annulating adamantane (**1**) (n = 1) to diamantane (**18**) (n = 2), or diamantane to triamantane (**19**) (n = 3), only one "homologue" can result. However, the next annulation of triamantane to tetramantane (n = 4) can yield three isomeric tetracatamantanes, **20–22**. In order to obtain a regular catamantane, the three axial hydrogens to be replaced on annulation by the trimethylenemethane system must belong to the same cyclo-



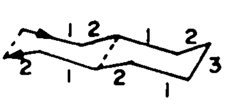
12312

35



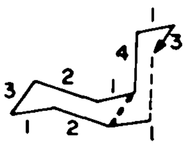
1231432

36



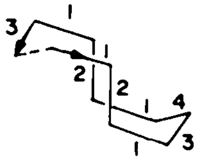
121231212

37



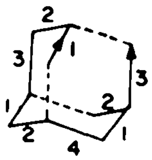
121321413

38



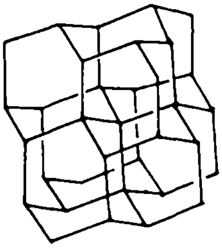
121341213

39



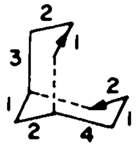
12312411(2)3

40



41

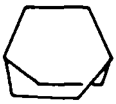
12312411(2)3



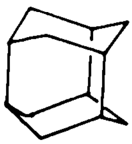
12312412

42

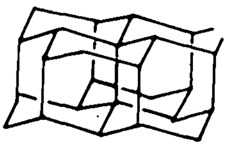
hexane ring. In triamantane and higher polymantanes there exist groups of three axial hydrogen atoms (e.g. those indicated by short lines in formula 19) which do not fulfill this condition: their replacement by net C_4H_4 annulation does not lead to a polymantane, but to a ring system containing a bicyclo[2.2.2]octane unit (43) with eclipsed bonds and boat-shaped cyclohexane rings. Such ring systems are not a portion of the cubic diamond lattice but of the "hexagonal diamond" lattice.[28] These two lattices are similar to the sphalerite (zinc blende) and wurtzite lattices, respectively. The recently synthesized hydrocarbon, iceane (44),[29] also fits on the wurtzite lattice.



43



44



1231

45

Models show that irregular catamantanes experience steric hindrance of hydrogen atoms, e.g. the pair of hydrogens indicated by the short lines in the smallest irregular catamantane 45 (with code 1231). If these two hydrogens are replaced in an irregular catamantane by a CH_2 bridge, a perimantane results with less steric crowding, e.g. 38.

In order to enumerate all possible polymantanes, the usual chemist's approach would be to annulate successively each member of the series, taking symmetry into account, and to determine how many "homologues" would result. Alternatively, the published list of all possible C-rotamers with their codes[26] may be regarded as the dualist graphs of polymantanes. When impossible structures and those which code the same perimantanes in a degenerate fashion are eliminated, a list of polyamantanes results. A mathematical approach would be to construct all allowed sequences of $n-1$ digits from the set 1, 2, 3, and 4, repeating each sequence with parentheses added wherever possible, and then eliminate redundancies. The C-rotamer approach is the easiest of the three to use. All these approaches, when applied to cases with $n = 1$-7 adamantane units, give the same results, presented in Table 2 for $n = 1$-6 and in Table 3 for $n = 7$. The numbers of polymantanes from Table 2 and 3 are summarized in Table 1. Starting with $n = 6$, there exist codes for branched systems where the digit sequence differs from all unbranched systems with the same n. In Tables 2 and 3, the codes for each value of n are listed in increasing numerical order (ignoring brackets and commas).

Table 1. Numbers of polyhexes, staggered C-rotamers, and polymantanes, ignoring enantiomerism

	Polyhexes				C-Rotamers				Polymantanes					
n	Catafusenes		Perifusenes	Total	Acyclic		Cyclic	Total	Catamantanes				Perimantanes	Total
									Regular		Irregular			
	Linear[a]	Branched			Linear[a]	Branched			Linear	Branched	Linear	Branched		
1	1	0	0	1	1	0	0	1	1	0	0	0	0	1
2	1	0	0	1	1	0	0	1	1	0	0	0	0	1
3	2	0	1	3	1	0	0	1	1	0	0	0	0	1
4	4	1	2	7	2	1	0	3	2	1	0	0	0	3
5	10	2	10	22	4	3	0	7	3	3	1	0	0	7
6	25	12	45	82	10	14	1	25	7	10	2	4	1	24
7	70	53	210	333	25	68	2	95	13	33	9	31	2	88

[a] Note that the number of linear catafusenes for a given n is equal to the number of linear C-rotamers with n+1.

Table 2. All possible polymantanes with n = 1 to 6 ignoring enantiomerism.

n	Catamantanes										Perimantanes			Total number of Polymantanes
	Regular					Irregular					Irregular			
	Linear			Branched		Linear			Branched		Cyclic			
	Code	Sym.	Formula	Code	Sym.	Code	Sym.	Formula	Code	Sym.	Code	Sym.	Formula	
1		T_d	$C_{10}H_{16}$	-	-	-	-	-	-	-	-	-	-	1
2	1	D_{3d}	$C_{14}H_{20}$	-	-	-	-	-	-	-	-	-	-	1
3	12	C_{2v}	$C_{18}H_{24}$	-	-	-	-	-	-	-	-	-	-	1
4	121	C_{2h}	$C_{22}H_{28}$	1(2)3	C_{3v}	-	-	-	-	-	-	-	-	3
	123	C_2												
	1212	C_{2v}		12(1)3	C_1									
5	1213	C_1	$C_{26}H_{32}$	12(3)4	C_s	1231	C_s	$C_{25}H_{30}$	-	-	-	-	-	7
	1234	C_2		1(2,3)4	T_d									
	12121	C_{2h}		121(2)3	C_1									
	12123	C_1		12(1)32	C_1									
	12131	C_1		121(3)4	C_s	12132	C_1		12(1)31	C_s	12312	D_{3d}	$C_{26}H_{30}$	
6			$C_{30}H_{36}$					$C_{29}H_{34}$						24
	12134	C_1		12(1)34	C_1	12314	C_1		123(1)2	C_1				
	12321	C_i		12(1,3)4	C_1				123(1)4	C_1				
	12324	C_2		12(3)12	C_s				12(3)41	C_s				
	12341	C_2		1(2)3(1)2	C_{2h}									
				1(2)314	C_1									
				12(3)14	C_1									
				1(2)3(1)4	C_2									

Table 3. All possible heptamantanes ignoring enantiomerism

Catamantanes										Perimantanes			
Regular, $C_{34}H_{40}$				Irregular						Irregular			
Linear		Branched		Linear			Branched			Cyclic			Total
Code	Sym.	Code	Sym.	Code	Sym.	Formula	Code	Sym.	Formula	Code	Sym.	Formula	
121212	C_{2v}	1212(1)3	C_1	121231	C_1	$C_{33}H_{38}$	12(12)31[a]	C_1	$C_{33}H_{38}$	121321	C_s	$C_{30}H_{34}$	
121213	C_1	121(2)31	C_1	121323	C_s	"	121(2)32	C_1	"	123124	C_s	"	
121232	C_1	1212(3)4	C_s	121324	C_1	"	1213(1)2	C_1	"				
121234	C_1	121(2)34	C_1	121341	C_1	"	12(1)3(1)2	C_1	"				
121312	C_1	12(12)34[a]	C_s	123132	C_1	"	12(1)314	C_1	"				
121314	C_1	121(2,3)4	C_s	123134	C_1	"	12(1)3(1)4	C_1	"				
121342	C_1	1213(1)4	C_1	123142	C_1	"	12(1)321	C_1	"				
121343	C_2	121(3)21	C_1	123143	C_2	$C_{32}H_{36}$	1213(2)4	C_1	"				
123214	C_1	121(3)23	C_1	123421	C_s	$C_{33}H_{38}$	12(1)341	C_1	"				
123231	C_s	121(3)24	C_1				12(13)41[a]	C_s	"				
123234	C_2	12(1)324	C_1				12(1,3)41	C_s	"				
123241	C_1	12(1)3(2)4	C_1				121(3)42	C_1	"				
123412	C_2	12(13)32[a]	C_3				12(1)342	C_1	"				88
		12(13)34[a]	C_1				12(13)43[a]	C_1	"				
		121(3)41	C_1				123(1)23	C_1	"				
		12(1,3)42	C_1				1(2)31(2)3	C_s	"				
		121(3)43	C_1				123(1)24	C_1	"				
		12(1,3)43	C_2				1(2)3124	C_1	"				
		12(3)1(2)3	C_1				123(1,2)4	C_1	"				
		12(3)124	C_1				1(2)31(2)4	C_1	"				
		12(3)1(2)4	C_1				12(3)132	C_1	"				
		1(2)3(1)24	C_1				1231(3)4	C_1	"				
		1(2)3(1,2)4	C_s				12(31)41[a]	C_{3v}	$C_{32}H_{36}$				
		1(2)3132	C_1				123(1)42	C_1	"				
		12(3)134	C_1				12(3)142	C_1	$C_{33}H_{38}$				
		1(2)3134	C_1				1(2)3(1)42	C_1	"				
		12(3)1(3)4	C_1				123(1)43	C_1	"				
		1(2)31(3)4	C_2				123(2)14	C_1	"				
		1(2)3142	C_1				1234(1)2	C_1	"				
		1232(1)4	C_1				12(3)4(1)2	C_1	"				
		123(2)41	C_1				1(2)34(1)2	C_{2v}	$C_{32}H_{36}$				
		12(3,4)12	C_{2v}										
		123(4)21	C_1										

[a] Symbols (12), (13) or (31), without commas, code "ethyl-like" branches of two adamantane units.

Starting with n = 4, there exist different polymantanes with the same digit sequence but differing in the presence of parentheses. An important feature of the code is its uniqueness for a given polymantane, and vice versa. Tables 2 and 3 also contain the symmetry of the polymantane expressed by its point group (Schönfliess symbol) and the molecular formula.

Nomenclature of polymantanes

The code, enclosed in square brackets, may be used for nomenclature purposes, being followed by the name composed of the Greek numeral for n and the suffix mantane. If desired, the specifications "cata" or "peri" may be inserted, although these are redundant and therefore are not mandatory: the code or the molecular formula indicates whether the polymantane is a regular or an irregular catamantane, or a perimantane. Thus, the smallest irregular catamantane is [1231]pentamantane (45), and the smallest perimantane is [12312]hexamantane (35). The former may also be called [1231]pentacatamantane, and the latter [12312]hexaperimantane.

As is apparent from the tables, duality (enantiomerism) was not taken into account either in the enumeration, or in the codes. If one wishes to include the enantiomers of polymantanes, then all those with point groups C_1, C_2 or C_3 must be counted twice. Since the smallest chiral polymantane is [123]tetramantane (21), from n = 4 onwards the totals will differ from those of Table 1, namely: 4 tetramantanes, 10 pentamantanes, 40 hexamantanes and 160 heptamantanes. If one wishes to code antipodal enantiomers differently, the solution proposed for C-rotamers may be adopted:[26] giving up the principle of the minimal number for the code, and applying the permutation (1) (2) (3, 4), the code of a chiral polymantane can be converted into the code of its enantiomer. Thus, the two antipodes of the smallest chiral polymantanes would be [123]tetramantane and [124]tetramantane.

The problem of positional numbering is not solved by this nomenclature proposal. Perhaps it would be best to retain the von Baeyer scheme for this purpose, rather than to introduce confusion by means of a new alternative.

Among extensions of the polygonal cell animal problem, the list of unsolved graph-theoretical problems[24] includes one polyhedral cell animal, namely the cubic cell because cubes are the only regular polyhedra which fill the space.[30] The enumeration of polymantanes is related to the above problem. An adamantane unit is a regular tetrahedron having methylene bridges in place of each edge; however, models of polymantanes consisting of face-sharing tetrahedra are unsuitable because tetrahedra are not space-filling whereas the diamond lattice does fill the space.

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