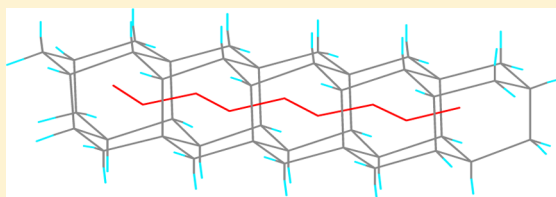


Partitioned-Formula Periodic Tables for Diamond Hydrocarbons (Diamondoids)

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ABSTRACT: Isomeric diamond hydrocarbons (diamondoids or polymantanes) with the same number n of adamantane units share the same molecular formula $C_Q(CH)_T(CH_2)_S$ and can be divided into valence isomers (denoted as $Q-T-S$) by partitioning the number $C = Q + T + S$ of their carbon atoms according to whether they are quaternary, tertiary, or secondary. Vertices of *dualists* are the centers of adamantane units, and dualist edges connect vertices of adjacent adamantane units (sharing a chair-shaped hexagon). Dualists of diamondoids are hydrogen-depleted skeletons of staggered alkane or cycloalkane rotamers. Diamondoids with acyclic dualists can be classified as *catamantanes*, those having dualists with chair-shaped six-membered rings as *perimantanes*, and those having dualists with higher-membered rings that are not perimeters of hexagon-aggregates as *coronamantanes*. Diamondoids with n adamantane units may be classified into regular catamantanes when the molecular formula is $C_{4n+6}H_{4n+12}$, and irregular polymantanes (catamantanes or perimantanes) when the number of carbon atoms is lower than $4n + 6$. The derivation is presented of formula-periodic tables of regular and irregular diamondoids that allow a better understanding of the shapes and properties of these hydrocarbons for which many applications are predicted.



INTRODUCTION

The recent discovery that mixtures of various diamond hydrocarbons (diamondoids for brevity) are found in crude oil and natural gas condensates from offshore stations in the U.S. Nophlet Formation (Gulf of Mexico) makes this class of substances attractive for many uses.^{1–3} The high volatility, high melting points, and resistance to oxidation of these compounds provide an explanation for their easy isolation. They may be separated and isolated in pure state. Their formation by catagenesis in oil deposits is due to their high thermodynamic stability, having the lowest steric strain among naphthenes. Because they clogged natural gas pipelines, they were first considered as a nuisance. Although hexamethylene-tetramine (urotropine) with the same geometry as adamantane has been known for more than a century because it results easily from the reaction of formaldehyde with ammonia, adamantane (hexamethylene-tetramethine, Figure 1) was first discovered in 1933 as a constituent of petroleum.⁴ Inorganic compounds such as P_4O_6 were also found to have the same geometry as adamantane.

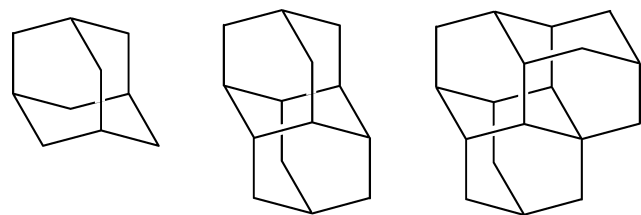


Figure 1. Carbon scaffolds of adamantane, diamantane, and triamantane.

As seen in Figure 1, diamondoids (polymantanes) are saturated hydrocarbons whose carbon atoms are parts of the diamond lattice. In the following we shall use the term “adamantane units” for indicating the components of diamondoids. Although the first member of the series, adamantane, was isolated from petroleum a long time ago and then synthesized by Prelog using a lengthy route,⁵ no further progress in the synthesis of higher members was made till Schleyer demonstrated that Lewis-acid catalysis may convert their valence isomers into such “diamondoid hydrocarbons” or polymantanes; indeed, hydrogenation of the cyclopentadiene dimer and treatment with anhydrous aluminum chloride afforded adamantane.^{6,7} Cupas, Schleyer, and Trecker prepared analogously diamantane (initially proposed as “congressane”—a synthetic challenge) from the photodimer of norbornene.⁸ The structural analysis by X-ray diffraction contributed to the award of the 1985 Nobel Prize for Chemistry to Karle.⁹ For triamantane, two starting materials were used: Schleyer and co-workers rearranged a bis-cyclopropanated polycyclic dimer of cyclooctatetraene in the presence of a sludge catalyst made from $AlBr_3$ and tert-butyl bromide;¹⁰ McKervey used Binor-S in a higher-yield reaction.¹¹ Among the tetramantane isomers (see further below), only the rod-like structure could be made synthetically (also by McKervey and co-workers).¹² Two early reviews on diamondoids were published.¹³ Schleyer’s publications continued to provide information on the chemistry of diamondoids.¹⁴

The mechanism of these rearrangements involves multistep 1,2-migrations in carbocations. Reaction graphs were first

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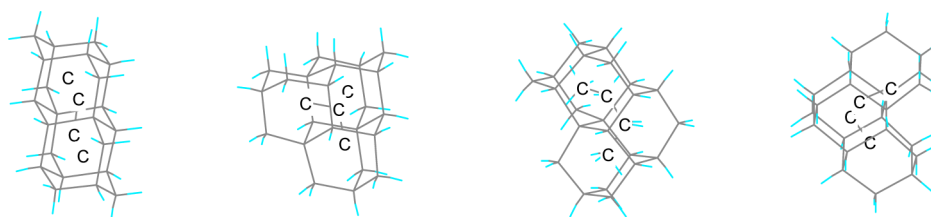


Figure 2. The four possible tetramantanes: the achiral [121]tetramantane, the achiral [1(2)3]tetramantane, and the two chiral enantiomers [123]tetramantane and [124]tetramantane. Dualists are presented as carbon skeletons of alkanes inside the corresponding diamondoids.

devised by Balaban et al.^{15,16} and were extensively used by Whitlock and Siefken,¹⁷ as well as by Schleyer and co-workers, for explaining these rearrangements;^{18,19} in the words of ref 17 “adamantane may be conceived as a bottomless pit, into which rearranging molecules may irreversibly fall”.

Thanks to the efforts of Dahl, Carlson, and their co-workers,^{1–3} natural diamondoids from petroleum with up to 11 adamantane units could be separated and identified; the lower members with 1 to 3 adamantane units could be isolated in kilogram amounts. Even the two enantiomeric tetramantanes could be separated by HPLC using methylated γ -cyclodextrin columns in reverse-phase mode.²⁰ A collaboration between Balaban and Klein with Carlson and Dahl allowed the finding of quantitative structure–property relationships among gas chromatographic retention times, HPLC elution volumes, and structures of various diamondoid isomers.²¹ Resistance to pyrolysis and oxidation of diamondoids and methylated homologues facilitates their isolation.

NOMENCLATURE AND CODING OF POLYMANTANES

The von Baeyer nomenclature of polycyclic compounds, adopted by IUPAC, is complicated. For example, the literature names of the three unique diamondoids with $n = 1$ –3 adamantane units shown in Figure 1 are tricyclo[3.3.1.1^{3,7}]-decane for adamantane, pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{6,11}]-tetradecane for diamantane, and heptacyclo[7.7.1.1^{3,15}.0^{1,12}.0^{2,7}.0^{4,13}.0^{5,11}]-octadecane for triamantane.

In 1978, a systematic nomenclature and enumeration of diamond hydrocarbons were advanced by Balaban and Schleyer.²² Earlier, on the basis of their dualists, Balaban and Harary had similarly classified benzenoid hydrocarbons into catafusenes, perifusenes, and coronafusenes.^{23,24} A dualist of a benzenoid has the centers of hexagons as vertices, and its edges connect vertices in condensed rings (i.e., rings sharing two carbon atoms). Unlike normal graphs where bond lengths and angles do not matter, in dualists they do.

Polymantanes are portions of the diamond network, just as benzenoids are portions of the graphite lattice. The idea of dualists was extended to polymantanes. Vertices of dualists are the centers of adamantane units, and edges connect vertices of adjacent adamantane units (sharing a chair-shaped hexagon). Dualists of polymantanes are hydrogen-depleted skeletons of staggered alkane or cycloalkane rotamers. These rotamers were investigated graph-theoretically earlier.²⁵ Having elaborated the outline of the dualist-based coding and enumeration of diamondoids,²⁵ the present author proposed a collaboration to Schleyer who accepted, and the result was the 1987 *Tetrahedron* paper which contains two tables with point symmetry groups and codes for all possible constitutional isomers of diamondoids (ignoring stereoisomerism): one isomer each for $n = 1, 2$, and 3; 3 isomers for $n = 3$; 6 for n

$= 5$; 24 for $n = 6$; and 88 isomers for $n = 7$.²² Unlike the honeycomb lattice of benzenoids that has the triangular lattice as its dualist, polymantanes are self-dual, with the caveat about highly branched staggered alkanes mentioned by Klein.²⁶ It should be mentioned that Klein and co-workers described formula periodic tables of all acyclic hydrocarbons.²⁷

There are four possible orientations of bonds around a vertex of a dualist of polymantanes, and they are denoted by digits 1 through 4. Conventionally, the new name of a polymantane uses the orientations of edges in the longest nonbranched chain of the dualist, selecting the smallest number from all possible sequences of digits reflecting the edge orientations. Branches are symbolized by digits in round brackets. For further details on nomenclature, the initial reference should be consulted.²²

When there is no cycle in the dualist, the diamondoid hydrocarbon is a *catamantane*; when the dualist contains one or more chair-shaped hexagons, the diamondoid hydrocarbon is a *perimantane* and when the dualist contains a larger ring but no hexagon, it is a *coronamantane* (till now, no coronamantane has been characterized experimentally).

Figure 2 exemplifies the proposed names for the three possible tetramantanes, the last of which is chiral, producing two mirror images of one another. Because there is no interconversion between such enantiomers, they are distinct molecules and their codes accommodate this feature by abandoning the requirement for “the smallest number”, as one can see in the caption of Figure 2.

In Figure 3, two stereoviews of one and the same enantiomeric [123]tetramantane indicate that the dualist overlaps with the diamondoid’s carbon scaffold in the “square projection” but appears centered in the “chickenwire projection”.

For pentamantanes, ignoring enantiomerism, there are six possible catamantanes (three with linear dualists and three with

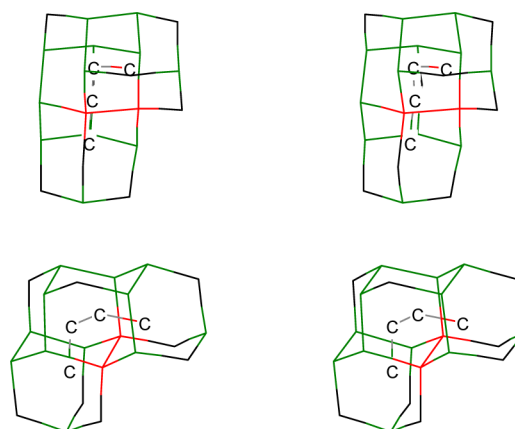


Figure 3. Two stereoviews of [123]tetramantane.

branched dualists shown in Figure 4 as stereoviews) and one irregular catamantane, with code 1231, shown together with its

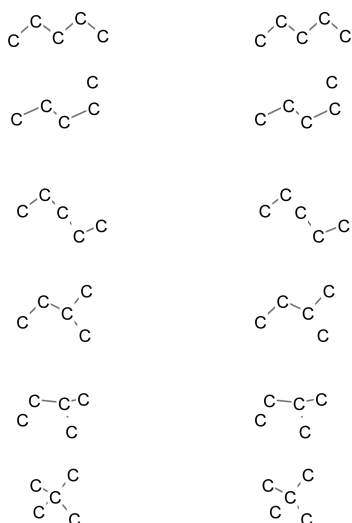


Figure 4. Stereoview of the dualists for regular pentamantanes with codes [1212], [1213], [1234], [12(1)3], [12(3)4], and [1(2,3)4].

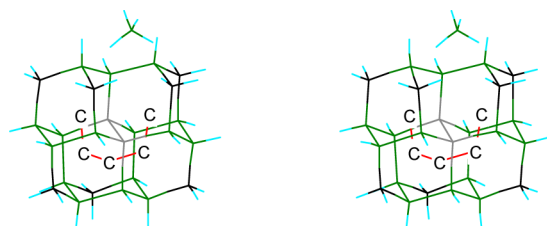


Figure 5. Stereoview of the irregular pentamantane with its dualist [1231].

dualist, again in stereoview, in Figure 5. In this figure one can also see that one more CH_2 group, shown above the [1231]pentamantane, can close an additional adamantane unit, adding two edges to the dualist which will become a 6-membered ring, converting the pentamantane into the smallest perimantane, [12312]hexamantane. We will call such an irregularity as in [1231]pentamantane “a proximity”. Catamantanes may accumulate several proximities, as for instance in [123143]heptamantane with two proximities.

The code for the dualist of the smallest perimantane represented by chair-shaped cyclohexane is 12312. Whereas all benzenoid catafusenes are isomeric, catamantanes can be regular (and in this case all such systems with the same number of adamantane units are isomeric) or irregular (when their dualist code includes a sequence such as *abca*), and then, they are no longer isomeric. Perimantanes do not have simple relationships between the number of adamantane units and their molecular formulas. More about regular and irregular catamantanes and about perimantanes will be presented in the following section.

One has now a natural source of such interesting compounds including rod-like molecules with up to 11 adamantane units, chiral molecules such as [1234]pentamantane, and several perimantanes. The rod-like molecules have dualists with alternating [1212...] codes. They can be functionalized at the

top and bottom tertiary carbon atoms on substituting the unique hydrogen by a halogen or another functional group. Such rigid molecular blocks may be used as spacers with a definite length in drug design, or in directing intramolecular attack on a definite position of the molecule, using the strategy brilliantly inaugurated by Breslow.²⁸ The functionalized chiral diamondoids building blocks may also be used in synthesizing biologically active compounds with definite configuration.

Drexler advocated the use of rigid nanotubes with definite length in molecular motors,²⁹ a field that nature has arrived at by molecular evolution (exemplified by the machinery that synthesizes ATP from inorganic phosphate). One can manufacture carbon nanotubes consisting of benzenoid rings, but their length and helicity are hard to control, and their functionalization at the ends is not as straightforward. By contrast, functionalized diamondoids rods can be obtained more readily and have similar rigidities.

All benzenoid catafusenes with the same number of rings are isomeric, and their enumeration has advanced steadily.^{30–32} Only Kekuléan benzenoid systems are stable, and this feature has also been taken into account. Dias has produced formula periodic tables of Kekuléan benzenoids that include catafusenes and perifusenes.^{33–36} When enumerating all possible benzenoids, there is a possibility of excluding or including nonplanar systems (helicenes), by taking three-dimensional structures into account. No such escape into the fourth dimension exists for diamondoids.

■ POSSIBLE APPLICATIONS OF REGIOSELECTIVELY FUNCTIONALIZED DIAMANTOIDS

With the advent of readily available lower diamondoids from petroleum, a host of possible applications can be envisaged. Prominent among these are applications of rod-shaped molecules functionalized at both ends. Examples of biological activities exhibited by such molecules are the curare-like bis-quaternary ammonium compounds used as muscular relaxants: two positive charges at a certain distance interact with acetylcholine esterase causing its inhibition.³⁷ Numerous other biological activities have been linked to molecular features at certain distances and angles, and many biomedical companies carry out their drug design by devising molecules with the corresponding features.

There are other nanorod-like molecules,^{38,39} such as carbon nanotubes; however, they are *mixtures* of similar but not identical molecules.⁴⁰ By contrast, one can prepare and functionalize regioselectively diamondoids as *pure substances*. Since the reactivities of tertiary and secondary C–H bonds in diamondoids differ, it is possible to achieve a regioselective functionalization. Grouping diamondoids according to valence-isomeric classes having definite numbers of tertiary (CH) and secondary (CH_2) hydrogen atoms is therefore of highest importance in this regard.⁴¹

Schreiner and his co-workers (together with Dahl and Carlson who provided the diamondoids from petroleum) investigated thoroughly the regioselectivity of diamondoid functionalization in a series of papers.^{42–50} It has long been known that the tertiary C–H bonds of adamantane can be more readily halogenated than the secondary C–H bonds.⁴³ For diamantane it was observed that alcohol formation by oxidation with *meta*-chloroperbenzoic acid favors medial-tertiary over apical-tertiary attack; higher yields are achieved by nitroxylation by anhydrous HNO_3 followed by hydrolysis; interestingly, apical substitution is favored by longer reaction

times. For fluorination, AgF halogen exchange and alcohol conversion using $\text{Et}_2\text{N}-\text{SF}_3$ proved to be methods of choice.⁴⁴ Photoacetylation of diamondoids with diacetyl gives predominantly apical acetyl derivatives owing mainly to polarizability effects, with steric factors playing a minor role.⁴⁵ Bis-apical rod-like functionalized diamondoids are the most promising candidates for applications. The global shape of the diamondoid also influences the regioselectivity.^{46,47} A fundamental finding of Schreiner's research group was that the formation of higher diamondoids occurred via a homolytic mechanism involving sequential addition of isobutane fragments to diamondoids.⁴⁸ Oxa- and thia-diamondoids were also prepared;⁴⁹ the influence of type and positions of heteroatoms was studied in order to predict the band gap tuning in nanodiamonds.⁵⁰

■ FORMULA PARTITION PERIODIC TABLE OF REGULAR DIAMONDROID VALENCE ISOMERS

Regular catamantanes with n adamantane units have the molecular formula $\text{C}_{4n+6}\text{H}_{4n+12}$. However, it is important to survey the *grouping of atoms according to the partition into secondary, tertiary, and quaternary carbon atoms*. Valence isomers (that rearrange to afford polymantanes) have the same molecular formula, the same number of rings, and the same partition. However, here we also impose the added restriction that valence isomers must contain only chair-shaped six-membered rings. Such valence isomers are described by *partitioned molecular formulas*. Earlier enumerations of valence isomers for adamantane allowed also many other types of valence isomers.⁴¹ It will become apparent that partitions of regular catamantanes depend on the number and type of branches of the dualist, i.e. on the vertex degree of the branch origin in the dualist.

Table 1 presents the beginning of the *formula periodic table of diamondoid valence isomers*; a more developed version (but perforce in more condensed form) is shown in Table 2, which

Table 1. For Regular Catamantanes, Partitions of Degrees of Carbon Atoms (Middle Rows in Each Cell: Quaternary–Tertiary–Secondary Carbon Atoms) and Partitions of Vertex Degrees of Dualists (Lowest Row: Numbers of Vertices with Degree 1, 2, 3, 4 separated by commas)

units n	molecular formula	zero branches	one branch
		carbon atoms (quat–tert–sec) dualist degree partition (degrees 1, 2, 3, 4)	carbon atoms (quat–tert–sec) dualist degree partition (degrees 1, 2, 3, 4)
1	$\text{C}_{10}\text{H}_{16}$	$(\text{CH})_4(\text{CH}_2)_6$ 0–4–6 0, 0, 0, 0	
2	$\text{C}_{14}\text{H}_{20}$	$(\text{CH})_8(\text{CH}_2)_6$ 0–8–6 1, 1, 0, 0	
3	$\text{C}_{18}\text{H}_{24}$	$\text{C}(\text{CH})_{10}(\text{CH}_2)_7$ 1–10–7 2, 1, 0, 0	
4	$\text{C}_{22}\text{H}_{28}$	$\text{C}_2(\text{CH})_{12}(\text{CH}_2)_8$ 2–12–8 2, 2, 0, 0	$\text{C}_3(\text{CH})_{10}(\text{CH}_2)_9$ 3–10–9 3, 0, 1, 0

encompasses regular catamantanes with up to eight adamantane units.

Data for triamantane and the three tetramantanes are repeated in Table 2 without specifying the partitioned molecular formula. Regular catamantanes with $n \geq 2$, whose dualists have no branches, share the same partition: $\text{C}_{n-2}(\text{CH})_{2n+4}(\text{CH}_2)_{n+4}$. When the dualist has a single branch, the partition is $\text{C}_{n-1}(\text{CH})_{2n+2}(\text{CH}_2)_{n+5}$. When two branches are present, two cases are possible: for the partitioned molecular formula with one degree-4 vertex in the dualist, the partition of vertices is $\text{C}_{n+1}(\text{CH})_{2n-2}(\text{CH}_2)_{n+7}$; for two degree-3 branching vertices in the dualist, the partitioned molecular formula is $\text{C}_n(\text{CH})_{2n}(\text{CH}_2)_{n+6}$. In these cases, and all other cases with more complicated partitions, the numbers of carbon and hydrogen atoms add up to $4n + 6$ and to $4n + 12$, respectively, as long as there are no proximities and the catafusene is a regular one.

Some explanations are needed for Table 2 which contains in condensed form information on partitions of the number C of carbon atoms (separated by hyphens) and on partitions of the sum n of vertex degrees of dualists (separated by commas, and indicating the number of adamantane units). The first row contains parameter b , loosely associated with branch numbers of the dualist (but only for 0 and 1); the correct branch numbers of the dualist are shown in the second row. Thus for the unique triamantane with zero branches encoded as [12] with the partitioned molecular formula $\text{C}(\text{CH})_{10}(\text{CH}_2)_7$, one sees 1–10–7 (meaning $Q-T-S$ values) in the column labeled 0.

Now let us discuss the numbers separated by dashes for the partition of the n vertex degrees in the dualist. Any dualist of a diamondoid with zero branches has **two end points**, so that one sees all entries of column 0 having boldface 2 as the first number of the quadruplet separated by commas. This quadruplet shows the numbers of vertices in the dualist for degrees 1, 2, 3, and 4 (an end point has degree 1). A steady increase of the second digit from top to bottom for all entries indicates that the vertices of degree 2 increase with increasing number of adamantane units. The last two numbers separated by commas are 0, 0 because there are no vertices with degree 3 or 4.

Column labeled 1 presents valence isomers of diamondoids whose dualists have one branch, hence have **3 end points** of the dualist, plus **1** vertex of degree 3 (boldface digits). The last two numbers separated by commas are 1, 0 because there are no vertices with degree 4.

Columns labeled 2 and 3 correspond to valence isomers of diamondoids whose dualists have two branches and, hence, have **4 end points** of the dualist. However, now there are two possibilities, namely either with **2** vertices of degree 3 (column 2) or **1** vertex of degree 4 (column 3) again as boldface digits. In the latter case, the two branches are geminal.

Columns labeled 4 and 5 present valence isomers of diamondoids whose dualists have three branches and, hence, have **5 end points** of the dualist. Again, there are two possibilities: three vertices of degree 3 or one vertex of degree 4 plus one vertex of degree 3.

Column labeled 6 displays valence isomers of diamondoids whose dualists have four branches and, hence, have **6 end points** of the dualist. Again there are several possibilities: two vertices of degree 4, 1 vertex of degree 4 plus two vertices of degree 3, or four vertices of degree 3. Only the first of these possibilities can be attained by octamantanes.

Table 2. For Regular Catamantanes, Partitions of Degrees of Carbon Atoms (Upper Row: Quaternary–Tertiary–Secondary Carbon Atoms) and Partitions of Vertex Degrees of Dualists (Lower Row: Numbers of Vertices with Degree 1, 2, 3, 4)

C\b		0	1	2	3	4	5	6
<i>n</i> units	formula	zero branches	one branch	two branches		three branches		four branches
18	C ₁₈ H ₂₄	1–10–7						
3		2, 1, 0 0						
22	C ₂₂ H ₂₈	2–12–8	3–10–9					
4		2, 2, 0, 0	3, 0, 1, 0					
26	C ₂₆ H ₃₂	3–14–9	4–12–10		6–8–12			
5		2, 3, 0, 0	3, 1, 1, 0		4, 0, 0, 1			
30	C ₃₀ H ₃₆	4–16–10	5–14–11	6–12–12	7–10–13			
6		2, 4, 0, 0	3, 2, 1, 0	4, 0, 2, 0	4, 1, 0, 1			
34	C ₃₄ H ₄₀	5–18–11	6–16–12	7–14–13	8–12–14	9–10–15		
7		2, 5, 0, 0	3, 3, 1, 0	4, 1, 2, 0	4, 2, 0, 1	5, 0, 1, 1		
38	C ₃₈ H ₄₄	6–20–12	7–18–13	8–16–14	9–14–15	10–12–16	9–14–15	12–8–18
8		2, 6, 0, 0	3, 4, 1, 0	4, 2, 2, 0	4, 3, 0, 1	5, 1, 1, 1	5, 0, 3, 0	6, 0, 0, 2

A spectacular symmetry of this periodic table of regular catamantanes $C_{4n+6}H_{4n+12}$ is apparent on examining Table 1. Practically all partitions of C in can be expressed in terms of parameters n and b indicating that the numbers of quaternary and secondary carbon atoms increase according to the number n of units and number b of branches, whereas the number of tertiary CH groups increases twice as fast. The three components of the triplet Q – T – S indicating the numbers of C, CH, and CH₂ groups, respectively are

$$Q = n + b - 2 = S - 6 \quad (1)$$

$$T = 2(n - b + 2) \quad (2)$$

$$S = n + b + 4 \quad (3)$$

In other words, regular catamantanes have the following partitioned formula: $C_{n+b-2}(CH)_{2n-2b+4}(CH_2)_{n+b+4}$. Still unexplained is the unique exception for the regular octamantanes with dualists having three branching points of degree 3, which according to the above formulas ought to have the carbon atom partition 11–10–17, but we found instead 9–14–15 (with dualist degree partition 5, 0, 3, 0). Table 2 exhibits remarkable symmetries along rows, columns, or diagonals. Tables with all isomers of diamondoids (ignoring stereoisomerism) are available only up to $n = 7$, and the above exception would have not been detected if some of the hundreds of octamantanes would not have been investigated. This exception proves that there may be still unknown features in the partitioned-formula periodic table, making Table 2 a nontrivial problem-hiding puzzle. A preliminary look at regular catamantanes with $n > 8$ adamantane units showed that the column 5 in Table 2 will start to be filled with values having expected symmetries only for $n \geq 10$.

In conclusion, all regular catamantanes with n adamantane units are isomeric and have the same molecular formula $C_{4n+6}H_{4n+12}$; however, the partition of carbon and hydrogen atoms, i. e. grouping these isomers into valence isomeric classes, depends on the vertex degrees of their dualists or, in other words on how many branches there are in the dualist graph, and whether these branches are separate or geminal (in the former case branches originate in a vertex of degree 3 and in the

latter case of degree 4). Several partitioned formulas have been indicated following Tables 1 and 2.

■ FORMULA PERIODIC TABLE OF IRREGULAR CATAMANTANE/PERIMANTANE VALENCE ISOMERS

Now let us examine how with this formula periodic table of irregular catamantane and perimantane valence isomers one can determine the molecular formula of diamondoids. First, we will discuss how one can generate new diamondoids by adding one adamantane unit to an existing diamondoid. In order to do this, one should be aware that only staggered conformations of C–C bonds yielding chair-shaped cyclohexane rings are allowed in the diamond lattice. Let us start with a “perhydrographene” quasi-flat sheet of carbon atoms having hydrogens attached on both sides to all starred and nonstarred carbon atoms, respectively. When adding four carbon atoms (an isobutane fragment) in order to form an adamantane unit (Figure 6), one should avoid the left-hand situation because it will produce tub-shaped cyclohexane rings as in lonsdaleite, and therefore, one must follow the right-hand approach.

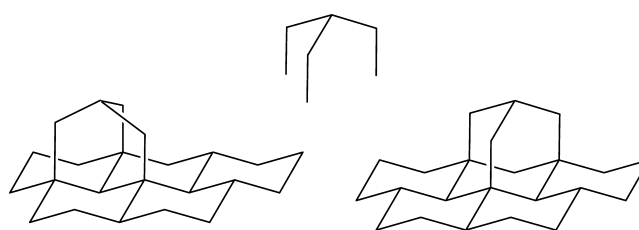


Figure 6. Two possibilities of attaching an isobutane fragment to “perhydrographene”: only the right-hand possibility is allowed.

Now let us consider how one attaches a new adamantane unit to a catamantane for obtaining a new adamantane unit starting from [123]tetramantane. As shown in Figure 7, one may either add an isobutane fragment with four carbon atoms, obtaining thereby the regular [1234]pentamantane or only a propane fragment with three carbon atoms obtaining the

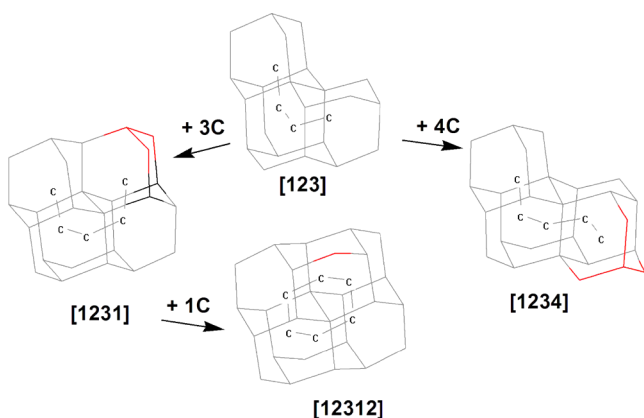


Figure 7. Stepwise additions of one adamantane unit starting from [123]tetramantane: on the right-hand side, adding the red isobutane fragment one obtains the regular [1234]pentamantane; on the left-hand side, by adding to [123]tetramantane a propane fragment, one obtains the irregular [1231]pentamantane. From the latter, in order to obtain the perimantane coded as [12312]hexamantane (the smallest perimantane), one needs to add just one carbon atom.

irregular [1231]pentamantane. From the latter, one may add just one carbon atom yielding [12312]hexamantane, the smallest perimantane. In Figure 7, the added fragments are shown in red.

To use a plastic image, irregular catamantanes, perimantanes, or coronamantanes have convoluted dualists that seem to be kneaded from hoof-shaped fragments (for irregular catamantanes), from chair-shaped rings (for perimantanes), or from larger rings, such as 8-membered or 10-membered rings in staggered conformation (for coronamantanes). Figure 8 presents a coronoid octadecamantane. Catamantanes, perimantanes and coronamantanes have $n - 1$ digits in their codes but might have n digits.

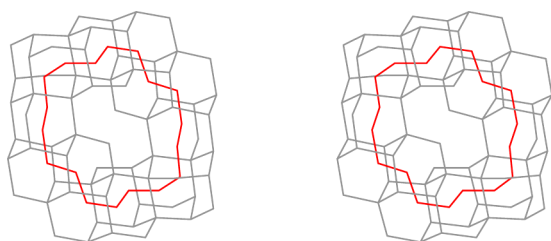


Figure 8. Stereoview of [12123242312123242]coronamantane with an 18-membered dualist (red).

Irregular catamantanes and perimantanes have $C < 4n + 6$ and a difference between the numbers of H and C atoms that is lower than 6. On looking at a dualist of a diamondoid, a proximity occurs when one has a continuous sequence of four edges belonging to the same chair-cyclohexane; in the code of the diamondoid this corresponds to repeating the same digit after two interposed different digits. The smallest nonbranched catamantane with one irregularity is [1231]pentamantane $C_2(CH)_{16}(CH_2)_7$, and the smallest nonbranched catamantane with two irregularities is [123143]heptamantane. There are three irregular branched catamantanes with $n = 7$, namely [12(31)41]heptamantane, [123(1)42]heptamantane, and [1(2)34(1)2]heptamantane. All these four heptamantanes have the partitioned formula $C_5(CH)_{18}(CH_2)_9$. The smallest perimantane with a 6-membered ring as dualist is [12312]-

hexamantane; there are two perimantanes with $n = 7$, namely [123124]heptamantane having axial methylcyclohexane as dualist, and [121324]heptamantane having equatorial methylcyclohexane as dualist.

For irregular catamantanes, no simple relationship between partitions and the position in Table 3 can be detected, because even with same numbers of proximities or branches, diamondoids are no longer isomeric. It is also found that for the same numbers n of adamantane units and b (branches + proximities), more than one partition of the carbon atoms can occur.

Still, although relationships 1–3 no longer apply, Table 3 does conserve some of the remarkable features of Table 1, exemplified by the column labeled 0. One can also observe the trivial result that all tertiary carbon atoms (CH groups) in diamondoids correspond to even numbers in Tables 2 and 3. The molecular hydrogen-depleted graph of diamondoids has vertices of degrees 2, 3, and 4; a well-known result of graph theory states that every graph has an even number of odd vertices.

CONCLUSIONS

Using dualists for modeling diamondoids was patterned after benzenoids, and since Dias found out interesting features of his formula periodic tables of benzenoids, it is not surprising that the formula periodic table of regular diamondoids also shows a high symmetry. Whereas benzenoids encounter complications when including helicenes, with diamondoids such complications, namely proximities, arise when adamantane units are so close to each other that less than four carbon atoms are needed to form a new unit.

Diamondoids contain quaternary, tertiary, and secondary carbon atoms; specifying them provides more detail than the molecular formula, and this partitioning allows the construction of formula periodic tables according to the number n of adamantane units and to features of the dualist such as the number of branches. For regular catamantanes a pronounced symmetry of this table is found. Irregular catamantanes and perimantanes, however, lead to a partitioned-formula periodic table with more exceptions. In the future, in order to understand better the carbon atom partitions for diamondoids, it will be necessary to develop computer programs for enumerating all diamondoid isomers with n values closer to the present highest value ($n = 11$) for isolated diamondoids from petroleum, and for finding their partitions in terms of decomposing C and n values into contributing terms. For all diamondoids examined in the present paper the ratio between hydrogen and carbon atoms decreases with increasing numbers of carbon atoms, branching points, proximities, and dualist ring formation, approaching the value of 1. When there are many internal rings in the dualist, diamondoid hydrocarbons with H/C ratio lower than 1 are possible, such as that shown in Figure 9 which has a H/C ratio of 0.76. The larger a diamond crystal (with all dangling bonds saturated with hydrogen atoms), the closer is its H/C ratio to zero.

There are analogies between considering: (i) neutron stars as chemical elements with very high atomic numbers Z having huge numbers of neutrons and few protons; (ii) natural crystals of graphite as benzenoid hydrocarbons with very high numbers h of benzenoid rings; and (iii) natural crystals of diamond as diamondoid hydrocarbons with very high numbers n of adamantane units. In the last two cases, there are huge numbers of carbon atoms and few peripheral hydrogen atoms.

Table 3. Irregular Catamantanes and Perimantanes^a

0		1		2		3		4		5		6	
irregular catamantanes												perimantanes	
zero branches				one branch				two branches					
units <i>n</i>	one proximity		two proximities		one proximity		two proximities		one proximity		two proximities		
5	2–16–7		2, 3, 0, 0 (C ₂₅ H ₃₀)										
6	3–18–8				4–16–9								2–18–6
	4–16–9												
	2, 4, 0, 0 (C ₂₉ H ₃₄)				3, 2, 1, 0 (C ₂₉ H ₃₄)								0, 6, 0, 0 (C ₂₆ H ₃₀)
7	4–20–9		5–18–9		5–18–10		5–18–9		7–14–12		5–18–9		4–18–8
	5–18–10				6–16–11								
	2, 5, 0, 0 (C ₃₃ H ₃₈)		2, 5, 0, 0 (C ₃₂ H ₃₆)		3, 3, 1, 0 (C ₃₃ H ₃₈)		3, 3, 1, 0 (C ₃₂ H ₃₆)		4, 2, 0, 1 (C ₃₃ H ₃₈)		4, 1, 2, 0 (C ₃₂ H ₃₆)		1, 5, 1 0 (C ₃₀ H ₃₄)

^aThe same conventions apply as for Table 2, except that diamondoids with equal *n* are not isomeric; molecular formulas are now inscribed in parentheses in each cell of the table.

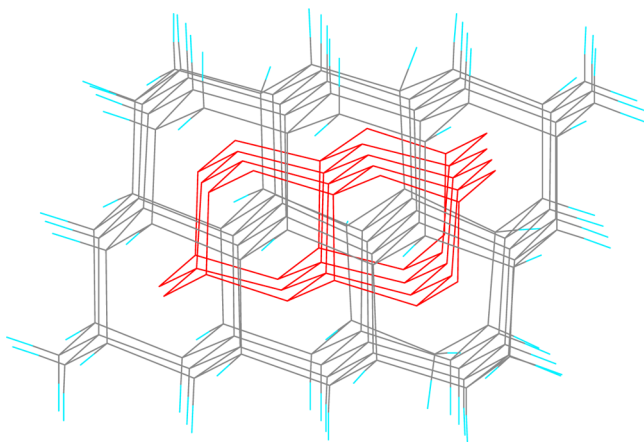


Figure 9. Large diamondoid hydrocarbon, C₁₀₀H₇₆, with *n* = 46 adamantane units (C–C bonds are black, C–H bonds are black + blue) with its red-colored dualist.

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Notes

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