

Carbon Materials: Chemistry and Physics 6  
*Series Editors: Franco Cataldo · Paolo Milani*

Mircea Vasile Diudea  
Csaba Levente Nagy *Editors*

# Diamond and Related Nanostructures

 Springer

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## **CARBON MATERIALS: CHEMISTRY AND PHYSICS**

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### **VOLUME 6: DIAMOND AND RELATED NANOSTRUCTURES**

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 Springer

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# Preface

Diamond is renowned for its beauty as well as for its superlative physical qualities. The rigor of its composition determines its exceptional thermal conductivity and hardness, traits that have found numerous industrial applications (e.g., as heatsink in electronics and in cutting, drilling, or polishing) and boosted the demand for diamond and diamond-like carbon.

A diamond crystal is in fact one molecule with macroscopic dimensions. When moving from molecules to materials, the model representing primary atomic arrangements undergoes transformations both in concept and experimental realization, as well as in the computational treatment. Following the latest developments and discoveries in the field, this book provides a thorough description of the diamond (and its relatives) in different hypostases.

Chapter 1 introduces the classical diamond through the eye of a chemist. Here the basic molecular substructures, adamantane and diamantane, are presented when they group together to build the star of materials: the diamond (indicated in our book as  $D_6$ ).

Chapter 2 examines the synthesis by chemical vapor deposition of diamond (and diamond-like carbon) films deposited on various surfaces and the analysis of these deposits.

Chapter 3 introduces the chemistry of a new diamond, named diamond  $D_5$ , which is suggested being seeded by the small cage  $C_{17}$ .

Chapter 4 describes some exotic carbon clathrates with  $sp^3$  carbon networks and calculates their electronic structure.

Chapter 5 analyzes the diamond  $D_5$ , a hyper-diamond structure with both translational and rotational symmetry, as encountered in quasicrystals.

Chapter 6 presents the fivefold symmetry which dominates the newly discovered world of quasicrystals. Such symmetry is built up by self-assembly of small cages, eventually called fullerenes, that form larger spherical multi-shell cages whose energetics is described.

Chapter 7 is drawn on the seed  $C_{17}$  and other substructures of  $D_5$  to evaluate their thermal stability.

Chapter 8 calculates the energetics and topology of lattices built up by nanotube junctions, as observed in diamond-related networks consisting of  $sp^2$  carbon.

Chapters 9 and 10 provide graph theoretical descriptions, in terms of counting polynomials, of the classical diamond and some newer diamondoids.

Chapter 11 describes nanotube junctions that could join to form a hypergraphene.

Chapter 12 presents polybenzenes, diamond-like structures with benzene-patched  $sp^2$  networks.

Chapter 13 analyzes fullerenes with negative curvature that could be involved in the construction of some carbon phases.

Chapter 14 offers an algebraic approach to the design of molecules having non-crystallographic symmetry.

Chapter 15 discusses carbon networks in the solid state, approached by DFT calculations.

Chapter 16 examines the diamond network drawing by using topological coordinates.

Chapter 17 treats the problem of filling the Euclidean space via a higher-dimensional space and non-crystallographic symmetries, as encountered in quasicrystals.

Chapter 18 gives a mathematical approach, in terms of group theory, to the symmetries encountered in the diamond  $D_5$ .

Finally, Chapter 19 provides a gallery of new structures, either space filled or spongy ones, possibly populating the quasicrystal world.

This unique volume brings together the major findings on the subject and will therefore be a source of inspiration and understanding for advanced undergraduates, graduates, and researchers with an interest in physics, graph theory, crystallography, and computational and synthetic chemistry.

Cluj-Napoca, Romania  
December 11, 2012

Mircea V. Diudea  
Csaba L. Nagy

# Acknowledgements

We would like to thank Franco Cataldo and Paolo Milani, series editors of “Carbon Materials: Chemistry and Physics” series, for ably identifying the need of a book on Diamond and Related Nanostructures.

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Last but not least, our warmest thanks go to all the respected contributors of this book.

Cluj-Napoca, Romania  
December 11, 2012

Mircea V. Diudea  
Csaba L. Nagy





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# Chapter 1

## Diamond Hydrocarbons and Related Structures

Alexandru T. Balaban

**Abstract** Among the two long-known allotropic forms of carbon,  $sp^2$ -hybridized multilamellar graphite is the thermodynamic stable form at normal temperature and pressure, whereas the denser  $sp^3$ -hybridized diamond becomes favored at very high pressures. Portions of graphene sheets with dangling bonds connected with hydrogen atoms are planar polycyclic benzenoid hydrocarbons (benzenoids). Similarly, portions of the diamond lattice with dangling bonds connected with hydrogen atoms are diamond hydrocarbons (diamondoids). Dualists of benzenoids consist of vertices in the centers of benzenoid rings and of edges connecting vertices corresponding to benzenoid rings sharing CC bonds. Analogously, dualists of diamondoids consist of vertices in the centers of adamantane units and of edges connecting vertices corresponding to adamantane units sharing six-membered rings. The diamond lattice is self-dual, whereas the honeycomb (hexagonal) and the triangular lattices are reciprocally dual. Encoding benzenoid structures can be achieved by using digits 0, 1, and 2, whereas encoding diamondoid structures (ignoring stereoisomers) can be achieved by using digits 1, 2, 3, and 4. The naming and encoding of diamondoid structures according to the Balaban-Schleyer proposal has now been generally accepted. The discovery and isolation of lower diamondoids in petroleum allowed a recent surge of interest in their properties and applications. Successive sections of this chapter are presenting regularities in the diamond lattice, where Cartesian coordinates can be integers. Then dualists of benzenoids followed by dualists of diamondoids are discussed, with similarities and differences. The latter dualists can be conveniently viewed as staggered rotamers of alkanes. By analogy with benzenoid catafusenes, perifusenes, and coronoids, dualists allow the classification of diamondoids into regular/irregular catamantanes

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(with acyclic dualists), perimantanes, and coronamantanes (with 6-membered or larger rings, respectively). This analogy allows a simple enumeration of all possible constitutional isomers of diamondoids. Stereoisomers of the chiral diamondoids are also discussed. The history of diamondoids is briefly discussed. A recently proposed partitioned-formula periodic table for diamondoids presents interesting symmetries, especially for regular catamantanes. On the basis of distance matrices for diamondoid dualists, one can obtain molecular invariants characterizing diamondoid structures. With such invariants, it was possible to rationalize HPLC and GC-MS chromatographic data for naturally occurring diamondoids. Finally, the chemical functionalization of diamondoids for various applications carried out by Schreiner and his coworkers is reviewed.

## 1.1 Introduction: Carbon Allotropes

Instead of the impersonal style that is customary for journal articles leading to awkward phrases in which authors refer to themselves using the 3rd person singular, in this book chapter, I will not shy from using the 1st person singular.

Although the element carbon occupies the 14th place (0.08 %) among other elements on earth's crust, oceans, and atmosphere, its importance for life places it at the top. Its electronegativity and atomic radius are midway between the extremes, so that carbon can combine with itself, forming stable covalent chains irrespective of their length. One other element, namely divalent sulfur, shares this property, but the results are only various allotropic forms of the element sulfur, unlike the infinite variety of organic and inorganic structures based on carbon chains. Alternating Si–O atom pairs also provide a rich assortment of structures characterizing most of the rocks in earth's crust.

The two long-known, naturally occurring carbon allotropes, namely diamond and multilayer graphite, have  $sp^3$ - and  $sp^2$ -hybridized carbon atoms, respectively. Their properties are in sharp contrast, as seen in Table 1.1. Diamond has a three-dimensional lattice in which each carbon atom has tetrahedral configuration with bond lengths of 1.54 Å and bond angles  $\alpha = 109.5^\circ$  ( $\cos\alpha = -1/3$ ;  $\text{tg}(\alpha/2) = \sqrt{2}$ ). Graphite has two-dimensional planar layers of benzenoid rings whose carbon atoms

**Table 1.1** Contrasting properties of diamond and multilayer graphite

Property	Diamond	Multilayer graphite
Aspect	Transparent, highly refractive	Opaque, black
Crystalline system	Cubic	Hexagonal
Density ( $\text{g} \times \text{cm}^{-3}$ )	3.514	2.266
Hardness (Mohs scale)	10	Between 1 and 2
Electrical conductivity	Low	High
Thermal conductivity	High	Low
Thermodynamic stability	Unstable	Stable



are 1.42 Å apart with bond angles of 120°; the interlayer distance is 3.35 Å. In this context, one should mention that graphite is converted under high pressure into synthetic diamond at temperatures around 2,000 °C. The thermodynamic instability of diamond at room temperature should allow its conversion into graphite (as described in 1884 by Jules Verne and Paschal Grousset in *The Southern Star*), but actually the activation energy is so high that diamonds *are almost* forever; nevertheless, this conversion can be carried out by heating diamond at 1,000 °C in the absence of oxygen. One should be aware that the high energy of dangling bonds at graphite sheet edges can be overcome by inter-sheet forces only for huge numbers and dimensions of sheets; otherwise, for relatively small numbers of carbon atoms ( $10^3$ – $10^4$ ), the stable forms are the third allotropic forms (fullerene onion-like spheroidal or nanotubular particles).

Because of these superficial dangling bonds that are normally occupied by hydrogen atoms, one can consider that diamond is an “honorary saturated hydrocarbon” and graphite an “honorary peri-condensed aromatic hydrocarbon” with negligibly small hydrogen-to-carbon ratios. By analogy with heavier stable nuclides whose nuclei must contain much larger numbers of neutrons than protons, one can also consider that dwarf neutron stars are “honorary superheavy atomic nuclei” with negligibly small proton-to-neutron ratios.

Natural diamonds are believed to have formed deep in the earth at high pressure and temperature; then tectonic processes have brought them in certain places closer to the surface. Each diamond crystal is one molecule with macroscopic dimensions.

With perfect  $sp^2$ -hybridization, a unilayer planar carbon sheet (called *graphene* by Boehm et al. 1962, 1994) was first obtained by Geim and Novoselov (2007), who were awarded the 2010 Nobel Prize for Physics for their studies of this material which is one-atom thick and has numerous applications owing to its amazing properties. Each graphene sheet is also one macromolecule.

The large family of the third allotropic form of carbon known as fullerenes is quasi-spherical polyhedra consisting of benzenoid rings plus 12 pentagons. They were discovered in 1985 by Kroto, Smalley, and Curl who used mass spectrometry and who were awarded the 1996 Nobel Prize for Chemistry (Curl 1997; Kroto 1997; Smalley 1997). All lower fullerenes obey the “isolated pentagon rule” starting with buckminsterfullerene  $C_{60}$  (truncated icosahedron, an Archimedean solid or semiregular polyhedron) and followed by  $C_{70}$ . Double-capped single-wall nanotubes are fullerenes with oblong structure. After Krätschmer and Huffman extracted fullerenes from soot by appropriate solvents (Krätschmer et al. 1990), research on fullerenes increased immediately.

Open-ended single-wall cylindrical carbon nanotubes (SWNTs, resulting by theoretical folding of graphene sheets) were prepared in 1991 by Iijima (1991) (earlier reports by Russian scientists in 1952 (Radushkevich and Lukyanovich 1952) and by other Japanese scientists (Oberlin et al. 1976) in 1976 were largely ignored). According to Coxeter’s vectors  $m$  and  $n$  on the honeycomb crystal lattice (Coxeter 1971), one can fold graphene sheets to yield a zigzag SWNT when  $m = 0$ , an armchair SWNT when  $m = n$ , and a chiral SWNT when  $m \neq n$ . Differences in

bandgap and electrical conductance between these three types of nanotubes can be correlated with  $|m-n|$  values: only when this difference is a multiple of 3 do circles in Clar structures (Clar 1972) overlap in congruent fashion on folding the graphene sheet; other foldings of graphene sheets explain similarly property differences among nanocones or nanotori (Balaban and Klein 2009; Klein and Balaban 2011; Balaban 2011). Whereas many fullerenes such as  $C_{60}$  and  $C_{70}$  can be prepared as *substances* (pure compounds with identical molecules), so far SWNT are *mixtures* of similar but different molecules, like many natural and synthetic polymers.

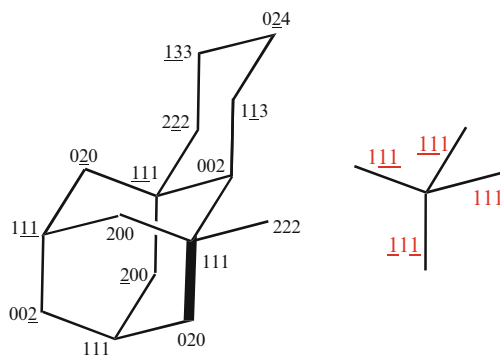
In addition to these four classes of carbon allotropes (graphite-graphene, diamond, fullerenes, and nanotubes), one should mention the existence of (1) amorphous carbon; (2) lonsdaleite, found in meteorites (Fron del and Marvin 1967; Pan et al. 2009; Bundy 1967; He et al. 2002), a relative of diamond (whereas in diamond all hexagons are in chair conformation with staggered C–C bonds, in lonsdaleite some 6-membered rings have eclipsed bonds as in wurtzite or iceane); and (3) other predicted carbon nets (Sheng et al. 2011; Zhu et al. 2011), such as Diudea’s diamond  $D_5$  (Diudea 2010; Diudea et al. 2011; Diudea and Nagy 2012).

Finally, one should discuss whether we can have a one-dimensional sp-hybridized carbon allotrope (a mythical polyynes allotrope, often mentioned in the literature as carbyne, a long chain of triply bonded carbon atoms, or a long cumulene) (Kroto 2010; Heimann et al. 1999; Baughman 2006; Itzhaki et al. 2005; Chalifoux and Tykwinski 2009; Lagow et al. 1995; Xue et al. 2004; Tobe and Wakabayashi 2005). The detection of interstellar and circumstellar molecules by radio, microwave, or infrared spectroscopy led to the identification of polyynes and their nitrile or dinitrile derivatives. However, one must take into account that these molecules are not in condensed phase. Acetylene is explosive when compressed (therefore it can be stored at higher pressure only in solution) and polyacetylenes even more so. The huge energy release on polymerization of polyynes makes their existence unlikely in condensed phase (Heimann et al. 1999). Several structures  $R-(C\equiv C)_n-R$  with various bulky or electron-acceptor end-caps R have been synthesized for  $n < 45$ , but this seems to be the approximate limit.

## 1.2 The Three-Dimensional Diamond Lattice

Vertices of the diamond lattice can be given integer coordinates by using a cubical unit cell four units across. With these coordinates, the points of the structure have coordinates  $(x, y, z)$  in the Euclidean three-dimensional space satisfying the equations

$$x = y = z(\text{mod } 2) \text{ and} \\ x + y + z = 0 \text{ or } 1(\text{mod } 4).$$



**Fig. 1.1** Integer coordinates ( $xyz$ ) for carbon atoms in the diamond lattice. *Left*: carbon atom coordinates for an adamantane unit with a fused 6-membered ring and one attached carbon atom (*minus signs* are represented by underlined digits). *Right*: ongoing from the central vertex to its four neighboring vertices, the *red numbers* indicate changes in the  $xyz$  coordinates

There are eight points (modulo 4) that satisfy these conditions:

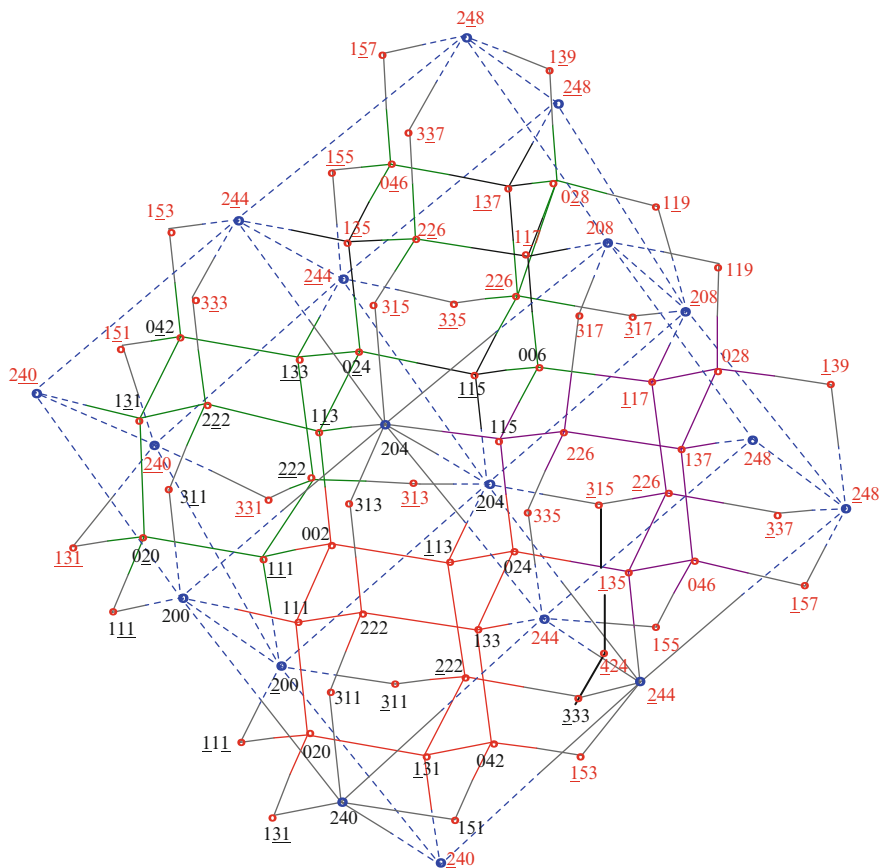
$$(0, 0, 0), (0, 2, 2), (2, 0, 2), (2, 2, 0), (3, 3, 3), (3, 1, 1), (1, 3, 1), \text{ and } (1, 1, 3).$$

All of the other points in the integer lattice may be obtained by adding multiples of four to the coordinates  $x$ ,  $y$ , and  $z$  of these eight points. In this integer lattice, adjacent points connected by C–C bonds are at distance  $\sqrt{3}$  apart. A triplet of even numbers is always connected with a triplet of odd numbers. In Figs. 1.1 and 1.2, one can see this diamond lattice with integer coordinates. For economy of space, minus signs are written under each digit, instead of being placed before each digit. In Fig. 1.2, full red lines delineate adamantane units, and blue dashed lines indicate cubic cells.

The origin of the rectangular Cartesian axes has been arbitrarily selected to coincide with the center of an octahedral “empty” space inside a central adamantane cell, and the coordinate axes are along the directions to the corners of the octahedron.

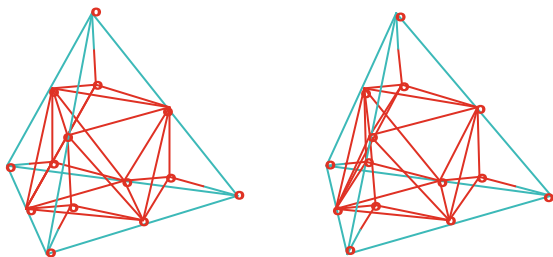
An interesting feature of the smallest unit (the adamantane scaffold) with its ten carbon atoms is the fact that six of these atoms symbolized by vertices (points) of the lattice form an “empty” regular octahedron, whereas the other four points lie at the centers of four regular tetrahedra fused to four alternant faces of the total of eight octahedron faces. This fusion yields a larger tetrahedron, with doubled linear extensions. It is known that the dihedral angle of the octahedron is  $\alpha$ , whereas the dihedral angle of the tetrahedron is  $\beta = 180^\circ - \alpha$ , so that the three-dimensional space can be filled by an assortment of octahedra and tetrahedra sharing faces, with two octahedra sharing an edge (Fig. 1.3).

In Table 1.2, one may see the coordinates of the carbon atoms at the eight corners of the cube situated on the right side of Fig. 1.2; the two parts of this table are for vertices of virtual tetrahedra within the cube.



**Fig. 1.2** Integer coordinates for the diamond lattice; four cubic cells are shown with *blue dashed lines* and C–C bonds by *red lines*. *Minus signs* are indicated under the corresponding digits

**Fig. 1.3** Stereo view of one adamantane cell with an octahedron and four tetrahedra



**Table 1.2** Integer coordinates for C atoms at cube corners in Fig. 1.2

$x$	$y$	$z$
-2	0	8
2	4	8
2	0	4
-2	4	4
2	0	8
-2	4	8
-2	0	4
2	4	4

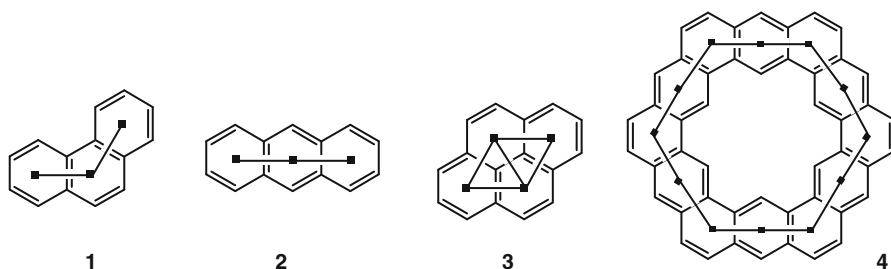
### 1.3 Dualists of 2D Polycyclic Aromatic Hydrocarbons (Benzenoids)

In 1968, I published with two coworkers a theoretical estimation of possible new two-dimensional and three-dimensional carbon lattices and nets (Balaban et al. 1968). In what started a fruitful collaboration I had with Frank Harary (Balaban and Harary 1968), the dualists of polycyclic benzenoids allowed a rigorous graph-theoretical study of such polycyclic aromatic hydrocarbons. One takes *a portion of an infinite graphene plane or an infinite diamond lattice* and defines a *dualist* of that portion by vertices that are centers of the cyclic cells (benzenoid rings or adamantane units, respectively) and by edges connecting vertices in adjacent cells. Dualists are similar to, but not identical with, graphs because angles between edges do matter (Balaban and Harary 1968; Balaban 1969, 1982).

Historically, benzenoids have been classified as cata-condensed (catafusenes) when all C or CH carbon atoms are on the periphery and as peri-condensed when there exist internal carbon atoms (necessarily without hydrogen). Dualists provide a simpler classification (catafusenes have acyclic dualists, whereas perifusenes have 3-membered rings) and allow an easy definition of a third type of benzenoids, coronoids, having dualists with larger rings. In Fig. 1.4, the isomeric phenanthrene (**1**) and anthracene (**2**) are catafusenes, pyrene (**3**) is a perifusene, and kekulene (**4**) is a coronoid.

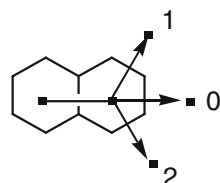
For catafusenes, we developed a coding system based on the dualist, as indicated in Fig. 1.5, based on the angles in the dualist longest continuous line (Balaban and Harary 1968; Balaban 1969, 1982). Starting from one end of the dualist, and examining the angle at each vertex, one assigns digit 0 for a straight annelation (angle  $180^\circ$ ) and digit 1 or 2 for a kinked annelation (angle  $120^\circ$  or  $240^\circ$ ), selecting as the canonical code the smallest number resulted from all digits. This means that one has to compare all endpoints and all kink notations.

For nonbranched catafusenes, it is simple to devise canonical notations for all isomeric catafusenes with four benzenoid rings  $C_{18}H_{12}$ , as seen in Fig. 1.6. For a branched catafusene such as triphenylene, one selects the longest linear path for the dualist, indicating in round parentheses the code of the branching line; if the branch has only one benzenoid ring as in triphenylene, **10**, a dot denotes this single branching benzenoid ring.

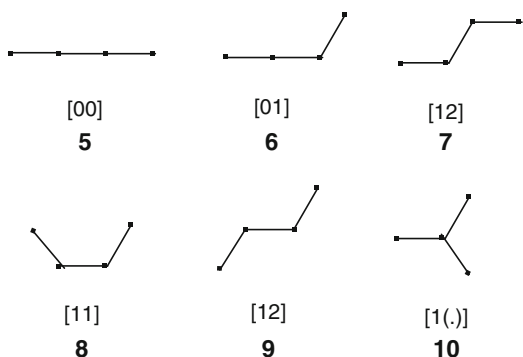


**Fig. 1.4** Two isomeric catafusenes  $C_{14}H_{10}$  (**1** and **2**), a perifusene  $C_{16}H_{10}$  (**3**), and a coronoid  $C_{48}H_{24}$  (**4**)

**Fig. 1.5** Coding scheme for catafusenes based on dualist angles at each annelation step



**Fig. 1.6** Dualists and codes for all isomeric catafusenes  $C_{18}H_{12}$  with four benzenoid rings, **5–10**



Interesting correlations for properties of benzenoids were made possible by using dualists: resonance energies (Balaban 1970), electrochemical potentials (Singh et al. 2006), and rates of Diels-Alder cycloaddition with maleic anhydride (Balaban et al. 1985). In collaborations with the Roumanian graph-theorist Tomescu, I introduced the term “isoarithmic” for benzenoids whose codes differ only in permutations between digits 1 and 2 (Balaban and Tomescu 1983) such as **8** and **9**: they have exactly the same numbers of Kekulé resonance structures in one-to-one correspondence and most of their properties are quasi-identical. In other words, on replacing in catafusene codes digits 1 and 2 by lowercase L which looks like digit 1, the catafusenes whose L-transform of 3-digit codes (looking like binary numbers) is identical should have very similar properties (Balaban 1977); similar ideas have been independently developed by Gutman (Balaban and Randić 2011).

In the 1930s, Eric Clar formulated his theory about aromatic sextets in benzenoids (Clar 1972); it can be summarized in postulating that benzenoid rings in cata- or perifusenes compete for  $\pi$ -electron sextets, resulting, for instance, that a sextet in acenes can belong to only one ring, whereas in zigzag catafusenes  $C_{4n+2}H_{2n+4}$ , there are  $n/2$  or  $(n+1)/2$  such Clar circles, for instance, one Clar circle in benzene and naphthalene and two Clar circles in phenanthrene (**1**) or in the three tetracatafusenes **7**, **8**, and **9** which have the same L-transform code. In the graphene lattice, Clar circles lie along poly-*para*-phenylene pathways. The dualist of this honeycomb lattice is a triangular lattice and vice versa.

When mathematical chemists started to enumerate all possible benzenoids, an interesting divergence occurred: one could consider benzenoids as being flat portions of the graphene lattice or as being assemblies of benzenoid rings sharing CC bonds, allowing to climb into the 3rd dimension. In the latter case, one could include helicenes, which are normal, stable catafusenes, and in a consolidated report, we pleaded for this approach, which complicates the calculations. Interesting findings were found by Dias who constructed “formula periodic tables” of benzenoids.

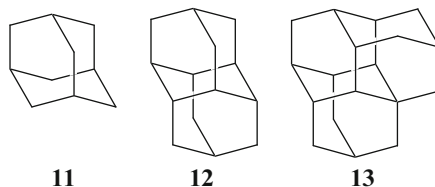
Before leaving the benzenoids, I would like to mention collaborations with my lifelong friend Milan Randić (a series of joint publications on numerical characterization of cata- or peri-condensed benzenoids according to partitions of  $\pi$ -electrons among adjacent benzenoid rings) (Randić and Balaban 2008; Balaban and Randić 2008); with Ivan Gutman on related topics for heteroanalogs of benzenoids (Balaban et al. 2007a); with Douglas J. Klein and his coworkers on fullerenes, nanocones, and nanotubes (Balaban et al. 1994a, b; Klein and Balaban 2006); with Roald Hoffmann (Merz et al. 1987) or D. J. Klein for combined  $sp^2$ – $sp^3$  hybridized lattices (Balaban et al. 1994a, b; Balaban and Klein 1997); and with Roger Mallion (Balaban and Mallion 2012), Milan Randić (Randić et al. 2012), or Patrick W. Fowler (Balaban et al. 2010) on ring currents in benzenoids.

## 1.4 Dualists of 3D Polycyclic Diamondoid Hydrocarbons and Staggered Alkane Rotamers

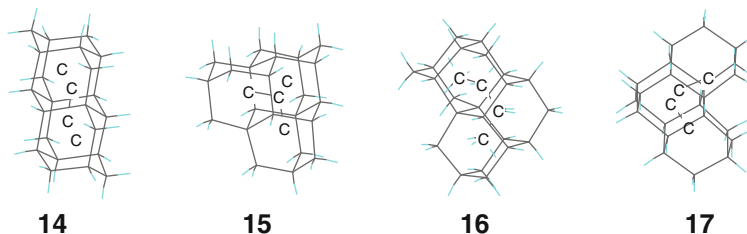
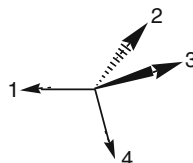
From two-dimensional dualists, it was easy to think about a similar approach involving three-dimensional polycyclic hydrocarbons (diamond hydrocarbons or diamondoids). Electronic factors and the tetrahedral bond angle  $\alpha = 109.5^\circ$  impose staggered conformations of alkanes that allow again an approach based on discrete mathematics, using dualists. In this case, however, there is no climbing to a higher dimension analogous to helicenic structures of benzenoids; on the other hand, one can still distinguish between catamantanes and perimantanes according to whether the dualist is acyclic or cyclic. The diamond lattice is self-dual.

In Fig. 1.7, one can see the single isomers of adamantane (**11**), diamantane (**12**), and triamantane (**13**). The four tetrahedral directions around a vertex are denoted by digits 1–4 as in Fig. 1.8, and again the canonical code for the staggered conformation

**Fig. 1.7** Adamantane  
(**11**,  $C_{10}H_{16}$ ), diamantane  
(**12**,  $C_{14}H_{20}$ ), and triamantane  
(**13**,  $C_{16}H_{24}$ )



**Fig. 1.8** The four tetrahedral directions



**Fig. 1.9** The four possible tetramantanes: the achiral [121]tetramantane, the achiral [1(2)3]tetramantane, and the two chiral enantiomers [123]tetramantane and [124]tetramantane

of an alkane has the minimal number resulting from sequential reading of the directions along the longest linear chain. Their dualists are represented by the carbon scaffolds of methane, ethane, and propane.

When there are branches along the longest linear chain of the dualist, their directions are enclosed in round brackets; as in the case of the benzenoids, codes are enclosed in square brackets.

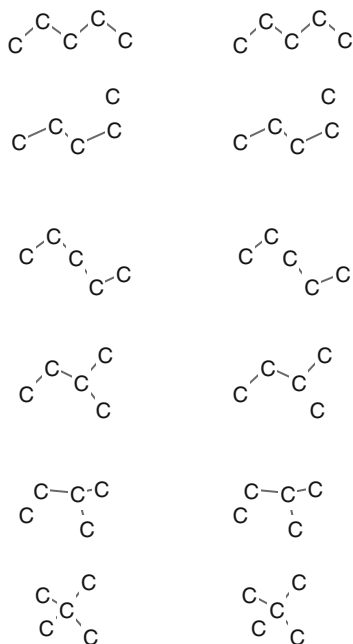
Starting with  $C_4$  alkanes, isomers and staggered conformational rotamers are possible, with the associated tetramantanes. The two isomers are *n*-butane and isobutane; the staggered conformational rotamers are the *anti*- and *gauche* *n*-butane. Only the latter is chiral. Figure 1.9 presents the four possible tetramantanes with their dualists indicated by the carbon skeleton of the corresponding alkane.

## 1.5 Isomers of Diamondoids

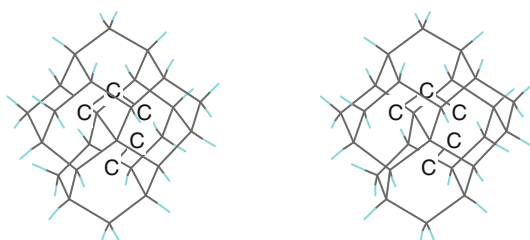
Pentanes give rise to three isomers and to seven rotamers (ignoring enantiomerism). Six of the corresponding pentamantanes are regular having molecular formula  $C_{26}H_{32}$ , with dualists shown as stereo views in Fig. 1.10. The seventh pentamantane



**Fig. 1.10** Stereo view of the dualists for regular pentamantanes with codes [1212], [1213], [1234], [12(1)3], [12(3)4], and [1(2,3)4]



**Fig. 1.11** Stereo view of the irregular pentamantane with its dualist [1231]



with dualist code [1231] is irregular having molecular formula  $C_{26}H_{30}$ , and it is shown as stereo view with its dualist in Fig. 1.11. One can see that the ends of the dualist are close to each other. When the dualist is a chair-shaped hexagon, the corresponding hexamantane is the smallest possible perimantane. In Table 1.3, one can see all possible catamantanes with one to six adamantane cells.

After having enumerated all possible staggered rotamers of alkanes (Balaban 1976a, b; Balaban and Baciu 1978), I have noticed marked similarities with isomers of benzenoids. Since Paul von Ragué Schleyer was the world's authority on adamantane and polymantanes, I wrote to him in 1978 suggesting collaboration, and the result was a paper (Balaban and Schleyer 1978) that used the code I had proposed, which is much simpler than the von Baeyer IUPAC nomenclature (Eckroth 1967). For example, the literature names of the three unique diamondoids with  $n = 1-3$  adamantane units are tricyclo[3.3.1.1<sup>3,7</sup>]decane for adamantane; for diamantane pentacyclo[7.3.1.1<sup>4,12</sup>.0<sup>2,7</sup>.0<sup>6,11</sup>]tetradecane; and for triamantane the IUPAC name is heptacyclo[7.7.1.1<sup>3,15</sup>.0<sup>1,12</sup>.0<sup>2,7</sup>.0<sup>4,13</sup>.0<sup>5,11</sup>]octadecane.

**Table 1.3** Catamantanes with  $n = 1-6$  adamantane units

$n$	Regular					Irregular				
	Linear			Branched		Linear			Branched	
	Code	Sym	Formula	Code	Sym	Code	Sym	Formula	Code	Sym
1		$T_d$	$C_{10}H_{16}$							
2	1	$D_{3d}$	$C_{14}H_{20}$							
3	12	$C_{2v}$	$C_{18}H_{24}$							
4	121	$C_{2h}$	$C_{22}H_{28}$	1(2)3	$C_{3v}$					
	123	$C_2$								
5	1212	$C_{2v}$		12(1)3	$C_1$					
	1213	$C_1$	$C_{26}H_{32}$	12(3)4	$C_s$	1231	$C_s$	$C_{25}H_{30}$		
	1234	$C_2$		1(2,3)4	$T_d$					
6	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	$C_1$	$C_{29}H_{34}$	12(1)31	$C_s$
	12134	$C_1$	$C_{30}H_{36}$	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	$C_{2h}$					

## 1.6 Brief History of Diamondoids

Adamantane (hexamethylene-tetramethine, Fig. 1.1) was first discovered as a constituent of petroleum (Landa and Machacek 1933). Inorganic compounds such as  $P_4O_6$  were also found to have the same geometry as adamantane. Urotropine (hexamethylene-tetramine), which has the same geometry as adamantane, has been known for a long time because it is easily formed from formaldehyde and ammonia. Adamantane was then synthesized by Prelog using a lengthy route (Prelog and Seiwerth 1941a, b); 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. Schleyer’s synthesis of adamantane (Schleyer 1957, 1990) was based on the fact that all C–H and C–C bonds are staggered, without any angular or conformational strain, so that being the most stable among all isomers, it is formed by the  $AlCl_3$ -catalyzed rearrangement of any  $C_{10}H_{16}$  saturated isomer; Schleyer’s synthesis started from the hydrogenated dimer of cyclopentadiene. Analogously, the dimer of norbornene rearranged (Cupas et al. 1965) to diamantane (congressane was its challenging name for the 1963 IUPAC meeting in London), and triamantane was obtained similarly using bis-cyclopropanated polycyclic dimer of cyclooctatetraene with a sludge of  $AlBr_3$  and *tert*-BuBr as catalyst (Williams et al. 1966); McKervey used another

hydrocarbon, Binor-S, in a higher-yield reaction (Burns et al. 1976). Among the tetramantane isomers, only the rodlike structure could be made synthetically, also by McKervey and coworkers (McKervey 1980).

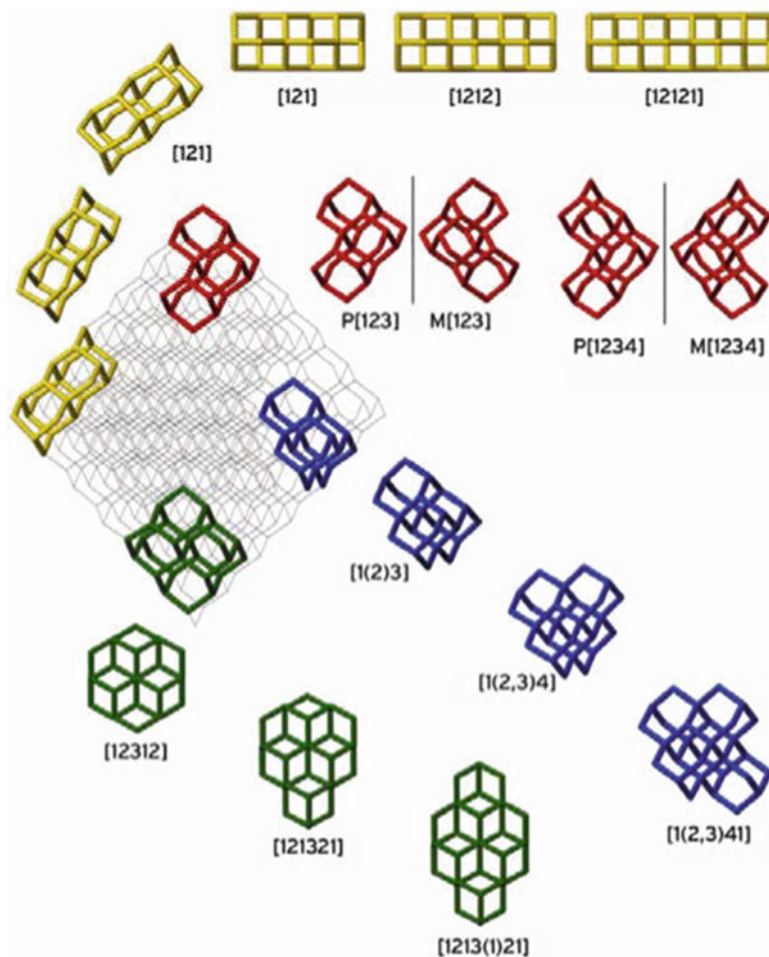
The X-ray diffraction of diamantane confirmed its structure and contributed to the award of the 1985 Nobel Prize in Chemistry to Jerome Karle (Karle and Karle 1965). Yet another link to this fascinating field was provided by using my reaction graphs (Balaban et al. 1966; Balaban 1994) for explaining the mechanism of the complicated rearrangements involved in these syntheses of polymantanes (Whitlock and Siefken 1968; Gund et al. 1975; Engler et al. 1973). Two early reviews on diamondoids were published by Fort Jr (Fort and Schleyer 1964; Fort 1976), and a very recent book has been published in 2012 (Mansoori et al. 2012). Since 1986, I have published three reviews on carbon and its nets (Balaban 1986a, b, 1989, 1998).

The recent discovery that mixtures of various diamondoids are found in crude oil and natural gas condensates (at concentrations 1–100 ppm) from offshore stations in the US Norphlet Formation (Gulf of Mexico) makes this class of substances attractive for many uses (Dahl et al. 1999, 2003a, b). The high volatility, high melting points (e.g., 268 °C for adamantane, which sublimates; 237 °C for diamantane; and 221 °C for triamantane), 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 no steric strain. Because they clogged natural gas pipelines, they were first considered as a nuisance.

Figure 1.12 represents four series of higher diamondoids as successive “adamantane analogs” indicated by four different colored carbon frameworks superimposed on a gray diamond lattice and shown separately with their notation. The yellow diamondoids are regular nonbranched rodlike zigzag catamantanes; the blue diamondoids are regular branched catamantanes; perimantanes are colored green. In the case of the red-colored chiral diamondoids (having primary helicity), enantiomeric pairs are displayed with **P/M** notations. Members of each series have been found and isolated from petroleum (Schreiner et al. 2009).

## 1.7 Degree Partitions of Dualist Vertices and Carbon Atom Partitions of Diamondoids

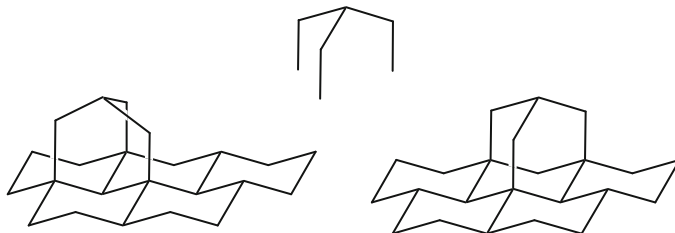
An interesting observation was made about isomers of diamondoids with  $n$  adamantane units. We recall that such  $[n]$ diamondoids are classified as catamantanes with acyclic dualists, perimantanes with dualists having one or more 6-membered rings, and coronamantanes when their dualists have larger rings that are not envelopes of smaller six-membered rings. Catamantanes can be regular when they have molecular formulas  $C_{4n+6}H_{4n+12}$  and irregular catamantanes or perimantanes when the number of carbon atoms is lower than  $4n + 6$  and as a consequence, the ratio C/H is higher than  $n/(n + 6)$ . To add one more adamantane unit to a regular diamondoid



**Fig. 1.12** Examples of four structure series of higher diamondoids

in order to form a new regular diamondoid, one needs to replace four C–H bonds by an isobutane ( $\text{CH}_4$ ) fragment. It is important to realize that such a replacement needs to be done properly, because otherwise boat-shaped cyclohexane rings would result, as seen in Fig. 1.13.

Diamondoids having an acyclic dualist where four edges have close-situated extremities (called “proximities”) need a smaller fragment to produce a new adamantane unit, and the product is an irregular catamantane or a perimantane. A proximity has a code that includes a sequence of digits containing a repetition of type *abca*. Dualists of irregular catamantanes have five vertices along a chair-shaped hexagon, causing hydrogen atoms of the corresponding repeating adamantane units to approach too closely. Dualists of perimantanes have an even more extended



**Fig. 1.13** The two possibilities of attaching to “perhydrographene” an isobutane fragment  $(\text{CH})_4$  shown above together with four “dangling bonds”: only the right-hand possibility is allowed, producing an adamantane unit with chair-shaped 6-membered rings in staggered conformations; the left-hand alternative yields tub-shaped 6-membered rings having bonds in eclipsed conformations

repetition of type *abcbab*. As it may be seen in Table 1.3, the smallest irregular  $[n]$ diamondoid has  $n = 5$ , and the smallest perimantane has  $n = 6$ .

Isomers of diamondoids with up to six adamantane units are enumerated in Table 1.3 and those with  $n = 7$  adamantane units in Table 1.4. In an earlier paper (Balaban 1986a), I have discussed all 262 possible valence isomers of adamantane, i.e., all molecules having the same partition of four CH and six  $\text{CH}_2$  groups. Valence isomers constitute a subclass of isomers characterized by having the same distribution of vertex degrees in the constitutional hydrogen-depleted graph. Interconversions between valence isomers of annulenes have been thoroughly discussed in reviews and a 3-volume book (Balaban et al. 1986).

Recently, applying a more restrictive condition for partitioning the C, CH, and  $\text{CH}_2$  groups, we have produced *partitioned-formula periodic tables for diamondoids*. For benzenoids, Dias has published extensively interesting findings in his formula periodic tables (Dias 1982, 1984, 1985, 1987, 1990). A remarkable symmetry can be observed in Table 1.5 displaying regular catamantanes (Balaban 2012). Adamantane, diamantane, and triamantane have a single isomer each, and therefore Table 1.5 starts with triamantane. Rows characterize regular diamondoid isomers with the same  $n$  sharing the same molecular formula. The partition of the  $4n + 6$  carbon atoms is shown by a triplet separated by hyphens (*Q-T-S* indicating the numbers of quaternary, tertiary, and secondary carbon atoms or C, CH, and  $\text{CH}_2$  groups with vertex degrees 4, 3, and 2 of the hydrogen-depleted constitutional formula). Now, looking at the  $n$  vertices of the dualist, the columns show, under each triplet, a quadruplet separated by commas indicating the numbers of vertices with vertex degrees 1, 2, 3, and 4 (in red). Columns are labeled with a number starting with 1. For columns labeled 3 and 4, the dualist has 0 and 1 branches, respectively. Columns labeled 5 and 6 are for dualists having two branches; the smallest regular catamantane with a dualist having two branches and no degree-4 vertex is a hexamantane.

By means of partitioning the C carbon atoms into triplets and the  $n$  adamantane units into quadruplets according to the vertex degrees, the result is a formula periodic table of diamondoids allowing a better understanding of their topological and geometrical shapes. One should be aware that so far, we have discussed

**Table 1.4** Of all 88 possible constitutional isomers of heptamantane

Catamantanes								Perimantanes	
Regular				Irregular					
Formula: C <sub>34</sub> H <sub>40</sub>				Formula: C <sub>33</sub> H <sub>38</sub>				C <sub>30</sub> H <sub>34</sub>	
Linear		Branched		Linear		Branched		Cyclic	
Code	Sym	Code	Sym	Code	Sym	Code	Sym	Code	Sym
121212	C <sub>2v</sub>	1212(1)3	C <sub>1</sub>	121231	C <sub>1</sub>	12(12)31	C <sub>1</sub>	121321	C <sub>s</sub>
121213	C <sub>1</sub>	121(2)31	C <sub>1</sub>	121323	C <sub>s</sub>	121(2)32	C <sub>1</sub>	123124	C <sub>s</sub>
121232	C <sub>1</sub>	1212(3)4	C <sub>s</sub>	121324	C <sub>1</sub>	1213(1)2	C <sub>1</sub>		
121234	C <sub>1</sub>	121(2)34	C <sub>1</sub>	121341	C <sub>1</sub>	12(1)3(1)2	C <sub>1</sub>		
121312	C <sub>1</sub>	12(12)34	C <sub>s</sub>	123132	C <sub>1</sub>	12(1)314	C <sub>1</sub>		
121314	C <sub>1</sub>	121(2,3)4	C <sub>s</sub>	123134	C <sub>1</sub>	12(1)3(1)4	C <sub>1</sub>		
121342	C <sub>1</sub>	1213(1)4	C <sub>1</sub>	123142	C <sub>1</sub>	12(1)321	C <sub>1</sub>		
121343	C <sub>2</sub>	121(3)21	C <sub>1</sub>	123143	C <sub>2</sub>	1213(2)4	C <sub>1</sub>		
123214	C <sub>1</sub>	121(3)23	C <sub>1</sub>	123421	C <sub>s</sub>	12(1)341	C <sub>1</sub>		
123231	C <sub>s</sub>	121(3)24	C <sub>1</sub>			12(13)41	C <sub>s</sub>		
123234	C <sub>2</sub>	12(1)324	C <sub>1</sub>			12(1,3)41	C <sub>s</sub>		
123241	C <sub>1</sub>	12(1)3(2)4	C <sub>1</sub>			121(3)42	C <sub>1</sub>		
123412	C <sub>2</sub>	12(13)32	C <sub>3</sub>			12(1)342	C <sub>1</sub>		
		12(13)34	C <sub>1</sub>			12(13)43	C <sub>1</sub>		
		121(3)41	C <sub>1</sub>			123(1)23	C <sub>1</sub>		
		12(1,3)42	C <sub>1</sub>			1(2)31(2)3	C <sub>1</sub>		
		121(3)43	C <sub>1</sub>			123(1)24	C <sub>1</sub>		
		12(1,3)43	C <sub>1</sub>			1(2)3124	C <sub>1</sub>		
		12(3)1(2)3	C <sub>1</sub>			123(1,2)4	C <sub>1</sub>		
		12(3)124	C <sub>1</sub>			1(2)31(2)4	C <sub>1</sub>		
		12(3)1(2)4	C <sub>1</sub>			12(3)132	C <sub>1</sub>		
		1(2)3(1)24	C <sub>1</sub>			1231(3)4	C <sub>1</sub>		
		1(2)3(1,2)4	C <sub>s</sub>			12(31)41	C <sub>3v</sub>		
		1(2)3132	C <sub>1</sub>			123(1)42	C <sub>1</sub>		
		12(3)134	C <sub>1</sub>			12(3)142	C <sub>1</sub>		
		1(2)3134	C <sub>1</sub>			1(2)3(1)42	C <sub>1</sub>		

constitutional formulas, ignoring chirality. The partition of carbon atoms in diamondoids according to the vertex degrees of their constitutional hydrogen-depleted carbon scaffolds is indicated by the following relationships.

$$\text{Quaternary C groups : } Q = n + b - 2 = S - 6 \quad (1.1)$$

$$\text{Ternary CH groups : } T = 2(n + b + 2) \quad (1.2)$$

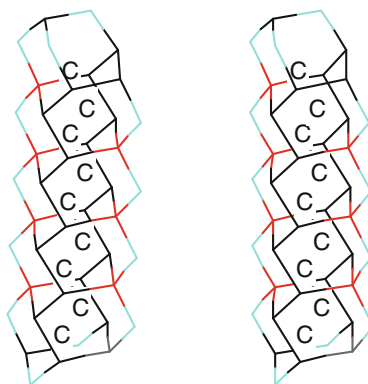
$$\text{Secondary CH}_2 \text{ groups : } S = n + b + 4 \quad (1.3)$$

In other words, the above relationships are translated as C<sub>n+b-2</sub>(CH)<sub>2n+2b+4</sub>(CH<sub>2</sub>)<sub>n+b+4</sub> for representing the partitioned formula for regular catamantanes, where the parameter *b* stands for the number of branches plus the number of

**Table 1.5** 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)

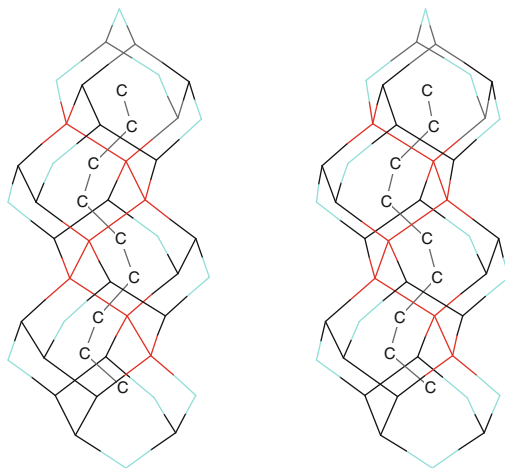
1	2	3	4	5	6	7	8	9
Cells	Formula	Zero branches	One branch	Two branches		Three branches		Four branches
3	$C_{18}H_{24}$	1-10-7 <b>2, 1, 0, 0</b>						
4	$C_{22}H_{28}$	2-12-8 <b>2, 2, 0, 0</b>	3-10-9 <b>3, 0, 1, 0</b>					
5	$C_{26}H_{32}$	3-14-9 <b>2, 3, 0, 0</b>	4-12-10 <b>3, 1, 1, 0</b>		6-8-12 <b>4, 0, 0, 1</b>			
6	$C_{30}H_{36}$	4-16-10 <b>2, 4, 0, 0</b>	5-14-11 <b>3, 2, 1, 0</b>	6-12-12 <b>4, 0, 2, 0</b>	7-10-13 <b>4, 1, 0, 1</b>			
7	$C_{34}H_{40}$	5-18-11 <b>2, 5, 0, 0</b>	6-16-12 <b>3, 3, 1, 0</b>	7-14-13 <b>4, 1, 2, 0</b>	8-12-14 <b>4, 2, 0, 1</b>	9-10-15 <b>5, 0, 1, 1</b>		
8	$C_{38}H_{44}$	6-20-12 <b>2, 6, 0, 0</b>	7-18-13 <b>3, 4, 1, 0</b>	8-16-14 <b>4, 2, 2, 0</b>	9-14-15 <b>4, 3, 0, 1</b>	10-12-16 <b>5, 1, 1, 1</b>		12-8-18 <b>6, 0, 0, 2</b>
9	$C_{42}H_{48}$	7-22-13 <b>2, 7, 0, 0</b>	8-20-14 <b>3, 5, 1, 0</b>	9-18-15 <b>4, 3, 2, 0</b>	10-16-16 <b>4, 4, 0, 1</b>	11-14-17 <b>5, 2, 1, 1</b>		13-10-19 <b>6, 1, 0, 2</b>
10	$C_{46}H_{52}$	8-24-14 <b>2, 8, 0, 0</b>	9-22-15 <b>3, 6, 1, 0</b>	10-20-16 <b>4, 4, 2, 0</b>	11-18-17 <b>4, 5, 0, 1</b>	12-16-18 <b>5, 3, 1, 1</b>	13-14-19 <b>5, 2, 3, 0</b>	14-12-20 <b>6, 2, 0, 2</b>

**Fig. 1.14** Stereo view of the nonbranched zigzag regular [121212121]nonamantane



degree-4 vertices in the dualist. The two nonbranched regular nonamantanes presented in Figs. 1.14 and 1.15 are isomers with molecular formula  $C_{42}H_{48}$  and have completely different geometries (the former is achiral whereas the latter is chiral owing to its helicity), yet their partitions are exactly the same:  $C_7(CH)_{22}(CH_2)_{13}$ . In both figures, red vertices correspond to quaternary C atoms and blue vertices to secondary  $CH_2$  groups.

**Fig. 1.15** Stereo view of the nonbranched helical regular [123412341]nonamantane



There is a perfect symmetry according to columns, rows, and diagonals in Table 1.5: boldface red numbers show the constant nonzero numbers in each column. The red numbers of degree-2 vertices increase steadily in each column with increasing  $n$ . In the triplet of each row, the numbers  $Q$  and  $S$  of the same parity increase steadily from left to right, whereas the even numbers  $T$  decrease steadily from left to right.

There are still some aspects of the partitioned-formula periodic tables that are incompletely understood, especially for the irregular catamantanes and the perimantanes (Balaban 2012).

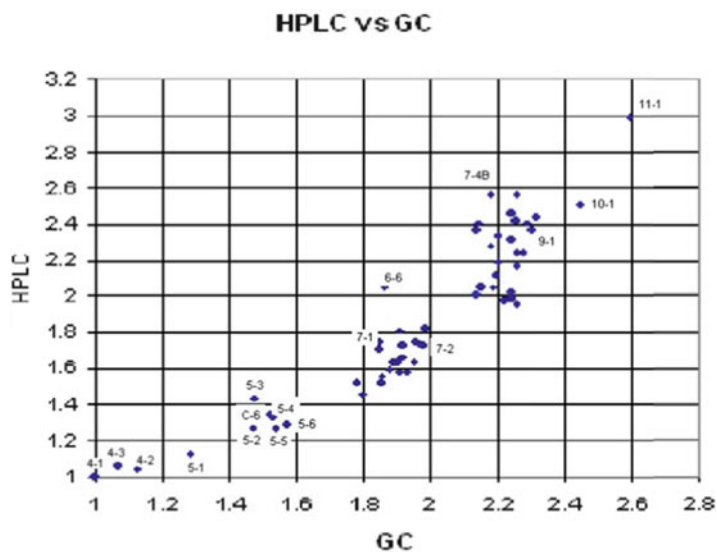
## 1.8 Chromatographic Separation and Identification of Diamondoids from Petroleum

In collaboration with Drs. Carlson and Dahl from Chevron and with Professor Klein from Texas A&M University Galveston, graph-theoretical matrices of diamondoid dualists were converted into molecular invariants characterizing diamondoid structures. With the help of these invariants, quantitative structure–property correlations were obtained using the data provided by Chevron (Balaban et al. 2007a, b). In Fig. 1.15, one can see that most tetramantanes and pentamantanes can be separated and identified by a combination of high-performance liquid chromatography (HPLC) and gas chromatography plus the corresponding mass spectra (GC-MS). Regular diamondoids have higher molecular weights than irregular diamondoids with the same number of carbon atoms. Only identified compounds are displayed in Table 1.6, but in the article (Balaban et al. 2007b) and in Fig. 1.16, many other unidentified diamondoids were included.



**Table 1.6** Chromatographic data of identified diamondoids from petroleum

Higher diamondoid code	Compound reference number	Molecular formula	M <sup>+</sup> ( <i>m/z</i> ) base peak	GC/MS relative retention times*	ODS HPLC relative elution volumes*
[1(2)3]	4;1	C <sub>22</sub> H <sub>28</sub>	292	1	1
[121]	4;2	C <sub>22</sub> H <sub>28</sub>	292	1.069	1.055
[123]	4;3	C <sub>22</sub> H <sub>28</sub>	292	1.126	1.036
[1(2,3)4]	5;1	C <sub>26</sub> H <sub>32</sub>	344	1.284	1.126
[12(1)3]	5;2	C <sub>26</sub> H <sub>32</sub>	344	1.473	1.269
[1212]	5;3	C <sub>26</sub> H <sub>32</sub>	344	1.479	1.431
[1213]	5;4	C <sub>26</sub> H <sub>32</sub>	344	1.529	1.323
[12(3)4]	5;5	C <sub>26</sub> H <sub>32</sub>	344	1.543	1.269
[1234]	5;6	C <sub>26</sub> H <sub>32</sub>	344	1.57	1.287
[12312]	C-6	C <sub>26</sub> H <sub>30</sub>	342	1.523	1.341
[12121]	6;6	C <sub>30</sub> H <sub>36</sub>	396	1.868	2.039
[121321]	7;1	C <sub>30</sub> H <sub>34</sub>	394	1.847	1.743
[123124]	7;2	C <sub>30</sub> H <sub>34</sub>	394	1.917	1.664
[121212]	7;4B	C <sub>34</sub> H <sub>40</sub>	448	2.185	2.521
[12312412]	9;1	C <sub>34</sub> H <sub>40</sub>	444	2.292	2.396
[1231241(2)3]	10;1	C <sub>38</sub> H <sub>43</sub>	456	2.451	2.503
[123(1,2)42143]	11;1	C <sub>39</sub> H <sub>38</sub>	508	2.599	2.987

**Fig. 1.16** Plot of the HPLC eluent volumes versus the GC retention times of diamondoid

**Table 1.7** Molecular invariants ( $D$ -eigenvalues) and chromatographic data

Diamondoid	$n$	$D$ -eigenv.	GC/MS	HPLC	Type
[1(2)3]	4	6.87	1.000	1.000	4-cata
[121]	4	7.79	1.069	1.055	4-rod
[123]	4	7.15	1.126	1.036	4-cata
[1(2,3)4]	5	10.58	1.284	1.126	5-bundle
[12(1)3]	5	11.08	1.473	1.269	5-cata
[1212]	5	12.27	1.479	1.431	5-rod
[1213]	5	11.88	1.529	1.323	5-cata
[12(3)4]	5	10.04	1.543	1.269	5-cata
[1234]	5	10.53	1.570	1.287	5-cata
[12121]	6	17.74	1.868	2.039	6-rod
[12312]	6	12.44	1.523	1.341	6-bundle
[121321]	7	16.89	1.847	1.743	7-bundle
[123124]	7	15.88	1.917	1.664	7-bundle
[121212]	7	24.17	2.185	2.521	7-rod
[12312412]	9	21.84	2.292	2.396	9-bundle
[1231241(2)3]	10	24.74	2.451	2.503	10-bundle
[123(1,2)42143]	11	29.65	2.599	2.987	11-bundle

One may observe that in Fig. 1.16, all three tetramantanes appear at the lower left (GC around 1.1), followed by an isolated spot corresponding to C-6, the peri-hexamantane with a chair hexagon as dualist (GC around 1.3). The next cluster has six points corresponding to the pentamantanes (GC around 1.5); the topmost point (with HPLC around 1.4) is due to the rodlike pentamantane. Catamantanes from the hexamantane group and perimantanes from the heptamantane group form the next cluster between GC 1.75 and 2.0; the topmost point with HPLC 2.04 is the rodlike hexamantane; also two perfused heptamantanes with dualists isomorphic to methylcyclohexane were identified in this cluster: the equatorial [121321]heptamantane with GC around 1.85 and the axial [123124]heptamantane with GC around 1.92. The next cluster with GC between 2.1 and 2.35 contains diamondoids from the octamantane and nonamantane groups, mostly perimantanes, including the nonamantane having a dualist graph isomorphic to bicyclo[3.3.1]nonane. The last two points with GC around 2.5 and 2.6 correspond, respectively, to the decamantane having as its dualist the adamantane skeleton and to its undecamantane homolog having one extra vertex attached to a “tertiary carbon” of the adamantane-like dualist (Table 1.7).

From the distance matrix of the dualist, one can easily obtain the largest eigenvalue, and this is one possible molecular invariant for the corresponding diamondoid (Table 1.6). As seen in Fig. 1.17, a satisfactory correlation ( $R^2 = 0.9842$ ) was obtained for the HPLC elution volumes.

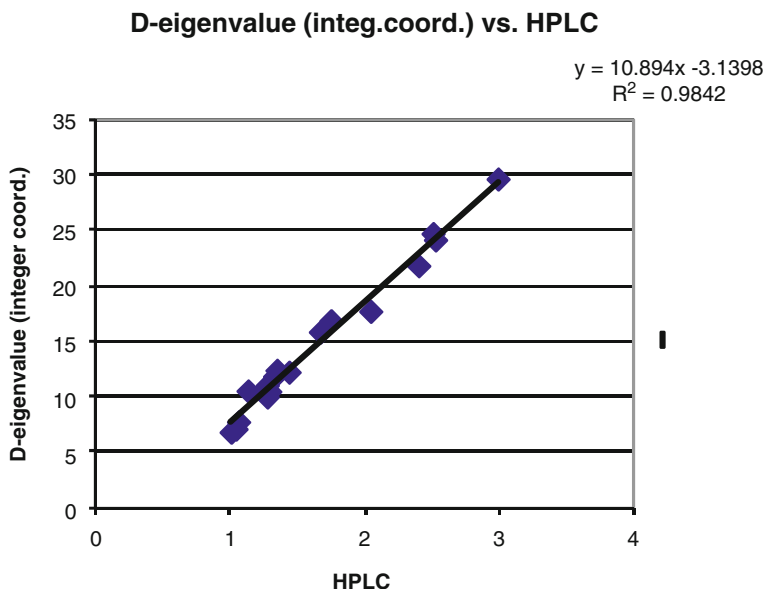


Fig. 1.17 Plot of D-eigenvalues for idealized coordinates vs. HPLC relative elution values

## 1.9 Applications and Uses of Diamondoids

Lower diamondoids are readily available from petroleum, so that many possible applications are imminent. Prominent among these are applications of rod-shaped molecules functionalized at one or both ends, securing thus exactly fitting distances between functional groups matching protein receptor sites. There are other nanorod-like molecules (Balaban et al. 2007b; Schwab et al. 1999, 2005) such as carbon nanotubes; however, these nanotubes are *mixtures* of similar but not identical molecules. By contrast, one can prepare and functionalize regioselectively diamondoids as *pure substances*. Due to different reactivities of tertiary and secondary C–H bonds in diamondoids, it is possible to achieve a regioselective functionalization. Apical positions in rodlike diamondoids starting with diamantane or [121]tetramantane (with zigzag dualists as in Fig. 1.14) are especially attractive. Grouping diamondoids according to valence-isomeric classes having definite numbers of tertiary (CH) and secondary (CH<sub>2</sub>) hydrogen atoms is therefore of highest importance in this regard.

Schreiner and his coworkers (together with Dahl and Carlson who provided the diamondoids from petroleum) investigated thoroughly the regioselectivity of diamondoid functionalization in a series of 30 papers, only a few of which can be mentioned here (Schreiner et al. 2011; Fokin et al. 2005; Schwertfeger et al. 2008, 2009; Fokin et al. 2009a, b, c, d; Dahl et al. 2010; Fokina et al. 2012; Wang et al. 2011; Schreiner et al. 2009; Schwertfeger et al. 2010a, b; Richter et al. 2009; Fokin

and Schreiner 2009; Roth et al. 2010). It has long been known that the tertiary C–H bonds of adamantane can be more readily halogenated than secondary C–H bonds (Schwertfeger et al. 2008). For diamantane, it was observed (Fokin et al. 2005) that alcohol formation by oxidation with *meta*-chloroperbenzoic acid favors medial-tertiary over apical-tertiary attack; higher yields are achieved by nitroxylation by anhydrous nitric acid followed by hydrolysis; interestingly, apical substitution is favored by longer reaction times. For fluorination, AgF halogen exchange and alcohol conversion using Et<sub>2</sub>N–SF<sub>3</sub> proved to be methods of choice (Schwertfeger et al. 2009). Photoacetylation of diamondoids with diacetyl gives predominantly apical acetyl derivatives owing mainly by polarizability effects, with steric factors playing a minor role (Fokin et al. 2009a). Bis-apical rodlike functionalized diamondoids are the most promising candidates for applications. The global shape of the diamondoid also influences the regioselectivity (Fokin et al. 2009b). 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 (Dahl et al. 2010). Oxa- and thia-diamondoids were also prepared (Fokin et al. 2009d). Bis-apical [121]tetramantane-dicarboxylic acid and its dimethyl ester were prepared in 77 and 69 % yields, respectively, starting from the corresponding diol derivative and converting into the dibromo derivative, which was treated with H<sub>2</sub>SO<sub>4</sub> and HCOOH in a Koch-Haaf reaction (Fokina et al. 2012). The influence of type and positions of heteroatoms was studied in order to predict the band gap tuning in nanodiamonds (Fokin and Schreiner 2009). Helical [123]tetramantane [102] (Schreiner et al. 2009) and the smallest perimantane (Fokin et al. 2009b) were isolated and studied for reactivity. Phosphorylated diamondoids and diamondoid-modified DNA were also prepared (Wang et al. 2011; Schwertfeger et al. 2010a, b). A recent paper in *Nature* reports the preparation of dimeric diamondoids with the longest yet reported C–C bond lengths between quaternary carbon atoms; their thermal stability and high melting points are due to attractive dispersion forces [91] (Schreiner et al. 2011). Schreiner’s review (Schwertfeger and Schreiner 2010) and Hopf’s comments on diamondoids (Hopf 2003) made it clear that some of the diamondoids from petroleum may be considered as nano-jewels, i.e., diamonds of 10<sup>–20</sup> carats (1 carat = 200 mg).

Small diamond crystals from outer space have been first detected in meteorites (Hopf 2003; Lewis et al. 1987; Anders and Zinner 1993; Jones et al. 2004; Pirali et al. 2007) and then identified in interstellar infrared spectra. At the lower dimensions such nanodiamonds are probably diamondoids with all peripheric “dangling bonds” of the diamond lattice saturated with hydrogen atoms.

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