Diamond hydrocarbons revisited: partitioned formula tables of diamondoids

Alexandru T. Balaban

Abstract Isomeric diamondoids with the same number n of adamantane units (or cells), which share the same molecular formula $C_Q(CH)_T(CH_2)_S$, can be divided into valence isomers by partitioning the number C of their carbon atoms according to whether they are Quaternary, Tertiary, or Secondary: $C = Q + T + S$. Each [n]diamondoid has a dualist (or inner dual) with n vertices (situated at centers of adamantane units), and edges connecting vertices of adjacent adamantane units sharing a chair-shaped hexagon of carbon atoms. Such a dualist is characterized by a quadruplet of indices (denoted as p, s, t, q for primary, secondary, tertiary, or quaternary) specifying again the connectivity of each vertex by assimilating it with a virtual carbon atom. The diamond lattice is self-dual. Dualists help in classifying diamondoids as catamantanes with acyclic dualists, perimantanes with dualists having chair-shaped six-membered rings, or coronamantanes with dualists having only higher-membered rings. In turn, catamantanes can be either regular when they have formulas $C_{4n+6}H_{4n+12}$, or irregular when the numbers of carbon and hydrogen atoms are lower than the above values for the given numbers n of adamantane units. Regular catamantanes can have branched or non-branched dualists and they are isomeric when having the same n. Partitioned formulas reflect the branching patterns, encoded in their dualists. Partition formulas and codes are presented for all possible diamondoids with up to 7 adamantane units. A remarkable symmetry is observed for the table of partition periodic table of regular catamantanes with up to 7 adamantane units. Isomeric irregular catamantanes with six or more adamantane units may be valence-isomeric (or *homomeric*, sharing both the molecular and the partitioned formulas), or *heteromeric* when they have different partitioned formulas.

A. T. Balaban (✉)
Department of Marine Sciences, Texas A&M University at Galveston,
200 Seawolf Parkway, Galveston, TX 77553, USA
e-mail: balabana@tamug.edu

1 Definitions

Molecules are formed by connecting atoms via covalent bonds, and they can be modeled by molecular graphs consisting of vertices representing atoms and edges representing covalent bonds. Hydrocarbons, in particular alkanes and cycloalkanes, consist of tetravalent carbon atoms and monovalent hydrogen atoms. In the following, hydrogen-depleted graphs show only the carbon atoms of hydrocarbons. Alkanes and cycloalkanes are *constitutionally isomeric* if they share the same molecular formula. In addition to constitutional isomers molecules can be stereoisomeric if their three-dimensional structure is taken into account; in particular, molecules with the same constitutional formula are *enantiomeric* (chiral) if they are not superimposable on their mirror image. Thus, two heptanes are the smallest enentiomeric alkanes: 1,2-dimethylpentane and 3-ethylhexane, but only the hydrogen-depleted graph of the latter is the smallest identity graph of an alkane, devoid of any symmetry element, so that its automorphism group has only the identity operation.

Molecular fragments such as CH_k, with k having values between 0 and 3 have been important tools for quantitative structure-activity relationships [1]. In the present context, they allow a closer characterization of molecular structure than constitutional molecular formulas. Thus, the nine constitutional isomers of heptane having molecular formula C_7H_{16} can be subdivided into five *partitioned-formulas* (or *valence-isomers*), namely: (i) heptane $(CH_3)_2(CH_2)_5$; (ii) 3-ethylpentane, 2- and 3-methylhexanes $(CH_3)_3(CH_2)_3(CH)$; (iii) 2,2- and 3,3-dimethylpentanes, $(CH_3)_4(CH_2)_2C$; (iv) 2,3- and 2,4-dimethylpentanes $(CH_3)_4(CH_2)(CH)_2$; (v) 2,2,3-trimethylbutane $(CH_3)_5(CH)C$. For experimental chemists investigating valence-isomers of annulenes (cubic graphs) the three-volume book on this topic proved to be a useful tool [2].

2 Introduction

Polycyclic aromatic hydrocarbons (benzenoids) consist of fused benzenoid rings. Planar benzenoids can be viewed as portions of graphene with peripheral hydrogen atoms. In the late 1960s a proposal was published [3,4] to represent the structure of benzenoids using their dualists (inner duals, consisting of vertices at the centers of benzenoid rings, and of edges connected vertices in adjacent rings that share a CC bond). This approach allowed the classification of benzenoids as cata-condensed (catafusenes), peri-condensed (perifusenes), or corona-condensed (coronoids) according to whether their dualists were acyclic, had three-membered rings, or larger rings, respectively. Moreover, for catafusenes one could encode their structure by using a 3-digit code using digit 0 for straight annelation and digits 1 or 2 for kinked annelation. It was shown later that the number of adjacent zero-digits provided a simple parameter for correlations with properties of benzenoids such as color, redox potential, or reactivity in Diels–Alder cycloadditions with dienophiles [5–7].

Diamondoids (or diamond hydrocarbons) have carbon skeletons that are portions of the diamond lattice, consisting of adamantane units (cells) with peripheral hydro-
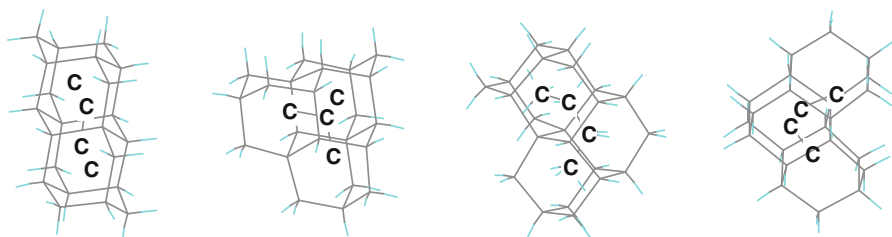
Fig. 1 The four possible tetramantanes: the achiral [121]tetramantane, the achiral [1(2)3]tetramantane, and the two chiral enantiomers [123]tetramantane and [124]tetramantane. Dualists are presented as carbon skeletons of alkanes inside the corresponding diamondoids

gen atoms. By analogy with benzenoids, dualists of [n]diamondoids can be defined as the geometrical assembly of n vertices at centers of adamantane units; when two adamantane units share a chair-shaped hexagon of carbon atoms, the corresponding vertices of the dualist are connected by an edge. Thus, an [n]diamondoid has a dualist (or inner dual) with n vertices (situated at centers of adamantane units), characterized by a quadruplet of indices (denoted as *p, s, t, q* for primary, secondary, tertiary, or quaternary) specifying again the connectivity of each vertex by assimilating it with a virtual carbon atom. The diamond lattice is self-dual. Dualists help in classifying diamondoids as *catamantanes* with acyclic dualists, *perimantanes* with dualists having chair-shaped six-membered rings, or *coronamantanes* with dualists having only higher-membered rings. Due to the fact that the C–C bonds in the diamond lattice are in staggered conformation, dualists of catamantanes are identical to the carbon skeletons of staggered alkanes. It had been shown by Klein and coworkers that with increasing numbers of carbon atoms highly branched alkanes have some size limitations [8–10]. Also by analogy with benzenoids, an encoding system for staggered alkanes and cycloalkanes was proposed in the mid-1970s [11–13], which was then extended for encoding diamondoid structures in 1978, in a collaboration between Balaban and Schleyer [14]. This system uses for dualists digits 1, 2, 3, and 4 for the four orientations around a tetrahedral carbon atom, aiming at getting the lowest number on reading sequentially the digits starting from one end of the dualist. Branches are enclosed in round brackets, and the whole code is enclosed in square brackets.

IUPAC names using the von Baeyer convention are complicated, as seen for adamantane (tricyclo[3.3.1.1^{3,7}]decane). Diamantane with $n = 2$ (pentacyclo[7.3.1 .1^{4,12}.0^{2,7}.0^{6,11}]tetradecane) has code [1]. Triamantane (heptacyclo[7.7.1.1^{3,15}.0^{1,12}. 0^{2,7}.0^{4,13}.0^{5,11}]octadecane) is encoded as [12]. Starting with $n = 4$, [n]polymantanes have more than one isomer. For $n = 4$ we have an achiral non-branched [121]tetramantane, an achiral branched [1(2)3]tetramantane, and a chiral pair of enantiomeric [123]tetramantanes (Fig. 1). In the following, enantiomerism will be ignored, and all discussions will be about constitutional isomers.

3 Regular catamantanes

As mentioned above, [n]catamantanes have dualists that correspond to the carbon skeletons of staggered alkanes. Regular catamantanes correspond to molecular formulas $C_{4n+6}H_{4n+12}$, meaning that all regular catamantanes with the same n are
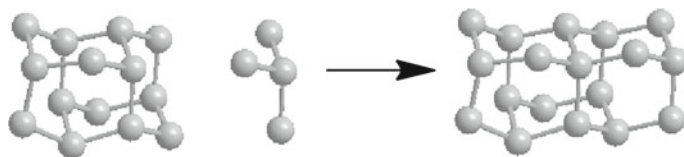
Fig. 2 Conversion of diamantane to triamantane by addition of an isobutane fragment

isomeric. Whenever the dualist includes a sequence of 5 virtual carbon atoms belonging to the same chair-shaped hexagon (a hoof-like sequence), the code contains a repeating digit *a* such as *abca*; the carbon endpoints of that sequence approach each other so much that this "proximity" leads to an irregularity manifested in the fact that the number of carbon atoms of the [*n*]diamondoid is less than $4n + 6$, and the number of hydrogen atoms is less than $4n + 12$; we call such systems "irregular catamantanes". They will be examined in a later section.

In a recently published article [15], diamondoids were shown to present interesting regularities when their molecular formulas were expanded as $C_Q(CH)_T(CH_2)_S$ in order to display the *valence-isomeric* (or *partitioned*) *formulas*. Thus, regular [*n*]catamantanes with molecular formulas $C_{4n+6}H_{4n+12}$ having non-branched dualists have partitioned formula $C_{n-2}(CH)_{2n+4}(CH_2)_{n+4}$. For dualists with *b* branches they have partitioned formulas $C_{n+b-2}(CH)_{2n-2b+4}(CH_2)_{n+b+4}$. The numbers of quaternary, tertiary, and secondary carbon atoms (*Q*, *T*, and *S*, respectively) in regular catamantanes are therefore:

$$Q = n + b - 2 = S - 6 \tag{1}$$
$$T = 2(n - b + 2) \tag{2}$$
$$S = n + b + 4 \tag{3}$$

Graph-theoretical arguments indicate that *T* is always an even number, and that the parity of *Q* and *S* numbers must be identical (either both even or both odd).

Let us discuss how a regular [*n*]polymantane $C_{4n+6}H_{4n+12}$ can be converted into a regular [*n* + 1]polymantane $C_{4n+10}H_{4n+16}$ by the addition of an isobutane fragment C_4H_4; such a process was shown experimentally by Dahl, Carlson, Schreiner and coworkers to take place in an actual chemical reaction [16]. Figure 2 shows the "diamondoid-homologation" of a non-branched diamondoid into another non-branched diamondoid, namely the conversion of diamantane to triamantane. It is easy to see that in this process the following changes take place: one CH and 3 CH_2 groups are added, one CH group becomes a C atom, and two CH_2 groups become 2 CH groups. The net result is:

$$Q-T-S \rightarrow (Q+1)-(T+2)-(S+1) \tag{4}$$

When one branch is added, the following changes occur as shown in Fig. 3 that presents a similar "homologation" of triamantane to [1(2)3]tetramantane. In this process the following changes occur: one CH and 3 CH_2 groups are added, two CH groups become C atoms, and one CH_2 group becomes a CH group. The net result is:
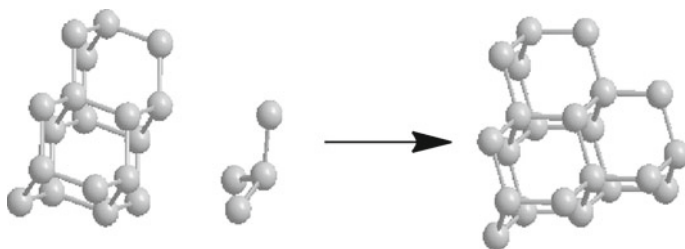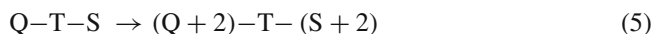
Fig. 3 Conversion of triamantane to [1(2)1]tetramantane by addition of an isobutane fragment

$$Q-T-S \rightarrow (Q+2)-T-(S+2) \tag{5}$$

The number of branches and their type (geminal or non-geminal) is easily seen by looking at the dualist: vertices of degree 3 in the dualist correspond to non-geminal branches, and vertices of degree 4 correspond to pairs of geminal branches. On denoting by p, s, t, q the degrees of dualist vertices (in all following Tables this sequence will be shown in boldface characters), the number of adamantane units is the sum of these four numbers, and the total number of branches is $b = p - 2$.

The codes for all possible constitutional isomers of diamondoids with n up to 7 were presented in ref. 14. For the regular diamondoids with n = 3 to 7, Table 1 indicates the partitioned formulas; it is ordered according to increasing n (vertically) and increasing b (horizontally). A remarkable symmetry can be observed in this Table: values of Q–T–S vary along descending pathways (in the direction "6 o'clock") according to (4); values of Q–T–S vary according to eq. (5) on diagonals (in direction "5 o'clock").

The remarkable regularities for the variation of the seven digits characterizing each homomeric class of regular catamantanes displayed in Table 1 are as follows.

The numbers of carbon and hydrogen atoms are $4n + 6$ and $4n + 12$, respectively.
With b as the number of branches, $Q = n+b-2$; $T = 2n-2b+4$; $S = n+b+4$.
Q and S increase monotonously by 1 from left to right and from top to bottom.
T decreases monotonously by 2 from left to right and by 1 from top to bottom.
$p + s + t + q = n$
$p + 2 = t + q/2 = b$
s increases monotonously by 1 from top to bottom.
p, t, and q do not change from top to bottom.

Codes of all constitutional isomers of polymantanes with $n = 3$–7 were not indicated in Ref. [15] but sequences of Q–T–S and p, s, t, q for regular catamantanes with $n = 3$–8 were included in that paper. Therefore Table 2 presents additionally these sequences for regular octacatamantanes with $n = 8$, but with only one example in each case, because till now a complete enumeration of all diamondoids with $n > 7$ is not available.

With one exception shown by the regular [1(2)3(2)1(3)4]octamantane, the symmetry of variations for sequences Q–T–S and p, s, t, q that had been observed in Table 1 according to (4) and (5) continues for $n = 8$. The exception, which had been noted in the preceding paper [15], involves the unique possible chiral valence isomer

Table 1 Partitioned formula periodic table of all possible diamondoids with 3–7 adamantane cells: first line: Q–T–S; second line: **p, s, t, q**; subsequent lines: diamondoid codes

Cells *n*	Formula	Zero branches	One branch	Two branches (non-geminal)	Two branches (geminal)	Three branches
3	$C_{18}H_{24}$	1-10-7 **2, 1, 0, 0** [12]				
4	$C_{22}H_{28}$	2-12-8 **2, 2, 0, 0** [121], [123]	3-10-9 **3, 0, 1, 0** [1(2)3]			
5	$C_{26}H_{32}$	3-14-9 **2, 3, 0, 0** [1212], [1213], [1234]	4-12-10 **3, 1, 1, 0** [12(3)4], [12(1)3]		6-8-12 4, 0, 0, **1** [1(2,3)4]	
6	$C_{30}H_{36}$	4-16-10 **2, 4, 0, 0** [12121], [12123], [12131], [12134], [12321], [12324], [12341]	5-14-11 **3, 2, 1, 0** [121(2)3], [12(1)32], [121(3)4], [12(1)34], [12(3)12], 1(2)3(14), [12(3)14]	6-12-12 **4, 0, 2, 0** [1(2)3(1)2], [1(2)3(1)4]	7-10-13 **4, 1, 0, 1** [12(1,3)4]	
7	$C_{34}H_{40}$	5-18-11 **2, 5, 0, 0** [121212], [121213], [121232], [121234], [121312], [121314], [121342], [121343], [123214], [123231], [123234], [123241], [123412]	6-16-12 **3, 3, 1, 0** [1212(1)3], [121(2)31], [1212(3)4], [121(2)34], [12(1)234], [1213(1)4], [121(3)21], [121(3)23], [121(3)24], [12(1)324], [12(13)12], [12(1)(3)34], [121(3)41], [121(3)43], [12(3)124], [1(2)3(1)32], [12(3)134], [1(2)3142], [1232(1)4], [123(2)41], [123(4)21]	7-14-13 **4, 1, 2, 0** [12(1)3(2)4], [12(3)1(2)3], [12(3)1(2)4], [1(2)3(1)24], [12(3)1(3)4], [1(2)31(3)4]	8-12-14 **4, 2, 0, 1** [121(2,3)4], [12(1,3)42], [12(1,3)43], [12(3,4)12]	9-10-15 **5, 0, 1, 1** [1(2)3(1,24]

Table 2 Continuation of Table 1 for valence isomeric regular octamantanes but with only one example for each case

Cells	Formula	Zero branches	One branch	Two branches		Three branches		Four branches
				Non-geminal	Geminal	Geminal	Non-geminal	
8	$C_{38}H_{44}$	6–20–12	7–18–13	8–16–14	9–14–15	10–12–16	9–14–15	12–8–18
		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**
		[1212121]	[1212(1)34]	[1(2)313(1)2]	[121(3,4)21]	1(2)3(2,4)13	[1(2)3(2)1(3)4]	1(2,3)4(1,2)3

The code [1(2)3(2)1(3)4] corresponds to the first example shown in Fig. 4

Fig. 4 Dualists of 3 octamantane valence isomers, namely a regular [1(2)3(2)1(3)4]octamantane and two irregular octamantanes: [1(2)3(2)1(2)1]octamantane having one proximity, and [1(2)3(1)4(1)2]octamantane with two proximities

corresponding to the staggered dualist of [1(2)3(2)1(3)4]octamantane (the first dualist of Fig. 4). All other stereoisomers are irregular because they have one or two proximities, as shown by the second and third examples of Fig. 4, respectively. This exception is a challenge for explanation and exploration involving further regular catamantanes with n > 8.

4 Irregular diamondoids

When adamantane units approach closely they generate proximities, wherein some diamondoid homologations need a fragment with less than four carbon atoms. The simplest proximity is shown in Fig. 5, involving adding a propane fragment to the regular [123]tetramantane $C_{22}H_{28}$. The result is an irregular pentamantane $C_{25}H_{30}$ with the partitioned formula $C_2(CH)_{16}(CH_2)_7$. It can be seen that in this case the homologation adds only three carbons and two hydrogens. For irregular catamantanes and for all perimantanes, homologations may involve even smaller numbers of C and H atoms, and as a consequence *irregular diamondoids with the same numbers of adamantane units are no longer isomeric*. Similarly to Table 1, one can see in Table 3 codes of all irregular [n]diamantanes with their codes for n = 5, 6 and 7 adamantane units.

One can observe for the first time in Table 3 that irregular catamantanes with the same number n of adamantane cells need not be isomeric. Moreover, even when they are isomeric they may differ in their partitioned formula, as in the case of the two non-branched irregular hexa-catamantanes [12132] and [12314] shown in Fig. 6. These isomeric but *heteromeric* diamondoids are not valence-isomeric. The
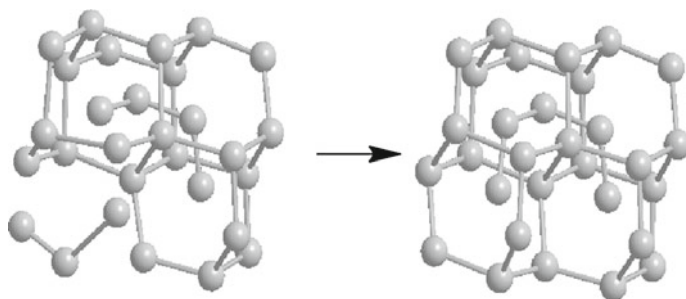
Fig. 5 Conversion of [123]tetramantane into the irregular [1231]pentamantane (one proximity) by addition of a propane fragment. In this figure, dualists are placed in the centers of diamondoids

Table 3 Irregular heptamantanes

	I r r e g u l a r c a t a m a n t a n e s						Perimantanes
n	Zero	branches	One	branch	Two	branches	
	One proximity	Two proximities	One proximity	Two proximities	One proximity	Two proximities	
5	$C_{25}H_{30}$ 2 16 7 **2, 3, 0, 0** [1231]						
6	$C_{29}H_{34}$ 3-18-8 4-16-9 **2, 4, 0, 0 2, 4, 0, 0** [12132]] [12314]		$C_{29}H_{34}$ 4-16-9 **3, 2, 1, 0** [12(1)31] [123(1)2] [12(3)41] [123(1)4]				$C_{26}H_{30}$ 2-18-6 **0, 6, 0, 0** [12312]
7	$C_{33}H_{38}$ 4-20-9 5-18-10 **2, 5, 0, 0 2, 5, 0, 0** [121231] [121323] [123132] [121324] [123134] [121341] [123142]	$C_{32}H_{36}$ 5-18-9 **2, 5, 0, 0** [123143] [123421]	$C_{33}H_{38}$ 5-18-10 6-16-11 **3, 3, 1, 0 3, 3, 1, 0** [12(12)31] [12(1)314] [121(2)32] [12(1)321] [1213(1)2] [12(1)342] [1213(2)4] [1(2)3124] [12(1)341] [123(2)14] [12(13)41] [1234(1)2] [121(3)42] [1231(3)4] [12(13)43] [123(1)23] [123(1)24] [12(3)132] [12(3)142] [123(1)43]	$C_{32}H_{36}$ 5-18-9 **3, 3, 1, 0** [12(31)41] [123(1)42]	$C_{33}H_{38}$ 7-14-12 6-16-11 **4, 2, 0, 1 4, 1, 2, 0** [12(1,3)41] [12(1)3(1)2] [123(1,2)4] [1(2)31(2)3] [1(2)3(2)4] [1(2)3(1)42]	$C_{32}H_{36}$ 5-18-9 **4, 1, 2, 0** [12(3)4(1)2] [1(2)34(1)2]	$C_{30}H_{34}$ 4-18-8 **1, 5, 1, 0** [123124] [121321]

The first two lines contain the Q–T–S partition of the diamondoid, the second line the **p, s, t, q** sequence of the dualist vertex degrees, and the following lines contain the corresponding heptamantane codes

explanation can be found by examining the "face" involved in the three-dimensional operation ("capping") analogous to the annulation of benzenoids by adding a new ring to an existing benzenoid. On attaching an isobutane "cap" to the smallest irregular [1231]pentamantane, one forms three new C–C bonds to a "hexagonal face" of one of its two final adamantane units. The new bonds may either involve one secondary and two tertiary carbon atoms, or one tertiary and two secondary carbon atoms. In the former case the hexamantane will have one more quaternary carbon atom than in the latter case.

Figure 7 displays the three possible perimantanes with 6 and 7 adamantane units: the dualist of [12312]hexamantane is a chair-shaped hexagon of vertices (denoted in
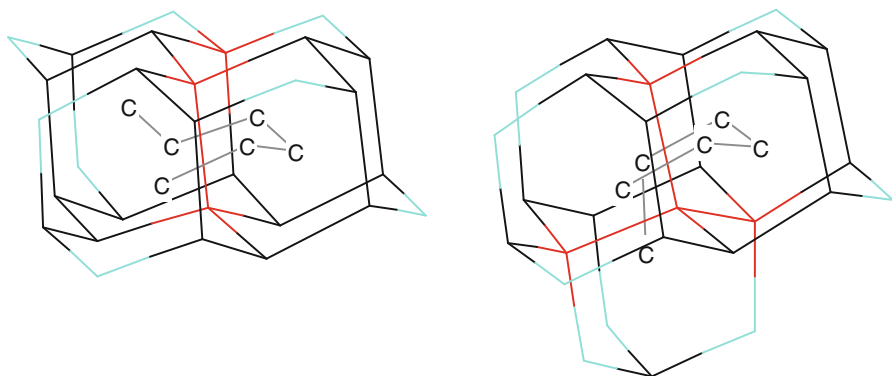
Fig. 6 Two isomeric (but not valence-isomeric) irregular catamantanes $C_{29}H_{34}$ with one proximity: [12132]hexamantane $C_3(CH)_{18}CH_2)_8$ and [12314]hexamantane $C_4(CH)_{16}CH_2)_9$; dualists, placed in the centers of diamondoids, are carbon skeletons of staggered hexanes
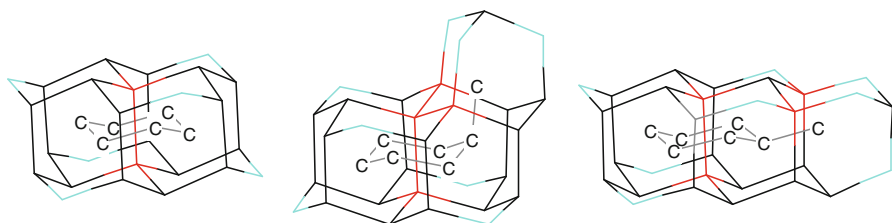

Fig. 7 The smallest perimantanes: [12312]hexamantane, and the two homomeric valence-isomeric axial [123124]heptamantane and equatorial [121321]heptamantane. Dualist conventions as in Fig. 6

Fig. 7 by letters C); dualists of the other two perimantanes in Fig. 7 have the extra vertex either in axial or equatorial geometry, but they are homomeric.

Again one can see in Table 3 that some heptamantanes are isomeric and homomeric, whereas other ones are isomeric and heteromeric. Thus, when increasing the number of adamantane units of the smallest irregular [1231]pentamantane by two, this can be done either by two "cappings" with isobutane fragments at both final adamantane units of the smallest irregular [1231]pentamantane (yielding [121323]- or [121324]hexamantane), or by adding one diamantane to one final end of [1231]pentamantane (yielding all other non-branched irregular heptamantanes of Table 3). In the latter case, just as seen earlier for the heteromeric irregular hexamantanes, one finds again that the new C–C bonds may lead to the formation of different numbers of quaternary carnon atoms in the newly formed heptamantane, affording heteromeric (although isomeric) irregular hepta-catamantanes.

5 Discovery, syntheses, natural occurrence, uses, and importance of diamondoids

A very brief review follows about this very interesting class of hydrocarbons. Adamantane was first identified in petroleum by Landa, who discovered in 1933 that this

hydrocarbon has a high melting point (268 °C) and yet it is volatile, subliming under normal pressure [17]. The spherical symmetry of adamantane influences the packing in crystalline state, which is responsible for the thermal behavior. After Prelog and Seiwerth [18,19], found in 1941 synthetic pathways for obtaining adamantane Schleyer discovered serendipitously in 1957 a much simpler high-yield synthesis of adamantane by Lewis-acid catalyzed rearrangement of polycyclic valence isomers [20], and then extended this finding to diamantane (congressane) [21] and triamantane [22]. The role of the Lewis acid is to form carbocations that rearrange by rapid 1,2-shifts towards the more stable diamondoid structures with lower steric strain [23–25]. Schleyer continued to enrich the synthetic chemistry and mechanistic understanding of these rearrangements [26–28]. However, among higher diamondoids only [121]tetramantane could be obtained by such rearrangements [29–32]. Recent reviews about diamondoids have been published or are in print [33–35].

The next episode was the unexpected discovery of a rich source of diamondoids with n = 1 to 11 in petroleum. At the end of the twentieth century, Dahl, Carlson and coworkers from Chevron [36–38] developed methods based on the thermal stability and inertness towards oxidation for isolating and purifying diamondoids, and then initiated a series of collaborations with other chemists, including the present author [39]. It was thus possible to find quantitative structure-property relationships with retention times in gas chromatography and in high-performance liquid chromatography. With Schreiner and his coworkers, the Chevron authors developed regioselective methods for substitutions of diamondoids, finding that the normal higher reactivity of tertiary hydrogens may be reversed under special reaction conditions [40–45].

Analytical methods are available for petroleum characterization by its diamondoid content [33]. Other possible uses of diamondoids may take advantage of their electronic and spectral properties [46,47], The discovery that substituted adamantane such as derivatives of 1-aminoadamantane (amantadine) possess antiviral activity stimulated research on other substituted diamondoids. Rod-like substances with substituents at definite distances, able to interact with protein receptors, are promising target molecules in this approach. Whereas diamondoids are *pure substances*, and their regioselectively functionalized derivatives are ideal starting materials, other rod-like hydrocarbons derived from nanotubes are *mixtures* with various degrees of polydispersity.

6 Conclusions

Each of the *n* adamantane units of any [*n*]diamondoid can have 1, 2, 3, or 4 adjacent adamantane units that share a chair-shaped hexagon of carbon atoms. This situation is reflected in the corresponding sequence *p, s, t, q* of the dualist, respectively. The dualist consists of virtual vertices placed in the center of each adamantane unit which are connected by an edge whenever two adamantane units are adjacent. Dualists mirror carbon chains of staggered rotamers of alkanes or cycloalkanes, and as such in this paper they are depicted as graphs with vertices represented by C atoms. Acyclic dualists characterize catamantanes, whereas dualists containing six-membered rings characterize perimantanes. When acyclic dualists have vertices belonging to five of the

six vertices that could complete a chair-shaped hexagon, then this constitutes a proximity and the catamantane is irregular. Regular catamantanes with the same number n of adamantane units are isomeric and homomeric, whereas irregular catamantanes with the same number n of adamantane units may not be isomeric; even when they are isomeric, they may be heteromeric.

For the first time, all possible constitutional isomers of diamondoids with up to 7 adamantane units have been assigned partitioned formulas indicating by the sequence Q–T–S the numbers of C, CH, and CH_2 groups in their molecular formulas. It was found that regular [n]catamantanes with up to 7 adamantane cells exhibit a remarkable symmetry when the combined Q–T–S and *p, s, t, q* sequences are arranged in Table 1 according to increasing n and b values. Since the reactivity of secondary and tertiary hydrogens in substitution reactions differs, it is important to have a clear picture of the numbers of such CH_2 and CH groups. Rod-like catamantanes such as [121]tetramantane functionalized at the most distant tertiary carbon atoms are interesting target molecules for the synthesis of medicinal drugs.

Let us consider as examples planar polycyclic aromatic hydrocarbons (kekulean PAHs or benzenoids), where the numbers of possible isomers were evaluated by computer programs; a huge progress could be observed from the situation in 1987 (constructive enumeration for PAHs with up to $h = 15$ benzenoid rings) [48] to 1998 ($h = 21$ benzenoid rings) [49,50] and the present situation ($h = 26$) [51,52]. Parallel non-constructive) algorithms allowed in 2002 finding the numbers for up to $h = 35$ [53], and in 2009 for up to $h = 50$ [54]. There is an urgent need for a comparable effort from computational chemists to produce partitioned formulas of diamondoids (constructive, if possible).

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