Helical [n]catamantanes and all-trans-perhydroacenic [n]perimantanes

Balaban, Alexandru T.; Rücker, Christoph

Published in:
Arkivoc

DOI:
10.3998/ark.5550190.p008.352

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

Citation for pulished version (APA):
Balaban, A. T., & Rücker, C. (2013). Helical [n]catamantanes and all-trans-perhydroacenic [n]perimantanes: Structures and von Baeyer IUPAC numbering of carbon atoms. *Arkivoc*, *2014*(2), 346-361. Article CV-8352NP. https://doi.org/10.3998/ark.5550190.p008.352

Helical [*n*]catamantanes and *all-trans*-perhydroacenic [*n*]perimantanes: structures and von Baeyer IUPAC numbering of carbon atoms

Alexandru T. Balaban [a] **and Christoph Rücker** [b]

[a] *Texas A&M University at Galveston, 200 Seawolf Parkway, Galveston, TX 77551, USA*
[b] *Leuphana University Lüneburg, Scharnhorststr. 1, D-21335 Lüneburg, Germany*
E-mail: balabana@tamug.edu, christoph.ruecker@uni-leuphana.de

Dedicated to Professor Rosa Claramunt on the occasion of her 65th anniversary

---

Abstract

[*n*]Diamondoids are hydrocarbons whose carbon skeleton is a portion of the diamond lattice, and contains *n* adamantane cells (or units) sharing chair-shaped hexagons of carbon atoms. When centers of these adamantane units are connected by lines, the resulting construction is called the dualist of the diamondoid, and it also is similar to a portion of the diamond lattice. While these hydrocarbons can be distinguished by the Balaban-Schleyer nomenclature system, substituted derivatives are to be described by the IUPAC von Baeyer nomenclature that attributes a unique number (locant) to each carbon atom within a molecule. In this paper, von Baeyer names and corresponding atom numberings were obtained by the computer program POLCYC for members of two classes of diamondoids: [*n*]catamantanes whose dualists are tight helices, and [*n*]perimantanes whose dualists are *all-trans*-perhydroacenes; general numbering schemes were derived for these compound classes. The structures and some regularities in their structural properties are discussed.

Keywords: Diamond hydrocarbons; [*n*]diamondoids; regular helical catamantanes; perimantanes; IUPAC nomenclature

---

Introduction

Diamondoid hydrocarbons (diamondoids, for short) have carbon skeletons that are portions of the diamond lattice and consist of adamantane cells (or units) sharing chair-shaped hexagonal rings.[1,2] The number *n* of such adamantane cells is reflected in the name of [*n*]diamondoids (e.g. triamantane for the unique diamondoid isomer with *n* = 3). There is an analogy between diamondoids and polycyclic benzenoid hydrocarbons (benzenoids, for short) whose carbon skeleton is a portion of graphene. Two adjacent benzenoid rings share a CC bond. According to this analogy, the structures of diamondoid and benzenoid hydrocarbons are characterized by their dualists, consisting of vertices in the centers of the constituent units and of edges connecting vertices corresponding to adjacent units.[3,4] Whereas the dualist of the graphene lattice is a triangular lattice (and vice-versa), the diamond lattice is self-dual, i. e. the dualist of the diamond lattice is itself a diamond lattice. As a side remark, the 2D square lattice and the 3D cubic net are also self-dual.

Diamondoids with n adamantane units are classified as [n]catamantanes and [n]perimantanes according to whether their dualists are acyclic or have six-membered rings, respectively. [n]Catamantanes are regular if they have molecular formulas $C_{4n+6}H_{4n+12}$ and irregular if their numbers of C or H atoms are smaller. Dualists of catamantanes are staggered rotamers of alkanes. Accordingly, starting with tetramantane, constitutional isomerism is possible; additionally, stereoisomerism is also possible because the *gauche* rotamer of butane is chiral. After Schleyer's $AlCl_3$-catalyzed synthesis of adamantane, based on the fact that diamondoids are the most stable among all polycyclic isomers, diamantane, triamantane and [121]tetramantane were synthesized by cationic rearrangements of isomeric polycyclic hydrocarbons.[5,6]

The discovery of efficient procedures for isolating diamondoids from petroleum [7] opened up a source of raw materials for anchoring functional groups on precise locations, based on the higher reactivity of tertiary (CH) groups than of secondary (CH_2) groups. Biologically active derivatives of diamondoids offer hopes for drug design based on the hydrophobicity and antiviral properties of diamondoid derivatives such as adamantylamine.

For various diamondoid structures, Balaban and Schleyer [3] proposed a naming and coding system based on the four directions around an sp^3-hybridized carbon atom and encoded by digits 1, 2, 3, and 4 according to a simple procedure. This system is generally accepted at present. However, for specifying the structures of substituted diamondoids, the more general von Baeyer nomenclature system adopted by IUPAC provides a general and unambiguous solution.[8,9] C. and G. Rücker devised the computer program POLCYC for naming polycyclic compounds and numbering carbon atoms therein according to the IUPAC Nomenclature Rules.[10] This program was instrumental to the present paper.

In a previous paper,[11] the present authors showed that there exists a general scheme for applying IUPAC Nomenclature Rules for long blade-like (or flat rod-like) regular catamantanes with zigzag dualists consisting of two repeating digits 121212… Repeating patterns for dualists consisting of three repeating digits 123123123… correspond to irregular catamantanes involving close approach of diamondoid CH_2 groups, so that such series do not appear to be of any interest. By contrast, when four different digits are involved in the dualists' repeating pattern 123412341234…, the result is a series of *"tight helical" regular catamantanes*. It is of interest because each member of the series is chiral (point group C_2), and because, as in the series of zigzag catamantanes, there is a regularity that will be analyzed and presented in this paper. Also, like the blade-like zigzag catamantanes, naturally-occurring chiral diamondoids (such as

[123]tetramantane and helical regular catamantanes) may offer attractive starting materials for functionalization in order to design chiral medicinal drugs. A second class of interesting diamondoids for which von Baeyer IUPAC nomenclature and carbon atom numbering is described in the present paper is characterized by having dualists corresponding to *all-trans* perhydroacenes.

Structure, atom numbering, and nomenclature for tight helical regular catamantanes

The molecular formula of these helical diamondoids $C_{4n+6}H_{4n+12}$ is partitioned[12,13] for quaternary, tertiary and secondary carbon atoms as follows: $C_{n-2}(CH)_{2n+4}(CH_2)_{n+4}$. All quaternary carbon atoms form a single non-branched path which has $n - 2$ vertices and is identical to the dualist of the tight [n–2] diamondoid helix. Less tight helical diamondoids are possible. Figure 1 presents dualists of a tight and a less tight diamondoid helix.

We consider that the smallest tight helical diamondoid is [1234]pentamantane, whose dualist exhausts all four tetrahedral directions; it has five adamantane cells and is chiral. By abdicating from the postulate of "lowest number" in the 4-digit notation, one might code enantiomers as [123]- versus [124]tetramantane, and [1234]- vs. [1243]pentamantane. The smallest chiral diamondoid ([123]tetramantane) was isolated from petroleum as both enantiomeric forms by an elaborate procedure.[14] Based on the upper right view of Figure 1, one should expect properties of the tight diamondoid helices to show a modulo-4 variation versus the number n of adamantane units, as the two ends of the dualist can occur in four different reciprocal situations, since the projection of the dualist brings the four tetrahedral directions along the sides of a square.

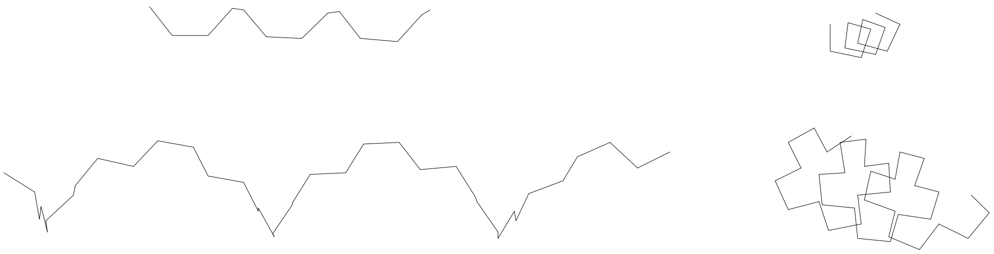

Figure 1. Upper row: two views for the dualist of tight helical [123412341234]tridecamantane. Lower row: two views for the dualist of a less tight helical polymantane with 38 adamantane units. In the upper right view, the helix axis connects centers of the square projections of the dualist.

The tight helical diamondoids will be shown in planar projections. As an example, Figure 2 displays a projection of the tridecamantane helix. Further schemes with right angles as in Figures 3, 4, and 5 will allow us to see four paths along the winding staircase representation as in the left part of Fig.1. The two terminal adamantane units can be easily distinguished, as only they have a tertiary CH group connected to three secondary CH_2 groups.

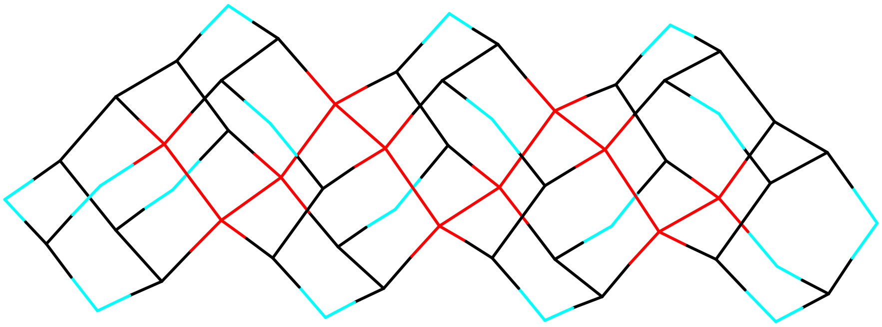

Figure 2. The hydrogen-depleted tight helical [123412341234]tridecamantane. Carbon atoms are color-coded: red for quaternary, black for tertiary, and blue for secondary carbon atoms.

As an example of a diamondoid helix, Figure 3 presents [123412341234]tridecamantane (formula $C_{58}H_{64}$, or according to partition $C_{11}(CH)_{30}(CH_2)_{17}$), with the numbering of carbon atoms corresponding to its IUPAC name, heptacosacyclo[$27.27.1.1^{13,45}.0^{1,32}.0^{2,23}.0^{2,27}.0^{3,54}.0^{5,22}.0^{6,19}.0^{6,53}.0^{7,50}.0^{9,18}.0^{10,15}.0^{10,49}.0^{11,46}.0^{15,44}.0^{16,41}.0^{19,40}.0^{20,37}.0^{23,36}.0^{24,33}.0^{26,31}.0^{35,56}.0^{36,53}.0^{39,52}.0^{40,49}.0^{43,48}$]octapentacontane.

We will use a planar projection of the tightest possible helical arrangements of diamondoids. This projection (Fig. 3a) mimics the alignment shown in Figure 2 for the tridecamantane helix as an example, such that one of the two adamantane-end-units having a tertiary carbon atom (CH group No. 29 in Fig. 3) connected to three secondary carbon atoms appears in the lower left side. The quaternary carbon atom that is a second neighbor of that CH group will always be number 1 in the IUPAC numbering, as displayed in Figure 4. The other adamantane-end-unit will appear on the right side of the projection in four different geometries, as will be shown in Figure 5. Returning to Figures 2 and 3, one sees that (apart from the two adamantane-end-units) there are four long quasi-horizontal zigzag paths along the main ring with vertices symbolizing repeating –C–CH–CH_2–CH– sequences. We will use the following names for these paths: the two *outer paths* in Figure 3a, which have numbers 2 to 10 and 34 to 42, and the two *inner paths*, running in the opposite direction, that have numbers 48 to 56 and 16 to 24. In the 3D model of the molecule, there are no such things as ‘outer’ or ‘inner’ paths, but rather the four paths (Fig. 3a) form the four ridges of a long rod-like molecule that has a square cross section when viewed along the helix axis (Fig. 3b). In the right-handed helical enantiomer shown here the first path (atoms 2 - 10) is the south-east quadrant in Figure 3b, atoms 16 - 24 form the south-west quadrant, atoms 34 - 42 the north-west quadrant, and atoms 48 - 56 the north-east quadrant, each of the four paths forming a right-handed helix in itself.

The main ring is indicated in Figure 3a by thick lines, and the two bridgehead atoms have numbers 1 and 29. These two atoms divide equally the main ring of 56 atoms, and there is the 1-atom main bridge between atoms 1 and 29, as well as the 1-atom secondary bridge between atoms 13 and 45. In Table 1 one can see the numbering of red-colored quaternary carbon atoms (obtained by the computer program POLCYC up to $n = 17$). They form a continuous sequence.

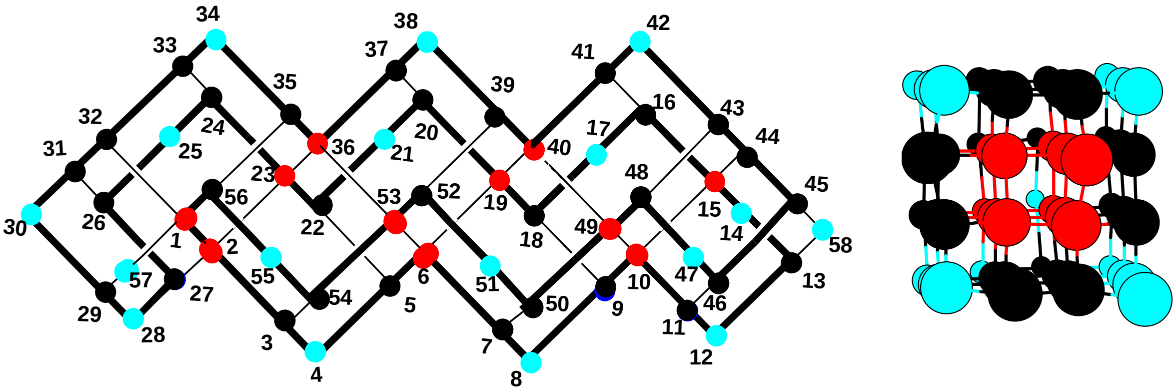

Figure 3. (a) Von Baeyer IUPAC numbering of carbon atoms in [123412341234]tridecamantane (left part). The main ring is shown with thick lines. The color coding is as in Figure 2. (b) Cross-sectional view of the same molecule along the helix axis. Atoms of the foremost adamantane unit were removed for clarity (right part).

Table 1. For tight helical diamondoids with *n* adamantane units, the partition of quaternary, tertiary, and secondary carbon atoms (totaling 4*n*+6 carbon atoms), and in columns A to O the numbering of adjacent quaternary carbon atoms (colored red in Figures 2 to 5)

n	Formula	C	CH	CH_2	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
5	$C_{26}H_{32}$	3	14	9	1	2	7												
6	$C_{30}H_{36}$	4	16	10	1	2	11	24											
7	$C_{34}H_{40}$	5	18	11	1	2	11	24	29										
8	$C_{38}H_{44}$	6	20	12	1	2	15	28	33	6									
9	$C_{42}H_{48}$	7	22	13	1	2	15	28	37	6	11								
10	$C_{46}H_{52}$	8	24	14	1	2	19	32	41	6	15	36							
11	$C_{50}H_{56}$	9	26	15	1	2	19	32	45	6	15	36	41						
12	$C_{54}H_{60}$	10	28	16	1	2	23	36	49	6	19	40	45	10					
13	$C_{58}H_{64}$	11	30	17	1	2	23	36	53	6	19	40	49	10	15				
14	$C_{62}H_{68}$	12	32	18	1	2	27	40	57	6	23	44	53	10	19	48			
15	$C_{66}H_{72}$	13	34	19	1	2	27	40	61	6	23	44	57	10	19	48	53		
16	$C_{70}H_{76}$	14	36	20	1	2	31	44	65	6	27	48	61	10	23	52	57	14	
17	$C_{74}H_{80}$	15	38	21	1	2	31	44	69	6	27	48	65	10	23	52	61	14	19

In Table 1, columns B, F, J, N, with constant values, represent “concave bend corner atoms” on the outer lower path of the main ring following the initial carbon (number 1). For odd *n* values, the main ring is evenly divided by the 1-atom main bridge between bridgehead atoms numbered 1 and 2*n*+3. For even *n*, the main ring is unevenly divided by the 1-atom main bridge between bridgeheads 1 and 2*n*+5. Columns D, H, L represent “concave bend corner atoms” on the outer upper path with numbers increasing stepwise by 4,0,4,0,… for increasing *n*. Columns C, G, K, O in the table correspond to carbon atoms that are situated next to carbons from columns D, H, L along the upper inner path with numbers increasing stepwise by 4,0,4,0,… for increasing *n*. Columns E, I, M in the table correspond to carbon atoms that are connected to carbons from columns D, H, L along the lower inner path with numbers increasing stepwise by 4. One can observe that some columns become repeated at different heights: C, G, K, O; also D, H, L; also E, I, M. On each row, values in columns *z* and *z*+4 (where *z* denotes a letter from B to O, i. e. except for *z* = 1) differ by alternatively adding or subtracting 4: for example with *n* = 17, values for entries in columns C, G, and K are 31, 27, and 23 (–4 series); in columns D, H, L values are 44, 48, and 52 (+ 4 series); in columns E, I, M values are 69, 65, and 61 (– 4 series).

The left part of planar projections for all such helical diamondoids, containing the carbon atom numbered 1, is the same and is illustrated in Figure 4. The right part, however, presents modulo-4 differences, in agreement with Table 1, and is shown in the four parts of Figure 5.

The *floor function* $\lfloor n/2 \rfloor$ denotes the largest integer not greater than *n*/2, or in other words the “largest integer part” of *n*/2. In Figures 4 and 5 we use the notation: $\lfloor n/2 \rfloor = x$. The general algorithm for IUPAC numbering and nomenclature of the tight helical diamondoids is explained by Figure 4 (for the initial part of the helical catamantanes, containing the carbon atom numbered 1, covering all four cases of the modulo-4 rules) and Figure 5 (which covers separately these four cases).

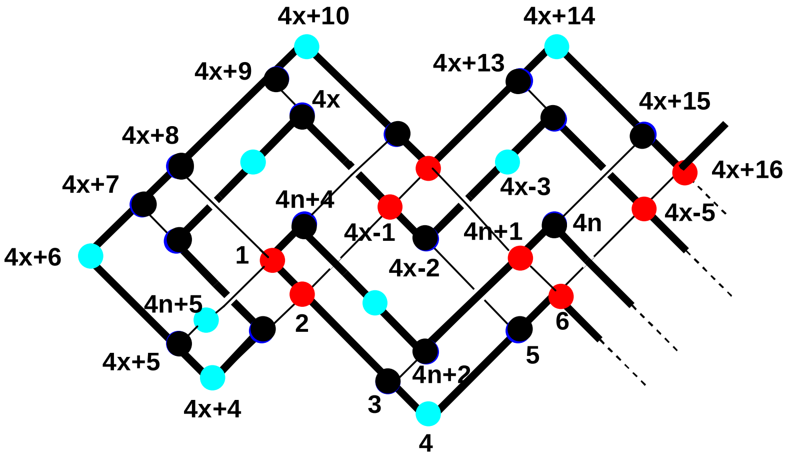

Figure 4. The left part of planar projections for all helical [*n*]diamondoids, containing the carbon atom numbered 1, with the general numbering of carbon atoms as a function of the number *n* of adamantane units using the floor function.

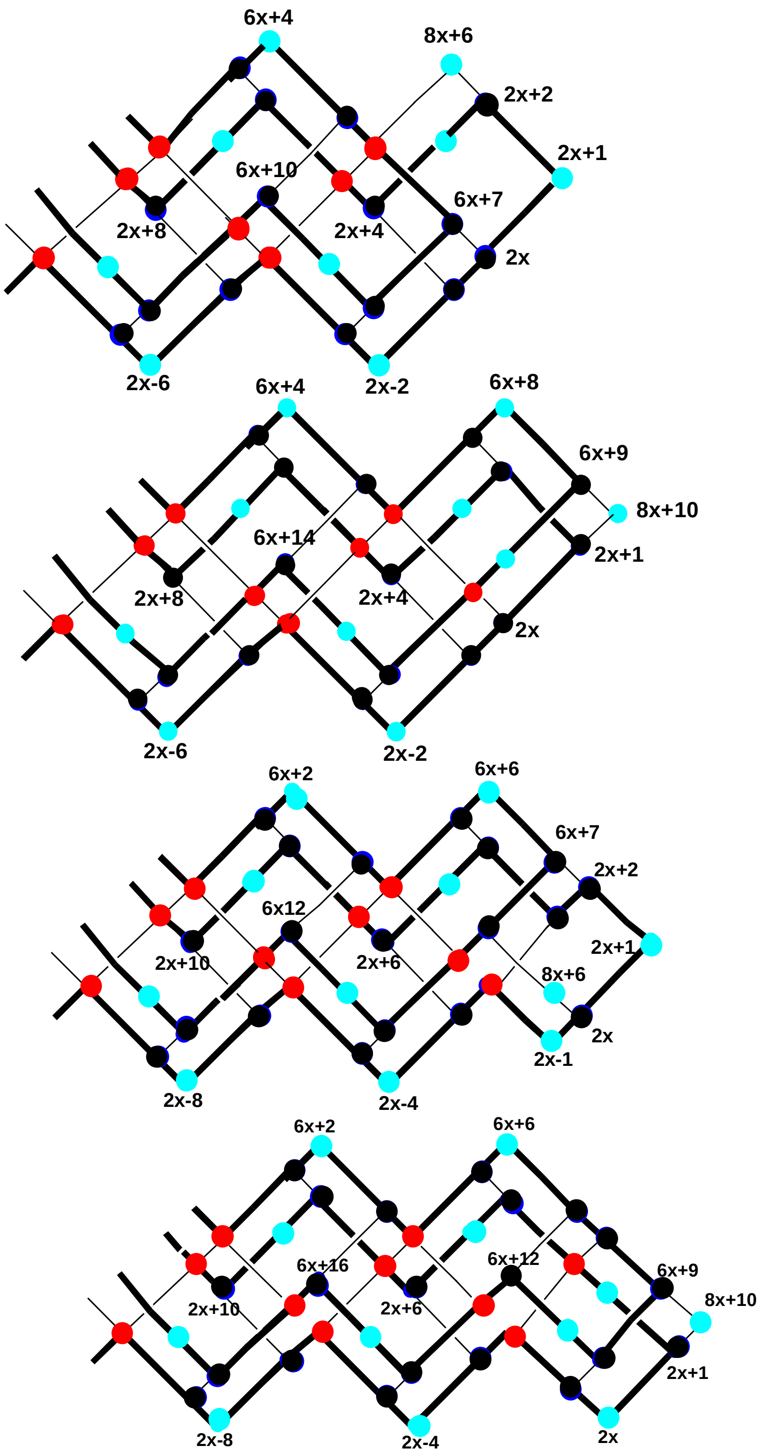

Figure 5. The right part of planar projections for all helical [*n*]diamondoids with the general numbering of carbon atoms as a function of the number *n* of adamantane units using the floor function; *n* values from top to bottom are: 2 (mod 4), 3(mod 4), 0 (mod 4) and 1(mod 4).

Stereochemical aspects in helical catamantanes

For substituted derivatives of helical catamantanes, numbering of carbon atoms allows us to differentiate hydrogens attached to tertiary carbon atoms, but not those attached to secondary carbon atoms. In a CH_2 group located on a ridge of the molecule, the two hydrogen atoms can be distinguished as 'pointing to the center' and 'pointing to the end' of the molecule; see Figure 6. As one can see in Figure 6, two invariants of the diamondoid helix are its axis and the helicity (positive for right-handed thread, and negative for left-handed thread which turns anticlockwise as it moves away from the observer).

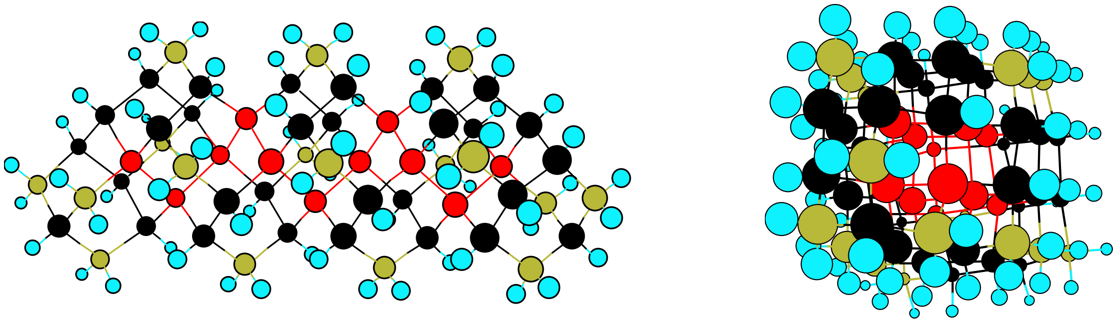

Figure 6. Helical [123412341234]tridecamantane with all its hydrogens (blue) in side-view and front-view. Here the secondary carbon atoms are not blue but olive.

Structure, atom numbering, and nomenclature for perimantanes having as dualists "geometry-preserving" graphs corresponding to *all-trans*-perhydroacenes

An interesting class of perimantanes has dualists that are the "geometry-preserving" graphs corresponding to hydrogen-depleted *all-trans*-perhydroacenes. The smallest such perimantane has a chair-shaped hexagon as dualist; it was identified in, and isolated from petroleum and is known as cyclohexamantane (see Fig. 7, top).[15] Its code using the Balaban-Schleyer system is [123123]perimantane; it contains n = 6 adamantane cells. In 2003 a "von Baeyer"-like name dodecacyclo[$12.12.0.0^{2,11}.0^{3,16}.0^{5,18}.0^{6,11}.0^{7,20}.0^{9,22}.0^{10,25}.0^{12,17}.0^{12,21}.0^{13,24}$]hexacosane and the corresponding numbering scheme were published and said to be the approved IUPAC numbering for cyclohexamantane.[15] This name, however, though correctly describing the structure, was not correct in the sense of IUPAC rule VB-6-4, which states "The superscript locants of the secondary bridges shall be as small as possible when considered as a set in ascending numerical order, a decision being made at the first point of difference".[8] In 2009 a different numbering scheme for cyclohexamantane was used,[16] corresponding to the correct von Baeyer IUPAC name as given here: dodecacyclo[$12.12.0.0^{1,6}.0^{2,23}.0^{3,20}.0^{5,18}.0^{7,16}.0^{9,26}.0^{10,15}.0^{12,25}.0^{13,22}.0^{14,19}$]hexacosane. Obviously, two different numbering schemes of a parent compound would result in two names for a monosubstituted derivative, confusingly differing in locant numbers. This again emphasizes the desirability for IUPAC names and the corresponding numbering schemes for polycycles to be constructed by a computer program.

The second member of this class has as dualist the graph corresponding to *trans*-decalin, see Figure 7, second structure. Its IUPAC name is nonadecacyclo[$20.16.0.0^{1,6}.0^{2,35}.0^{3,20}.0^{3,32}.0^{4,29}.0^{5,26}.0^{7,24}.0^{9,38}.0^{10,23}.0^{12,37}.0^{13,22}.0^{14,35}.0^{15,20}.0^{16,33}.0^{18,31}.0^{19,28}.0^{21,26}$]octatriacontane. The Balaban-Schleyer code, which is [123(1)2312323]perimantane, distinguishes it from the perimantane having as dualist the graph of *cis*-decalin. The latter diamondoid has code [123(1)2412423]-perimantane, and the IUPAC (von Baeyer) name nonadecacyclo[$18.18.0.0^{1,26}.0^{2,35}.0^{3,28}.0^{4,21}.0^{6,29}.0^{7,22}.0^{9,30}.0^{10,27}.0^{11,32}.0^{13,26}.0^{13,34}.0^{14,37}.0^{16,25}.0^{17,38}.0^{19,24}.0^{22,27}.0^{28,33}$]octatriacontane.

In Table 2 we present data for the first perimantanes with *all*-*trans*-perhydroacene graphs as dualists. Their IUPAC names were generated by the POLCYC program up to k = 5; for higher k values the required computer time would be unreasonably high.

Table 2. The smallest perimantanes with *all*-*trans*-perhydroacene graphs as dualists

n	k	**Formula**	**Partition**	**Main ring**	**Perhydroacenic dualist**	**Abbreviation** *a*-*t*-H-*k*
6	1	$C_{26}H_{30}$	$C_2(CH)_{18}(CH_2)_6$	12 + 12	cyclohexane	*a*-*t*-H-mono
10	2	$C_{38}H_{40}$	$C_6(CH)_{24}(CH_2)_8$	20 + 16	decalin	*a*-*t*-H-di
14	3	$C_{50}H_{50}$	$C_{10}(CH)_{30}(CH_2)_{10}$	24 + 24	perhydroanthracene	*a*-*t*-H-tri
18	4	$C_{62}H_{60}$	$C_{14}(CH)_{36}(CH_2)_{12}$	32 + 28	perhydrotetracene	*a*-*t*-H-tetra
22	5	$C_{74}H_{70}$	$C_{18}(CH)_{42}(CH_2)_{14}$	36 + 36	perhydropentacene	*a*-*t*-H-penta
26	6	$C_{86}H_{80}$	$C_{22}(CH)_{48}(CH_2)_{16}$	44 + 40	perhydrohexacene	*a*-*t*-H-hexa
30	7	$C_{98}H_{90}$	$C_{26}(CH)_{54}(CH_2)_{18}$	48 + 48	perhydroheptacene	*a*-*t*-H-hepta

In the following we use the number k of six-membered rings in the dualist as parameter for perimantanes having dualists isomorphic with *all*-*trans*-perhydroacenes. Below we give, for k = 3,4,5, the name of the dualist, in parentheses a shorthand notation for the dualist, and finally the corresponding perimantane's IUPAC name.

trans,*trans*-Perhydroanthracene (*a*-*t*-H-tri, k = 3):
hexacosacyclo[$24.24.0.0^{1,6}.0^{2,43}.0^{3,24}.0^{3,40}.0^{4,37}.0^{5,34}.0^{7,32}.0^{8,49}.0^{9,30}.0^{11,48}.0^{12,29}.0^{14,47}.0^{15,28}.0^{16,45}.0^{17,26}.0^{18,43}.0^{19,24}.0^{20,41}.0^{22,39}.0^{23,36}.0^{25,34}.0^{27,32}.0^{28,49}.0^{45,50}$]pentacontane, see the middle structure in Figure 7;

trans,*trans*,*trans*-Perhydrotetracene (*a*-*t*-H-tetra, k = 4):
tritriacontacyclo[$32.28.0.0^{1,10}.0^{2,55}.0^{3,8}.0^{3,32}.0^{4,53}.0^{5,30}.0^{5,50}.0^{6,47}.0^{7,44}.0^{9,42}.0^{11,40}.0^{12,61}.0^{13,38}.0^{15,60}.0^{16,37}.0^{18,59}.0^{19,36}.0^{20,57}.0^{21,34}.0^{22,55}.0^{23,32}.0^{24,53}.0^{25,30}.0^{26,51}.0^{28,49}.0^{29,46}.0^{31,44}.0^{33,42}.0^{35,40}.0^{36,61}.0^{57,62}$]dohexacontane, see the fourth structure in Fig. 7;

trans,*trans*,*trans*,*trans*-Perhydropentacene (*a*-*t*-H-penta, $k = 5$):
tetracontacyclo[$36.36.0.0^{1,10}.0^{2,63}.0^{3,8}.0^{3,36}.0^{4,61}.0^{5,34}.0^{5,58}.0^{6,55}.0^{7,52}.0^{9,50}.0^{11,48}.0^{12,73}.0^{13,46}.0^{14,71}.0^{15,44}.0^{17,70}.0^{18,43}.0^{20,69}.0^{21,42}.0^{22,67}.0^{23,40}.0^{24,65}.0^{25,38}.0^{26,63}.0^{27,36}.0^{28,61}.0^{29,34}.0^{30,59}.0^{32,57}.0^{33,54}.0^{35,52}.0^{37,50}.0^{39,48}.0^{40,73}.0^{41,46}.0^{42,71}.0^{65,74}.0^{67,72}$]tetraheptacontane, see Figure 7, last structure.

A polycyclic compound is said to be Hamiltonian if all its non-H atoms can be arranged along the given bonds on a single ring (which is then called a Hamiltonian cycle).[17] The structural element of a tertiary (or quaternary) C atom surrounded by three secondary C atoms is sufficient for non-Hamiltonicity, i.e. in such a substructure one secondary C atom necessarily is left out of the main ring. This substructure, corresponding to a primary vertex of the dualist, is found at both ends of a zigzag catamantane [11] and of a tight helical catamantane (Figures 2 to 6). These compounds therefore have at least two carbon atoms out of the main ring, which is reflected in their IUPAC names. In contrast, the perimantanes considered here lack such terminal adamantane cells, and not surprisingly have all their C atoms on the main ring (a Hamiltonian cycle), as reflected in their IUPAC names by zeros at the third and all following positions within the square brackets.

The zero-atom main bridge for odd numbers k of 6-membered rings in the dualist divides equally the main ring, [$a.a.0.0^{1,y}.0\ldots$]. For even numbers k, it divides unequally the main ring, [$a.b.0.0^{1,y}.0\ldots$], with $a - b = 4$. Figure 7 presents the first five members (k = 1, 2, 3, 4, and 5) of this class of [*n*]perimantanes.

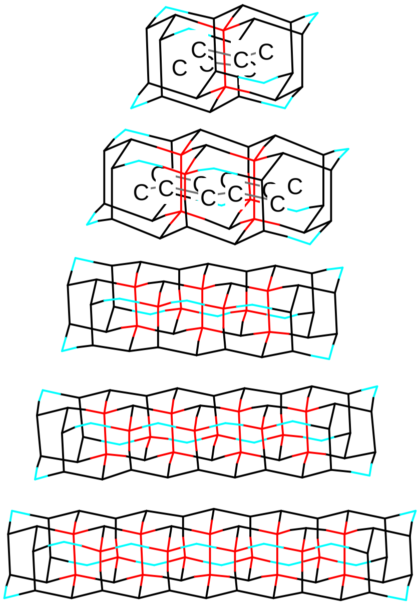

Figure 7. From top to bottom: perimantanes having as dualists *all-trans* perhydroacenes with k = 1, 2, 3, 4, and 5.

In Figure 7 the color codes for secondary, tertiary, and quaternary carbon atoms are as in Figure 2. In the first two cases the dualists are displayed in gray with vertices indicated by letter

C. In the remaining cases the dualist is not shown and the projection shows the six long quasi-horizontal paths closer to being almost straight: the two mostly *black* paths are sequences of tertiary carbons, each ending by two secondary carbons; they enclose the *red/black* paths, which, in turn, enclose the *red/blue* paths. Figures 9a,b will show the geometry of these diamondoids.

With n indicating the number of adamantane cells, one obtains:

- the number of six-membered rings of the dualist is $k = (n–2)/4$;
- the molecular formula is $C_{12k+14}H_{10k+20}$ partitioned into $C_{4k–2}(CH)_{6k+12}(CH_2)_{2k+4}$;
- for odd k, the equal halves of the main ring have $a = 6k+6$; for even k, the unequal portions of the main ring have $a = 6k+8$ and $b = 6k+4$.

It may be seen in Figure 7 that in all these perimantanes there are six quasi-straight horizontal paths from one extremity to the other, organized in three pairs with atom numberings in opposite directions (as will be seen in Fig. 8): ignoring the lateral extremities, the *black* pair of paths has only tertiary carbon atoms; the *red/black* pair has alternating tertiary and quaternary carbon atoms, and the *red/blue* pair has alternating secondary and quaternary carbon atoms.

Again we will use a planar projection mimicking the trends that are visible in Figure 7, such that the above six paths appear on horizontal quasi-straight lines. The quaternary carbon atom closest to, and at the right side of the middle of the upper red/black path, in this particular projection, will have number 1; the numbering continues from left to right till it reaches the last quaternary carbon atom on this path, then it goes on to the adjacent tertiary carbon atom on the upper black path, following along the periphery with the lower black path till its end, from whence it follows the lower red/black and the lower red/blue paths. With a loop involving four carbon atoms, the numbering continues on the upper red/blue and then red/black paths, reaching finally carbon atom numbered 1, thus completing the Hamiltonian circuit. Thus, in other words, the numbering of carbon atoms along the Hamiltonian circuit, which constitutes the main ring, starts from the bridgehead quaternary atom numbered 1 of the red/black path with tertiary and quaternary carbon atoms, runs along the black paths, followed by the red/black path containing the central quaternary atom numbered $6k+8$ for odd k or $6k+10$ for even k (which is the second bridgehead), and continues along the red/blue paths. Another observation is that the carbon atom numbering of the extremities in terms of k jumps by 4 along odd numbers when moving from a path to the next one ($3k$, $7k$, $11k$ for the left-hand extremity, $5k$ and $9k$ for the right-hand extremity), whereas in the inner part of the six paths the numbering jumps by 2 along even numbers ($4k$, $6k$, $8k$, $10k$, $12k$); see Figure 8. All differences in numbering between odd and even k arise only from the equal/unequal division of the main ring by the main bridge, for odd/even k values, respectively.

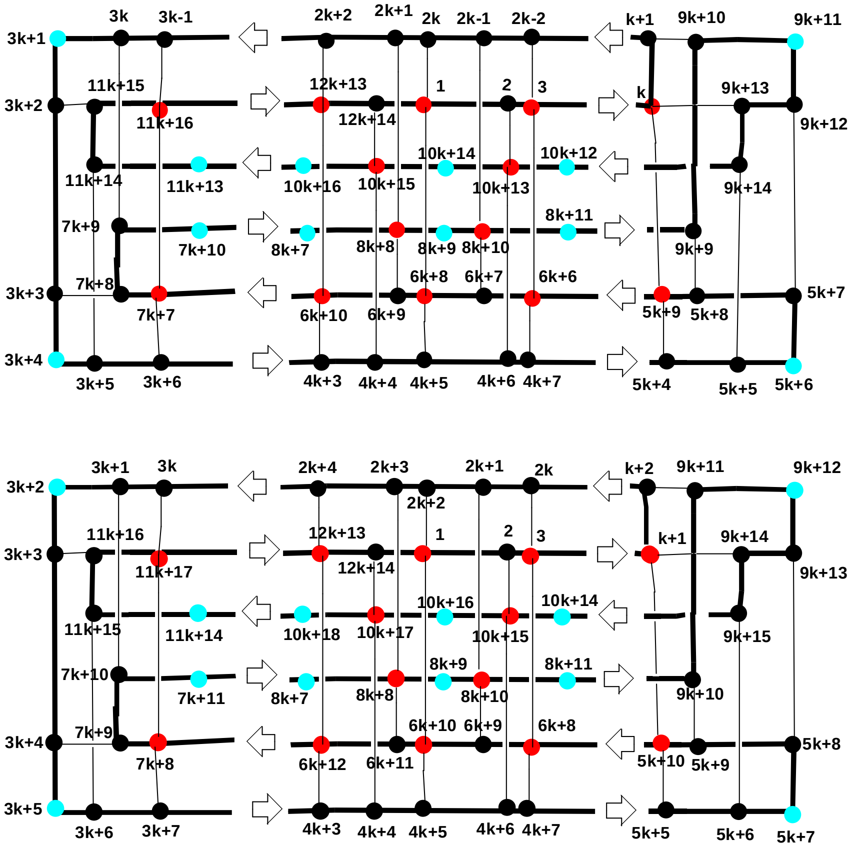

Figure 8. General scheme for numbering carbon atoms in perimantanes that have dualists corresponding to *all-trans* perhydroacenes with odd k >1 (upper part) and even k >2 (lower part). All broken-line crossings are randomly assigned, without geometrical significance.

Stereochemical aspects in perimantanes that have as dualists all-trans perhydroacenes

All these molecules exhibit mirror symmetry (point group C_{2h}, except for the k = 1 case, which has point group D_{3d}) and thus are achiral, but most substitutions of a hydrogen atom will destroy that symmetry and thus create chirality. Here, just as for zigzag catamantanes where there is the symmetry plane of the blade-like coplanar dualist,[11] the median plane of the dualist allows one to distinguish the diastereomers of substituted compounds by the orientation of the substituent(s) relative to that plane, equatorial or axial. An example is provided in Figure 9a for the case k = 2, showing all hydrogen atoms in equatorial or axial relationship to the median plane of the *trans*-decalin dualist.

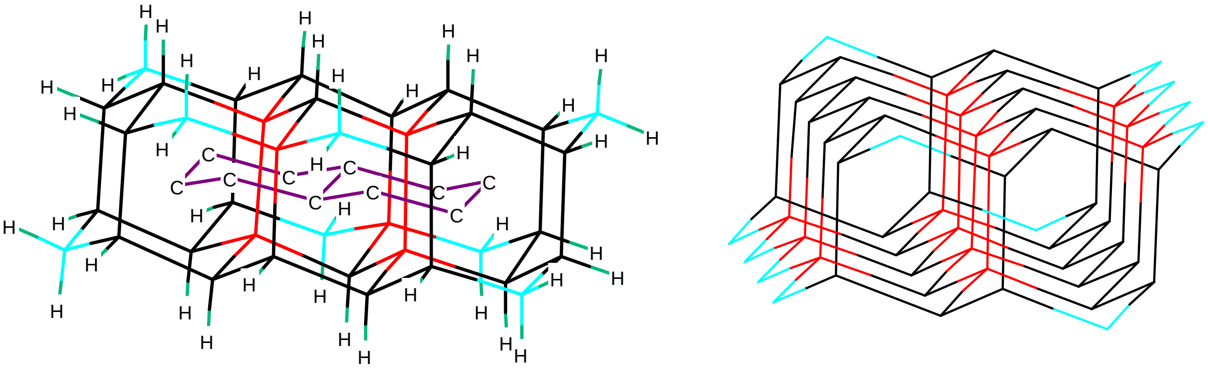

Figure 9. (a) Left part: side-view of the perimantane with *k* = 2 showing all hydrogen atoms and the *trans*-decalin-like dualist that provides a median reference plane; the two hydrogens connected to each secondary carbon atom are distinguished by having two different orientations with respect to this plane, equatorial and axial. (b) Right part: view along quaternary atoms of the perimantane with *k* = 4 indicating that the red/blue paths are the most distant from the center.

Concluding remarks

For two classes of diamondoids that may have interesting applications after regioselective functionalization we have determined their general nomenclature and carbon atom numbering according to the von Baeyer (IUPAC) rules: (i) tight-helical regular catamantanes, and (ii) perimantanes having as dualists *all-trans* perhydroacenes. In the former case, chirality is an important asset, and in the latter case the flat geometry provides interesting spatial relationships between possible substituents. Another potentially attracting aspect is in using such systems as building blocks for supramolecular assemblies, after proper substitution with functional groups.

How does it come that in the helical catamantanes (just as in the zigzag catamantanes [11]) the IUPAC numbering commences close to the end of the molecule, whereas in the perimantanes numbering starts close to the molecule's center? In the case of zigzag and helical catamantanes, the structure element $CH_2{-}CH(CH_2){-}CH_2$, occurring at both ends of these molecules, prevents them from being Hamiltonian, i. e. from having a von Baeyer name of the form [$a.b.0.0^{x,y}$...]. Since by the IUPAC rule VB-5 the main bridge must be as long as possible, one of the CH_2 groups in such a substructure must be the main bridge, resulting in a von Baeyer name of the form [$a.b.1.1^{x,y}.0$...]. The atom forming the one-atom main bridge is necessarily an immediate neighbor of both main bridgehead atoms, one of which by definition is atom number one. In other words, the atom number one is necessarily an immediate neighbor of one of the CH_2 atoms in the above substructure, which is located at the end of the molecule, therefore atom number one itself is located near the end of the molecule. In the case of the perimantanes with perhydroacene dualists, we have no substructure preventing Hamiltonicity. Now IUPAC rule VB-6-1 states that the main bridge (a zero-atom bridge) should divide the all-atom main ring as symmetrically as possible. The main bridgeheads must be close to, or coincide with the center of the molecule in order to have a symmetrical division of the main ring. Thus, as was to be expected, the properties of the von Baeyer names of these compounds are based on the interaction between the structures (given by Nature) and the man-made rules.

The helical (and the zigzag) catamantanes are all graph-theoretically (gt-) planar compounds, i.e. their structural formulas can be written on a planar surface without any crossing lines, given unlimited flexibility of line lengths and angles. In contrast, the perimantanes with *trans*-perhydroacene dualists are all gt-nonplanar, being homeomorphs of the Kuratowski graph $K_{3,3}$, as was pointed out for the $k = 1$ member (cyclohexamantane) by Kuck.[18] There are few compounds known with this property, among them very few natural products, for thermodynamic and kinetic reasons.[19] In the case of cyclohexamantane and its higher analogs, there is at least no energetic obstacle to formation, in that the structures are almost free of strain, see Figure 9. According to molecular mechanics calculations, the steric energy per C atom in these compounds is not significantly different from that in gt-planar helical or zigzag catamantanes, see Figure 3 and reference 11. Another gt-nonplanar diamondoid is the superadamantane-5 ('adamantane of adamantanes'),[20] which is a homeomorph of Kuratowski's graph K_5. Therefore diamond is the only compound known to us that is gt-nonplanar due to both $K_{3,3}$ and K_5 type substructures, and at the same time the only K_5 type gt-nonplanar natural product of which we are aware.

Nature provides a rich source of synthetically inaccessible diamondoids that have four or more adamantane units. Several diamondoid hydrocarbons obtained from petroleum have already been used as starting materials for molecular components of nanosystems: chapter 4 of the book cited earlier provides many examples of such uses.[1]

It is known that hydrogens of diamondoids attached to tertiary carbon atoms can be substituted more readily than hydrogens attached to secondary carbon atoms. Regioselective functionalization at tertiary carbons situated at precise distances may offer pathways to biologically active products by interaction with proteins, inhibiting or activating such bio-catalysts. Unlike rod-like benzenoid nanotubes which are polydisperse mixtures of related but not identical molecules, diamondoids are pure compounds, with molecular shapes that are easily controllable. Functionalized diamondoids obtained by regioselective reactions offer a wide range of possible shapes in three dimensions.[14-16,21,22] In order to specify the location and stereochemistry of substituents, the von Baeyer nomenclature enhanced by stereochemical descriptors as advocated here is the best available system.

References

1. Mansoori, G. A.; de Araujo, P. L. B.; de Araujo, E. S. *Diamondoid Molecules: With Applications in Biomedicine, Materials Science*, Nanotechnology and Petroleum Science. World Scientific Publishing Co.: New Jersey, 2012. http://dx.doi.org/10.1142/7559
2. Balaban, A. T. in *Diamond and Related Nanostructures*, Diudea, M. V.; Nagy, C. L., Eds., Springer: Berlin, 2013.
3. Balaban, A. T.; Schleyer, P. v. R. *Tetrahedron* **1978**, *34*, 3599-3609. http://dx.doi.org/10.1016/0040-4020(78)88437-3
4. Balaban, A. T. *MATCH Commun. Math. Comput. Chem.* **1976,** *2*, 51-61.
5. Schleyer, P. v. R. *J. Am. Chem. Soc.* **1957**, *79*, 3292. http://dx.doi.org/10.1021/ja01569a086
6. Schleyer, P. v. R. in *Cage Hydrocarbons* Olah, G. A., Ed., Wiley-Interscience: New York, 1990, pp 1-38.
7. Dahl, J. E.; Liu, S. G.; Carlson, R. M. K. *Science* **2003**, *299*, 96-99. http://dx.doi.org/10.1126/science.1078239 PMid:12459548
8. Moss, G. P. *Pure Appl. Chem.* **1999**, *71*, 513-529. http://dx.doi.org/10.1351/pac199971030513
9. Renner, T.; Favre, H. A.; Powell, W. H. *Nomenclature of Organic Chemistry: IUPAC Recommendations 2012 and Preferred IUPAC Names*, Royal Society of Chemistry: London, 2013.
10. Rücker, G.; Rücker, C. *Chimia* **1990**, *44*, 116-120.
11. Balaban, A. T.; Rücker, C. *Cent. Eur. J. Chem.* **2013**, *11*, 1423-1430. http://dx.doi.org/10.2478/s11532-013-0275-7
12. Balaban, A. T. J. *Chem. Inf. Model.* **2012**, *52*, 2856-2869. http://dx.doi.org/10.1021/ci300406b PMid:23046064
13. Balaban, A. T. *J. Math. Chem.* **2013**, *51*, 1043-1055. http://dx.doi.org/10.1007/s10910-012-0130-7
14. Schreiner, P. R.; Fokin, A. A.; Reisenauer, H. P.; Tkachenko, B. A.; Vass; E.; Olmstead, M. M.; Bläser, D.; Boese, R.; Dahl, J. E. P.; Carlson, R. M. K. *J. Am. Chem. Soc.* **2009**, *131*, 11292-11293. http://dx.doi.org/10.1021/ja904527g PMid:19722641

15. Dahl, J. E. P.; Moldowan, J. M.; Peakman, T. M.; Clardy, J. C.; Lobkovsky, E.; Olmstead, M. M.; May, P. W.; Davis, T. J.; Steeds, J. W.; Peters, K. E.; Pepper, A.; Ekuan, A.; Carlson, R. M. K. *Angew. Chem. Int. Ed.* **2003**, *42*, 2040-2044.
    http://dx.doi.org/10.1002/anie.200250794
    PMid:12746817
16. Fokin, A. A.; Tkachenko, B. A.; Fokina, N. A.; Hausmann, H.; Serafin, M.; Dahl, J. E. P.; Carlson, R. M. K.; Schreiner, P. R. *Chem. Eur. J.* **2009**, *15*, 3851-3862.
    http://dx.doi.org/10.1002/chem.200801867
    PMid:19229930
17. Balaban, A. T.; Babic, Klein, D. J. *J. Chem. Educ.* **1995**, *72*, 693-698.
18. Kuck, D. in *Strained Hydrocarbons*: *Beyond the van't Hoff and Le Bel Hypothesis* Dodziuk, H., Ed., Wiley-VCH: Weinheim, 2009.
19. Rücker, C.; Meringer, M. *MATCH Commun. Math. Comput. Chem.* **2002**, *45*, 153-172.
20. Shen, M.; Schaefer, H. F.; Liang, C.; Lii, J. H.; Allinger, N. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 497-505.
    http://dx.doi.org/10.1021/ja00028a015
21. Fokin, A. A.; Gunchenko, P. A.; Novikovsky, A. A.; Shubina, T. E.; Chernyaev, B. V.; Dahl, J. E. P.; Carlson; R. M. K.; Yurchenko, A. G.; Schreiner, P. R. *Eur. J. Org. Chem.* **2009**, 5153-5161.
    http://dx.doi.org/10.1002/ejoc.200900600
22. Schwertfeger, H.; Würtele, C.; Hausmann, H.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A.; Schreiner, P. R. *Adv. Synth. Catal.* **2009**, *351*, 1041-1054.
    http://dx.doi.org/10.1002/adsc.200800787