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Nonclassical Carbon: From Theory to Experiment

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Abstract—Nonclassical organic compounds are defined as compounds comprising in their molecular or ionic structure nontetrahedral (planar, pyramidal, semiplanar, or inverted) tetra- or/and hypercoordinate carbon centers. The evolution of concepts was considered and accumulated theoretical and experimental data concerning the structure and dynamic transformations of nonclassical organic compounds were systematized. Computational analysis based on the methods and computational potential of modern quantum chemistry has presently gained a high predictive power and serves as a potent source of information on structural organization of nonclassical compounds.

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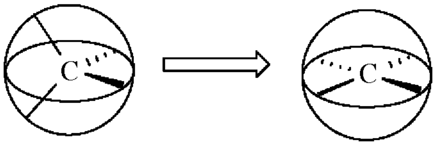
INTRODUCTION

Over the past decade the problem of nonclassical structures of organic and organometallic compounds has been highlighted in a fairly large number of reviews that summarized published data on all facets of research on molecules and ions with a nonstandard geometry and/or hypercoordinate carbon atom (nonclassical carbon) [1–10].

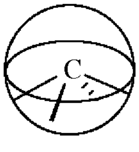
At present more and more research groups are being involved in studies on organic and organoelement systems with hypercoordinate main group elements. The enhanced interest in such systems has been stimulated, first, by the discovery of a principal solution of the problem of planar tetracoordinate carbon (PTC) and, second, by the vigorous progress of research into endofullerenes with various atoms and atomic groups in the fullerene cavity [11, 12]. Depending on the size of the cavity, the interaction of the central atom with fullerene surface atoms can be covalent through van der Waals in nature, and the central atom in a small-sized fullerene cavity can show capacity for hypercoordination.

We have not set ourselves the aim to cover in the present review the entire body of published data on nonclassical carbon. The review focuses in detail on fundamental works so that to represent the history of the origination of the concepts of nonclassical carbon, which gave impetus to systematic research into separate aspects of nonclassical carbon compounds, with the main emphasis put on evidence that has never been reviewed and summarized.

Classification of nonclassical carbon structural motifs starts with a description of configurations topologically differing from tetrahedral (configuration **1**), i.e. a configuration in which the four bonds all reside in a single semisphere. In the world's literature, the term "anti-van't Hoff–LeBel [13] tetracoordinate carbon cofigurations" is widely used, but we consider this term not fully appropriate. However, an antitetrahedral structure is, too, difficult to imagine. In



1 **2**



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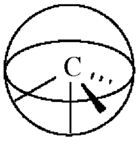

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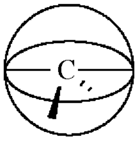

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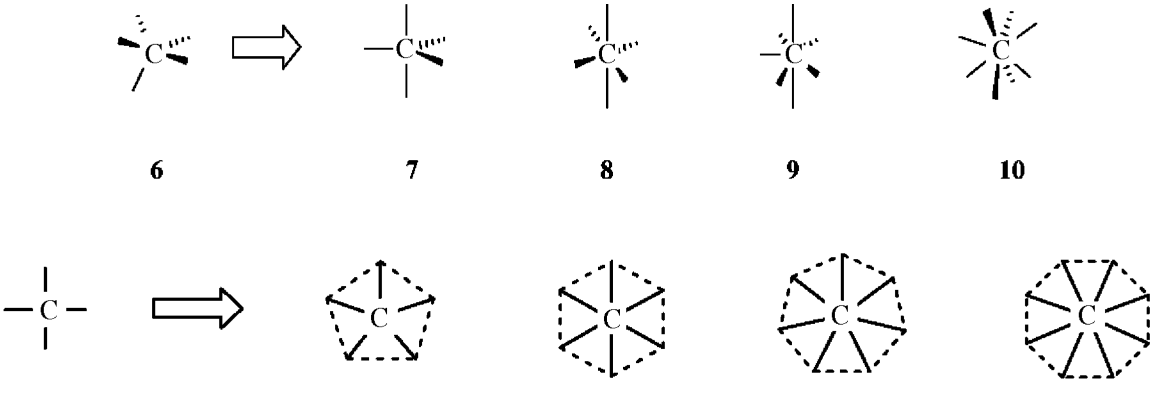
our opinion, all carbon configurations quantitatively differing from a tetracoordinate tetrahedral are more correct to define as nonclassical.

Nonclassical carbon configurations, in their turn, can be divided into nonclassical configurations of tetracoordinate carbon and hypercoordinate configurations. The nonclassical tetracoordinate configurations include planar (**2**), pyramidal (**3**), inverted or umbrella-type (**4**), and semiplanar (**5**). For the sake of brevity, in what follows we use the terms planar, pyramidal, inverted, and semiplanar carbon.

The nonclassical carbon configurations with more than four valence bonds and formed by four electron pairs include hypercoordinate carbon structures: penta- (**6, 7**), hexa- (**8**), hepta- (**9**), and octacoordinate (**10**) carbon centers.

Over the past years the concept of planar hypercoordinate carbon atom (structures **11—14**), developed from the concept of planar carbon, has exhibited a tremendous upgrowth (for the review of the problem of hypercoordinate planar carbon, see the paper of Gribanova et al. in this issue).


6 **7** **8** **9** **10**

2 **11** **12** **13** **14**

While the tetracoordinate carbon configurations topologically differing from tetrahedral configuration **1** are confined to simplexes **2**–**5**, octacoordinations like **10** and **14** in various compounds not nearly exhaust the list of possible carbon hypercoordinations. The question of what is the limiting carbon coordination in organic and organoelement compounds is still open.

Planar Tetracoordinate Carbon Atom

(Planar Carbon)

It is well known that it is a high rigidity of the tetrahedral configuration of the tetracoordinate carbon center in organic molecules that ensures existence and development of life on Earth. At the ab initio computational level, the theoretical explanation of the high stereochemical rigidity of the the tetrahedral configuration of the tetracoordinate carbon center in methane has first been advanced by Monkhorst in 1968 [14]. The referee has calculated the energy of the a planar D_{4h} configuration **2** of the methane molecule, as a possible transition state on the way of inversion (enantiomerization) of a tetrahedral T_d configuration **1**, involving no chemical bond cleavage. The simplest RHF/STO calculations with a minimum basis set showed that the energy gap between the T_d and D_{4h} configuration of methane is extremely large (250 kcal mol^{-1}). Modern precision calculations with very large basis sets result in more than halved gaps (up to ~110 kcal mol^{-1}) [1, 7]. However, the latter value still remains higher than or compare with the C—H dissociation energy in methane (~105 kcal mol^{-1}) or the CH_4®CH_2+H_2 dissociation energy (~110 kcal mol^{-1}) [15]. In 1970 Hoffmann, Alder, and Wilcox [16] suggested the reasons for the instability of a planar bond configuration of tetracoordinate carbon, based on an analysis of the correlation diagram of MOs of the tetrahedral and planar forms of methane (Fig. 1). As tetrahedral form T_d deforms into planar D_{4h}, one of the triply degenerate t_{1u} MOs sharply increases in energy and transforms into a nonbonding a_{2u} MO (carbon p_z AO) which accommodates two valence electrons; as a result, the four C–H bonds are provided by six, rather than eight electrons.

Hoffmann, Alder, and Wilcox [16] suggested a general strategy for stabilizing planar carbon in organic compounds, targeted at decreasing the energy

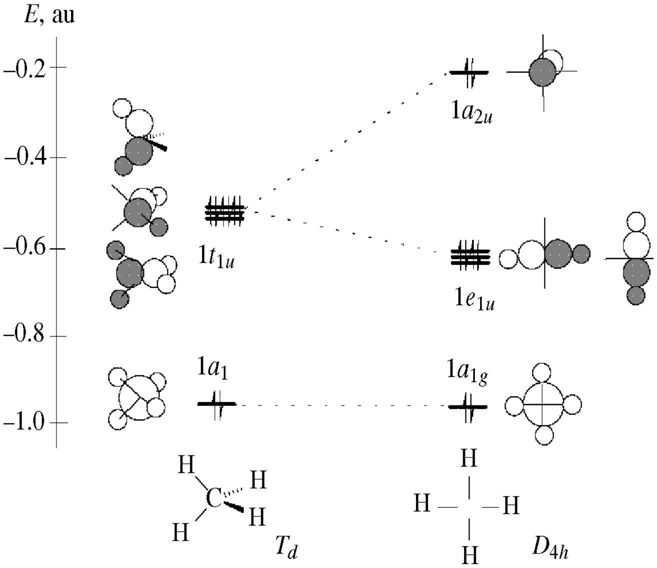
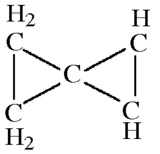


Fig. 1. Molecular orbital correlation diagram for tetrahedral T_d and square-planar D_{4h} configurations of methane.

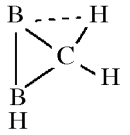
of the possible transition state of the enantiomerization reaction and on the formation of stable compounds under certain conditions. For the lone electron pair of the carbon atom ($1a_{2u}$) to be involved in chemical bonding. it should be delocalized over the perimeter of the ligands surrounding the carbon center. To this end, strong *p* acceptors should be introduced as substituents at the planar carbon center (first conditions), and powerful *s*-donor substituents should be introduce to increase the electron density on the four valence bonds (second condition). For further stabilization of the planar structure, it is desirable to incorporate the latter in an aromatic annulene ring (third condition). Later a new steric stabilization concept was suggested: To incorporate planar carbon in a strained frame, thus providing a mechanical preservation of the planar form (fourth condition).

Numerous theoretical and experimental data obtained over the past two decades gave conclusive evidence showing that a much diminished energy gap between the planar and tetrahedral (here and hereinafter, we generally refer to the tetrahedral topological form) structures with the four necessary stabilization conditions met provide the expected effect. The reviews [1–9] cover, quite comprehensively and in sufficient detail, both early theoretical and recent data for a wide range of organic, organoelement, and organometallic compounds, and, therefore, we do not need to review them anew. Here we will restrict ourselves by mentioning the most characteristic, in our opinion, compounds **15–27** [7—28] which not only can serve as objects for synthetic realization; in particular systems **20** have already been synthesized [21–24].

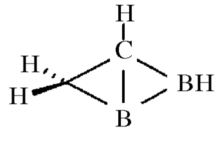
According to calculations, structures **15–27**



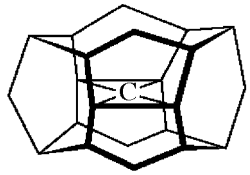
15 [7]



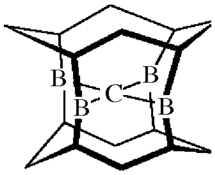
16 [7]



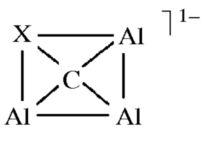
17 [7]



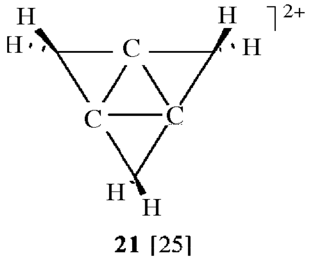
18 [18]



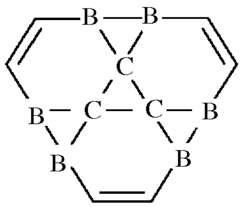
19 [19]



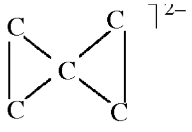
20 (X = Si, Ge) [20–24]



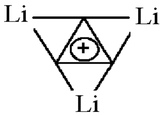
21 [25]



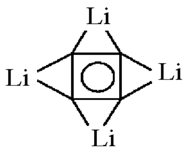
22 [26]



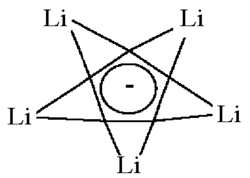
23 [27]



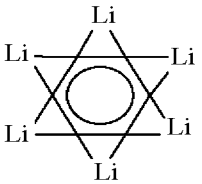
24 [28]



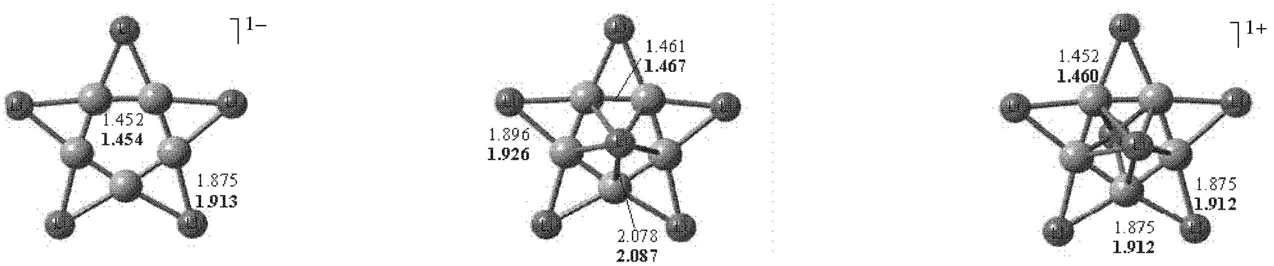
25 [28]



26 [28]



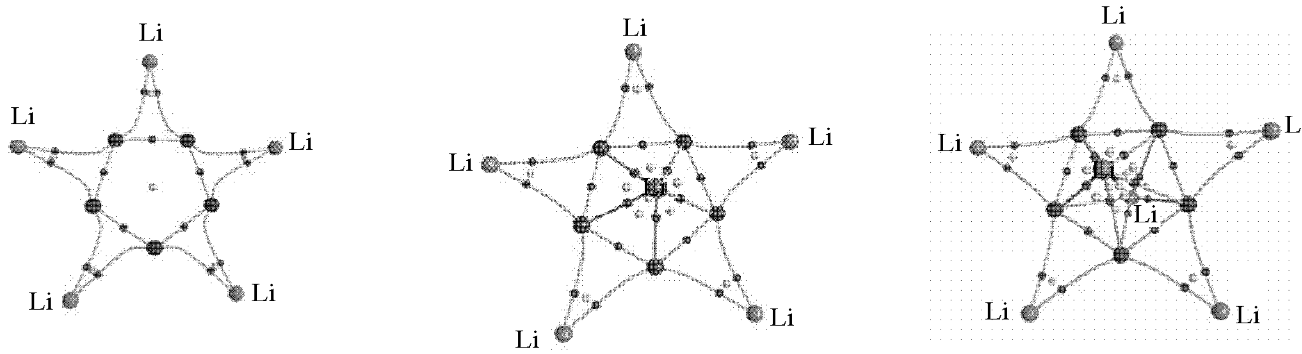
27 [28]



26, D_{5h}
$\omega_1 = 130$ (**119**) cm^{-1}

26a, C_{5v}
$\omega_1 = 136$ (**130**) cm^{-1}

26b, D_{5h}
$\omega_1 = 159$ (**158**) cm^{-1}

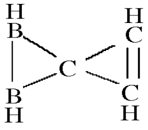


26, D_{5h} **26a**, C_{5v} **26b**, D_{5h}

Fig. 2. (Normal) B3LYP/6-31G** and (bold) MP2/6-31G** geometric characteristics (bond lengths) and lowest vibration frequencies for structures **26**. (Bottom) Molecular graphs for the same structures. Here and hereinafter, bond lengths are in Å.

correspond to minima on the potential energy surfaces (PES) and can be fairly stable compounds. Figure 2 depicts the structures of pentalithium cyclopentadienyl anion **26** and the corresponding molecular graphs [28].

Systems **28—31** [17, 26] which, like the above-mentioned structures correspond to minima on the PES and can serve not only as synthetic targets, but also as building blocks for further design on their basis of one-, two-, and three-dimensional polymeric or crystal structures, deserve special mentioning.



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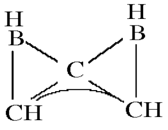

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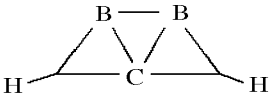

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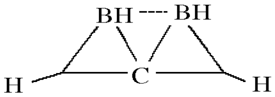
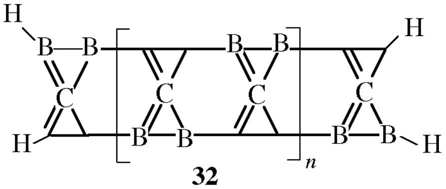
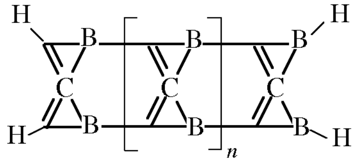


31

Monomers **28** and **29** can be used to construct regular polymeric tape structures **32** and **33** ($n = 0,1,2,3,\ldots$) containing, respectively, $2n+2$ or $n+2$ planar tetracoordinate carbon centers.

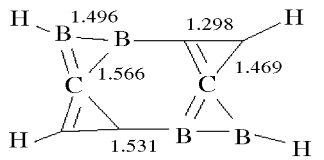


32



33

For structures **34–37** we give the B3LYP/6-31G** bond lengths in the planar nonclassical systems corresponding to minima on the PES [29], as well as the relative energies of the isomers. The most stable isomeric form is structure **35** formed of monomer **29** in the “head-to-tail” fashion.



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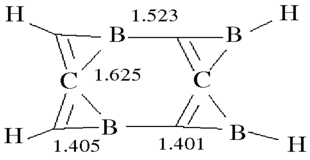

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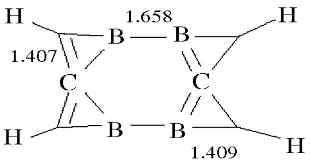

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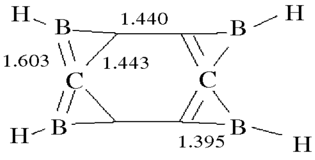
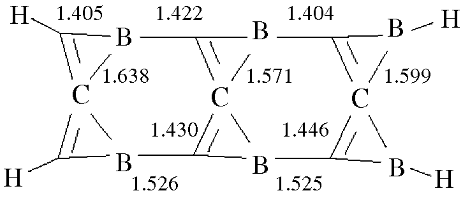


37

ΔE, kcal mol^{-1} 65.9 0 6.1 24.5

The stability of planar systems **34**–**37** is provided by the aromaticity not only of each of its three-membered ring, but also of the system as a whole. It can be expected that collective aromaticity effects will favor enhanced stability of extended systems **32** and **33,** as their chain length (*n*) will increase. Such systems can be exemplified by trimer **38** and tetramer **39,** constructed of monomer **29** in the "head-to-tail" fashion [29] (B3LYP/6-31G** bond lengths are given).



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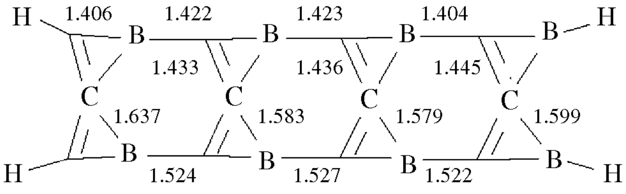

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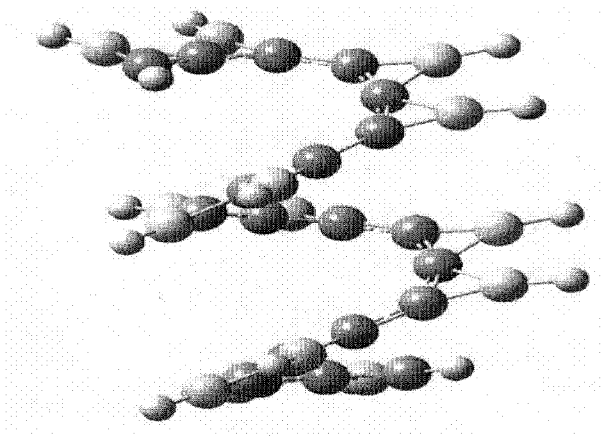
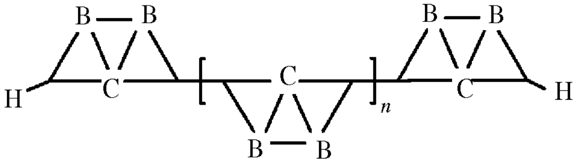


Fig. 3. Helical structure of polymer **41** (B3LYP/6-31G** calculation).

Monomeric units **30** and **31** can also be used to construct linear polymeric systems **40** and **41**, which can be considered as polyynes doped with strongly electron-acceptor ligands.



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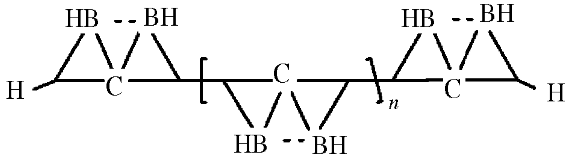
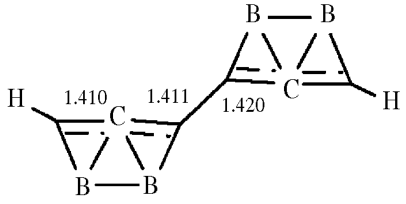


41

Figure 3 shows the structure of a spiral *cis* conformer of system **41**, $n = 6$.

Stable dimer **42** and trimer **43** constructed of monomer **30** feature equal C–C bond lengths (B3LYP/6-31G**), which implies strong conjugation along the polymeric chain.



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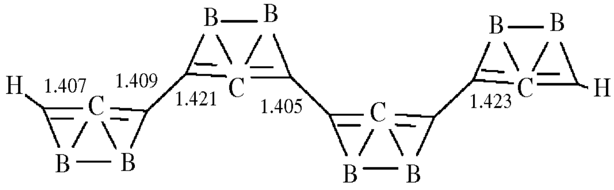
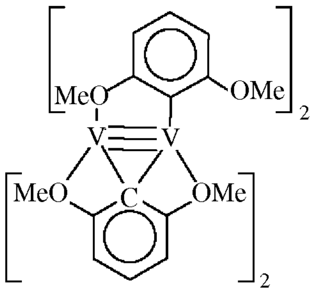


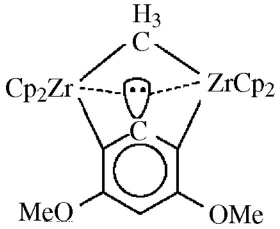
43

As the first experimental observation of a PTC compound we can mention an X-ray study of divanadium complex **44** [30].

In this and structurally similar diciirconocene complex **45,** the PTC configuration is realized by means of a multicenter bond formed by the sp^2 orbital of the phenyl anion, like is the case in the C_{2v} form of methane (see the reviews [3, 8, 9]). An example of compounds belonging to the abundant class of bimetallic complexes in which planar tetracoordinate carbon atoms form bonds with both transition and main group metal centers, is provided by complex **46** [31]. Almost planar carbon centers were found in associates of 2-lithiocyclopropene derivatives, such as **47** [32], and in a series of carbides, such as $Ca_4Ni_3C_5$ which has been thoroughly studies both experimentally [33] and theoretically [34].



44



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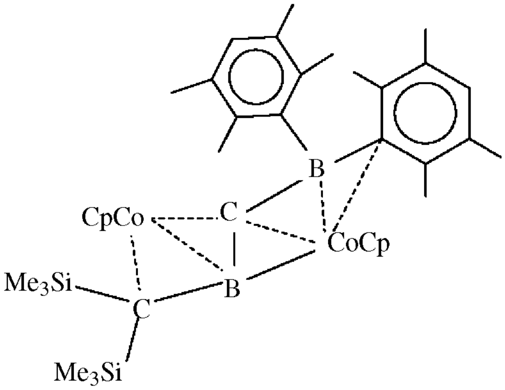

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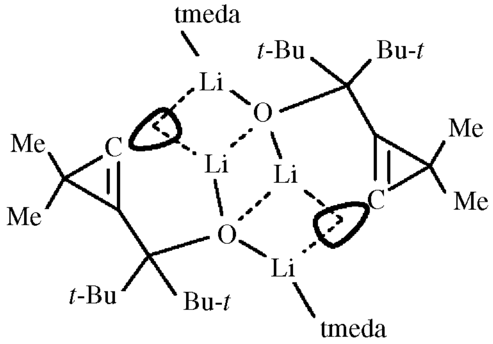


47

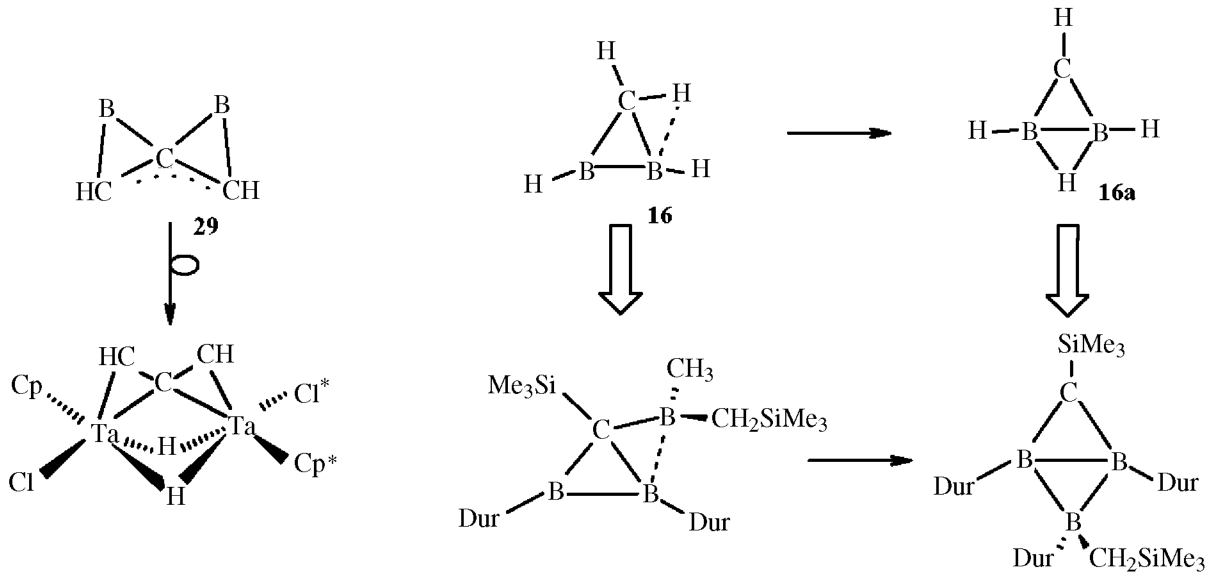
(Cp = cyclopentadienyl, tmeda = tetramethylethylenediamine).

Evidence for an analogous type of bonding of planar carbon in organoboron and corresponding organometallic compounds can be obtained from a comparison of system **29** [17] and a fairly recently иsynthesized ditantalum complex **48** [35].

The stability of pentaatomic anionic clusters **20** (X = Si, Ge) was first proved by ab initio calculations [20] and then this system was fixed experimentally in the gas phase and characterized by means of anion photoelectron spectroscopy [21–24]. Pentaatomic neutral radicals **20** (X = Si) can serve as a good basis structure for designing materials for spintronics [36]. Probably, the first example of a synthesized organoboron system with a planar carbon center is *C*-borylboracyclopropane **49** [37] which is a substituted analog of parent borane **16** [7].

The presence of a planar carbon center in **49** was confirmed by NMR spectroscopy [37]. Surprisingly, like borane **16** which, according to calculations in [7], undergoes low-barrier isomerization to **16a**, system **49** undergoes fast low-barrier isomerization to **50**.

The above-presented data serve as a good illustration for the fruitfulness of the concept of electronic stabilization of planar tetracoordinate



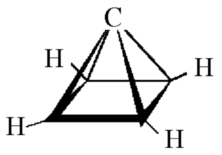
48 **49** **50**

Dur = 2,3,5,6-tetramethylphenyl.

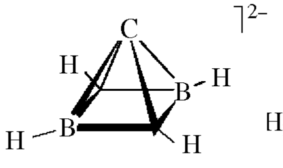
carbon, suggested by Hoffmann, Alder, and Wilcox, and evidences in fact the development of a new field: the chemistry of planar carbon.

Pyramidal Carbon

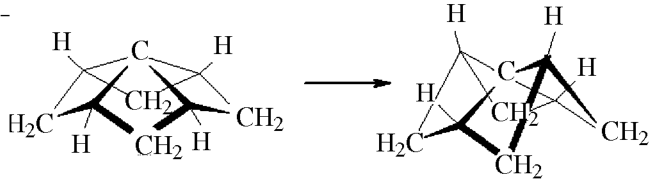
The concept of planar carbon is based on the idea of structural stabilization of the transition state of the inversion of tetrahedral form **1**, which probably passes through planar form **2**. However, already previous semiempirical and ab initio (RHF/DZ) calculations [1, 38] of the methane stereoisomerization path under the condition that the four C–H bonds remain equivalent over the whole reaction path showed that pyramidal structure **3** is preferred by energy over square-planar structure **2**. We were the first to analyze the stereoelectronic conditions for stabilization of pyramidal carbon in organic compounds and gave the first examples of systems **51**–**53** and other systems which can contain a pyramidal nonclassical form of carbon [39—41]. Thus the concept of pyramidal carbon was developed. Systems **51** and **52** feature a fairly high thermodynamic stability, whereas pyramidal fenestrane **53** readily, with a low activation barrier, isomerizes into tetrahedral isomer **54** [1].



51



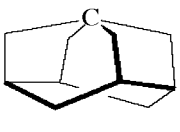
52



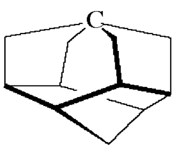
53 **54**

Like with planar carbon systems, there are two principal strategies for constructing compounds containing pyramidal carbon: electronic stabilization and steric enforcement of the pyramidal configuration of the carbon center. These two principles were realized in the design of systems **55**–**63** which are interesting for experimentation [1, 26, 42–46].

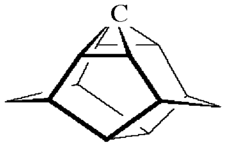
Surprisingly, pyramidal structure **60** almost compares in energy with tetrahedral form **61.** Forms **60** and **61** are separated by a low energy barrier, which implies a high degree of stereochemical nonrigidity of these two structures. Tetraborafenestrane **63,** unlike fenestrane **53** which is much more stable as tetrahedron **54**, is stable as pyramid **63** only, whereas



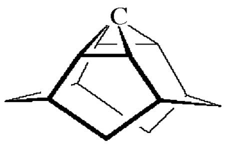
55 C_2



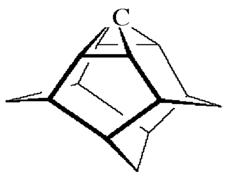
56 C_2



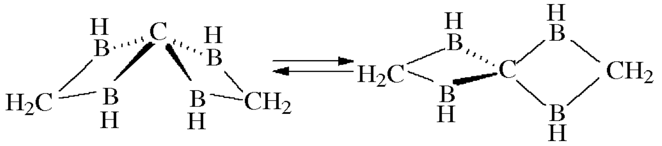
57 C_2



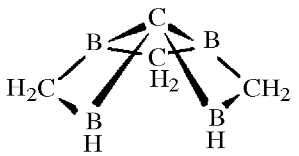
58 C_2



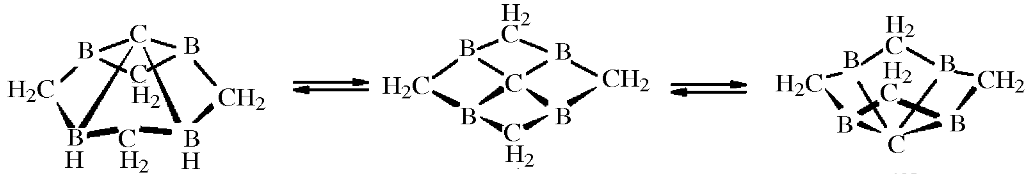
59 C_2



60 **61**



62 C_2



63a **64** **63b**

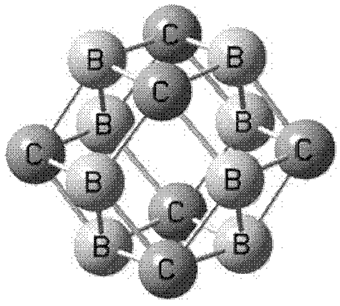
planar structure **64** is an intermediate in the inversion reaction **63a** ↔ **64** ↔ **63b**. Tetrahedral form **61** is not at all a stationary point on the corresponding PPS.

According to quantum-chemical calculations at different levels of theory, the apical carbon atom in all pyramidal carbon compounds bears a large negative charge, and the highest occupied molecular orbital is almost completely localized on this center, being, in essence, a lone-pair orbital. These circumstances are responsible for that these molecules have quite low ionization energies (4.5–5.0 eV) which compare with the ionization potentials of light alkali metals, as well as for the extremely high basicity of pyramidal carbon compounds. The calculated proton affinities of organic compounds with a pyramidal carbon center are the highest on record, even compared to those characteristic of proton sponges (see table).

Of interest is a fairly stable boron carbon cluster **65** whose carbon atoms all, according to B3LYP/6-311+G** calculations, have a pyramidal configuration of their four fairly short B–C bonds (~1.6 Å).

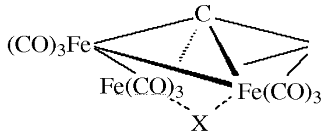
Gas-phase proton affinities (298 K) for pyramidal carbon structures

Compound	Calculation method	Proton affinity, kcal mol^{-1}	Reference
51 Pyramidane	CCD/6-311+G**	236.8	[45]
	HF/3-21G	253.3	cf. ref. [82] in [1]
	MP2/6-311+G**//MP2/6-31G*	230.6	[43]
55	MP2/6-311+G**//MP2/6-31G*	269.3	[43]
57	The same	280.1	[43]
58	The same	280.8	[43]
59	The same	281.8	[43]
Tetramethyl-**58**	The same	285.1	[43]
1.8-Bis(dimethylamino)naphthalene (proton sponge)	MP2/6-311+G**//HF/6-31G*	245.5	cf. ref. [102] in [1]
	Experiment	245.7	cf. ref. [103] in [1]

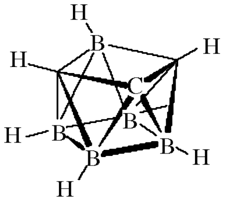


65

Of experimentally detected pyramidal carbon systems we would like to mention iron carbide cluster **66** and carborane **67** which is suggested as a stable $C_3B_5H_7$ system (cf. references in [1]).



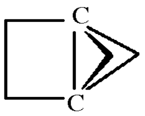
66



67

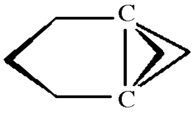
Inverted (Unmbrella) Carbon

The concept of inverted tetracoordinate carbon atom in organic compounds was advanced by Wiberg [47, 48] in 1968 on the basis of an analysis of the geometric structure of experimentally known or theoretically explored propellanes **68–73** and 1,3-dehydroadamantane **74** [49].



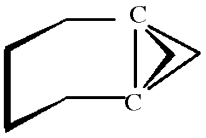
68

[2.1.1]propellane



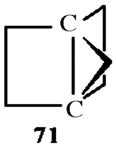
69

[3.1.1] propellane



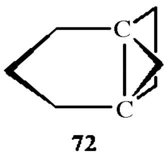
70

[4.1.1] propellane



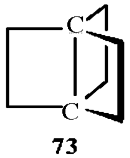
71

[2.2.1] propellane



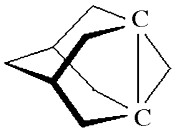
72

[3.2.1] propellane



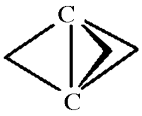
73

[2.2.2] propellane



74

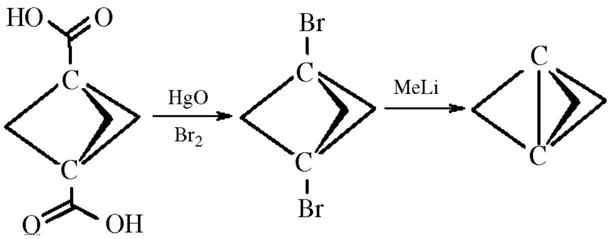
1,3-dehydroadamantane



75

[1.1.1] propellane

In the same works, the concept of inverted tetracoordinate carbon structure **4** as a nonclassical system of four bonds located on one side of a single plane was put forward. Almost simultaneously Wiberg formulated the task of synthesizing the parent, still unknown [1.1.1]propellane **75.** The first molecular mechanics and ab initio calculations showed that this structure is highly strained and instable. Manu leading chemists cast doubt in the feasibility of synthesis of such a system. However, Wiberg confided in the results of high-level ab initio calculations that gave evidence for the stability of this compound. In 1982 Wiberg and Walker [50] triumphantly announced the successful synthesis of [1.1.1]propellane from 1,3-dibromo-bicyclo [1.1.1]propellane by the following scheme:

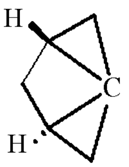


Thus, the theoretically predicted structure **75** has been realized in a real compound. A more detailed consideration of the concept of inverted carbon is given in the reviews [47, 48].

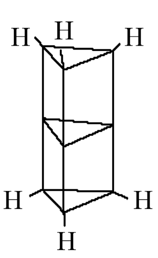
Semiplanar Carbon

The concept of semiplanar carbon was advanced in 1996 [51], and all stereoelectronic effects favoring such configuration were considered in [1]. Here we dwell only on recent works.

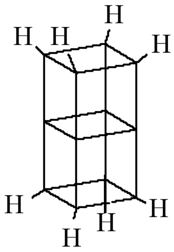
The semiplanar carbon configuration (bisphenoidal or "butterfly") is observed in certain organometallic compounds, as well as the theoretically predicted tricyclo[2.1.0.$0^{1,3}$]hexane [1, 8, 52] (**76**).



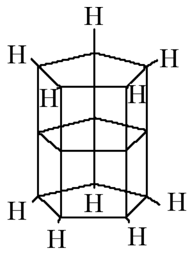
76 [52]



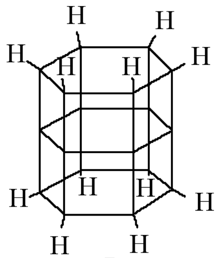
77, D_3



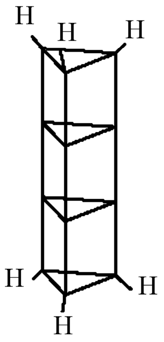
78, D_4



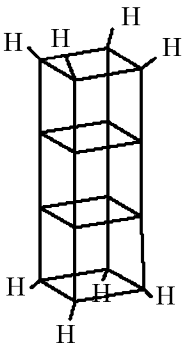
79, D_{5h}



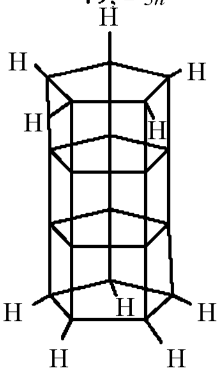
80, D_{6h}



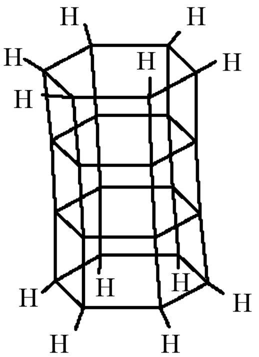
81, D_{3h}



82. D_{4h}



83. D_{5h}



84, D_{6h}

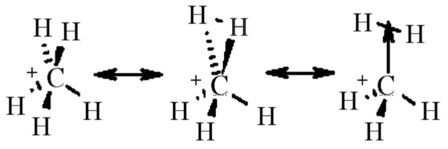
The most spectacular representatives of organic compounds containing several semiplanar carbon centers are polyprismanes **77**–**84** [53, 54].

The angle between the apical bonds of semiplanar carbon deviate from 180° by no more than 10°. Furthermore, a unique effect of negative Poisson's ratio (auxetics effect) [55] was discovered, i.e. polyprismane, when stretched along the C_n symmetry axis, expands perpendicularly to the applied force. whereas compression makes the system to compress. At the molecular level, this effect was discovered for the first time.

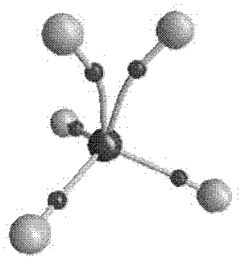
Pentacoordinate Carbon

The parent pentacoordinate carbon system is the methonium ion, specifically protonated methane **85** which was first detected by Talrose and Lyubomova in 1952 by mass spectrometry in the gas phase [56, 57], and 10 years later Olah and co-workers [58–60] detected this ion in superacid media by means of NMR spectroscopy. Note that the methonium ion is of great importance for astrophysics: Its microwave spectrum serves to detect the presence of methane in galactic clouds. This simplest protonated hydrocarbon is a prototype intermediate structure arising in ion-molecular interactions [61], and, what is the most important, in reactions of saturated hydrocarbons with electrophilic agents [10, 60–65].

The cation CH_5^+ is the most stable in the C_s conformation, and it is often considered as π complex **85a** of the CH_3^+ cation with the H_2 molecule [65–69]. However, as seen from Bader molecular graph **85c** [70] of the CH_5^+ cation, the central carbon atom is linked by bond paths with all the hydrogen atoms; at the same time, there is no bond path between two remote hydrogen atoms, which is necessary and sufficient evidence for the lack of a chemical bond between them.



85 **85a** **85b**

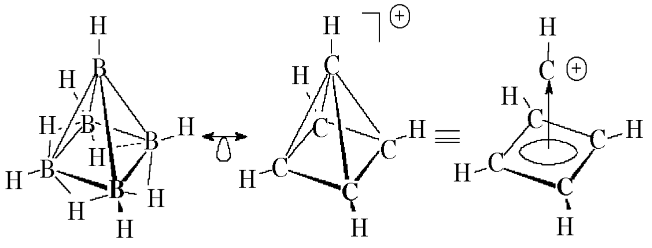


85c

Cation **85** is a highly stereochemically nonrigid system. It can undergo simultaneously two types of quite a low-barrier (<1 kcal mol^{-1}) rearrangements: rotation of remote hydrogen atoms about "the C_{3v} symmetry axis" of the methyl group and "mixing" of all the hydrogen atoms with each other. This means that the proton "mixing" in the methonium ion occurs as a barrierless process even at 0 K.

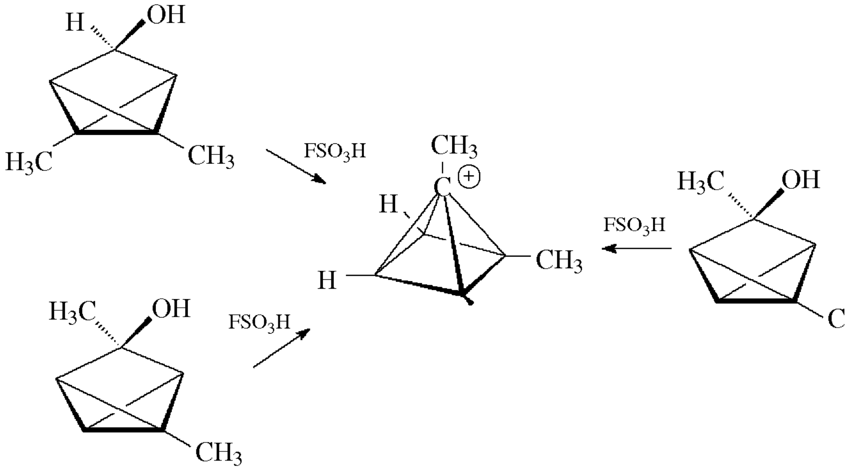
In this connection a question was raised as to whether CH_5^+ possesses a concrete structure at all. The methonium cation was suggested to be considered as an "intramolecular liquid" and its structure to be described by statistical functions rather than atomic coordinates (the paper concerning the structure of the methonium cation [66] is glaringly entitled "Cheshire Cat Smiles"). A powerful experimental evidence for the exceptionally high stereochemical nonrigidity (fluctionality) of the methonium cation was provided by Marx and Savin [67], who reported the observation (eventually, after long-standing wasted effort) of a high-resolution IR spectrum of this cation in a matrix of a small number (n = 1–6) of hydrogen molecules whose presence is necessary to retard the above-mentioned exchange processes. This spectrum contains about 900 spectral lines in the range 2770–3150 cm^{-1} and is much more complex than expected for a structure belonging to a certain definite symmetry type.

A huge body of experimental and theoretical data on pentacoordinate carvbon is presented in the monograph [73] and review [1], and, therefore, here we will dwell on selected most illustrative examples. Cation **86** is a spectacular representative of a purely hydrocarbon pentacoordinate carbon system. The possibility of existence of a stable pyramidal cation **86** with a pentacoordinate apical carbon atom, as an isoelectronic and isostructural analog of borane **87,** was first suggested by Williams in 1971 [74].



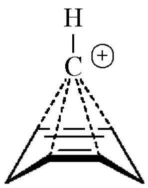
87 **86** **86a**

In 1972, two works were published almost simultaneously [75, 76], the first of which theoretically substantiated, based on an analysis of orbital interactions and extended Huckel computations, stability of cation **86**, and the other reported an NMR observation of the first derivative of pyramidal $(CH)_5^+$, prepared by the following scheme:



More recently, the detection of bishomo derivatives and other $(CH)_5^+$ analogs **88–93** in superacid media was reported [1, 77–79].

Let us now make a slight digression and touch upon the problem of the priority in studying the structures in question. On one of the meeting with the authors of the



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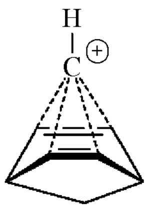

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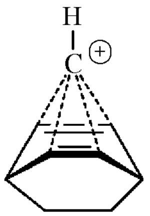

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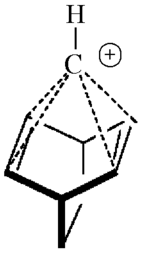

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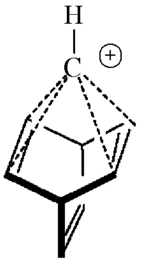

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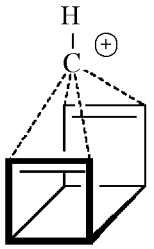

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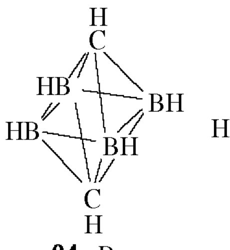
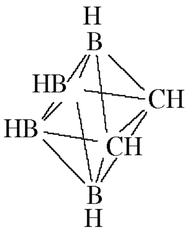
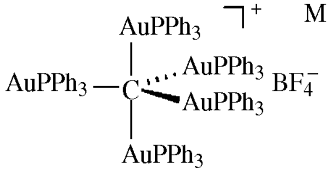


94, D_{4h}



95, C_{2v}



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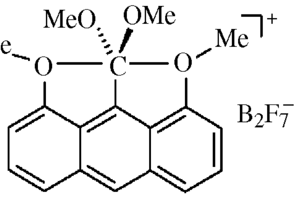


97

present review in late 1980s Schleyer told that the pyramidal system $C(CH)_4$ (pyramidane **51**) as a structure corresponding to a minimum on the PES, as well as its corresponding acid **86**, were also computed by his co-workers, but they did not attach significance to these results, decided to leave them unpublished and put away for good; as a result, pyramidane was first reported by Corey as late as 1982 [80]. However, it is the latter work that is considered by certain authors [81] as a pioneering on pyramidane. Generally speaking, scientific priority is not infrequently an oversensitive issue. As one of the recent examples we can mention here a dispute between two Noble Prize Winners for Chemistry Hoffmann and Corey [82–84]. The latter [81, 82], not referring to concrete publications, fairly aggressively states that the idea of conservation of orbital symmetry in pericyclic reactions belongs to him rather than to Woodward and Hoffmann [82–84].

Of well experimentally explored pentacoordinate carbon systems we can mention here 1,6- and 1,2-*closo*-carboranes **94** and **95** (cf. references in [1, 85]), as well as pentaaurated methonium ion **96** and salt **97** [86–88].

The C—O bond length in **97** is 2.44 Å, and this value is the largest of known covalent C–O bond lengths in all experimentally studied organic compounds on record.

The possibility of stabilization of a “frozen-transition-state” trigonal-bipyramidal pentacoordinate carbon in a compound like **97** was pointed out by Martin as far back as early 1980s [89, 90].

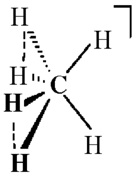
Hexa-, Hepta-, Octa- and Higher Carbon Coordinations

Stereoelectronic conditions for the realization of hexa- and higher carbon coodinations in organic and organoelement compounds are fairly comprehensively summarized in the reviews [1–3, 10]. Therefore, here we will only dwell on characteristic examples of higher coordinate carbon compounds and on the most recent publications.

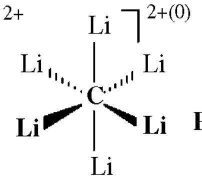
The simplest example of a hexacoordinate carbon system is provided by dirotonated methane CH_6^{2+} (structure **98)** which, according to ab initio calculations [91, 92], is stable in the C_{2v} form.

Like methonuim ion **85**, dication **98** is a stereochemically nonrigid structure: The energy barrier of the C–H hydrogen redistribution reaction in the gas phase is as low as 4.3 kcal mol^{-1} [93]. The unfavorable octahedral configuration of CH_6^{2+} is stabilized in its lithium **99** and organometallic derivatives like **100** [92–95]. Hexaaurated dication **100** was isolated preparatively as tetrafluoroborate and thoroughly studied experimentally [86].

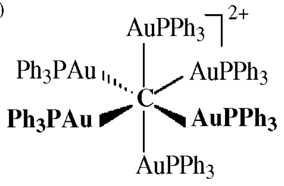
An outstanding example of a hexacoordinate carbon system is the hexamethylated pyramidal dication **101** prepared by Hogeween and Kwant in



98, C_{2v}



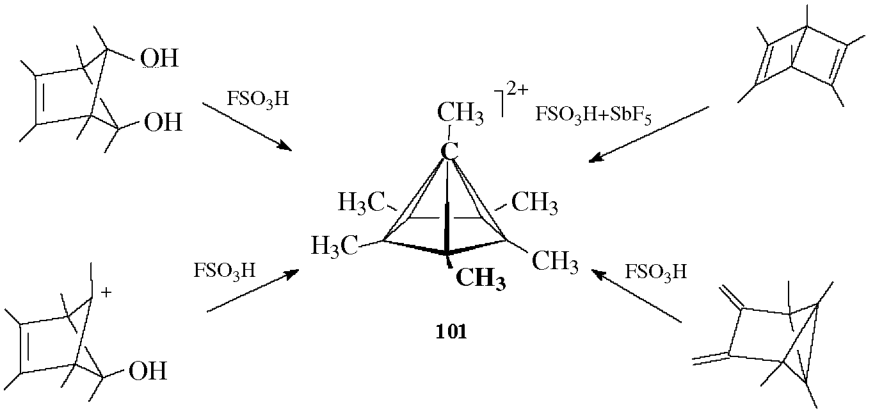
99, O_h



100

1973 (cf. review [96]) in superacid media from various precursors.

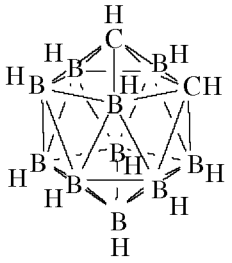
It is important to mention here that simultaneously derivatives of pyramidal dication **101** were detected at the laboratory of Acad. V.A. Koptyug in Novosibirsk, but the researcher found these data so surprising that decided not report before more thorough measurements would be made [97].



101

Carbon hexacoordination is realized in carboranes **102**, **103** and carbide clusters like **104** whose stability is provided by multicenter bonding.

We have fairly recently [98, 99] suggested new carcass hexacoordinate carbon systems **105** and **106**. These systems can also be used as building blocks for constructing one-dimensional extended structures containing several hexacoordinate centers.



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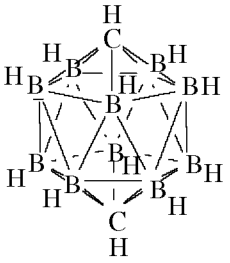

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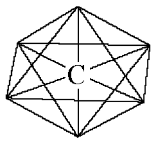
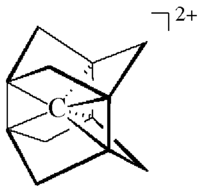


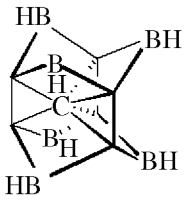
104

$CRu_6(CO)_{17}$,

$CFe_6(CO)_6^{2-}$



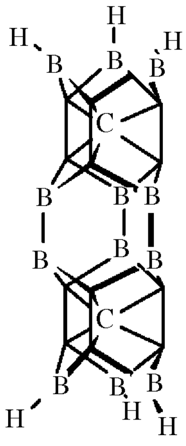
105



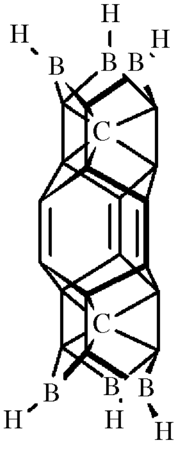
106

As shown by B3LYP/6-31G** DFT calculations [100], nonclassical systems **107–110** are fairly stable.

It is important to note that system **107** is stable in its ground $^3A_2''$ state which is lower than the singlet $^1A_1'$ state by 13.3 kcal mol^{-1}. At the same time, systems **108**, **109,** and **110** prefer the singlet state. There almost no structural differences in the triplet and singlet states of system **107**: Their bond lengths differ by no more than



107



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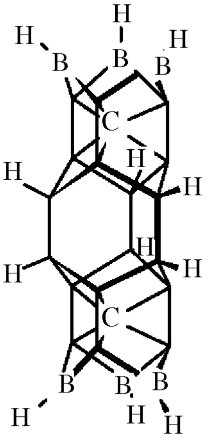

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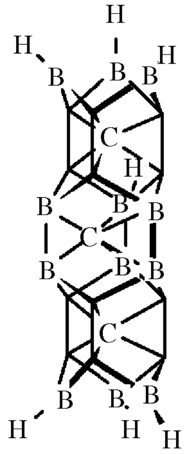
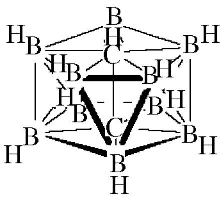


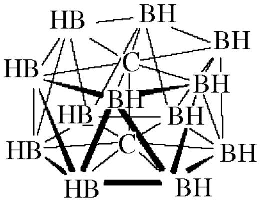
110

0.005 Å. The C_{end}–C bond lengths between the endohedral and carcass carbon atoms in systems **107**–**110** fall within the range characteristic of standard single C–C bond lengths in saturated hydrocarbons (1.54–1.57 Å). Therewith, the C_{end}–C bond lengths in the above systems gradually shorten compared to the respective bond length in monomer **106** (1.579 Å [98]), except for system **110** with three endohedral hexacoordinate centers, whose C_{end}–C bonds are slightly longer.

Interesting carborane systems with hexa- and heptacoordinate carbon atoms were constructed by Schleyer and co-workers [101] by means of B3LYP/6-311+G** calculations. The apical carbon atoms in carboranes **111** and **112** are bonded not only with their surrounding boron atoms, but also have an axial C–C bond.



111



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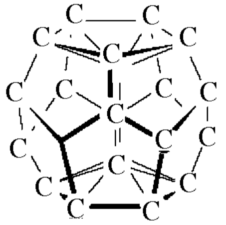
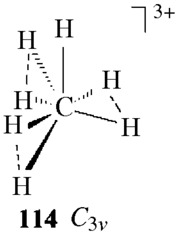


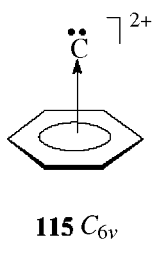
113 $C_2@C_{20}$

According to B3LYP/6-311+G** calculations [102], axial carbon chains are also contained in endofullerenes $C_2@C_{20}$ **113**, $C_2@C_{24}$, $C_4@C_{30}$, $C_2@C_{36}$, and other systems. Terminal atoms in the inner carbon chain are hexacoordinate and have fairly short C–C bonds.

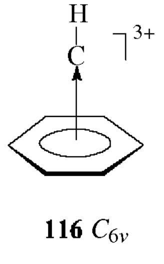
The simlest stable heptacoordinate carbon structure is triprotonated methane **114** whose eight valence electrons are distributed between three 3*c*–2*e* C–H_2 bonds and one 2*c*-2*e* C–H bond [92]. As follows from QCISD(T)/6-311G** calculations, the positive charge in **114** is all localized on hydrogen atoms (each bearing a charge of about +0.6 e), whereas carbon is charged negatively (q_C–1.27 e). Thus, the stability of this triply charged ion is provided mostly by electrostatic forces. Electrostatic interactions, too, contribute much in the stabilization of pyramidal cations with a six-membered basal ring. According to MP2/6-311+G** and B3LYP/6-311+G** calculations [103], di- and trications **115** and **116** whose apical carbon atoms are coordinated within, respectively, six and seven other centers, correspond, in compliance with the eight-electron rule, to fairly deep minima of the PES.



114 C_{3v}

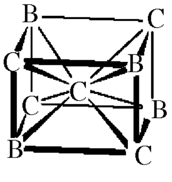


115 C_{6v}

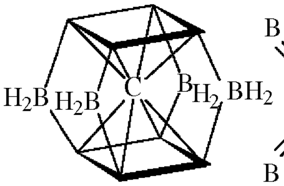


116 C_{6v}

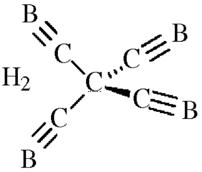
The fact that triprotonated methane **114** has only one 2*c*–2*e* C—H bond opens one more possibility for replacing this bond by a three-center 3*c*-2*e* C–H_2 bond, thus approaching the tetracation CH_8^{4+}. However, when the charge is +4, the Coulomb repulsion of hydrogen atoms which accommodate all positive charge becomes the predominating destabilizing factor. It was shown at the MP2/6-31G** level that CH_8^{4+} is an unstable ion, and an energy minimum was found for no one of the possible structure [62, 90]. At the same time, according to CCSD(T)/6-311+G** and B3LYP/6-311+G** calculations, carbon octacoordination is realized in boron–carbon systems **117** and **118** [104, 105].



117, T_d



118, D_{4h}



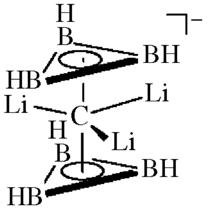
119, T_d

Bader topological analysis showed that the central carbon atom in systems **117** and **118** is octacoordinate and linked with all the eight peripheral atoms by single bonds whose lengths only slightly differ from standard values.

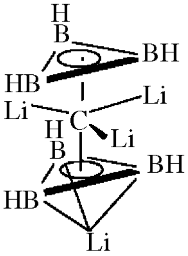
An interesting feature of these systems is an unusual stereochemistry of the ligand carcass formed of boron and carbon atoms and having, like two central carbon atoms in [1.1.1]propellane **75,** an umbrella bond configuration. The central octacoordinate carbon atoms in **117** and **118** bear a large positive Mulliken charge (~1.3 e). A possible classical isomer **119** of the $C(CB)_4$ molecule with a tetrahedral central carbon atom is, according to calculations, unstable and corresponds to a saddle point on the PES.

A ninecoordinate carbon atom, as follows from B3LYP/6-311+G** calculations and Bader analysis, is present in sandwich compounds **120** and **121** [2, 106–108].

The above-considered structures not nearly exhaust the list of theoretically explored nonclassical molecules. At present this field is progressing avalanche-like, and only over last months of 2007 several works concerning different facets of stability and structure of nonclassical systems have been published [10, 109, 110].



120, D_{3h}



121, C_s

CONCLUSIONS

Advances in theoretical simulation and huge progress in the development of computational capacities of modern quantum chemistry have it made quite reasonable to set such goals in searching for new structures, that had fairly recently been repudiated traditionally thinking researches with the reasoning of type “this may not be the case because this may never be the case”. At the same time, the experimental effort initiated by theoretical analysis has already culminated in the observation and preparation of a wide range of new nonclassical organic compounds. The theoretical search for such compounds is presently targeted at revealing stabilization factors and exploring the unusual dynamics and poperties of such molecules and ions in which the ligand environment of the carbon atom contains up to eight centers in a randomly specified spatial orientation. Such structural motifs are of considerable interest in terms of the design of new high-performance materials with unusual properties, and the progress of technics, especially of superlow-temperature laser deposition methods, gives good grounds to believe that theoretical predictions will be verified by experiment. It is not excluded that the situation in this field resembles the history of fullerenes.

The term “nonclassical compound” arose 50 years ago, when first examples of such structures had become reknown, and, therewith, the term itself was introduced to distinguish exceptions from usual rules. Seemingly, exceptions are now becoming impossible to distinguish from rules, and G. Olah, awarded the Noble Prise (1994) for his contribution in this field, believes that the division of structures into classical and nonclassical will gradually disappear from the language and practice of chemists as they will be gaining a deeper understanding of general principles of chemical bonding.

ACKNOWLEDGMENTS

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