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Theoretical Design of Planar Systems with Hypercoordinate *p* Elements of the Second Period in a Nonmetallic Environment

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Abstract—Theoretical approaches to stabilization and design of nonclassical compounds containing *p* elements of the second period (B, C, N, O, F) in a nonmetallic environment are considered. Structural diversity of such systems is demonstrated, and influence of steric and electronic factors on their stability is considered.

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INTRODUCTION

Since the mid-2000s accumulation of experimental and theoretical evidence for the existence of compounds with a nonstandard stoichiometry and an unusual coordination of the central atom, viz. hypercoordination, has commenced [1]. The structure of such nonclassical compounds does not fit into the concept of the tetrahedral carbon atom, suggested by Van't Hoff and Le Bel in 1874 and forming the basis of classical structural theory. The first theoretical challenge to the basic theoretical concept of tetrahedral tetracoordinate carbon was thrown down about 40 years ago, when R. Hoffmann, R. Alder, and K. Wilcox revealed principal factors favoring stabilization of systems with a planar coordination of bonds of tetracoordinate carbon (planar плоский tetracoordinate carbon) [2, 3], which gave rise to a splash in theoretical and experimental research into the structure and properties of nonclassical structures [1, 4–15]. These works and general evolution of concepts of nonclassical structures containing a planar tetracoordinate carbon atom are analyzed in another review in this issue (R.M. Minyaev and V.I. Minkin "Nonclassical Carbon: From Theory to Experiment").

The search for systems with a planar tetracoordinate carbon atom has fairly long focused on organometallic compounds, and the probability that planar carbon can be stabilized in a nonmetallic environment was considered to be low. The very fact that Siebert and Gunale in their review [10] published 30 years later the principles of stereoelectronic stabilization had been set up [2], mentioned unsuccessful attempts to detect planar carbon surrounded by boron-containing ligands is illustrative. Compounds in which planar tetracoordinate carbon and other main group atoms are stabilized in boron environment could only be detected in the past decade. Now it is boron-containing substituents that are considered as an exceptionally effective ligand environment for stabilizing planar hypercoordinate entities. The present review considers the principal approaches to forming planar hypercoordination[1] of *p* elements of the second period in a boron, as well as another nonmetallic environment.

Planar Tetracoordinate Carbon in Hydride Derivatives

As follows from the MO analysis of the electronic structure of methane, the instability of a planar molecular form is associated with destabilization of the HOMO formed by an unhybridized p_z orbital of carbon. Consequently, a planar carbon center is the

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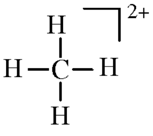
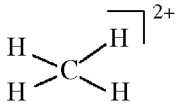
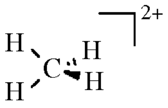
[1] Including carbon tetracoordination which can be characterized as planar hypercoordination.

most facile to form by oxidation of methane to the dication CH_4^{2+}, thus removing the destabilizing electron pair. Actually, according to ab initio and DFT calculations, the methane dication is stable in the planar form [16, 17]. As follows from B3LYP/6-311+G** calculations [17], the global minimum on the potential energy surface (PES) of the dication CH_4^{2+} belongs to structure **1** of D_{4h} symmetry. The other planar conformation **2** of C_{2v} symmetry corresponds to a local minimum and is less favored by as little as 1.3 kcal mol^{-1}. Tetragonal form **3,** too, corresponds to a minimum on the PES, but this structure is 56 kcal mol^{-1} less stable than **1**. High-level ab initio calculations [16] gave evidence in favor of a planar dication structure but inverted the relative stability of forms **1** and **2**. The stability of CH_4^{2+} in the gas phase was conformed by mass spectrometry [18, 19].

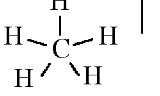

1, D_{4h}

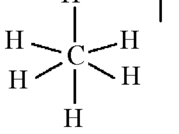

2, C_{4v}

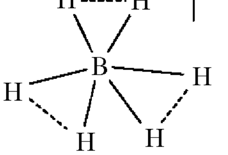

3, D_{2d}

The planar configuration is much stabilized even by partial oxidation of methane. As follows from DFT B3LYP/6-311+G** calculations, the radical cation $CH_4^{+\cdot}$ detected by mass spectrometry [1–19] is stable in the tetragonal form of D_{2d} symmetry [16]. However, the planar structure of D_{4h} symmetry is destabilized by as little as 17 kcal mol^{-1} than the CH_4 molecule (~150 kcal mol^{-1}).

Protonation of dication **1** gives rise to the trication CH_5^{3+} with a sextet of electrons around the carbon atom, which, too, is stabilized in planar form **4** of D_{5h} symmetry [20]. According to QCISD(T)/6-311G** calculations, C–H bonds in this electron-deficient system are much elongated (1.317 Å), and the CH bond order is as small as 0.56. The dissociation of **4** into methane dication and proton is a highly exothermic (275 kcal mol^{-1}) process with an activation barrier of 0.01 kcal mol^{-1}. This makes impossible experimental detection of the CH_5^{3+} particle which should undergo spontaneous decomposition in statu nascendi [20].


4, D_{5h}


5


6, D_3

Six-electron tetracation **5** cannot exist by electrostatic reasons (at the charge +4 the Coulomb repulsion of hydrogen atoms which accommodate the whole positive charge is the prevailing destabilizing factor), but is isoelectronic boron analog **6**, according to QCISD(T)/6-311G** results, is structurally stable and has a flattened D_3 configuration [20].

Planar Tetracoordinate Carbon in Polycyclic Systems

The principal strategy of stabilization of the planar configuration of carbon bonds was based on introduction of π-acceptor and σ-donor substituents to provide delocalization of the lone electron pair of planar carbon and compensation of the electron deficiency of σ bonds in the planar structure [2, 21]. Later a “sterical” or “mechanical” approach was suggested, involving steric compulsion of the carbon center to adopt the planar configuration, by its incorporation into small strained rings or into a rigid 3D frame [21].

According to our results, an optimal approach to stabilization of planar tetracoordinate carbon in polycyclic systems suggests a combination of factors: steric (incorporation of carbon in strained rings) and electronic (introduction of electron-acceptor boron-containing groups, aromatic filling of the π system) [22]. The effect of π-electron stabilization factors of

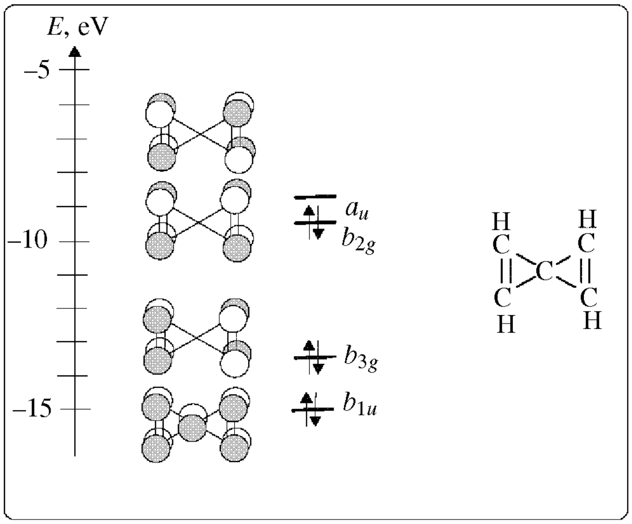
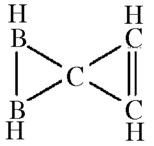


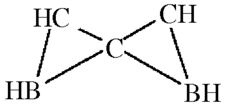
Fig. 1. Molecular π-orbital diagram of planar spiropentadiene.

the simplest bicyclic systems with three-membered rings is convenient to consider in terms of the molecular orbitals of a hydrocarbon system, viz. planar spiropentadiene.

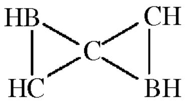
As seen from the diagram in Fig. 1, the simplest bicyclic systems contain only two bonding π orbitals which can be filled by four of the six available π electrons. Therefore, planar spiropentadiene is not a stable system and does not correspond to a local minimum in the PES of the C_5H_4 molecule. To stabilize the system, it is sufficiently to replace two peripheral carbon centers by boron atoms to obtain 1,2-diboraspiropentene **7** [22]. According to DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) calculations, structure **7** with a planar tetracoordinate central carbon atom corresponds to a minimum on the PES of the $C_3B_2H_4$ molecule. Structures with tetrahedral or pyramidal carbon centers correspond to higher order stationary points ($\lambda > 1$, here and hereinafter, relates to the number of negative eigenvalues of the Hesse matrix) and are destabilized with respect to planar form **7** by more than 50 kcal mol^{-1}.



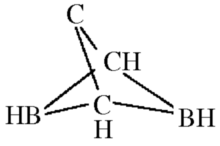
7, C_{2v}



8, C_{2v}



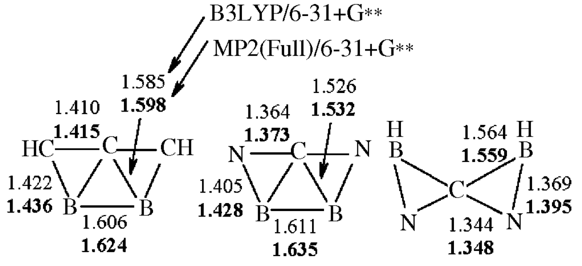
9, C_{2h}



10, C_{2v}

The stability of system **7** is provided by the "local" aromaticity of the three three-membered each having two π electrons. The calculations also result in two more stable $C_3B_2H_4$ structures with a planar tetracoordinate carbon centers, **8** and **9**, and, therewith, structure **8** is the most stable form containing planar carbon. According to MP2(full)/6-311+G** calculations, planar structure **8** is as little as 4.4 kcal mol^{-1} less favored by energy than carbenium structure **10** corresponding to the global minimum on the PES of the $C_3B_2H_4$ molecule. At the same time, DFT calculations at the B3LYP/6-311+G** level result in the opposite stability order of systems **8** and **10**: The global minimum on the PES corresponds to system **8**, whereas carbene isomer **10** is destabilized by 3.6 kcal mol^{-1}.

According to our calculations [23, 24], stabilization of planar tetracoordinate carbon is also possible in the other simplest bicyclic compounds **11–13** having a 4π-electron system. An additional stabilization factor in systems **11** and **12** is B–B interligand binding.



11, C_{2v} **12**, C_{2v} **13**, C_{2v}

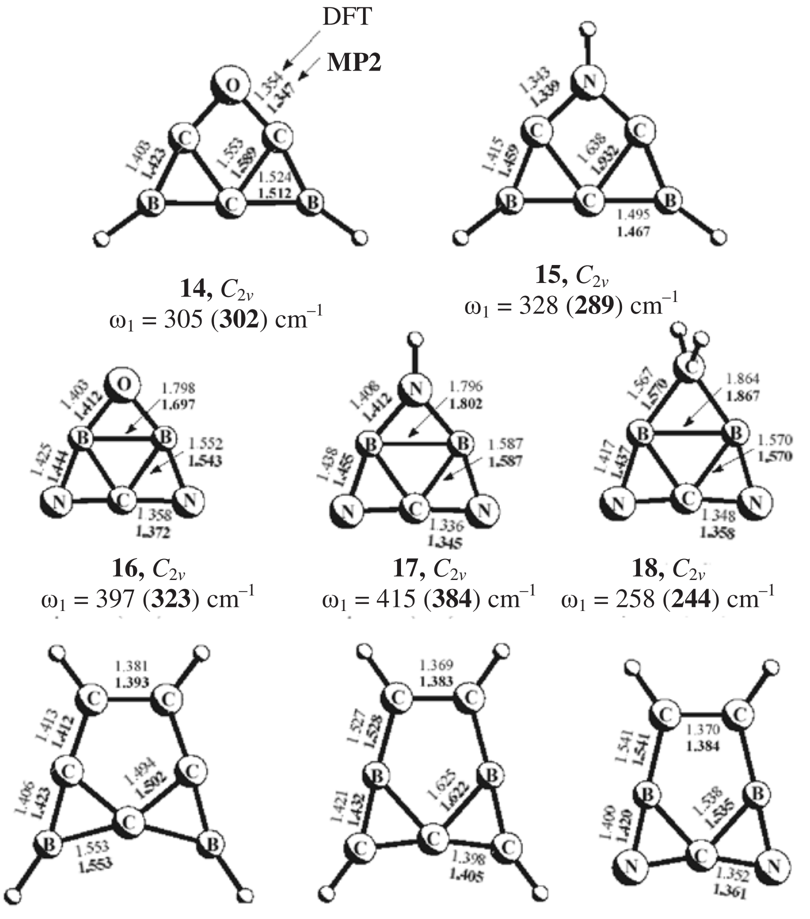
ω_1 = 455 (**420**) cm^{-1} ω_1 = 452 (**413**) cm^{-1} ω_1 = 211 (**214**) cm^{-1}

Here and hereinafter, bond lengths are in Å; ω_1 is the lowest harmonic vibrational frequency.

The considered simplest systems with planar tetracoordinate carbon can serve as stable structural blocks for constructing a broad range of compounds with extended molecular carcasses [22, 23]. Introduction of peripheral substituents to obtain polycyclic systems (Fig. 2) formed by fused rings endows the molecular carcass with additional rigidity and enhances stability of compounds with a planar tetracoordinate carbon center.

Charges systems with a planar carbon center can be transformed into stable neutral compounds by introducing appropriate substituents [22–25]. Let us consider this approach on an example of anion **22**. According to our B3LYP/6-311+G** calculations, planar structure **22** correspond to an energy minimum on the PES, but the MP2(full)/6-311+G** method places this structure into a first-order saddle point on the PES. Neutralization of the negative charge in anion **22** (and its additional stabilization) can be provided by introduction of electron-donor substituents (systems **23** and **24**). As follows from B3LYP/6-311+G** and MP2 (full)/6-311+G** calculations, structures **23** and **24** correspond to minima on the PESs.

Another approach to charge compensation is based on introduction of counter ions (for example, lithium cations). The calculations place the dilithium salt of **25** into a minimum on the PES. Introduction of lithium cations forms a hexacoordinate carbon center.



14, C_{2v}
$\omega_1 = 305$ (**302**) cm^{-1}

15, C_{2v}
$\omega_1 = 328$ (**289**) cm^{-1}

16, C_{2v}
$\omega_1 = 397$ (**323**) cm^{-1}

17, C_{2v}
$\omega_1 = 415$ (**384**) cm^{-1}

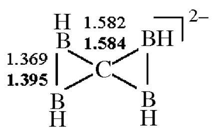
18, C_{2v}
$\omega_1 = 258$ (**244**) cm^{-1}

19, C_{2v}
$\omega_1 = 251$ (**244**) cm^{-1}

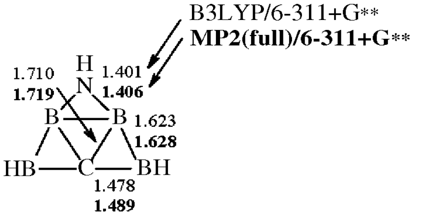
20, C_{2v}
$\omega_1 = 235$ (**223**) cm^{-1}

21, C_{2v}
$\omega_1 = 228$ (**225**) cm^{-1}

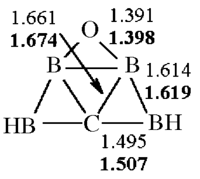
Fig. 2. Geometric characteristics (bond lengths) and lowest vibration frequencies of structures **14–21**, as given by DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) calculations.



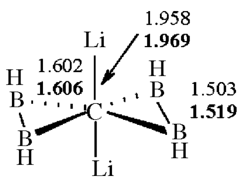
22, D_{2h}
$\omega_1 = 151$ (***i*112**) cm^{-1}



23, C_{2v}
$\omega_1 = 198$ (**174**) cm^{-1}

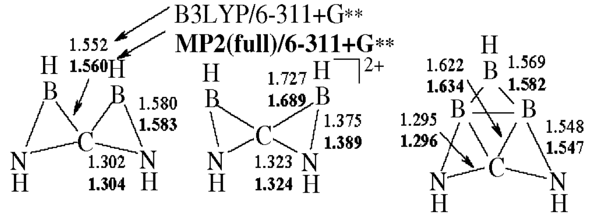


24, C_{2v}
$\omega_1 = 243$ (**239**) cm^{-1}



25, D_{2h}
$\omega_1 = 57$ (**71**) cm^{-1}

Directed modification can be used to stabilize initially unstable systems [23]. For example let us consider unstable structure **26** having six p electrons. The transition to dication **27**, while forming the required four-electron π system, provides no stabilization. According to calculations, dication **27** corresponds to a saddle point on the PES. Even though system **27** formally possesses all factors necessary to stabilize planar tetracoordinate carbon (electron-positive boron substituents, structural rigidity, and aromatic p system), electron-donor NH groups exert a strong destabilizing effect. At the same time, a peripheral π-acceptor BH group (system **28**) provides stabilization: Neutral compound **28**, according to DFT and ab initio calculations, corresponds to a stable structure on the PES.

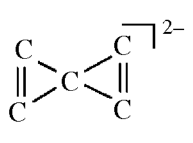


26, C_{2v} [λ = 3(**4**)] **27**, C_{2v} (transition state) **28**, C_{2v}

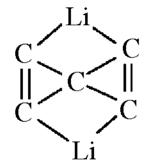
$\omega_1 = i322$ (i**106**) cm^{-1} $\omega_1 = 46$ (**133**) cm^{-1}

Thus, the stability of the considered nonclassical structures with a planar tetracoordinate carbon center is provided by a combined effect of electronic and steris factors: π-acceptor and σ-donor atoms adjacent to the carbon center; carbon atom incorporated in strained three-membered rings; strong interligand interaction; and aromatic π system with filled bonding and vacant antibonding orbitals. Introduction of peripheral atomic groups not only imparts additional rigidity to systems with planar tetracoordinate carbon. The same approach can be used for varying the electronic structure of these compounds: Electron-donor groups compensate for the p-electron deficiency of the central node (systems **23** and **24**), whereas electron-acceptor substituents neutralize excess p electrons (system **28**).

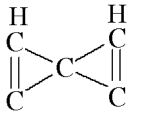
The results of research on the simplest biicyclic systems with a planar tetracoordinate carbon center are fully consistent with these conclusions. Thus, when the above conditions are met, planar carbon can be stabilized in a fairly unusual environment. The 4π-electron dianion **29** calculated by the CCSD(T), MP2, and B3LYP methods with the 6-311++G(2d) basis set is isostructural and isoelectroic to dianion **22** and corresponds to an energy minimum on the PES [26, 27]. Ligand carbenium-type carbon atoms have vacant p_π orbitals perpendicular to the molecular plane and are able, like BH groups, to function as π-acceptor substituents. According to the calculations, the HOMO of dianion **29** has a positive eigenvalue, which may prevent existence of this dianion [26, 27]. However, introduction of lithium cations as counterion decreases the HOMO energy to a negative value. The stabilizing effect of counterion is explained by that they enhance rigidity of the carcass and favor delocalization of the excess electron density of the planar carbon center. Unlike dianion **22** in which lithium counterion favor formation of a hexacoordinate carbon center (system **25**), counterion in anion **29** do not change the coordination characteristics of the carbon center (system **30**). The latter result is explained by the presence of σ-electron pairs in ligand carbon atoms, which favor counterion location in the system plane.



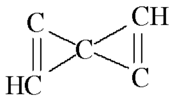
29, D_{2h}



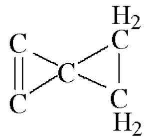
30, D_{2h}



31, C_{2v}

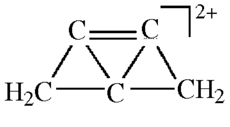


32, C_{2h}

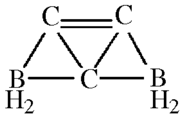


33, C_{2v}

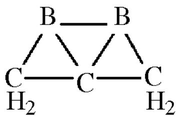
As shown by B3LYP/6-311+G** calculations [28], planar 4π-electron systems **31** and **32** with two π-acceptor carbene ligands are, too, structurally stable. System **33** with only one filled bonding p orbitals (two π electrons), while corresponding to a minimum on the PES, features an extremely low (~2 kcal mol^{-1}) activation barrier to three-membered ring opening [28].



34, C_{2v}



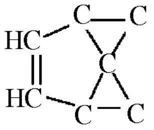
35, C_{2v}

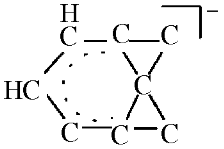


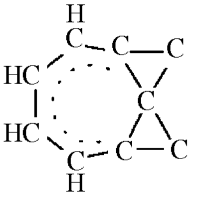
36, C_{2v}

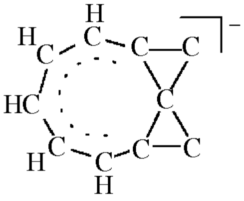
The additional interligand bonding realized in the series of isoelectronic stable planar systems **34**–**36** and their positional isomers isoelectronic and isostructural analogs of the previously suggested 4π-electron stable system $NB_2(BH_2)_2^-$ with planar tetracoordinate nitrogen [29] prevents decyclization by increasing substantially the barrier to this reaction (for example, ~30 kcal mol^{-1} for **36**) [28]. According to the calculation results in [28], systems **31**–**36** all have negative NICS indices (Nuclear Independent Chemical Shift is an index suggested to characterize magnetic properties associated with aromaticity), which provide evidence for aromaticity of these compounds. At the same time, the corresponding tetrahedral forms are antiaromatic. Thus, in the simplest systems with planar tetracoordinate carbon the 4n+2 aromaticity rule is formally violated, and the principal stability factor is the “local” aromaticity of each of the structural fragments.

According to our suggested strategy for modification of the simplest systems [22, 23, 25], the series of structures with a central plane entity CC_4 can be extended by introducing peripheral atomic groups. Such approach allows one to obtain abundant series of compounds like **37**–**40** whose stability has been confirmed by B3LYP/6-311++G(2d,2p) calculations [30].


37, C_{2v}


38, C_{2v}

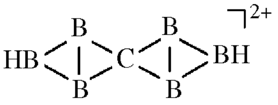

39, C_{2v}


40, C_{2v}

Structure **37** is an isoelectronic analog of the previously proposed [22] system **19** (see Fig. 2) whose BH groups are replaced by carbene carbon atoms. Further extension of the peripheral ring leads to compounds **38**–**40** which are less stable due to a less rigid carcass and lower aromaticity. The calculated lifetime of the least stable system **40** which has the lowest activation barrier to three-membered ring opening (2.5 kcal mol^{-1}), is 6.0 ps at 300 K. It is interesting to note that isomer **37** was detected in the interstar space, i.e. molecules containing planar carbon may be involved in space processes [30].

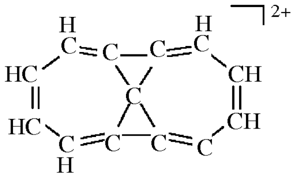
The three-membered rings in systems **37**–**39** feature negative NICS indices, i.e. they are aromatic [30]. The $4n+2$ rule is valid for systems **37** and **40** only (six and ten p electrons, respectively), whereas systems **38** and **39** contain only eight ($4n$) π electrons. These results provide evidence for the conclusion that “local” aromaticity of structural fragments involved in formation of a planar configuration of bonds is of principal importance.

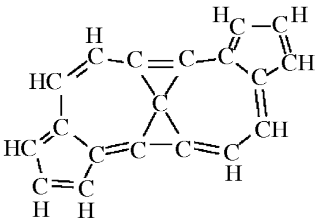
The above systems all are stabilized due to additional bonding between two central three-membered rings. At the same time, an approach to forming stable polycyclic systems, that involves no rigidity enhancement of the molecular carcass, may also prove effective. Thus, according to B3LYP/6-311+G** calculations [31], the expansion of structural node **22** on two sides with preservation of the four-electron p system does not disturb stability of the planar carbon center in **41**.

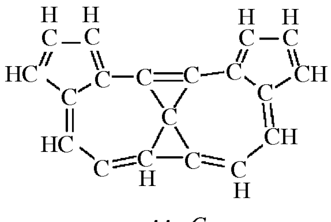

41, D_{2h}

As follows from an analysis of the electronic structure of compound **41**, the boron atoms attached to the central tetracoordinate planar carbon atom each contribute one π electron into the joint π system, which can be described in terms of *sp* hybridization. Thus, boron ligands behave as π-donor substituents. Peripheral boron atoms can be considered to have a classical sp^2 hybridization which provides interaction of their vacant *p* orbitals perpendicular to the molecular plane with π electrons of ligand boron atoms and delocalization of the π-electron density in system **41**. Molecular orbital analysis shows that dication **41**, like the above-described simplest nonclassical systems, has a stable π system with two filled bonding orbitals and vacant antibonding π orbitals.

The possibility of two-side expansion of a carcass comprising a planar carbon center is also exemplified by a B3LYP/6-311++G**//B3LYP/6-31G* study of systems **42**–**44** [32].


42, C_{2v}


43, C_{2h}

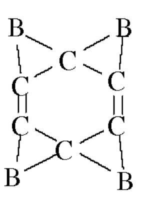

44, C_{2v}

Systems **43** and **44** do not adhere to the 4*n*+2 (eighteen electrons) rule, but their NICS indices show that these compounds are aromatic in nature. At the same time, the activation barriers to opening of the three-membered rings in **43** and **44** are low (2.2 and 1.4 kcal mol^{-1}, respectively), which leaves little chance for these systems to be detected under ordinary conditions. A possible synthetic approach to such compounds can involve low-temperature procedures, such as fixation in anrog matrix [32].

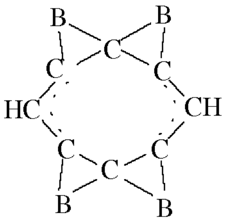
Compounds with Several Planar Carbon Centers

Structural blocks of the simplest planar carbon systems can be used for designing complex compounds containing one, two, or three planar carbon centers [24]. Systems **45**–**48** exemplify different modes of combining several (here two) basic blocks with a planar carbon center. This procedure only slightly affects geometric parameters of the planar forms and does not touch upon their stabilization mechanism.

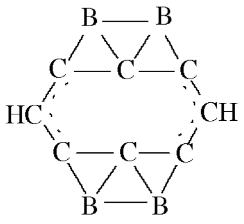
In lithium-containing compounds, the couterions can act as bridges between monomeric structural blocks. Thus structures like **30** can undergo polymerization to forms chains like **49**. Use of doulble-charged cations capable to tetracoordination (Zn^{2+}, Be^{2+}, etc.) allows construction of 3D systems of monomers with planar tetracoordinate carbon [33].



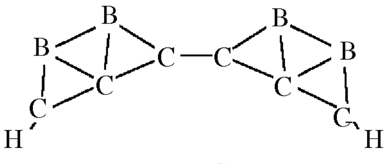
45, C_{2h}



46, C_{2h}

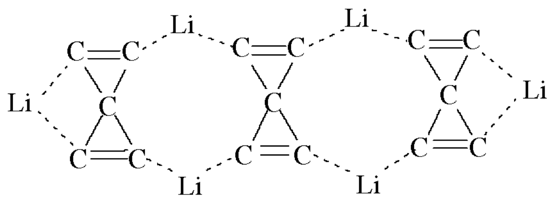


47, C_{2h}



48, C_{2v}

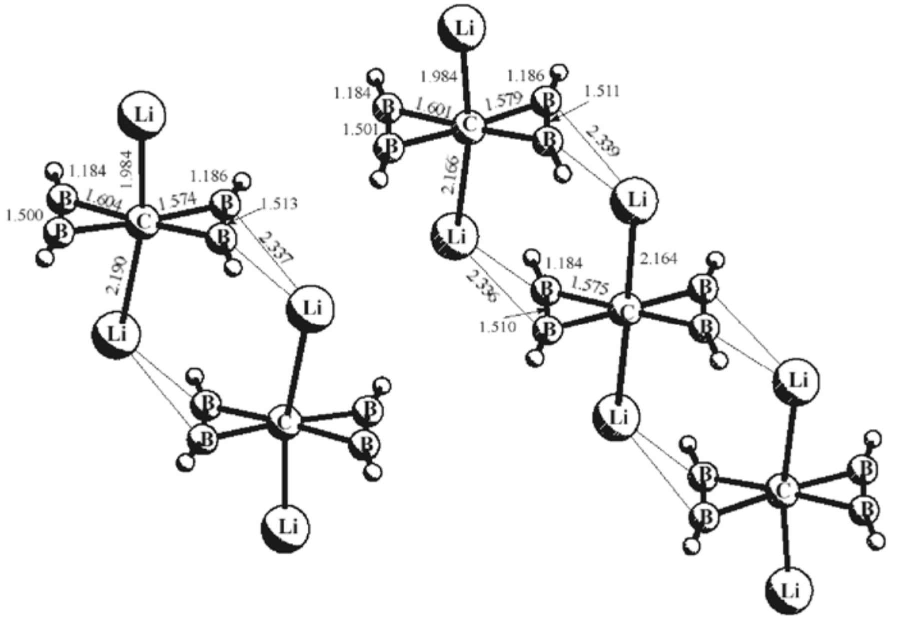
As two or more such monomers as hexacoordinate carbon system **25** approach each other, spontaneous polymerization with a high exothermic effect (about 50 kcal mol^{-1} for each pair of monomers) occurs. Figure 3 shows thus formed dimer **50** and trimer **51,** containing hexacoordinate carbon centers. The chain systems formed upon further polymerization preserve C_{2h} symmetry [34].



49, D_{2h}

One more type of complex systems with planar carbon is represented by molecules involving several nonclassical centers with a common ligand environment. Examples of such systems are provided by isoelectronic dianions **52** and **53** (Fig. 4) whose stability was confirmed by DFT B3LYP/6-311+G** and ab initio MP2(full)/6-311+G** calculations [34]. The two planar carbon centers in these systems are stabilized by a common boron environment. At the same time, the presence of bridging BH_2 groups makes possible formation of polymeric chains. Figure 4 shows thus formed trimeric aggregate **52a** in which each of the monomers contains two nonclassical carbon centers. The tetracoordinate carbon centers in the end monomers of system **52a** are slightly pyramidalized (~3°). Note that system **53** can polymerize either by inclusion of counterions, such as lithium (system **53a**), with simultaneous charge compensation or via bridging BH_2 groups (like **52a**). Thus, system **53** can be extended in both directions simultaneously, which allows nets with nonclassical carbon centers to be formed [34].

A still more exotic fashion of joining the simplest structural blocks is realized in systems containing several planar carbon centers directly bound to each other. Such systems are exemplified by molecules **54** [35] and **55**–**57** [24] whose stability was confirmed by B3LYP and MP2 (6-311+G** basis) calculations.

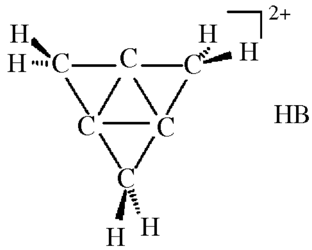


50, C_{2h}
$\omega_1 = 45\ \mathrm{cm}^{-1}$

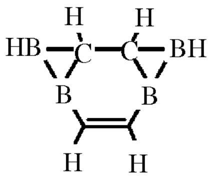
51, C_{2h}
$\omega_1 = 20\ \mathrm{cm}^{-1}$

Fig. 3. Geometric characteristics and lowest vibration frequencies of structures **50** and **51**, as given by DFT (B3LYP/6-311+G**) calculations.

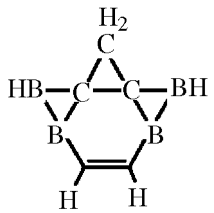
The principal factor favoring stability of all of these systems is that nonclassical carbon centers are incorporated into aromatic rings, i.e. stability is provided by "local" aromaticity. Evidence for this conclusion comes from analysis of MOs and calculation of NICS indices. At the same time, the 4*n*+2 rule, like with the simplest systems, is not always obeyed: Systems **56** and **57** have eight and twelve π electrons, respectively. Therewith, the factor of steric stabilization, associated with the presence of strained three-membered rings, is of importance here.



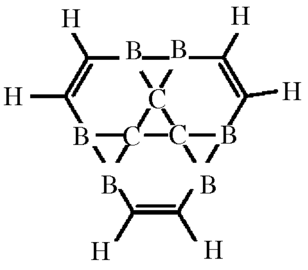
54, D_{3h}



55, C_{2v}

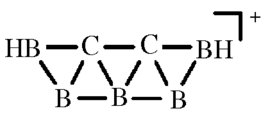


56, C_{2v}

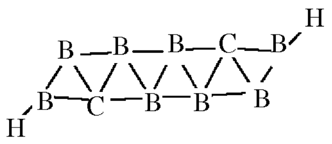


57, D_{3h}

A convenient structural carcass for forming nonclassical systems is provided by polyatomic boron clusters which allow various isoelectronic substitutions leading to systems with several planar carbon centers. The examples are compounds **58** and **59** and their derivatives, whose stability was predicted by B3LYP/6-311+G** calculations [31]. The fact that such systems comprise simultaneously one or several nonclassical boron centers.

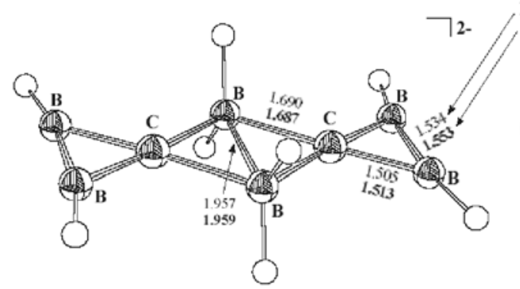


58, D_{2h}

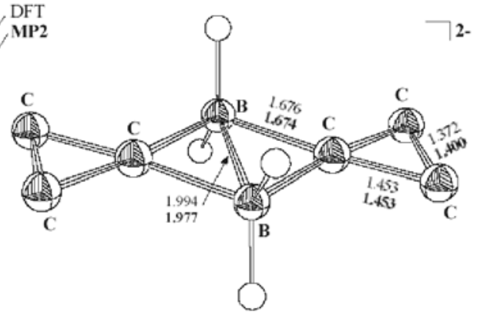


59, D_{2h}

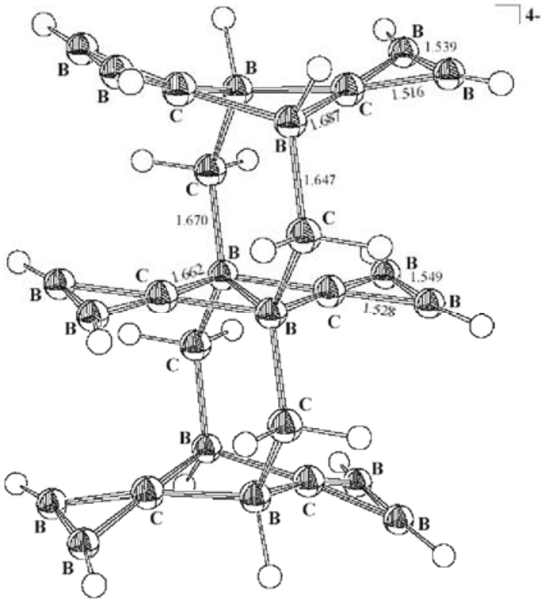
One more type of boron–carbon systems is represented by "wheel"-structured clusters like **60** [36]. Incorporation of a cyclic fragment C_n inside a boron ring can result in stabilization of several planar



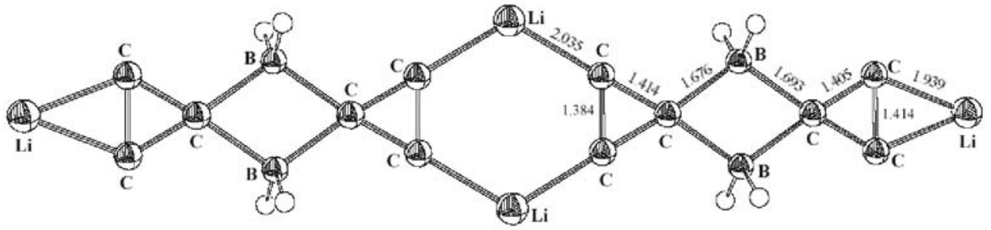
52, D_{2h}
ω_1 = 97 (**76**) cm^{-1}



53, D_{2h}
ω_1 = 125 (**123**) cm^{-1}



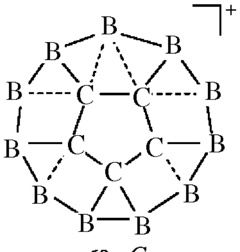
52a, D_{2h}
ω_1 = 18 cm^{-1}

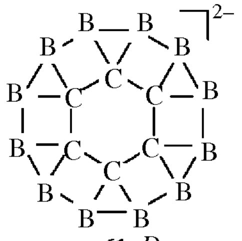


52a, D_{2h}
ω_1 = 13 cm^{-1}

Fig. 4. Geometric characteristics (bond lengths) and lowest vibration frequencies of structures **52** and **53**, as given by DFT (B3LYP/6-311+G**) and ab initio (MP2(full)/6-311+G**) calculations.

carbon centers bound to each other. According to B3LYP/6-311+G(2df) calculations, the 10π-electron cation $C_5B_{11}^+$ (structure **60**) contains fairly long C–B bonds (up to 1.74 Å). At the same time, the dianion $C_6B_{12}^{2-}$ (structure **61**) which is formally an antiaromatic system (fourteen π electrons) contains six internal planar carbon centers with C–B and C–C bond lengths of 1.662 and 1.496 Å, respectively [37].

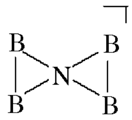

60, C_{2v}

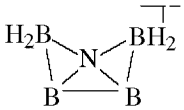

61, D_{6h}

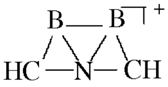
The 10π-electron analog $C_6B_{12}^{2+}$ is stabilized in C_{6v} symmetry with planarity disturbance. Each of the internal structural fragments CB_2 of dianion **61** is a 2π-electron aromatic ring, i.e., like with the simplest systems, the key stability factor is "local" aromaticity. It is noteworthy that systems like **60**, **61,** and their analogs are fluctuating: The inner ring fairly freely rotates with respect to peripheral (barrier <1 kcal mol^{-1}) [36, 37].

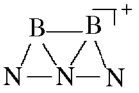
Planar Tetracoordinate Nitrogen

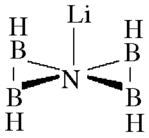
The strategy developed for searching compounds with planar tetracoordinate carbon is feasible for constructing systems with planar tetracoordinate nitrogen [29]. However, unlike the situation with planar carbon, fairly few stable planar tetracoordinate nitrogen systems have been found, on account of the fact that nitrogen is more electronegative than carbon and this hinder delocalization of the excess electron density of the planar center. Therefore, to stabilize planar nitrogen in the simplest bicyclic derivatives requires more severe conditions: Either four π-acceptor groups or a carcass with additional interligand binding [29]. Like with bicyclic derivatives of carbon, the necessary condition for stabilization of systems containing two three-membered nitrogenous rings is formation of a stable π system (four π electrons).

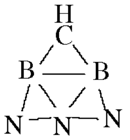

62, D_{2h}

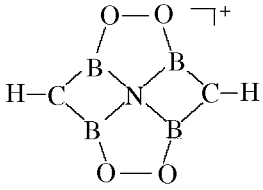

63, C_{2v}

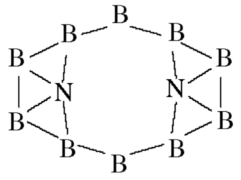

64, C_{2v}


65, C_{2v}


66, C_{2v}


67, C_{2v}


68, D_{2h}


69, D_{2h}

Examples of presently known systems with planar tetracoordinate nitrogen are provided by structures **62**–**69** whose stability was conformed by DFT (B3LYP/6-311+G**) and ab initio [MP2(full)/6-311+G**] calculations [29]. Like with compounds with planar tetracoordinate carbon, the charge of ionic systems can be compensated for by counterions, which in-creases the coordination number of nitrogen but douse not disturb planarity (the example is system **66**). Systems **63**–**65** contain only two π-acceptor centers, but they are stabilized due to interligand binding. The stabilizing effect of interligand binding can be assessed using isomers **62** and **63**, of which system **63** is 9.3 (DFT) and 15.1 (MP2) kcal mol^{-1} more favored by energy. Like with planar carbon derivatives, the carcass in the simplest nitrogenous systems can be extended for greater stability and charge compensation. An example is neutral compound **67** formed on the basis of cation **65**. It is interesting to note that **67** is isomeric to stable system **17** with planar tetracoordinate carbon atom. According to calculations, structure **17** is 67.0 (DFT) and 64.4 (MP2) kcal mol^{-1} energetically more favorable than **67**, which can be explained by more effective delocalization of the p_z-electron pair on carbon **17** than on nitrogen on **67**, since carbon is less electronegative than nitrogen.

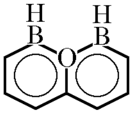
System **68** is the first example of a derivative of the fenestrane class (systems with a tetracoordinate carbon atom which serves as a common vertex for four fused carbocycles, from fenestra, the Latin for win-dow), proposed more than 35 years ago as a variant of stabilization of planar tetracoordinate carbon. However, despite a considerable effort, this type of structures for *p* elements of the second period has been realized neither theoretically nor experimentally [1, 4, 11]. Like with carbon derivatives, systems comprising two and more planar nitrogen centers can be formed. An example is neutral system **69** which is stable in the triplet state, and its aromatic π system is similar to that of naphthalene.

Thus, our calculations [29] point to the possibility of existence of a family of neutral and charged systems with a planar configuration of tetracoordinate nitrogen atom. Factors that determine stability and ways of modification of nonclassical derivatives of tetracoordinate nitrogen and carbon atoms are identical, but the less favorable electronic conditions for forming a planar nitrogen center constrict considerably the range of its derivatives.

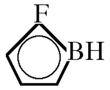
Hypercoordination of Oxygen and Fluorine in Planar Polycyclic Systems

When passing from carbon to more electronegative elements, planar configurations of tetracoordinate cental atoms get more difficult to stabilize, and already with nitrogen the range of known nonclassical compounds is quite limited. The situation with higher electronegativity central atoms is still more complicated, being more demanding both sterically and electronically. According to our calculations, stabilization of planar tetracoordinate oxygen and fluorine atoms in the simlest systems, like those considered above, proves to be hardly realizable. At the same time, for the nonstandard hypercoordinate state one can consider planar tricoordination for oxygen and dicoordination for fluorine.

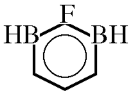
We suggested in [34, 38–40] a strategy for forming planar systems containing tricoordinate oxygen and di- and tricoordinate fluorine, which is a modified version of the strategy for forming planar tetracoordinate nodes. Hypercoordinate oxygen and fluorine systems are stabilized in conditions similar to those with a tetracoordinate planar center (aromaticity and boron environment). The simplest approach to stabilization of planar tricoordinate oxygen and and di- and tricoordinate fluorine derivatives is based on incorporation of a hypercoordinate center enclosed by boron substituents into an isoelectronic aromatic system. We made use of this approach to construct stable systems **70–72** with the nonstandard planar tricoordination of oxygen and dicoordination of fluorine [38, 40].



70, C_{2v}



71, C_s



72, C_{2v}

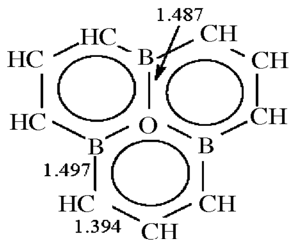
Oxygen compound **70** is stable due to strong cyclic π-electron delocalization (~60 kcal mol^{-1}), whereas in fluorine compounds **71** and **72** the contribution of aromatic stabilization is much smaller (~3 and 13 kcal mol^{-1}, respectively).

The same approach is suitable for constructing other polycyclic compounds containing planar tricoordinate oxygen atoms, such as **73**–**77** which, according to B3LYP/6-311+G** calculations, correspond to minima on the PES [34, 39]. The principal condition for stabilization of such systems, like with the above compounds with planar tetracoordinate centers, is enclosure of the central hypercoordinate atom by π-acceptor boron ligands and aromaticity of the resulting polycyclic system. Compounds **73–77** comprise stable π systems with filled bonding and vacant antibonding molecular orbitals. As the electronegativity of peripheral ligands (BH, CH, N) increases, bonds between the central oxygen atom and its enclosing boron ligands get shorter.

Planar tricoordinate fluorine derivatives, such as **78** and **79,** can be formed in the same way. The contribution of aromatic stabilization decreases in going from oxygen to fluorine derivatives [34, 39].

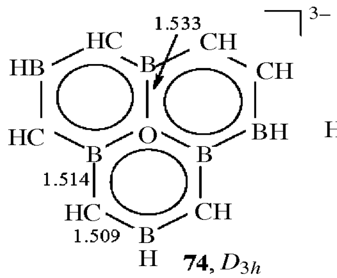
Note that stabilization of planar tetracoordinate oxygen and fluorine in a nonmetallic environment is still possible and can be realized by means of a rigid molecular carcass. Thus planar tetracoordinate *p*-element atoms of the second period are present in systems like **80** constructed on the basis of a dehydrated asterane carcass (asteranes are highly symmetrical star-shaped hydrocarbons formed of two parallel annulene fragments interlayed by a polymethylene pseudo-cycle; from astēr, the Greek for star [41, 42].

B3LYP/6-311+G**



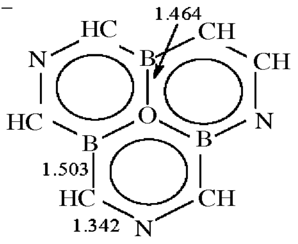
73, D_{3h}

ω_1 = 119 cm^{-1}



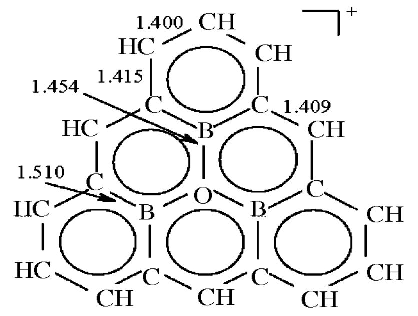
74, D_{3h}

ω_1 = 91 cm^{-1}



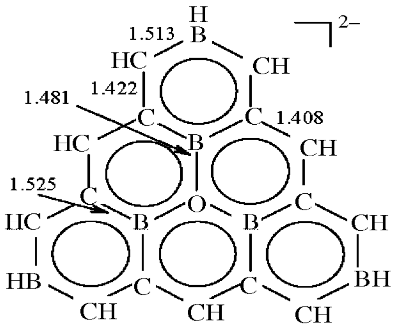
75, D_{3h}

ω_1 = 125 cm^{-1}



76, D_{3h}

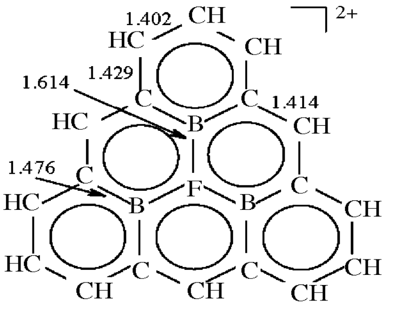
ω_1 = 63 cm^{-1}



77, D_{3h}

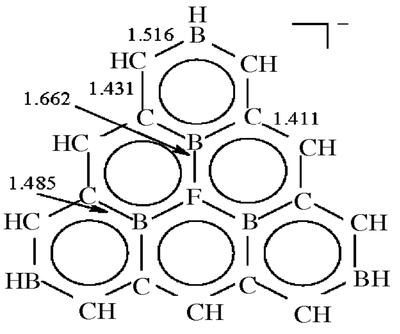
ω_1 = 76 cm^{-1}

B3LYP/6-311+G**



78, D_{3h}

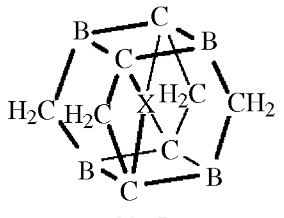
ω_1 = 63 cm^{-1}



79, D_{3h}

ω_1 = 77 cm^{-1}

Topological analysis of electron density distribution in terms of the Bader's Atoms In Molecules (AIM) theory [43] showed that the central atom in compounds **80** is tetracoordinate and forms bonds exclusively with basal carbon atoms whose unhybridized *p* orbitals are half-filled. Basal boron atoms with empty diagonal *p* orbitals do not form chemical bonds with the central atom.



80, D_{2h}

(X = C, N$^+$, O^{2+}, F^{3+})

Hypercoordination of Boron, Carbon, and Nitrogen in Planar Polycyclic Systems

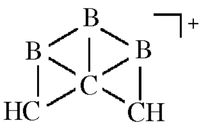
As shown above, additional strained rings formed in planar tetracoordinate carbon systems by introducing peripheral atoms or groups ensure enhanced stability of such compounds by enhancing rigidity of the molecular carcass. At the same time, such systems are constructed by forced distortion of their geometry and feature an only partially filled coordination space around the central atom (see Fig. 2), which creates additional coordination possibilities. Theoretical results show that, provided requirements for stabilization of planar configuration are met, the coordination number of the central atom can be increased not sacrificing system stability. Possibilities for stabilization of such compounds were predicted on an example of systems containing penta-, hexa-, hepta-, and octacoordinate atoms of elements of the second period in boron environment.

*Pentacoordinate carbon***.** Planar pentacoordinate carbon derivatives can be constructed by introducing appropriate groups in systems with a lanar tetracoordinate carbon center. Thus substitution in systems like **20**, **23**, or **24** of two-electron π-donor groups HC=CH, NH, or O by one-electron π-donor boron atoms makes it possible to increase the coordination number of the planar center and stabilize pentacoordinate carbon systems, such as **81** and **82**.

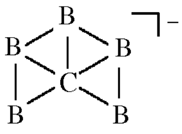
Evidence for the stability of such systems which were given the name hyparenes (hypercoordinate arenes) was obtained by DFT calculations [44]. Like with tetracoordinate carbon systems, systems with a pentacoordinate central atom can be extended by introducing peripheral groups (see, for example, **83**–**85**). Combining structural blocks with planar pentacoordinate carbon to form a system comprising several nonclassical centers is made relying on the same principles as with tetracoordinate carbon systems (for example, systems **86** and **87**). Like tetracoordinate systems, stable pentacoordinate carbon compounds should not necessarily obey the $4n+2$ rule. Thus **81**–**83**, like the parent tetracoordinate derivatives, are 4π-electron systems and can be formally considered as antiaromatic. Systems **84** and **85** have six π electrons, while **86** and **87,** ten and eight π electrons, respectively. At the same time, analysis of NICS aromaticity indices and proton chemical shifts provide evidence showing that systems **81**–**86** are aromatic in nature. According to the specified criteria, dimer **87** is antiaromatic, but it corresponds to a mini-mum on the PES, demonstrating a high stability of the constituent monomeric blocks [44].

The calculated Wiberg bond indices of pentacoordinate carbon in hyparenes are about 4, i.e. these systems obey the octet rule [44]. Due to the “deltahedral” multicenter bonding [45], the central pentacoordinate atom forms strong bonds whose characteristics are close to those of standard single bonds.

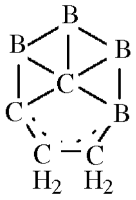
According to MP2/6-311+G** calculations, hyparenes with peripheral BH groups (for example, **88**–**90**), too, correspond to minima on the PES and are stabilized by π-electron delocalization [39]. Planar pentacoordinate nitrogen derivatives, like **91,** can be constructed in the same way [39].



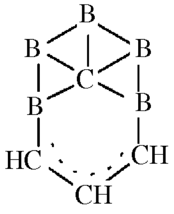
81, C_{2v}



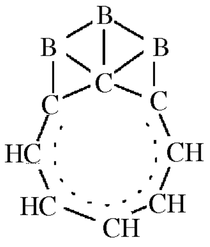
82, C_{2v}



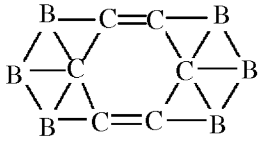
83, C_{2v}



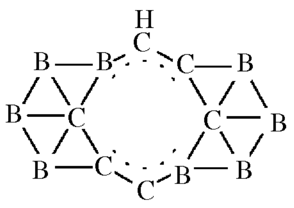
84,



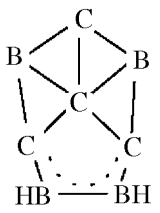
85, C_{2v}



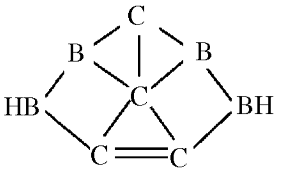
86, D_{2h}



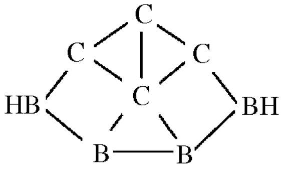
87, D_{2h}



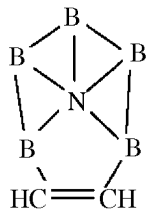
88, C_{2v}



89, C_{2v}

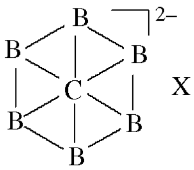


90, C_{2v}

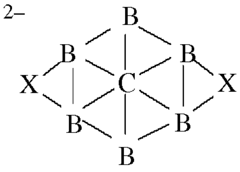


91, C_{2v}

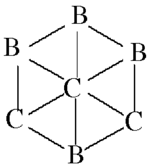
*Hexacoordinate carbon***.** According to quantum-chemical calculations, planar boron rings provide an exceptionally effective carcass for constructing hypercoordinate carbon systems [25, 46–48]. Carbon hexacoordination in a boron environment is realized systems like **92** [48] and **93** [25]. Stability of hexacoordinate carbon systems is provided by multicenter bonding between the central atom with its surrounding ligands.



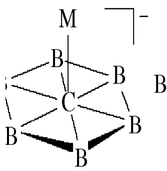
92, D_{6h}



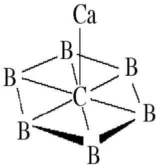
93, C_{2h}
(X = NH, O)



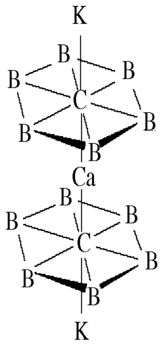
94, C_{2v}



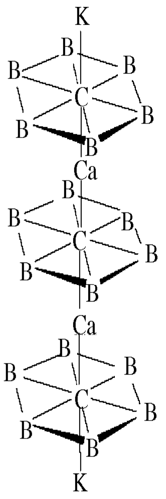
95a, C_{6v}
(M = Li, Na, K)



95b, C_{6v}



96, D_{6h}

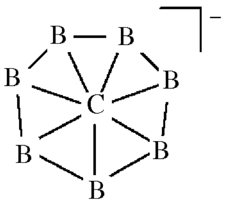


97, D_{6h}

Systems like **93** formally relate to the 4n type (eight π electrons) but have a stable π system with filled bonding and vacant antibonding orbitals. Along with this, the principal factors that operate to stabilize such systems are strong interligand binding, presence of strained three-membered rings, and π interaction of the central atom with ligand environment. Substitution of two boron atoms with carbon in 6π-electron dianion **92** gives rise to neutral compound **94** with hexa-coordination.

Like with tetracoordinate systems, the charge in anion **92** can be compensated by introduction of counterions to form structures **95** with a slightly pyramidalized carbon center [49]. According to B3LYP/6-311+G* calculations, such systems may primarily stabilized by π–d interaction, like in calcium derivatives. Couterions can function as bridging atoms for constructing chain polymers like **96** and **97** comprising several structural blocks.

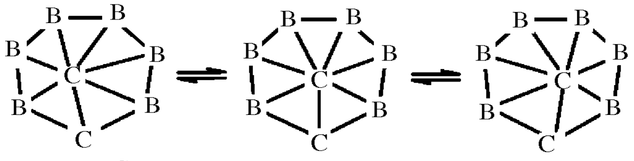
Heptacoordinate carbon. Systems with a higher coordination number of carbon can be stabilized in the same way. Anion **98** is a theoretically predicted example of a system containing planar heptacoordinate carbon [44, 50]. The extension of the ring in going from systems **92** and **93** to system **98,** is accompanied by elongation of bonds between the central atom with its surrounding boron ligands.



98, D_{7h}

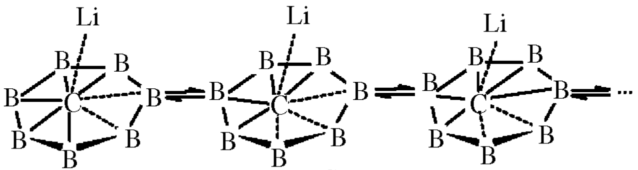
The negative charge in anion **98** can be compensated for by substitution of one of boron substituents by carbon (system **99**). However, the decrease of the symmetry leads to structural nonrigidity associated with low-barrier carbon migration over the ring: **99a** ↔ **100** ↔ **99b** ↔ **...**

Addition of lithium counterion to anion **98,** too, induces low-barrier carbon migration over the boron



99a, C_s **100**, C_{2v} (transition state) $\Delta E^{\neq} = 0.2$ kcal mol^{-1} **99b**, C_s

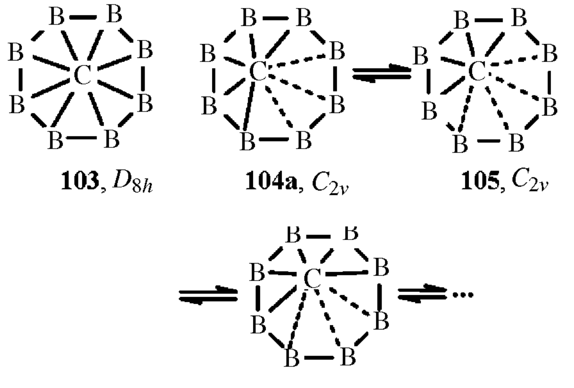
ring: **101a** ↔ **102** ↔ **101b** ↔... At the same time, calculations with inclusion of the zero-point energy show that structures **100** and **102** become the most stable, which allow the carbon atom in these systems to be considered heptacoordinate [50].



101a, C_s **102**, C_{2v} (transition state) $\Delta E^{\neq} = 0.2$ kcal mol^{-1} **101b**, C_s

Octacoordinate carbon. The further ring extension on passing to system CB_8 **103** is accompanied by lengthening of bonds between the central atom and ligands. According to DFT calculations, CB_8 possesses a fluctuating structure in which the “effective” carbon coordination number is 8 [44, 51]. System **103** of D_{8h} symmetry corresponds to a hilltop ($\lambda = 2$) on the PES of CB_8.

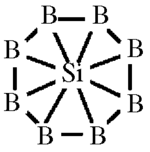
The energy minimum for a cyclic structure CB_8 corresponds to form **104** of C_{2v} symmetry with a pentacoordinate central carbon atom. Structure **104** is quite labile and uhdergoes fast topomerization **104a** ↔ **105a** ↔ **104b** ↔ **...**, where structures **105** of C_{2v} symmetry correspond to saddle points ($\lambda = 1$) on the PES of CB_8 and are transition states of low-barrier (1.3 kcal mol^{-1}) intracyclic C–B bond migration. The energy barrier resulting from calculations with harmonic ZPE correction is lower (0.9 kcal mol^{-1}). The very low barrier to isomerization provides evidence in favor “effective” octacoordination of carbon in the carcass of fluctuating system **103**. The fluctuation is associated with the size inconsistency between the central atom and ring, which gives rise to extreme C–B bond lengthening [44, 51].



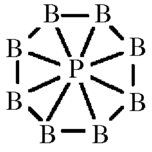
103, D_{8h} **104a**, C_{2v} **105**, C_{2v}

104b, C_{2v}

Evidence showing that size consistency between ring and hypercoordinate atom is of principal importance was obtained by B3LYP/6-311(2df) calculations [51] of silicon (**106**) and phosphorus (**107**) derivatives with larger size central atoms. Unlike the carbon analog, the phosphorus and silicon derivatives have a highly symmetric D_{8h} structure.



106, D_{8h}

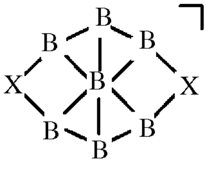


107, D_{8h}

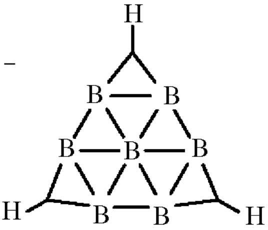
The considered molecules with hepta- and octacoordinate central atoms are stabilized due to formation of an aromatic π-electron system with three filled bonding orbitals [50, 51].

Hypercoordination of boron and nitrogen in planar boron cycles. Hypercoordination in systems with a planar carbon entity is effected via multicenter central atom–ligand interactions. The same type of bonding can be realized in similar structures with other hypercoordinate elements, especially in derivatives of boron which is prone to multicenter bonding.

According to DFT (B3LYP/6-311G**) and ab initio [MP2(full)/6-311G**] calculations, anions **108** isoelectronic to systems **93** and having a hexacoordinate boron feature a planar structure [46, 47]. Molecule **109** represent the structural type of a neutral derivative with an aromatic six-electron π system. Each B_2CH fragment isoelectronic to an aromatic cyclopropenyl cation possesses a local aromaticity and contributes two electrons into the common π-electron system. Like with anion **98**, introduction of Li^+ counter ions in system **108** endow it with structural nonrigidity associated with the low-barrier (~0.2 kcal mol^{-1}) migration of Li$^+$ over the basal plane [47].



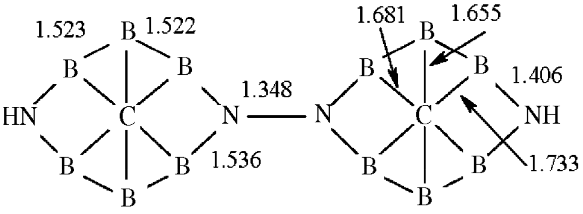
108, C_{2h}
(X = NH, O)



109, D_{3h}

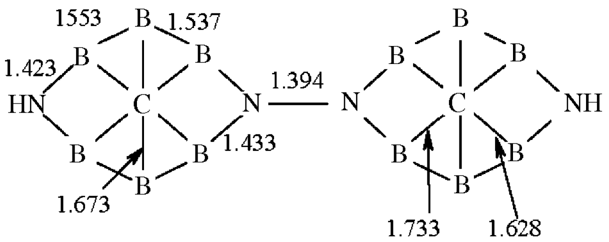
The presence of peripheral groups in systems **93** and **108** make possible formation of chain polymeric systems like **110** and **111**, that correspond to energy minima on the PES [52]. Elongation of the polymeric chains does not disturb stability of the system.

B3LYP/6-311+G**



110

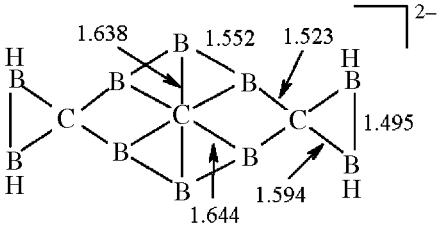
2Li



111

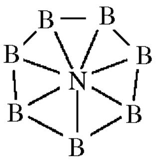
Theoretical studies showed that systems of planar hypercoordination are characterized by the so-called double aromaticity, which makes them stable and allows formation, on the basis of monomers with planar hypercoordinate central atoms, a variety of polymeric compounds promising in terms of synthetic applicability [53].

The stabilizing effect of boron environment in systems like **93** allows introduction as ligands of already two terminal planar tetracoordinate carbon entities. According to our B3LYP/6-311+G** calculations, planar dianion **112** corresponds to a minimum on the PES [34]. This nonclassical system includes three hypercoordinate entities (two tetracoordinate and one hexacoordinate) with a common ligand environment.

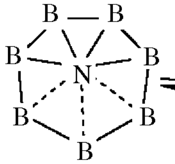


112, D_{2h}
$\omega_1 = 69$ cm^{-1}

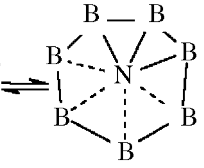
Like with planar tetracoordinate nitrogen derivatives, planar systems with a hypercoordinate nitrogen center have limited possibilities for stabilization, on account both of the higher electronegativity of nitrogen (compared to carbon), which hinders delocalization of excess electron density, and of its smaller atomic size, which results in lengthening and weakening of bonds with carcass atoms. System **113** of D_{7h} symmetry, isoelectronic to system **98** and having a heptacoordinate central nitrogen atom, corresponds, according to B3LYP/6-311+G(2df) calculations [50], to a hill of the PES (l = 2), that intervenes seven equivalent minima **114a**–**114g** and, correspondingly, seven saddle points **115a**–**115g** which are transition states of the topomerization reaction **114a** ↔ **115a** ↔ **114b** ↔**...** with a low energy barrier (1.2 kcal mol^{-1}).



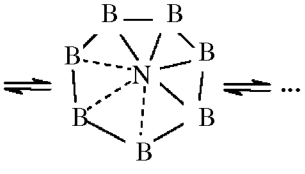
113, D_{7h}



114a, C_{2v}



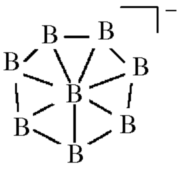
115, C_{2v}



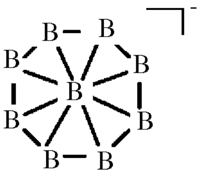
114b, C_{2v}

Thus, the highly symmetric D_{7h} form becomes less stable in going to a smaller size central atom. The size inconsistency between the central atom and cyclic carcass gives rise to structural nonrigidity which can be considered as the mechanism of adaptation of the hypercoordinate atom to its ligand environment. Calculations with inclusion of the zero-point energy result in a low migration barrier (0.8 kcal mol^{-1}), which implies "effective" heptacoordination of the nitrogen atom in system **113** [50].

It is important to note that evidence for the efficiency of the strategy for forming a system with planar hypercoordination, suggested in [25, 44, 46–48, 54, 55] was provided by the synthesis by the laser vaporization method of first compounds of this type&-clusters **116** and **117** comprising hepta- and octa-coordinate boron atoms in planar boron cycles [54]. A B3LYP/6-311+G** quantum-chemical study of a series of boron clusters, too, gave evidence for their stability associated with double aromaticity (NICS indices) [54].



116, C_{2v}



117, D_{8h}

CONCLUSIONS

The revealed principles of stabilization of systems with a planar hypercoordination of *p* elements of the second period in a nonmetallic environment are fairly universal and include the following general factors: (1) introduction of a hypercoodinate center in strained rings; (2) interaction of a hypercoodinate center with ligand environment; (3) strong ligand–ligand bonding; (4) aromaticity (filled bonding and vacant antibonding π orbitals) of a polyatomic system and sufficiently large gaps between the HOMO and LUMO; and (5) size consistency between the ligand carcass and hypercoordinate atom. With tetracoordinate systems, the latter factor is significant only if the central and ligand atoms much differ in parameters; the first factor should be omitted with systems with tricoordinate oxygen and fluorine atoms. Even though the possibities for hypercoordination get more limited with increasing electronegativity of the hypercoordinate center, it is still possible even for such highly electronegative elements as nitrogen, oxygen, and fluorine. Charged systems with hypercoordination can be additionally stabilized by counter ions which provide charge delocalization and enhance rigidity of the molecular carcass. Fuethermore, counter ions can function as bridges in forming polymeric systems with hypercoordination.

At present the interest in nonclassical systems is growing due to the possibility of synthesizing new systems with unusual properties. Thus metal-containing systems with planar tetracoordinate carbon are believed to hold promise for designing on their basis functional materials and nanolectronic devices for spintronics ("spin electronics" is a new field of electronics, which makes use of effects associated the spin states of electrons) [56], lithium–carbon clusters present interest for production of materials with increased electrical capacity [57], and nonclassical binary boron derivatives can possess superconductor characteristics [44]. Factors that stabilize the simplest nonclassical systems were found to operate in more complicated compounds many of which can de used for polymer production. Even though research into polymeric systems with hypercoordination has in fact been initiated only recently, here, too, new and unexpected results can be obtained.

ACKNOWLEDGMENTS

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