Russian Chemical Bulletin, International Edition, Vol. 55, No. 11, pp. 1893—1903, November, 2006

# Sandwich compounds of second-row elements: a quantum chemical study★

**T. N. Gribanova, R. M. Minyaev,★ and V. I. Minkin**

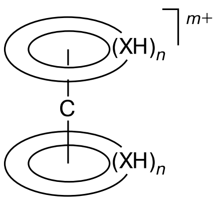
*Institute of Physical and Organic Chemistry at Rostov State University,*
*194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.*
*Fax: +7 (863 2) 434 667. E-mail: minyaev@ipoc.rsu.ru*

The structures and stabilities of a number of neutral and charged sandwich-type boron, carbon, and nitrogen compounds designed based on the cyclophane cage and obeying the "electron octet" rule were studied by the B3LYP/6-311+G** density functional method. The possibility of targeted modification of the electronic structures of such compounds by varying the basal or bridging atomic groups was investigated.

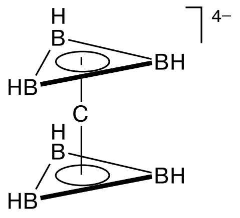
**Key words:** hypercoordinate boron, hypercoordinate carbon, hypercoordinate nitrogen, sandwich systems, quantum chemical calculations.

Search for and studies of compounds containing hypercoordinate main-group element atoms belong to the most intensively developing avenues of theoretical and experimental research.[1—3] An important problem in this field consists in elucidation of methods for targeted design of novel structural types of molecular systems that allow formation and stabilization of hypercoordinate centers.[1] In this connection, sandwich systems seem to be very attractive because their architectures allow the nature and coordination number of the hypercoordinate centers to be varied over a rather wide range. The electronic factors responsible for stability of the sandwich compounds of main-group elements have been studied in detail; they are summarized in the form of the "electron octet" rule[4,5] substantiated by the discovery of various sandwich compounds of alkali[6] and alkali-earth[7,8] metals and some of the third- to sixth-row elements (Si, Ge, Sn, Pb, P, As, Bi, *etc.*).[8,9] At the same time there are only a few examples of stable sandwich derivatives of second-row elements available at the moment.

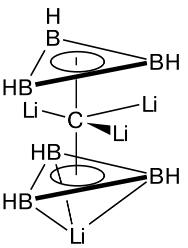
For the simplest carbocenes **1** (X = C) the "electron octet" rule implies the formation of systems bearing rather large positive charges ($m$ = 2 for **1**, $n$ = 3 and $m$ = 4 for **1**, $n$ = 4); stabilization of such species is precluded by electrostatic factors.[10] Additional stability can be achieved by replacing the carbon centers X by electropositive groups that favor stabilization of nonclassical configurations of the carbon atom.[3,4] For instance, B3LYP/6-311++G** calculations predicted that silicon-containing analog of carbocene **1** (X = Si, $n$ = 3, $m$ = 2) should be a stable compound.[11] At the same time this method of solving the stabilization problem of sandwich carbon-containing derivatives is still of limited use, being confirmed by a single successful example as yet. A much more efficient is the approach based on the replacement of the carbon centers in carbocenes by boron atoms (X = B) and additional stabilization of anionic systems thus formed by lithium counterions or bridging hydrogen atoms.[10,12]



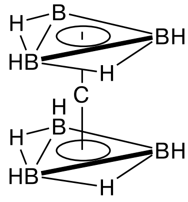
**1**, $D_{nh}$



**2**



**3**



**4**

According to MP2 and DFT calculations with the 6-311+G* basis set, the initially unstable anionic system **2** can be stabilized on going to neutral systems **3** or **4** that contain counterions.[10,12] This approach is fruitful,[12] being at present a unique efficient strategy of targeted design of sandwich derivatives of the second-row elements.

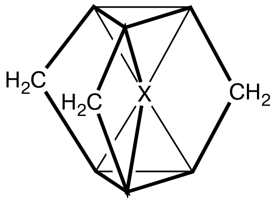
In this work we propose a novel method for design of hydrocarbon and hetero-substituted sandwich systems,

---

★ Dedicated to Academician O. M. Nefedov on the occasion of his 75th birthday.

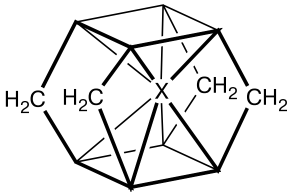
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1825—1835, November, 2006.

which is based on incorporation of a hypercoordinate atom of the second-row element into the "cyclophane" cage in which the basal rings are linked by some bridging atomic groups. In the case of hydrocarbon derivatives the "electron octet" rule is met by the systems **5** and **6**.



**5**, $D_{3h}$

X = $B^+$ (**a**), $C^{2+}$ (**b**), $N^{3+}$ (**c**)



**6**, $D_{4h}$

X = $B^{3+}$ (**a**), $C^{4+}$ (**b**), $N^{5+}$ (**c**)

According to calculations, the bridging groups do not only stabilize the sandwich configurations, but also provide the possibility of varying their electronic structures.

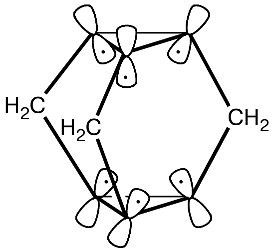
## Calculation Procedure

Density functional (DFT) quantum chemical calculations were carried out with the B3LYP three-parameter functional and the split-valence basis set 6-311+G(d,p)[13] using the Gaussian-98 program package.[14] The stationary points were identified by analytically calculating the force constant matrix. The topological analysis of the total electron density distribution according to Bader (AIM analysis[15]) was performed using an original AIMPAC program package.[16] The orbital interaction diagram was plotted using the results of EHT calculations.[17] Graphic images of the molecular structures shown below were plotted using the PD program (PLUTO node) incorporated into the PC MODEL program package;[18] the Cartesian atomic coordinates obtained after geometry optimization were used as the input parameters.

## Results and Discussion

**Sandwich derivatives based on hydrocarbon cage.** According to calculations, systems **5b**,**c** with $D_{3h}$ symmetry correspond to energy minima ($\lambda$=0)** on the potential energy surface (PES). The geometric parameters of systems **5b**,**c** are presented in Fig. 1 and their energy characteristics are listed in Table 1.

The AIM analysis of systems **5b**,**c** showed that the central atoms form six bonding paths involving carbon atoms in the basal fragments, thus being hexacoordinate. The formation of sandwich structure is ensured by the interaction of non-hybridized p-orbitals of the basal C atoms (they are directed toward the center of the cage) with the p-orbitals of the central atom. Bridging methylene units provide structural rigidity of the molecular cage and, as a consequence, additional stabilization of the sandwich systems.



The C—C bond lengths in system **5b** (1.479 Å) are much shorter than conventional single bond lengths (1.54 Å).[19] An increase in the electronegativity of the central atom on going to the nitrogen-containing derivative **5c** is accompanied by a decrease in the energy levels of its p-orbitals and an increase in the energy gap between the interacting fragment orbitals, which leads to weakening of the orbital interaction between the basal rings and the central atom. At the same time the calculated interatomic distances C—N (1.479 Å) are only slightly longer than conventional lengths of corresponding single bonds (1.47 Å).[19] A structural manifestation of the stronger (compared to the nitrogen-containing derivatives) interaction of the central atom with ligands in system **5b** is an appreciable compression of the outer cage (shortenuing of the bridging C—C bonds and the bonds within the basal fragments).

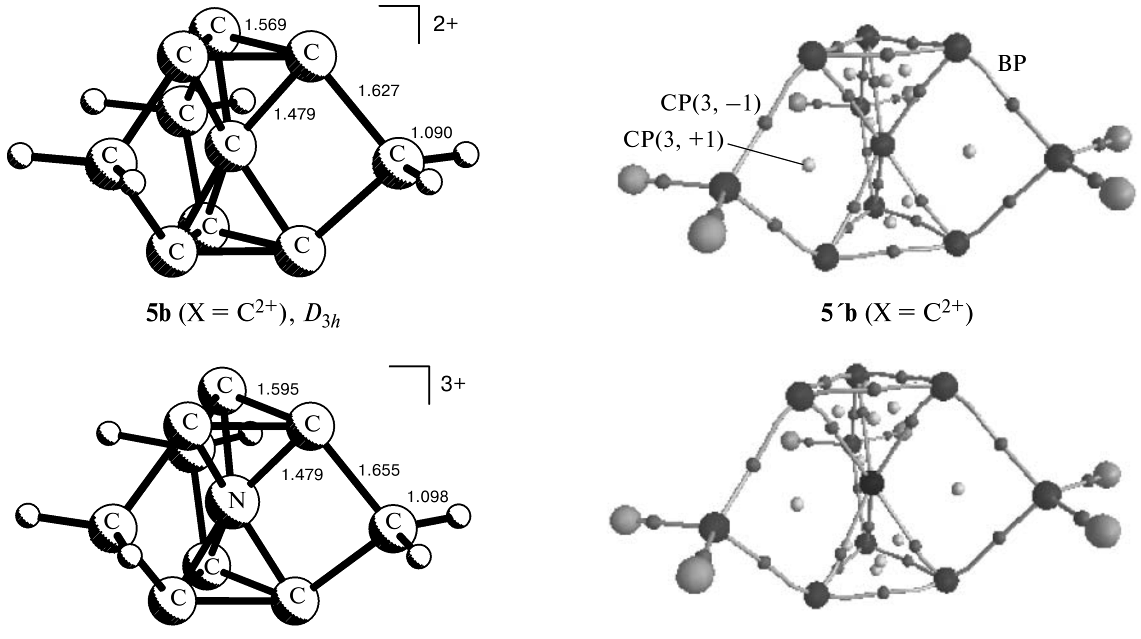
The central hexacoordinate carbon atom in compound **5b** bears a rather large positive Mulliken charge (3.5 e), which provides a decrease in the effective size of the central atom and reduces steric strain caused by incorporation of this atom into the molecular cage. The nitrogen-containing derivative is characterized by a much smaller charge on the central atom (1.3 e). For both systems **5b**,**c** our calculations predicted rather high first harmonic vibrational frequencies (see Table 1), which indicates kinetic stability of these compounds.

Unlike the carbon- and nitrogen-containing derivatives, the boron-containing system **5a** with $D_{3h}$ symmetry corresponds to a second-order stationary point on the PES because here the central atom is too large to be encapsulated within the molecular cavity; this causes destabilization of the sandwich structure. At the same time, enlargement of the cage on going to systems **6** containing four-membered basal rings allows the boron derivative to be stabilized. Namely, calculations showed that all systems **6a—c** with $D_{4h}$ symmetry correspond to energy minima on the PES. The geometric parameters of systems **6** are shown in Fig. 2 and their energy characteristics are listed in Table 1.

The AIM analysis showed that the central atom in systems **6** forms eight bonding paths involving the basal

---

** $\lambda$ is the index of a given stationary point equal to the number of negative eigenvalues of the Hesse matrix at this point.



**5b** ($X = C^{2+}$), $D_{3h}$

**5´b** ($X = C^{2+}$)

**5c** ($X = N^{3+}$), $D_{3h}$

**5´c** ($X = N^{3+}$)

**Fig. 1.** Geometric characteristics of structures **5**.

*Note.* Here and in Figs 2—7 we present the geometric characteristics of the structures corresponding to energy minima ($\lambda = 0$) on the PES obtained from B3LYP/6-311+G** calculations. The bond lengths are given in Ångstrøms. The Bader molecular gaphs of the corresponding structures are shown in the right side of Figs 2—7 (BP is the Bader bonding path, CP (3; –1) is the bonding-path stationary point; and CP (3, +1) is the ring stationary point).

**Table 1.** Energy characteristics of sandwich systems **5**, **6**, and **8**—**10** obtained from B3LYP/6-311+G(d,p) calculations

| Structure | X | Symmetry | $-E_{\text{tot}}$ | ZPE | $\varpi_1$ |
|---|---|---|---|---|---|
| **5b** | $C^{2+}$ | $D_{3h}$ | 383.361679 | 0.111443 | 201.4 |
| **5c** | $N^{3+}$ | $D_{3h}$ | 399.253436 | 0.107353 | 221.1 |
| **6a** | $B^{3+}$ | $D_{4h}$ | 485.180666 | 0.156855 | 289.6 |
| **6b** | $C^{4+}$ | $D_{4h}$ | 497.488069 | 0.152135 | 291.6 |
| **6c** | $N^{5+}$ | $D_{4h}$ | 512.992911 | 0.143663 | 284.7 |
| **8c** | $N^{3-}$ | $D_{4h}$ | 410.395645 | 0.133305 | 205.5 |
| **9** | $C^{4+}$ | $D_{2d}$ | 446.963527 | 0.153421 | 253.5 |
| **10** | $C^{4+}$ | $D_{2h}$ | 446.942363 | 0.152353 | 240.8 |

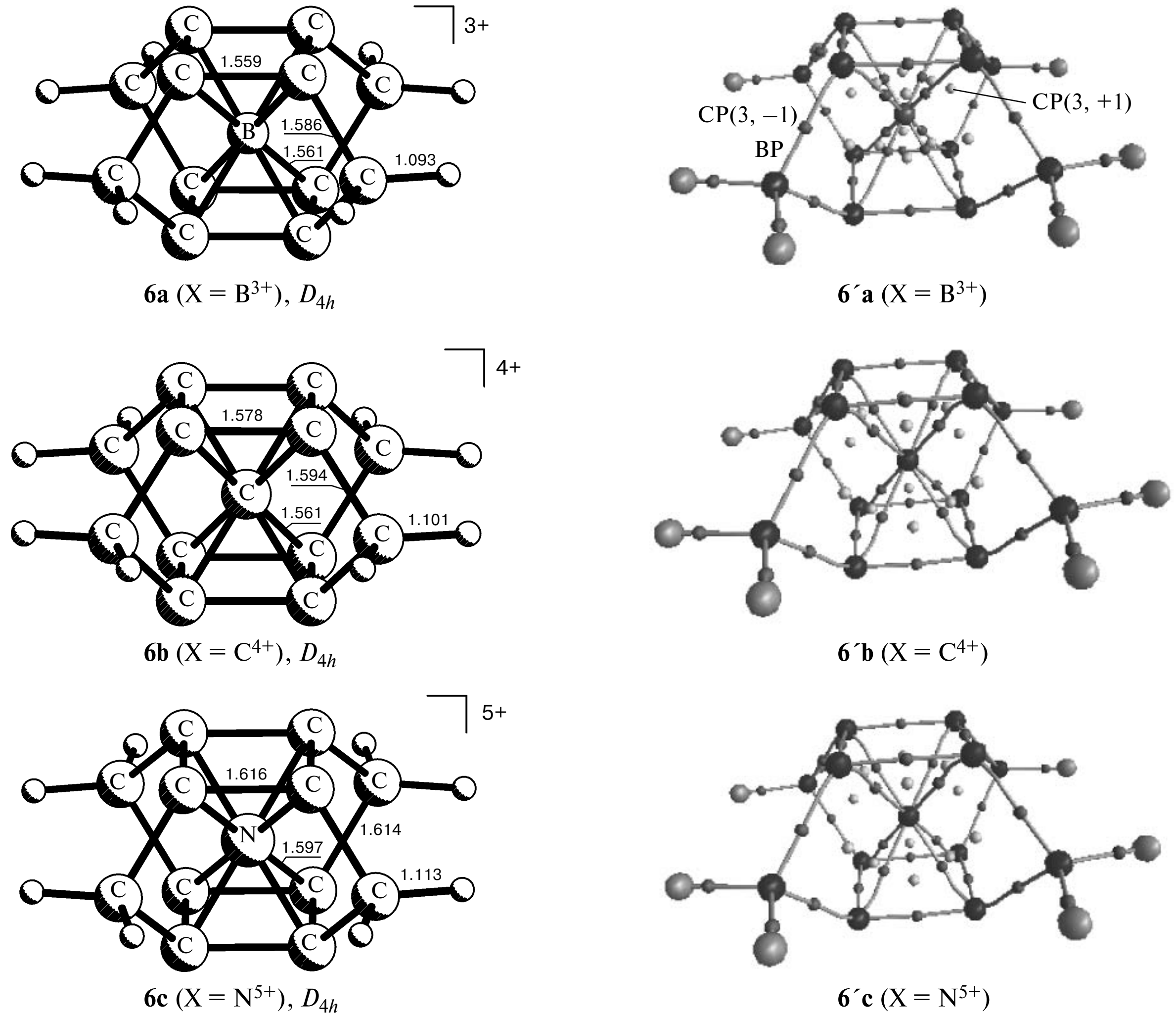
*Note.* $E_{\text{tot}}$/a.u. is the total energy (1 a.u. = 627.5095 kcal mol$^{-1}$); ZPE/a.u. is the zero-point vibrational energy; and $\varpi_1$/cm$^{-1}$ is the lowest harmonic vibrational frequency.

carbon centers, thus being octacoordinate (see Fig. 2). Enlargement of the inner cavity in systems **6** leads to elongation of the bonds between the central atom and the basal fragments compared to systems **5**. The C—C bond lengths in system **6b** (1.561 Å) only slightly exceed those of single C—C bonds. In the nitrogen-containing derivative the bonds between the central atom and ligands (1.597 Å) are considerably longer than covalent bonds N—C. The most efficient interaction between the hypercoordinate center and the basal rings occurs in the boron-containing derivative **6a** with the most diffuse p-orbitals of the central atom. The NBO analysis[20] of the electronic structure of systems **6** also revealed the smallest separation between the orbital energy levels of the interacting fragments for the boron-containing compound. This system is characterized by the most pronounced compression of the molecular cage (calculated interatomic distances B—C are 1.561 Å, being slightly shorter than typical single bond lengths, *e.g.*, 1.58 Å in $BMe_3$).[21]

Nonclassical compounds **5** and **6** containing hypercoordinate central atoms obey the "electron octet" rule, which is the necessary condition for stabilization of sandwich systems.[4] The correlation MO diagram (Fig. 3) shows that stabilization of systems **6** is due to the interaction between the s- and p-valence orbitals of the central atom and the $\pi$- and $\pi$*-MOs of the four-membered basal fragments, which leads to the formation of four bonding MOs (electron octet).

The bonding MOs in systems **5** are formed analogously.

**Sandwich structures containing hetero-substituted basal rings.** The stabilities of the sandwich derivatives **5** and **6** that obey the "electron octet" rule suggest the possibility of replacing basal-ring carbon atoms by heteroatoms in such a fashion that newly formed species remain isoelectronic to the initial system. When considering hypervalent sites, the most appropriate substituents are electron-



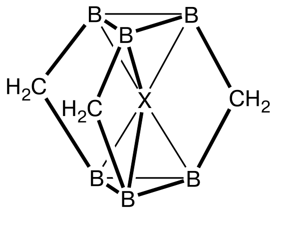
**6a** (X = $B^{3+}$), $D_{4h}$ **6´a** (X = $B^{3+}$)

**6b** (X = $C^{4+}$), $D_{4h}$ **6´b** (X = $C^{4+}$)

**6c** (X = $N^{5+}$), $D_{4h}$ **6´c** (X = $N^{5+}$)

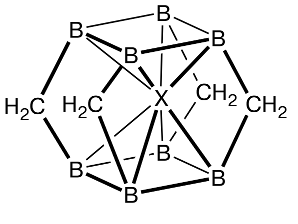
**Fig. 2.** Geometric parameters of structures **6** (for notations, see Fig. 1).

withdrawing boron ligands that were used to design a variety of nonclassical systems.[1,3] In this case the fulfilment of the "electron octet" rule implies transition to anionic systems **7** and **8**.



**7**, $D_{3h}$

X = $B^{5-}$ (**a**), $C^{4-}$ (**b**), $N^{3-}$ (**c**)



**8**, $D_{4h}$

X = $B^{5-}$ (**a**), $C^{4-}$ (**b**), $N^{3-}$ (**c**)

However, calculations of compounds **7** and **8** revealed only one stable system **8c** ($D_{4h}$ symmetry, Fig. 4, Table 1) corresponding to energy minimum ($\lambda = 0$) on the PES. No stationary points corresponding to all other sandwich derivatives **7** and **8** were located because of the lack of convergence.

Systems **7** and **8** contain boron atoms in the basal rings. Here one can expect a considerable increase in steric strain compared to the carbon-containing analogs **5** and **6**. This is due to incorporation of bulky boron centers into the three-membered and four-membered basal rings immobilized in quite rigid cages. System **8c** (unique stable species among compounds **7** and **8**) contains the smallest central atom and the largest volume of the outer cage and thus should experience a minimum steric strain.

Replacement of carbon atoms in the basal rings by bulkier boron atoms causes a significant extension of the basal rings (see Fig. 4) (calculated B—B distances are 1.790 Å, being slightly longer than conventional covalent bond lengths (1.75 Å)).[19] The B—N interatomic distances in system **8c** (1.692 Å) are much longer than the N—B single bond lengths; however, this is consistent with the donor-acceptor bond lengths (*e.g.*, 1.658 Å for $H_3B-NH_3$).[22] Weakening of the bonds between the cen-

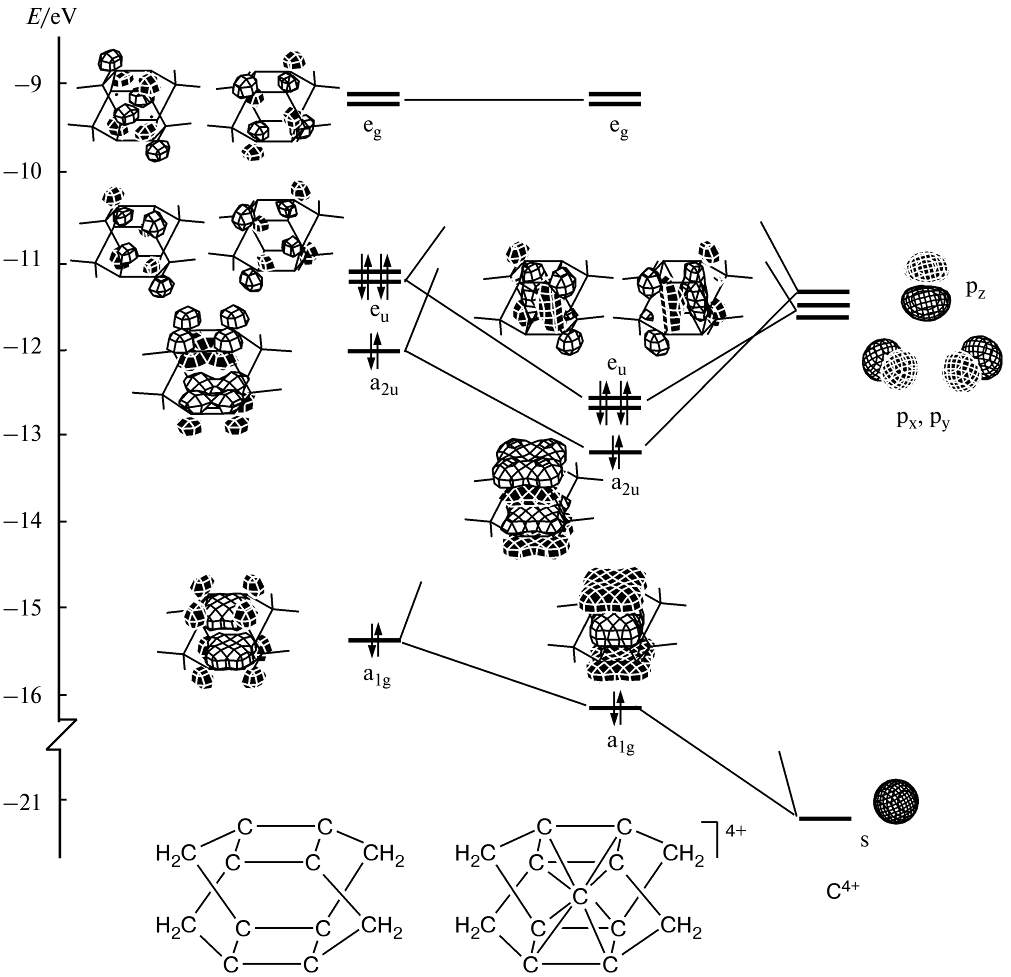
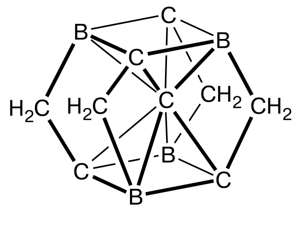


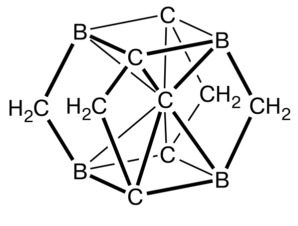
**Fig. 3.** Schematic correlation diagram illustrating the formation of the bonding MOs of system **6b** from fragment orbitals. The MO energy levels were obtained from EHT calculations.[17]

tral atom and ligands compared to system **6c** can be explained by both enlargement of the cage and less efficient fragment orbital interactions due to an increase in the energy gap between the orbitals owing to a decrease in the electronegativity of the basal atoms and an increase in their π-AO energy levels. The formation of an octacoordinate center in system **8c** was confirmed by the AIM analysis, which, however, indicates a somewhat different type of the bonding between the central atom and ligands (compared to systems **5** and **6**). The molecular graph **8´c** of structure **8c** (see Fig. 4) shows that the central nitrogen atom forms two banana-type bonding paths with each boron atom. A similar model for hypervalent bonding was reported in a study[23] of nonclassical systems $CB_6^{2-}$ and $C_3B_4$ containing hexacoordinate carbon centers.

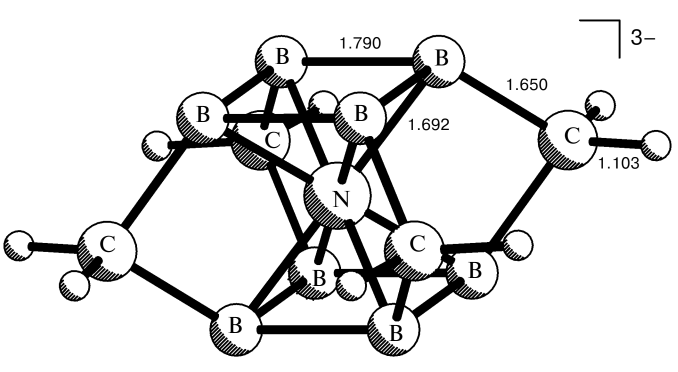
One can expect that experimental detection of systems **5**—**8** will be favored by framing them with counterions, because numerical theoretical studies[1,10,12,24] predict that counterions do not violate the stabilities and structures of nonclassical compounds; rather, they can additionally stabilize these species. At the same time it is important to elucidate the possibility of targeted modification of highly charged systems **5**—**8** that can lead to neutral or low-charged compounds. As an example of such a modification, we studied partial replacement of the basal ring atoms in such a manner that the newly formed system remains isoelectronic to the initial one. For instance, in the case of cationic system **6b** the positive charge can be compensated by replacing four carbon atoms by boron atoms (systems **9** and **10**).



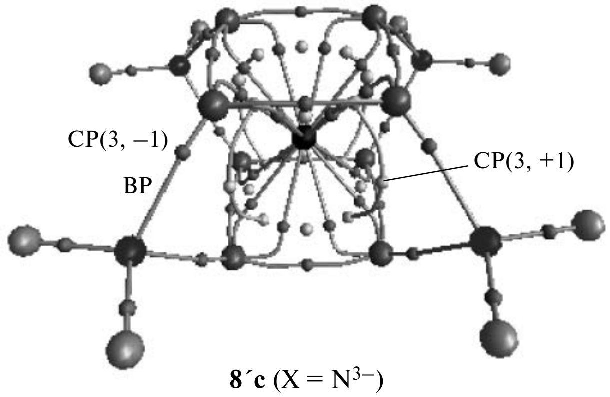
**9**, $D_{2d}$



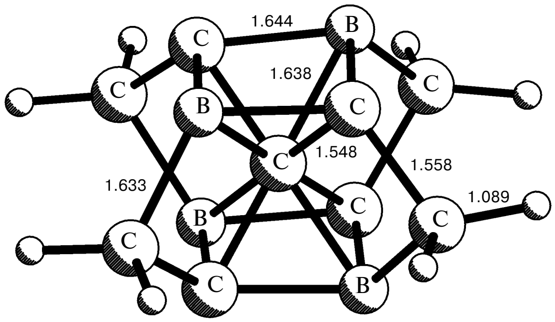
**10**, $D_{2h}$



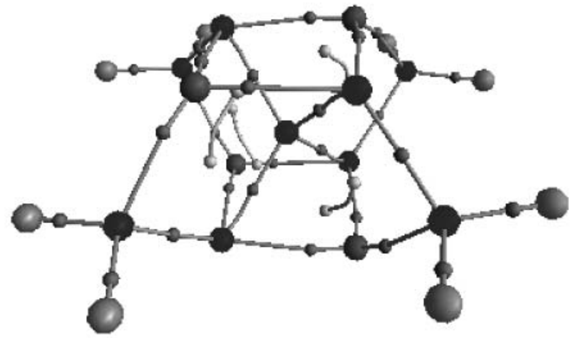
**8c** (X = $N^{3-}$), $D_{4h}$



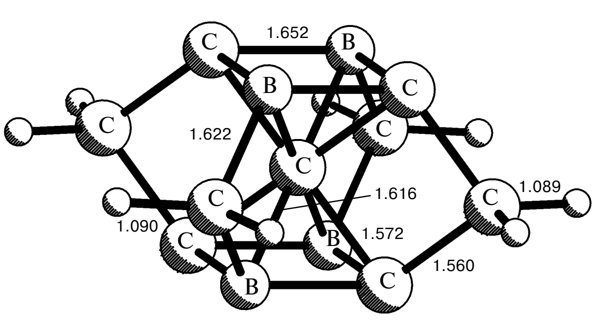
**8´c** (X = $N^{3-}$)



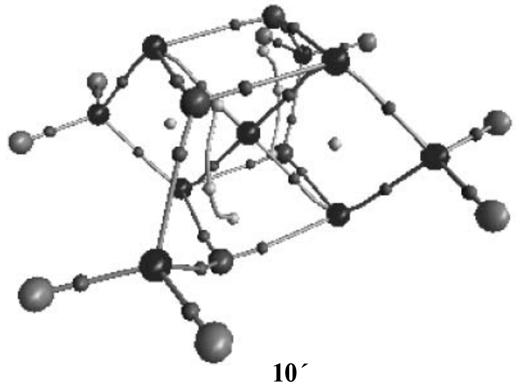
**9**, $D_{2d}$



**9´**



**10**, $D_{2h}$



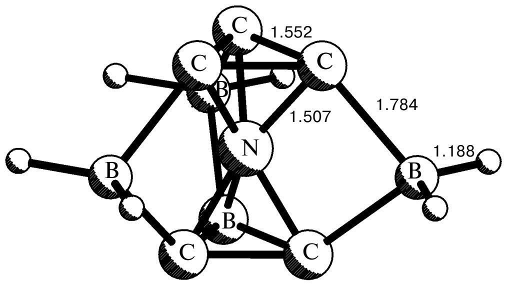
**10´**

**Fig. 4.** Geometric parameters of structures **8**—**10** (see Note to Fig. 1).

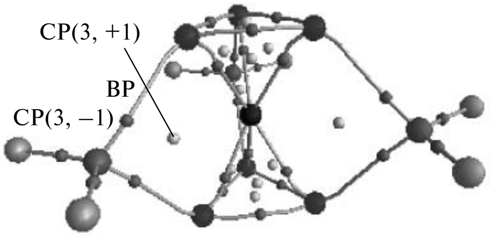
According to calculations, both neutral systems **9** and **10** (see Fig. 4, Table 1) correspond to energy minima ($\lambda = 0$) on the PES. However, this conclusion was not confirmed by the topological analysis of the electron density distribution despite rather short distances between the central carbon atom and the basal atoms and formal octacoordination of carbon in these compounds. According to the results of the AIM analysis, the central carbon atom in compounds **9** and **10** is tetracoordinate (see Fig. 4) and forms chemical bonds only with the basal carbon atoms having half-filled non-hybridized p-orbitals. The boron basal atoms having unfilled diagonally oriented p-orbitals form no chemical bonds with the central atom. System **9** is 13.3 kcal $mol^{-1}$ energetically more preferable and has a classical tetrahedral configuration of the bonding between the central atom and ligands; in system **10** the central carbon atom has a nonclassical planar bond configuration (see Fig. 4). Thus, this type of partial replacement of the basal atoms provides no conservation of the coordination number of the central atom, being at the same time promising in the design of novel types of systems containing planar tetracoordinate centers in the carbon environment of the carbon atoms.

**The nature of bridging atoms and the structure and stability of sandwich systems.** We also considered the possibility of modifying the systems **5**—**8** by varying the bridging fragments. In systems **5** and **6**, the positive charge can be compensated by replacing the bridging carbon centers by electron-deficient boron-containing groups (systems **11** and **12**, respectively).

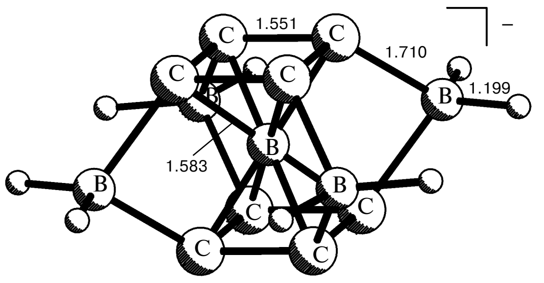
The MO analysis showed that the formation of the fourth covalent bond by the boron centers in systems **11** and **12** is ensured by accepting an extra electron from the π-system of the sandwich cage by each boron atoms. Therefore, these systems also obey the "electron octet" rule. According to calculations, system **11c** with $D_{3h}$ symmetry and systems **12a—c** with $D_{4h}$ symmetry correspond to energy minima on the PES. The geometric parameters



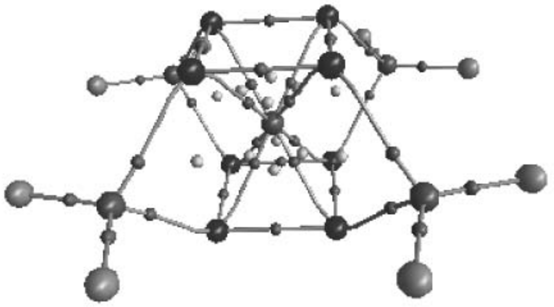
**11c** (X = N), $D_{3h}$



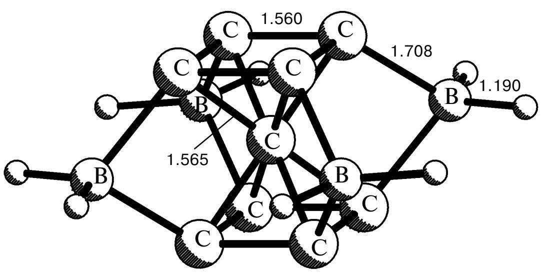
**11´c** (X = N)



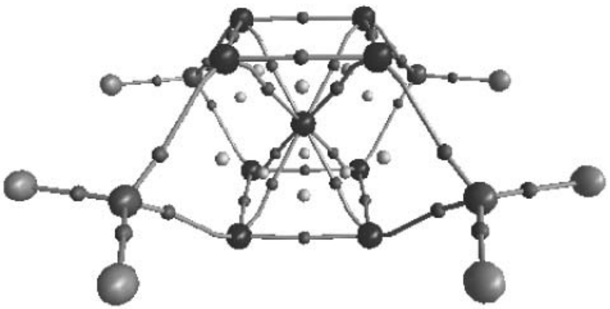
**12a** (X = B$^-$), $D_{4h}$



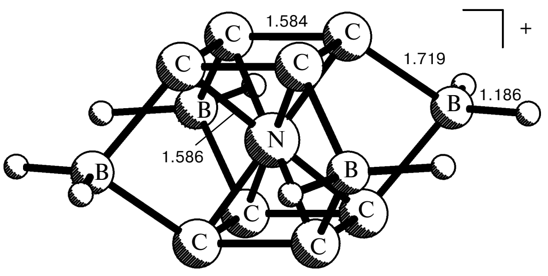
**12´a** (X = B$^-$)



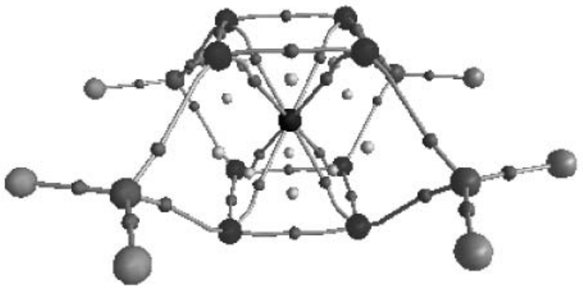
**12b** (X = C), $D_{4h}$



**12´b** (X = C)

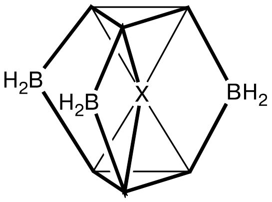


**12c** (X = N$^+$), $D_{4h}$



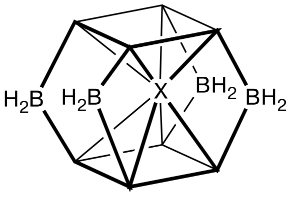
**12´c** (X = N$^+$)

**Fig. 5.** Geometric parameters of structures **11** and **12** (see Note to Fig. 1).



**11**, $D_{3h}$

X = $B^{2-}$ (**a**), $C^-$ (**b**), N (**c**)



**12**, $D_{4h}$

X = $B^-$ (**a**), C (**b**), $N^+$ (**c**)

of these systems are shown in Fig. 5 and their energy characteristics are listed in Table 2.

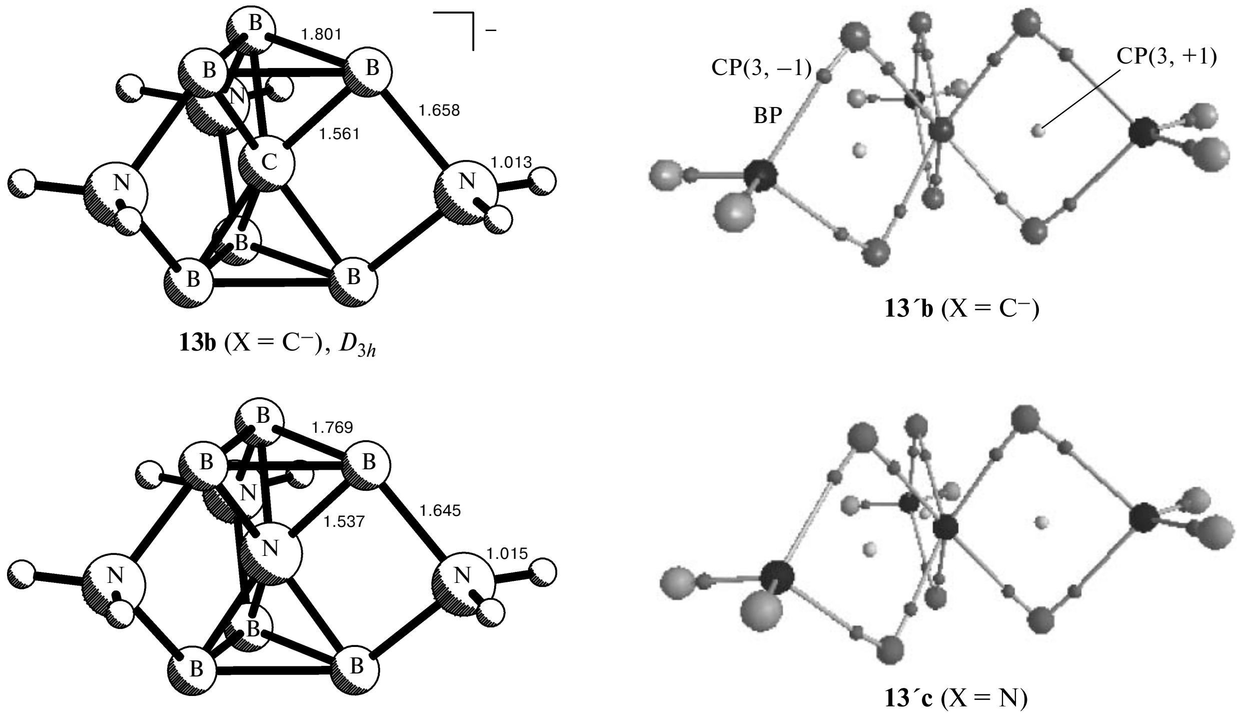
As to the carbon- and boron-containing derivatives **11a**,**b**, their structures with $D_{3h}$ symmetry correspond to the second-order stationary points on the PES. The nitrogen-containing system **11c**, although corresponding to an energy minimum on the PES, is characterized by a low first harmonic vibrational frequency (56 $cm^{-1}$), which indicates a low kinetic stability of the species. At the same time the AIM analysis of this system revealed the formation of a hexacoordinate nitrogen center (see Fig. 5). The calculated interatomic distances N—C (1.507 Å) are slightly longer than corresponding covalent bonds. Weakening of the bonds between the central atom and ligands compared to system **5c** is due to the incorporation of bulkier bridging boron atoms, resulting in an increase in the distances between the basal rings.

**Table 2.** Energy characteristics* of sandwich systems **11**—**15** obtained from B3LYP/6-311+G(d,p) calculations

| Structure | X | Symmetry | $-E_{tot}$ | ZPE | $\varpi_1$ |
|---|---|---|---|---|---|
| **11** | N | $D_{3h}$ | 361.002965 | 0.092795 | 55.8 |
| **12a** | $B^-$ | $D_{4h}$ | 433.650207 | 0.133237 | 196.2 |
| **12b** | C | $D_{4h}$ | 446.656146 | 0.133154 | 250.6 |
| **12c** | $N^+$ | $D_{4h}$ | 462.866148 | 0.128712 | 147.1 |
| **13b** | $C^-$ | $D_{3h}$ | 354.899847 | 0.107794 | 122.0 |
| **13c** | N | $D_{3h}$ | 371.565855 | 0.110965 | 211.6 |
| **14a** | $B^-$ | $D_{4h}$ | 447.513666 | 0.151406 | 223.2 |
| **14b** | C | $D_{4h}$ | 460.747919 | 0.154791 | 244.7 |
| **14c** | $N^+$ | $D_{4h}$ | 477.208843 | 0.154841 | 257.5 |
| **15** | $C^{4+}$ | $D_{2h}$ | 453.777172 | 0.144369 | 171.0 |

* See Note to Table 1.

The AIM analysis of systems **12a**—**c** showed that all of them have octacoordinate central atoms (see Fig. 5). The calculated lengths of the bonds between the basal carbon centers and the bridging boron atoms are 1.71—1.72 Å, being in the range of single C—B bond lengths in carboranes.[25] In all systems **12** the basal rings are slightly compressed compared to systems **6**. In the carbon- and boron-containing systems the bonds of the central atom with the basal centers are somewhat longer than in the cationic analogs **6**, whereas in the nitrogen-containing system the central bonds are shortened. At the same time



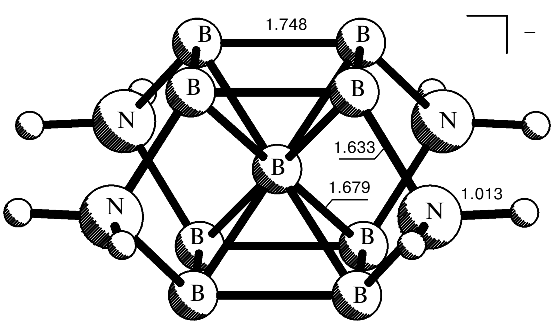
**13b** (X = $C^-$), $D_{3h}$

**13´b** (X = $C^-$)

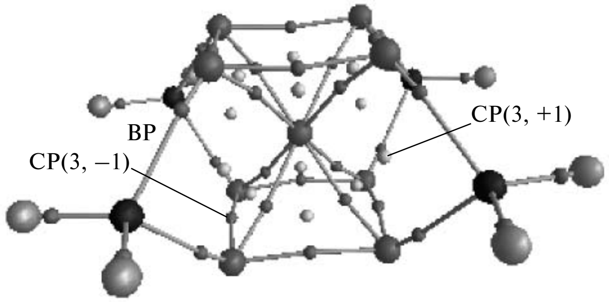
**13c** (X = N), $D_{3h}$

**13´c** (X = N)

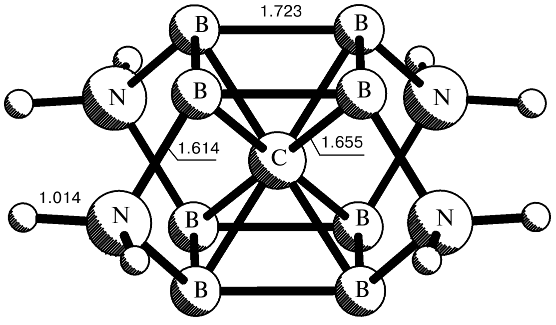
**Fig. 6.** Geometric parameters of structures **13** (see Note to Fig. 1).



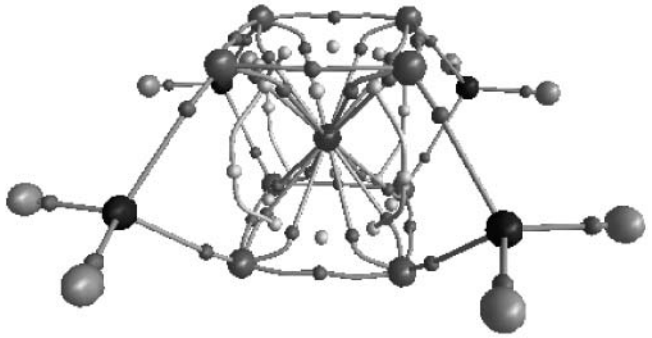
**14a** (X = $B^-$), $D_{4h}$



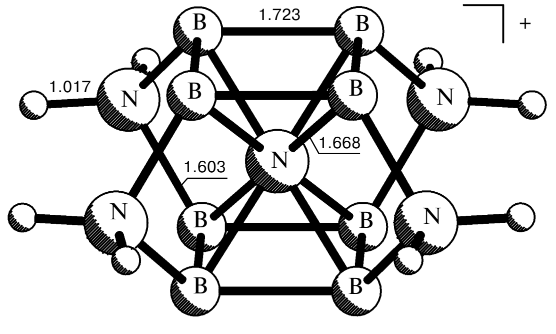
**14´a** (X = $B^-$)



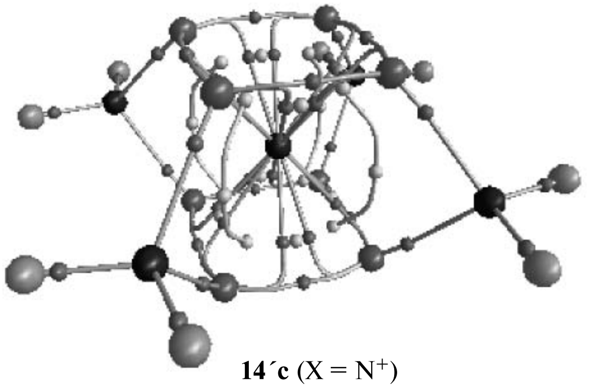
**14b** (X = C), $D_{4h}$



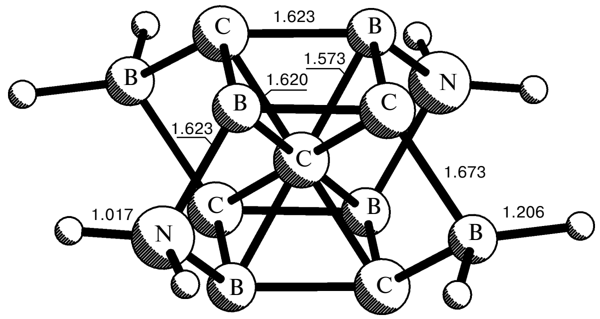
**14´b** (X = C)



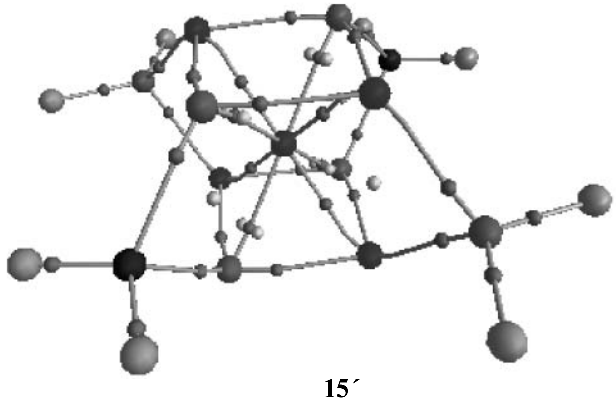
**14c** (X = $N^+$), $D_{4h}$



**14´c** (X = $N^+$)



**15**, $D_{2h}$

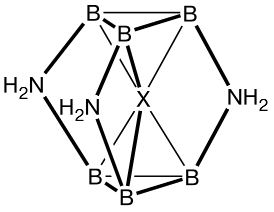


**15´**

**Fig. 7.** Geometric parameters of structures **14** and **15** (see Note to Fig. 1).

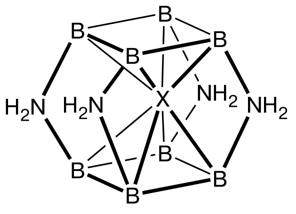
the calculated interatomic distances N—C noticeably increase on going from system **11c** containing three-membered basal rings to system **12c** containing four-membered basal rings, *i.e.*, the trends revealed for compounds **5** and **6** remain valid. Thus, replacement of the bridging atoms allows the electronic structure of the sandwich systems to be varied with conservation of the structural stability and trends of changes in the geometric characteristics.

The negative charges of systems **7** and **8** can be compensated analogously by replacing the bridging carbon atoms by electron-donating nitrogen-containing groups (systems **13** and **14**, respectively).



**13**, $D_{3h}$

X = $B^{2-}$ (**a**), $C^-$ (**b**), N (**c**)



**14**, $D_{4h}$

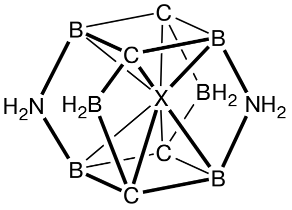
X = $B^-$ (**a**), C (**b**), $N^+$ (**c**)

According to calculations, all systems **13** and **14**, except **13a**, have $D_{nh}$ symmetry and correspond to energy minima ($\lambda = 0$) on the PES. System **13a** with $D_{3h}$ symmetry corresponds to a second-order stationary point ($\lambda = 2$) on the PES. Thus, incorporation of boron atoms into the molecular cages of all the systems containing three-membered basal rings (see above) is sterically unfavorable, whereas the less strained systems containing four-membered basal rings and the central boron atom are stable. The geometric parameters of the stable systems **13** and **14** are shown in Figs 6 and 7 and their energy characteristics are listed in Table 2.

According to the AIM analysis, systems **13** have hexacoordinate while systems **14** have octacoordinate central sites (see Figs 6 and 7, respectively). Compounds **13b**,**c** are characterized by rather long B—B distances within the basal rings, which, although lying in the range of single bond lengths in boranes and carboranes, do not correspond to chemical bonds. Thus, the boron basal atoms in these systems are dicoordinate (see Fig. 6) and only interact with the central and bridging atoms. The bonds between the basal fragments and the central atoms are only slightly longer than conventional single bonds.

The model for hypervalent bonding in systems **14b**,**c** is analogous to the model for compound **8c**. Here, two bent bonding paths connecting the central atom to each basal-ring atom are formed. In the boron-containing system **14a** each ligand forms a unique bonding path involving the central atom. The bonds formed by the boron basal atoms with the bridging nitrogen centers in systems **13** and **14** are much longer than covalent bonds, being at the same time consistent with the donor-acceptor B—N bond lengths.

Interestingly, hypercoordination in system **10** containing a tetracoordinate central atom can be induced by varying the bridging groups. According to calculations, a neutral system **15** (see Fig. 7, Table 2) derived from system **10** corresponds to a stable compound ($\lambda = 0$) on the PES and has an octacoordinate central carbon atom.



**15**, $D_{2h}$

The presence of electron-donating bridging $NH_2$ groups in compound **15** causes acceptance of the electron density by the boron basal atoms and formation of bonds with the central atom. The occurrence of an additional (compared to system **10**) interaction between the central carbon atom and the boron basal atoms is accompanied by noticeable shortening of the C—B distances in compound **15**, whereas the C—C bonds become somewhat longer.

Thus, the sandwich systems based on the "cyclophane" cage, which were analyzed in this work, belong to a novel type of stable nonclassical compounds containing hypercoordinate atoms of second-row elements. A key feature of these systems is the possibility of design of various structural modifications that make it possible to vary the electronic characteristics and geometric parameters without stability violation.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32538), the Council on Grants at the President of the Russian Federation (Program of Support of the Leading Scientific Schools, Grant NSh-4849.2006.3), and the Civil Research and Development Foundation (USA).

## References

1. V. I. Minkin and R. M. Minyaev, *Mendeleev Commun.*, 2004, 43.
2. E. D. Jemmis, E. G. Jayasree, and P. Parameswaran, *Chem. Soc. Rev.*, 2006, **35**, 157.
3. V. I. Minkin, R. M. Minyaev, and R. Hoffmann, *Usp. Khim.*, 2002, **71**, 989 [*Russ. Chem. Rev.*, 2002, **71**, 869 (Engl. Transl.)].
4. V. I. Minkin, R. M. Minyaev, and Yu. A. Zhdanov, *Nonclassical Structures of Organic Compounds*, Mir Publishers, Moscow, 1987.
5. J. B. Collins and P. v. R. Schleyer, *Inorg. Chem.*, 1977, **16**, 152.
6. M. Eiermann and K. Halner, *J. Am. Chem. Soc.*, 1992, **114**, 135.
7. R. A. Williams, K. F. Tesh, and T. P. Hanusa, *J. Am. Chem. Soc.*, 1991, **113**, 4843.

8. P. Jutzi and N. Burford, *Chem. Rev.*, 1999, **99**, 969.
9. F. Zaegel, J. C. Galucci, P. Meunier, R. Gautheron, M. R. Sivik, and L. A. Paquette, *J. Am. Chem. Soc.*, 1994, **116**, 6466.
10. R. M. Minyaev, V. I. Minkin, and T. N. Gribanova, *Mendeleev Commun.*, 2004, 96.
11. G. N. Srinivas, T. P. Hamilton, E. D. Jemmis, M. L. McKee, and K. Lammertsma, *J. Am. Chem. Soc.*, 2000, **122**, 1725.
12. R. M. Minyaev and T. N. Gribanova, *Izv. Akad. Nauk, Ser. Khim.*, 2005, **54**, 527 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 533].
13. J. B. Foresman and E. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Pittsburgh: Gaussian, Inc., 1996.
14. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M.W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98*, *Revision A.9*, Gaussian, Inc., Pittsburgh (PA), 1998.
15. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990.
16. J. R. Cheeseman, T. A. Keith, and R. F. W. Bader, *AIMPAC Program Package*, Hamilton, Ontario (Canada): McMaster University, 1992.
17. R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.
18. *PC MODEL*, Selena Software, Bloomigton, IN (USA), 1987.
19. J. Emsley, *The Elements*, Clarendron Press, Oxford, 1991.
20. A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
21. M. Hargittai and I. Hargittai, *The Molecular Geometries of Coordination Compounds in Vapour Phase*, Akademia Kiado, Budapest, 1975.
22. L. R. Thorn, R. D. Suenram, and F. J. Lovas, *J. Chem. Phys.*, 1983, **78**, 167.
23. C. Foroutan-Nejad, G. H. Shafiee, A. Sadjadi, and S. Shahbazian, *Can. J. Chem.*, 2006, **84**, 771.
24. R. M. Minyaev, V. I. Minkin, T. N. Gribanova, and A. G. Starikov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2219 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 2325].
25. J. Casanova, *The Borane*, *Carborane and Carbocation Continuum*, John Wiley and Sons, Chichester, 1998.

*Received July 18, 2005*