Planar hexacoordinated boron in organoboron compounds: an *ab initio* study

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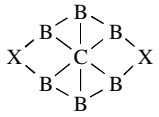
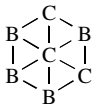
Ab initio [MP2(fu)/6-31G**, MP2(fu)/6-311G**] and DFT [B3LYP/6-31G**, B3LYP/6-311G**] calculations predict stable planar structures of the nonclassical compounds $BB_6(CH)_3$ and $BB_6X_2^-$ (X = NH, O) containing a hexacoordinated central boron atom.

Nonclassical organoelement systems, particularly those containing hypercoordinated planar centres are of considerable theoretical and practical interest.[1] Recently, unusual stable planar molecular systems **1** and **2** and their isomers containing planar hexacoordinated carbon centres have been predicted by *ab initio* calculations.[2,3]



X = NH, O

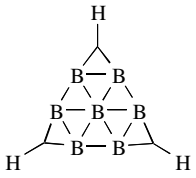
1, D_{2h}



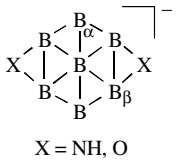
2, C_{2v}

These structures with a hexacoordinated planar carbon atom are stabilized through the multicentre interactions of the central atom with the ligands. One may expect that the same bonding type may also occur in similar structures of hypercoordinated central atoms of other main-group elements, particularly, in boron-containing compounds. A possibility of stabilization of such compounds is supported by theoretical works on boron clusters including planar or quasi-planar boron atoms.[4–6]

Here, we report on *ab initio* [MP2(fu)/6-31G**, MP2(fu)/6-311G**][7] and density functional theory [B3LYP/6-31G**, B3LYP/6-311G**][8] calculations on compounds **3** and **4** (X = = NH, O), which contain a hexacoordinated planar boron centre.



3, D_{3h}



X = NH, O

4, D_{2h}

According to the calculations, compounds **3** and **4** (X = NH, O) possess highly symmetrical planar structures and correspond to minima ($\lambda = 0$; hereafter, λ designates the number of hessian negative eigenvalues at a given stationary point) on the corresponding potential energy surfaces (PES). Their geometric and energy characteristics are listed in Table 1 and depicted in Figure 1.

The B_c–B bond lengths formed by the central boron (B_c) with the vicinal borons in **3** are about ~1.7 Å; this value is in the range of available experimental data[9] on BB single bonds. These bonds are 0.1 Å longer than the peripheral BB bonds. The multicentre type of bonding in the B_cB_6 coordination site is illustrated by the shapes of the respective molecular orbitals of **3** shown in Figure 2. An additional contribution to the stability of the planar polycyclic structure of **3** is provided by the interaction of the vacant p_z-orbital located at the B_c centre with the π-system of the ligand environment.

The molecule of **3** is a 6π-electron aromatic system with three occupied π-orbitals (Figure 3). Electron density corresponding to the $1a_2''$-orbital (Figure 3) is delocalised on the entire system, electron density defined by the $1e''$-orbitals is localised inside of the B_2CH fragments. Thus, these three π-orbitals are bonding.

According to Mulliken orbital population analysis, central boron in **3** possesses a vacant p_π-orbital and, thus, does not contribute

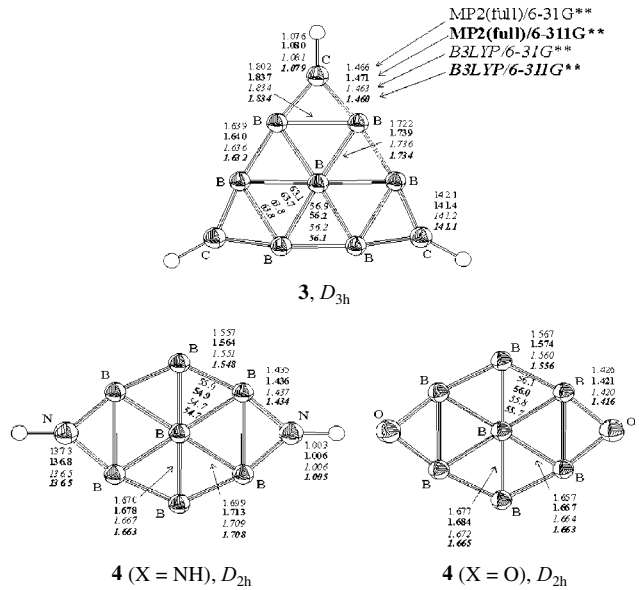
Table 1 *Ab initio* and DFT data for compounds **3** and **4**.[a]

Compound	Method	E_{tot}	λ	ZPE	ω_1
3	MP2(fu)/6-31G**	–288.986615	0	0.074912	63.8
	MP2(fu)/6-311G**	–289.207299	0	0.073563	71.7
	B3LYP/6-31G**	–289.947847	0	0.073959	119.3
	B3LYP/6-311G**	–290.005892	0	0.073558	115.2
4 (X = NH)	MP2(fu)/6-31G**	–283.772298	0	0.061120	87.4
	MP2(fu)/6-311G**	–284.019274	0	0.060076	93.4
	B3LYP/6-31G**	–284.677995	0	0.060390	120.6
	B3LYP/6-311G**	–284.757773	0	0.059998	91.7
4 (X = O)	MP2(fu)/6-31G**	–323.472887	0	0.036851	35.0
	MP2(fu)/6-311G**	–323.753393	0	0.036185	46.0
	B3LYP/6-31G**	–324.438428	0	0.036625	95.7
	B3LYP/6-311G**	–324.529137	0	0.036344	34.3

[a] E_{tot} (in a.u.) is the total energy (1 a.u. = 627.5095 kcal mol^{-1}); λ is the number of the negative hessian eigenvalues; ZPE (in a.u.) is the harmonic vibration zero-point correction; ω_1 (in cm^{-1}) is the lowest harmonic vibration frequency.

electrons into the total π-system. Each of the B_2CH fragments contributes two π-electrons to the total π-system of **3**. Therefore, it is π-isoelectronic to the aromatic cyclopropenyl cation and possesses 'local' aromaticity. Rather strong π-interaction inside the B_2CH fragments is evidenced by the short (1.46–1.47 Å) lengths of the BC bonds, which are considerably shorter than single BC bonds (1.6–1.7 Å)[10,11] and are close to the lengths of typical BC double bonds (~1.4–1.45 Å).[12] Compound **3** also has short peripheral BB bonds (1.64 Å) whose lengths are comparable with those of BB double bonds (~1.63 Å).[12]

The stability of anions **4** with central hypercoordinated boron is also due to the formation of multicentre bonds of the central atom with surrounding ligands. The calculated bond lengths BB_α and BB_β are in the range characteristic of standard single BB



3, D_{3h}

4 (X = NH), D_{2h}

4 (X = O), D_{2h}

Figure 1 Geometry parameters of the structures of **3** and **4** calculated by *ab initio* and DFT methods. The bond lengths and angles are indicated in angström units and degrees, respectively.

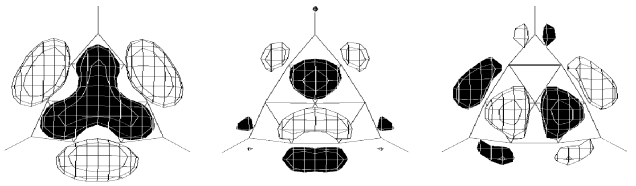


Figure 2 Shapes of multicentre σ-molecular orbitals in the structure of **3** [MP2(full)/6-31G** calculations].

bonds (~1.7 Å). A peculiar feature of systems **4** is very short B_α–B_β bonds (1.55–1.57 Å), which are appreciably shorter than experimentally determined BB double bonds (~1.63 Å).[12]

The π-electronic system of anions **4** contains eight π-electrons, two of which coming from the B_α centre. Thus, the valent state of the B_α atoms in **4** does not correspond to the 'classical' sp^2-hybridization with a vacant p_π-orbital. The electron occupation of the B_α p_π-orbitals is corroborated by the data of Mulliken population analysis indicating a large (about –0.3 e) negative charge on each of the B_α atoms.

As distinct from B_α, the valent state of other four boron atoms, B_β, may be described in terms of 'classical' sp^2-hybridization with a vacant p_π-orbital. Such a distinction facilitates the B_α–B_β charge transfer, leads to strong interligand π-interaction and contributes to stabilization of the planar system with hypercoordinated central boron. Another stabilising factor is the aromaticity of anions **4**: all bonding π-orbitals are occupied by electrons, whereas all antibonding π-orbitals remain vacant.

Note that all of the BN bonds in the polycyclic system of **4** (X = NH) are weaker than usual π-dative BN bonds: the calculated lengths of the BN bonds in **4** are equal to 1.44 Å, and they are notably longer than the experimental lengths of π-dative BN bonds (1.38–1.41 Å).[13] Similar effect of weakening π-interaction between B and N in the case of inclusion of boron atoms into BB double bonds is well known.[13]

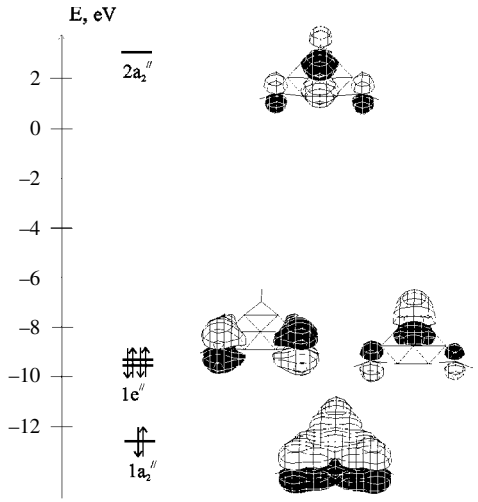


Figure 3 Occupation of π-orbitals in **3** [MP2(full)/6-31G** calculations].

The replacement of NH groups by a more electronegative oxygen atom leads to strengthening the BB_β bonds in **4** (X = O) and to weakening the B_α–B_β and B–B_α bonds. The latter effect leads to destabilization of the system. Nonetheless, the structure of **4** (X = O) corresponds to a minimum ($\lambda = 0$) on the PES. At the same time, low values of the first harmonic vibration frequencies point to the shallowness of this minimum and, consequently, to low kinetic stability of the structure of **4** (X = O).

In conclusion, the results of the calculations of hypothetical compounds **3** and **4** testify that there are three important factors leading to the stabilization of planar hexacoordinated central boron atom: (1) the π-interaction of hypercoordinated central boron with the ligands in its environment; (2) the strong interligand bonding and (3) the aromaticity of polycyclic systems (the occupation of all bonding and the vacancy of all anti-bonding π-orbitals).

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References

1 V. I. Minkin, R. M. Minyaev and Yu. A. Zhdanov, *Nonclassical Structures of Organic Compounds*, Mir, Moscow, 1987.
2 R. M. Minyaev and T. N. Gribanova, *Izv. Akad. Nauk, Ser. Khim*., 2000, 786 (*Russ. Chem. Bull*., 2000, **49**, 783).
3 K. Exner and P. v. R. Schleyer, *Science*, 2000, **290**, 1937.
4 J. E. Fowler and J. M. Ugalde, *J. Phys. Chem*., 2000, **104**, 397.
5 (*a*) I. Boustani, *Surface Sci*., 1997, **370**, 355; (*b*) I. Boustani, *Phys. Rev. B*, 1997, **55**, 1.
6 I. Boustani, A. Quandt and A. Rubio, *J. Solid State Chem*., 2000, **154**, 269.
7 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem*., 1993, **14**, 1347.
8 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.
9 M. Hildenbrand, H. Pritzkow and W. Siebert, *Angew. Chem., Int. Ed. Engl*., 1985, **24**, 759.
10 M. Hargittai and I. Hargittai, *The Molecular Geometries of Coordination Compounds in Vapour Phase*, Akademia Kiado, Budapest, 1975.
11 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Claredon Press, Oxford, 1986.
12 P. Power, *Inorg. Chim. Acta*, 1992, **198**–**200**, 443.
13 A. Moezzi, R. A. Bartlett and P. P. Power, *Angew. Chem., Int. Ed. Engl*., 1992, **31**, 1082.

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