

Planar tetracoordinated nitrogen in boron-containing compounds: a theoretical quantum-chemical study

Tatyana N. Gribanova, Ruslan M. Minyaev* and Vladimir I. Minkin

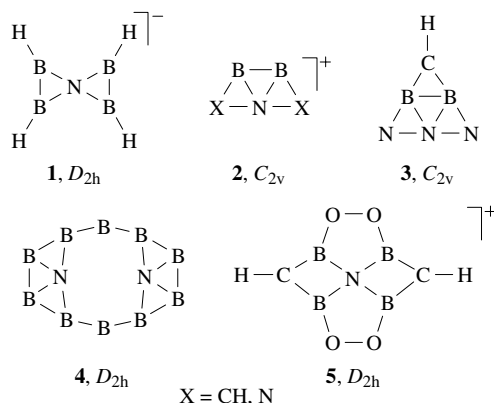
Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 8632 4346 67; e-mail: minyaev@ipoc.rsu.ru

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A series of stable non-classical structures of boron-containing compounds with planar tetracoordinate nitrogen atoms has been computationally designed based on density functional theory [B3LYP/6-311+G(*d,p*)] calculations.

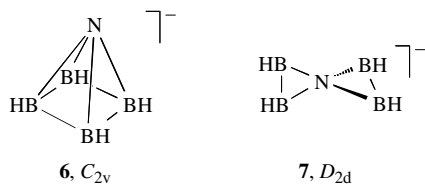
The strategy of stabilization of non-classical planar tetracoordinate carbon originally developed by Hoffmann, Alder and Wilcox¹ was later applied to a number of non-classical organo-element systems.^{2–5} An important principle of this strategy consists in attaching π -electron-withdrawing substituents to a planar carbon centre. In the case of tetracoordinated main-group elements more electronegative than carbon, this effect is less pronounced. The only theoretically predicted systems containing a planar tetracoordinated nitrogen are NAl_4^- and NSiAl_3 .⁶ Meanwhile, recent theoretical investigations^{4,5,7–9} showed that planar boron environments can serve as convenient frameworks for the stabilization of planar tetra- and hypercoordinated main-group centres.

Here, we report on density functional theory [B3LYP/6-311+G(*d,p*)]¹⁰ calculations of stable structures **1–5**, which contain planar tetracoordinated nitrogen centres.



The simplest boron framework encapsulating a planar tetracoordinated nitrogen is present in 3-aza-1,2,4,5-tetraboraspiro[2.2]pentane anion **1**. It corresponds to a minimum ($\lambda = 0$; hereafter, λ designates the number of negative hessian eigenvalues at a given stationary point) on the $\text{B}_4\text{H}_4\text{N}^-$ potential energy surface (PES). The calculated geometric characteristics of anion **1** are presented in Figure 1.

Other $\text{N}(\text{BH})_4^-$ structures with non-planar tetracoordinated nitrogen centres (pyramidal **6** and tetrahedral **7**) do not correspond to stable forms. The structure of **6** corresponds to a critical point with $\lambda = 2$, while the structure of **7** is located on a slope of the PES, i.e., it is not characterised by a stationary point on the PES.



The structural stability of **1** is determined by the combined effect of electronic (σ -donor and π -acceptor boron ligands) and steric (nitrogen centre included in two strained three-membered rings) factors,^{1,3} as well as the stability of its π -system. According

to MO analysis, anion **1** is characterised by a four-electron π -system with two occupied bonding and vacant antibonding π -orbitals (Figure 2) likewise the previously studied derivatives of planar tetracoordinated carbon.^{4,5}

The influence of counter-ions on the stability of **1** was studied using model system $\text{Li}^+\text{N}(\text{BH})_4^-$ **8**, which was found to be a minimum ($\lambda = 0$) on the respective PES. The Li^+ ion does not cause substantial deformation of the planar fragment $\text{N}(\text{BH})_4^-$ (Figure 1). Relatively small charge separation (the Mulliken charge at Li is 0.284 e), as well as a short N–Li distance (1.954 Å), which slightly exceeds the ordinary bond length, allows us to characterise the $\text{LiN}(\text{BH})_4$ complex as a covalent compound with a pentacoordinated nitrogen centre.

The $\text{N}(\text{BH})_4^-$ PES contains another isomer **9** with planar tetracoordinated nitrogen (Figure 1), which can be considered as the product of double 1,2-proton shift in **1**. According to

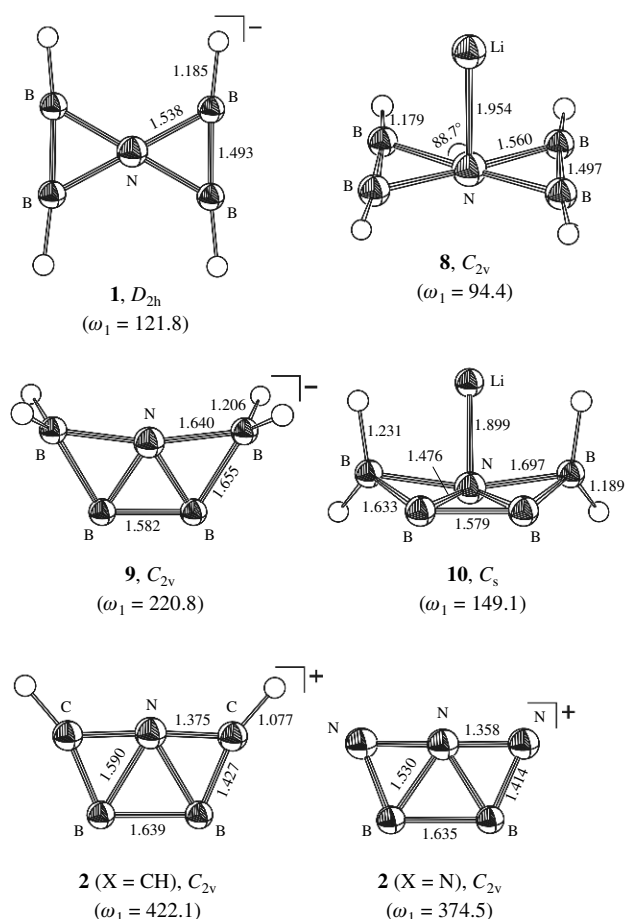


Figure 1 Geometry parameters (bond lengths are given in angstroms) and the smallest harmonic vibration frequency (ω_1 in cm^{-1}) of the stable ($\lambda = 0$) structures of **1**, **2**, **8–10** calculated by the B3LYP/6-311+G** method. The smallest harmonic vibration frequencies for the structures of **1**, **2** (X = CH), **8** correspond to the tetrahedral distortion, for structures of **2** (X = N), **9**, to the pyramidal distortion, and for the structure of **10**, to the twist distortion of the Li atom.

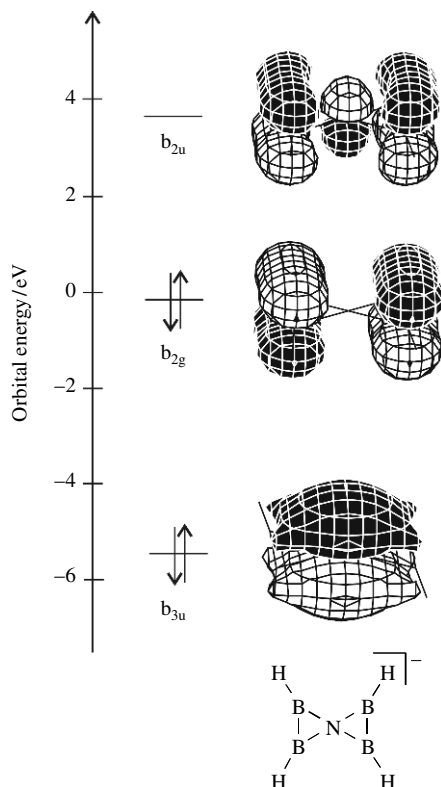


Figure 2 The shape and occupation of π -orbitals in **1**.

the calculations, isomer **9** is 9.3 kcal mol⁻¹ energy preferred to **1**. The attachment of Li leads to formation of complex **10** (Figure 1) with a rather short the Li...N distance and, similarly to isomer **1**, does not cause substantial deformations of the planar nitrogen centre and the peripheral boron surrounding in system **9**. As in the case of systems **1** and **9**, neutral system **10** is 8.2 kcal mol⁻¹ more stable than **8**. The increased stability of **9** is caused by additional stabilization due to strong inter-ligand BB bonding between the two equivalent three-membered rings. The computed inner BB bond length in **9** is 1.582 Å, which is shorter than experimentally determined double B=B bond lengths (~1.63 Å).¹¹

Analogous mechanism of stabilization of planar tetracoordinated nitrogen operates also in cationic systems **2**, which are isoelectronic to **1** (Figure 1), which correspond to energy minima ($\lambda = 0$) on the respective PESs. As for **1**, other forms of cations **2** (X = CH, N) with pyramidal or tetrahedral bond configurations at nitrogen do not conform to stable structures. Similarly to **9**, systems **2** (X = CH, N) are characterised by formation of strong inter-ligand BB bonds (1.64 Å). Each of the peripheral nitrogens in **2** (X=N) contributes one electron to the total π -system, whereas its sp^2 -type lone pair lying in the molecular plane belongs to the σ -system. In the formed 4π -electron system of **2**, significant splitting of the two bonding filled with electrons and antibonding π -MOs is observed.

Various structural modifications of systems **1** and **2** retaining planar tetracoordinated nitrogens centres are conceivable. One of them is represented by neutral compound **3** (Figure 3).

Note that compound **3** has stable ($\lambda = 0$) isomer **11** (Figure 3) with planar teracoordinated carbon. According to the calculations, **11** is 67.0 kcal mol⁻¹ more stable than **3**. This may be explained by more effective delocalization of the p_z electron pair located at less electronegative carbon as compared with that at nitrogen in **3**.²

Another interesting example of neutral non-classical systems is compound **4** (Figure 3) containing two planar teracoordinated nitrogen centres. As the calculations predict, the ground state of **4** is the $^3B_{3g}$ triplet. The principal factor determining the stabilization of **4** is the strong inter-ligand π -bonding of different boron ligands. Two boron atoms lying on the C_2 sym-

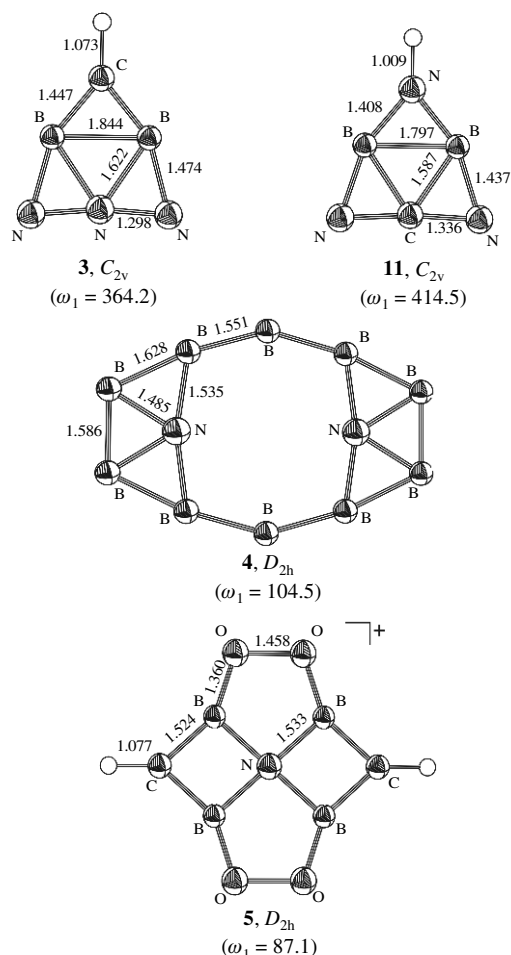


Figure 3 Geometry parameters (bond lengths are given in angstroms) and the smallest harmonic vibration frequency (ω_1 in cm⁻¹) of the stable ($\lambda = 0$) structures of **3–5** and **11** calculated by the B3LYP/6-311+G** method. The smallest harmonic vibration frequencies for the structures of **3**, **5**, **11** correspond to the pyramidal distortion, and for the structure of **4**, to the boat distortion.

metry axis and connecting two equivalent NB₄ fragments are sp -hybridised and contain one of the valence electrons in the p_π -orbital, which leads to formation of strong multicentre π -bonds with vacant p_π -orbitals of the neighbouring boron atoms. Stabilization of the 8π -electron system **4** is due to its transition to the triplet electronic state. Promotion of one π -electron to the vacant π -MO leads to occupation of five bonding π -MOs, the order and shape of which are similar to those of π -MOs of the aromatic system of naphthalene.

Another example of the non-classical system with a planar tetracoordinated nitrogen centre is fenestrane-like compound **5** (Figure 3), which was proposed as a suitable framework for stabilization of planar tetracoordinated carbon more than 30 years ago.¹ However, despite the intense search for such compounds,² no structures of this kind have been discovered theoretically or experimentally for the second row main-group elements. According to the calculations, the stable ground-state structure of **5** is the $^3B_{1u}$ triplet. Although small value of the lowest harmonic vibration frequency (87 cm⁻¹) can point to the rather low kinetic stability of **5**, this system is interesting as the first example of a stabilised *N*-fenestrane derivative.

Thus, our calculations point to the existence of a novel structural type of non-classical boron-containing systems with a planar tetracoordinated nitrogen centre, which are stabilised by the cumulative action of electronic and steric factors.

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