



## The inorganic analogues of *carbo*-benzene



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### ABSTRACT

Inspired by *carbo*-benzene, we have analyzed *in silico* the stability of *carbo*-borazine ( $C_{12}B_3N_3H_6$ ) and the *iminobora*-mer of borazine ( $B_9N_9H_6$ ). Both systems may be regarded as the inorganic analogues of *carbo*-benzene, being  $B_9N_9H_6$  the perfect case. Unlike aromatic *carbo*-benzene,  $C_{12}B_3N_3H_6$  and  $B_9N_9H_6$  can be classified as almost nonaromatic systems as indicated by the computed induced magnetic field. All these systems undergo dimerization very readily; therefore, they cannot be synthesized as such. However, akin to substituted *carbo*-benzene, the substitution of the hydrogen atom of  $C_{12}B_3N_3H_6$  and  $B_9N_9H_6$  by other groups could stabilize them.

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According to Chauvin's definition [1–3], a *carbo*-mer or [n]pericyclyne is an expanded molecule obtained by insertion of  $nC_2$  units within each bond of a molecule. The simplest example of a *carbo*-mer is acetylene. In case one imagines the *carbo*-mer of benzene, several possibilities can be anticipated. One of them is the unsubstituted ring *carbo*-mer called "*carbo*-benzene" (**1**, see Fig. 1). The molecule has two resonance structures, resembling one proposed by Kekulé for benzene. Interestingly, substituted derivatives of **1** are known [4–7], but the naked-skeleton itself (without possible external conjugation) remains as a synthetic challenge. Density functional theory (DFT) computations show that **1** adopts  $D_{6h}$  symmetry, satisfying the structural criterion to be considered as an aromatic system [8–10]. Other carbomers derived from rings or cages have been recently studied [11,12].

Let us consider the possibility of building an inorganic analogue of *carbo*-benzene. In 1940, Wiberg and Bolz proposed the alias of 'inorganic benzene' for borazine [13] based on the fact that all B–N bond lengths are equivalent, which is the landmark of aromaticity in hydrocarbons, and the number of  $\pi$ -electrons is the same as in benzene. However, the electronegativity difference between boron

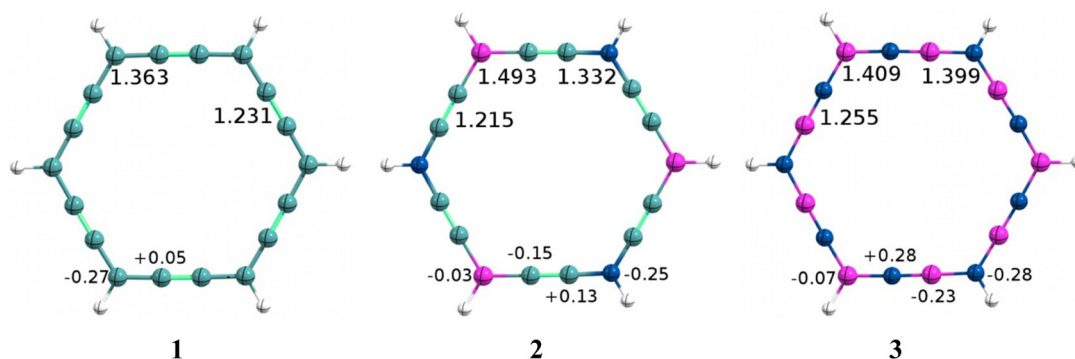
and nitrogen induces a decrease in its aromaticity [14,15]. Inspired by the beauty of *carbo*-benzene and the analogy between borazine and benzene, we think of the inorganic analogues of *carbo*-benzene. Molecule **2** ( $C_{12}B_3N_3H_6$ ) is formally the *carbo*-borazine. In order to build a carbon-free molecule, we have also decided to expand borazine by insertion of six B–N (azaborine) units. The result is the aesthetically pleasing structure of [6]pericyclyne or *iminobora*-mer of borazine ( $B_9N_9H_6$ , Molecule **3**). None of these molecules is discussed yet, but some extended structures based on this unit were studied *in silico* by Ivanovskii and co-workers [16]. Therefore, in this letter, we explore the viability of **2** and **3** as the inorganic analogues of *carbo*-benzene. The nature of the chemical bond is studied *via* molecular orbital analysis and electron delocalization in terms of the induced magnetic field.

The optimized structures and key geometrical parameters are displayed in Figure 1. The Cartesian coordinates and energies are given in the Supporting Information. All geometries are optimized at the PBE0/def2-TZVP level [17,18] in Gaussian 09 [19]. Frequency analysis shows that the planar structures of **1–3** are true local minima on the potential energy surfaces. The lowest frequencies for **1**, **2**, and **3** are 61, 48, and 37  $cm^{-1}$ , respectively. The HOMO–LUMO gaps are 3.15 (**1**) 4.54 (**2**), and 6.76 (**3**) eV and their stable wave functions suggest closed-shell singlet ground states.

Particularly, the computed C–C separations of **1**, 1.363 and 1.231 Å indicate a significant degree of electron delocalization. In the case of **2**, the C–C bond lengths (1.215 Å) are slightly shorter than that in **1**, a symptom of an electron delocalization

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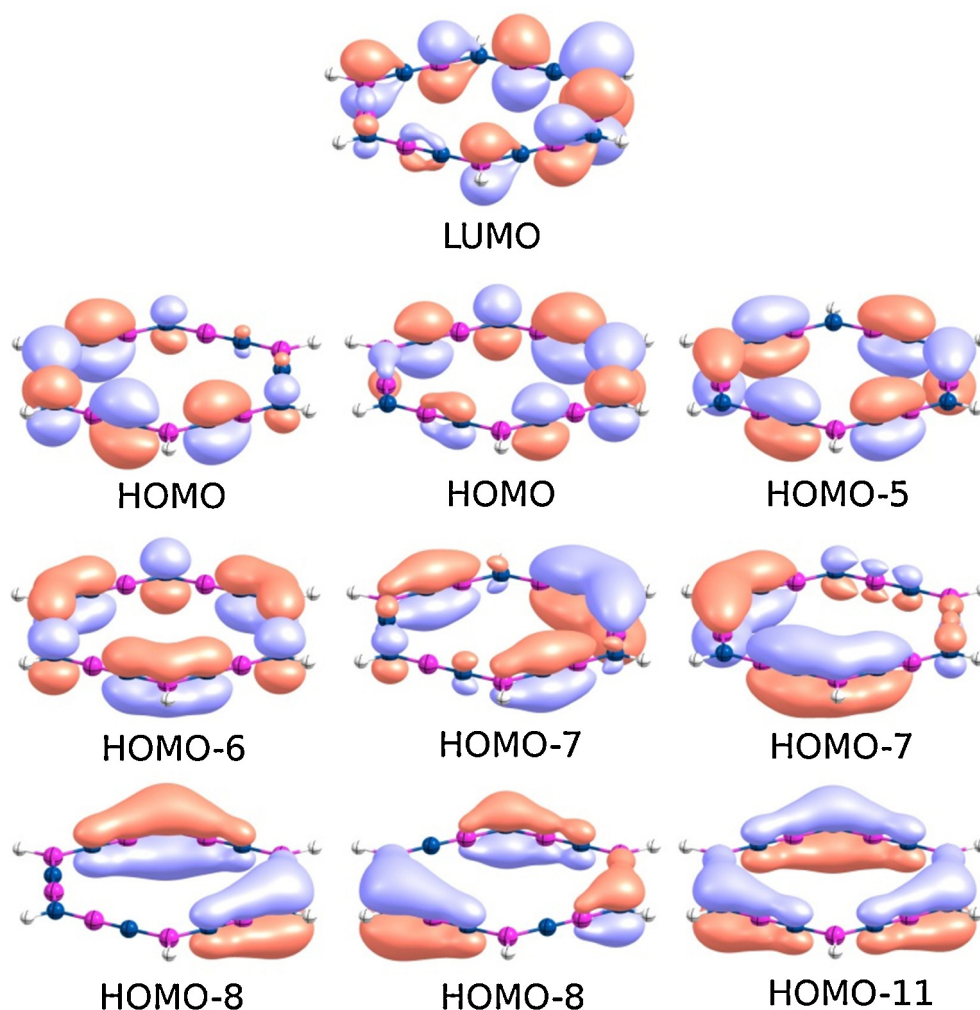


**Figure 1.** Optimized structures of **1–3** computed at the PBE0/def2-TZVP level. Bond lengths are in Å and NPA charges are in |e|.

reduction. For **3**, the B–N distances are 1.409, 1.252, and 1.400 Å. The longer B–N distances are slightly shorter than those computed for borazine at the same level (1.425 Å) and also slightly longer than the formal B=N double bond as in  $\text{H}_2\text{B}=\text{NH}_2$  (1.385 Å). So, structurally **3** exhibits a degree of delocalization.

Figure 2 depicts the nine  $\pi$ -MOs for **3**. While the HOMO is doubly degenerate and centred mainly on the nitrogen atoms, the LUMO is located on the boron atoms. Strictly, molecules **1–3** could be considered as aromatic (all have 18  $\pi$ -electrons, Figs. 1-SI and 2-SI). The natural population analysis (NPA) [20] derived atomic charges

show an interesting electron density distribution: (a) In **1**, the negative charge is concentrated at the corners of the hexagon. (b) In **2** and **3**, the charges at boron corners are close to zero and the nitrogen atoms at the corner are negatively charged (see Fig. 1). (c) In *carbo*-benzene, the  $\text{C}_2$  fragment is almost neutral, but in **2** the C–C bond is strongly polarized. (d) In the carbon-free compound, the boron and nitrogen natural charges of the B≡N fragment are 0.28 and  $-0.23$  |e|, respectively. Thus, the electronegativity difference (1.0 in Pauling units) between the N and B atoms alters the electron distribution in **3** compared to that in **1**, and modifies the



**Figure 2.** LUMO and the occupied  $\pi$ -molecular orbitals of **3**.

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