Computational Chemistry

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Boron–Boron Multiple Bond in $[B(NHC)]_2$: Towards Stable and Aromatic $[B(NHC)]_n$ Rings**

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Molecules containing boron–boron multiple bonds are of considerable current interest.[1–4] Because of the electron deficiency of the boron element, chemical bonding and structural features of boron-based compounds differ from those of the carbon counterparts. While carbon–carbon bonds exist in different hybridization states, boron–boron multiple bonds are rather scarce, and are in part a result of their high reactivities. In this context, recent isolation of molecules containing $B\equiv B$ bonds has marked an important breakthrough in boron chemistry.

In 2002, the OCBBCO complex was experimentally produced in an excess Ar matrix at 8 K by Zhou et al.[5] Although these authors subsequently reported that OCBBCO has low thermodynamic stability and rapidly undergoes unimolecular rearrangement to form more stable isomers such as OBBCCO and OBCCBO,[6] its existence under special experimental conditions as the first $B\equiv B$ molecule has attracted much attention.

In 2008, Wang et al.[7] also reported the existence of the $B_2(BO)_2^-$ anions in the gas phase. The $B_2(BO)_2^{2-}$ dianion was consequently proposed to be a stable compound containing a $B\equiv B$ bond. More interestingly, Braunschweig et al.[8] were recently successful in synthesizing the $R\rightarrow B\equiv B\leftarrow R$ complex with $R = {:}C\{N(2,6\text{-}i\mathrm{Pr}_2C_6H_3)CH\}_2$ or an N-heterocyclic carbene (NHC), which can be isolated at ambient temperature. Recall that stable neutral diborenes $R\rightarrow H_2B{-}BH_2\leftarrow R$ and $R\rightarrow HB{=}BH\leftarrow R$ were prepared earlier by Robinson et al.[9] Enhanced stability of diborane compounds containing R = NHC groups as compared to those containing CO and BO moieties is very peculiar, but such an effect has not been fully understood yet. The only reason, as pointed out by Frenking and Holzmann,[10] is that the donor strength of the NHC is much stronger than that of CO. However, previous studies showed that characteristics of chemical bonding in $(BR)_2$, $B_2(BO)_2^{2-}$, and OCBBCO are very similar to each other.[5,7,8,10] A better understanding of the stability and chemical bonding features of these species is thus necessary and helpful for the design of new compounds containing boron–boron multiple bonds.

In fact, molecules containing planar boron rings are quite attractive materials. While small boron clusters B_n, with n of up to 23, have planar or quasiplanar structures,[11,12] the well-known boron hydrides B_nH_n prefer cage-formed three-dimensional structures.[13] Schleyer et al.[14] attempted to theoretically design planar $(BCO)_n$ compounds in which the carbonyl CO groups are bound to B atoms of inner B_n rings. These authors showed that $(BCO)_n$ exhibited a structure and aromaticity comparable to those of the corresponding $(CH)_n$ hydrocarbons. However, Li et al.[15] subsequently demonstrated that $(BCO)_n$ is much less stable than its isomer $(CBO)_n$, in which the BO moieties are located around the inner C_n rings. These results can simply be understood by the fact that the OCB moiety is much less stable than its CBO isomer.[6] In view of the high stability of diborane compounds containing NHCs, an interesting and legitimate question arises as to whether the $[B(NHC)]_n$ with $n = 3$–6 could exist as stable compounds.

Herein, we re-examine the features of structure, chemical bonding, and stability of the boron compounds $(BL)_2$ with $L = {:}C\{N[2,6\text{-}(CH_3)_2C_6H_3]CH\}_2$ (NHC), CO, and BO. We find that π electrons are properly delocalized on the (X-B-B-X) chain. More importantly, such a π conjugation along the B-C-N chains determines the high stability of $[B(NHC)]_2$. The compounds $[B(NHC)]_n$ exhibit structural and aromatic characters similar to those of the corresponding hydrocarbons $(CH)_n$, and thus constitute challenging targets for experimental studies (Figure 1). Our predictions not only give more insight into the peculiar features of the molecules considered, but also suggest a promising novel type of planar boron rings.

The shapes of selected molecular orbitals (MOs) depicted in Figure S1 of the Supporting Information file show that the two HOMOs of each species are occupied by π electrons which are delocalized along the X-B-B-X chain rather than localized at the central B−B bonds. These observations are consistent with the Wiberg bond indices (WBI) of molecules. The WBI_{B-X} values of $B_2(BO)_2^{2-}$, OCBBCO, and **2** amount to 1.25, 1.31, and 1.18, respectively, and are considerably larger than the value of 0.92 for a single C−B bond (**1**).

The electron distribution of $(BL)_2$ is further considered using the electron localization function (ELF)[16] which has successfully been applied to analyze the chemical bonding of organic and inorganic compounds.[17,18] A localization using ELF leads to a partition of a total density into different basins where electrons are located. The plots of total ELF maps and electron populations in the associated basins are depicted in Figure 2. It can be seen that disynaptic B−X basins of $B_2(BO)_2^{2-}$, OCBBCO, and **2** contain 2.9, 3.3, and 3.0

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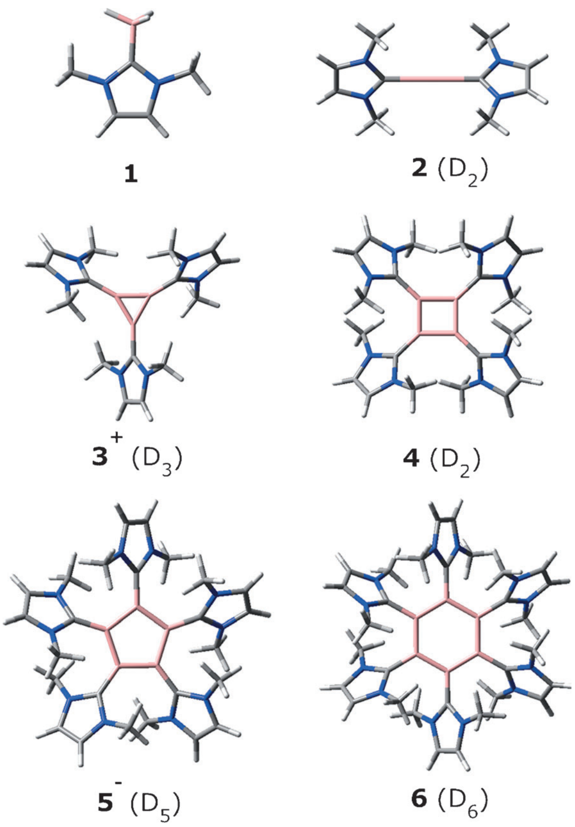

Figure 1. Shapes and point groups of $H_3B{-}L$ and $(BL)_n$ compounds with $n = 2$–6 [B3LYP/6-31+(d,p)].

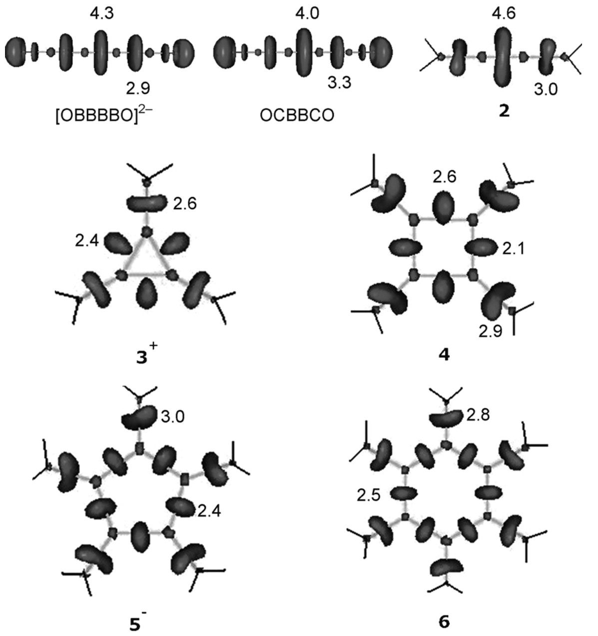

Figure 2. Plots of total ELF of compounds at bifurcation values of 0.85. Basins on NHC groups are removed from plots for simplicity.

electrons, respectively. Additionally, the electron population of disynaptic B−B basins only varies in a range of 4.0–4.6 electrons. These results confirm our above analysis that π electrons are not localized on the central B−B bonds, but they are rather delocalized over the X-B-B-X chain. As a consequence, the molecules $(BL)_2$ also exhibit a resonance structure L=B=B=L along with a more localized B≡B bond in the Lewis structure [L−B≡B−L].

In the simplest molecule $H_3B{-}NHC$ (**1**, Figure 1) which contains a B−C bond, the B−C bond length is equal to 1.599 Å, and considerably longer than the B−C distance of 1.486 Å of **2**. This difference lends support for the presence of delocalized π electrons in the B−C bonds of **2**. Analysis of the canonical molecular orbital (CMO) of **2** reveals that its π electrons, which occupy the HOMO−2 and HOMO−3, are also delocalized along B-C-N chains (Figure S1). In addition, while the MO corresponding to the central B−B σ bond lies at higher energy levels (HOMO−1) for $B_2(BO)_2^{2-}$ and OCBBCO, it shifts into a deeper valence area for **2** (HOMO−6). Such an electron reorganization is another reason for the high stability of **2**.

To design new molecules, the $(BL)_n$ cycloadducts with an appropriate charge to form closed-shell configurations with $n = 3$–6 were constructed by directly attaching the ligands (L) to the B atoms of the inner B_n rings. Geometrical optimizations and calculations of harmonic vibrational frequencies of all structures considered were carried out using the hybrid B3LYP functional in conjunction with the 6-31+G(d,p) basis set. The shapes of optimized structures are depicted in Figure 1. All inner B_n frameworks of complexes **3**$^+$, **5**$^-$, and **6** have planar shapes similar to those of corresponding $(CH)_n$ hydrocarbons. In most B_n rings, the B−B bond lengths in each ring are equal to each other. Calculations of harmonic vibrational frequencies reveal that they are true minima without any imaginary frequencies. Boron atoms of the inner B_4 ring of **4** are slightly distorted out of symmetric plane and form two short and two long B−B bonds. For the cation **3**$^+$, the B−B distances of 1.583 Å are close to those of (1.560 ± 0.018) Å for the B=B bond in RHB=BHR.[9] The B−B bond lengths of 1.680 Å for **6** are somewhat longer than the 1.560 Å for a B=B bond, but shorter than the (1.824 ± 0.004) Å of B−B bonds in $RH_2B{-}BH_2R$ (Table 1).[9]

The shapes of selected MOs of the adducts **3**–**6** depicted in Figure 3 reveal that **3**$^+$ has two π electrons occupying the HOMO−2 which is responsible for a π bond over the three-membered B_3 ring. Consequently, it satisfies the Hückel rule

Table 1: Geometrical parameters, natural charge populations on B, and WBI of the compounds considered in this study.[a]

	$d_{B\text{-}B}$ [Å]	$d_{B\text{-}C}$ [Å]	$q_{\lvert B\rvert}$	$WBI_{B\text{-}B}$	$WBI_{B\text{-}X}$
$B_2(BO)_2^{2-}$	1.490	–	−0.72	2.40	1.25
OCBBCO	1.457	–	−0.14	1.94	1.31
1	–	1.599	–	–	0.92
2 (D$_2$)	1.467	1.486	−0.17	2.05	1.18
3$^+$ (D$_3$)	1.583	1.535	−0.15	1.21	0.97
4 (D$_2$)	1.736	1.536	−0.15	0.90	1.05
	1.638			1.22	
5$^-$ (D$_5$)	1.700	1.528	−0.18	1.03	1.14
6 (D$_6$)	1.680	1.549	−0.17	1.05	1.05

[a] For details on the determinations of these values please see the Supporting Information.

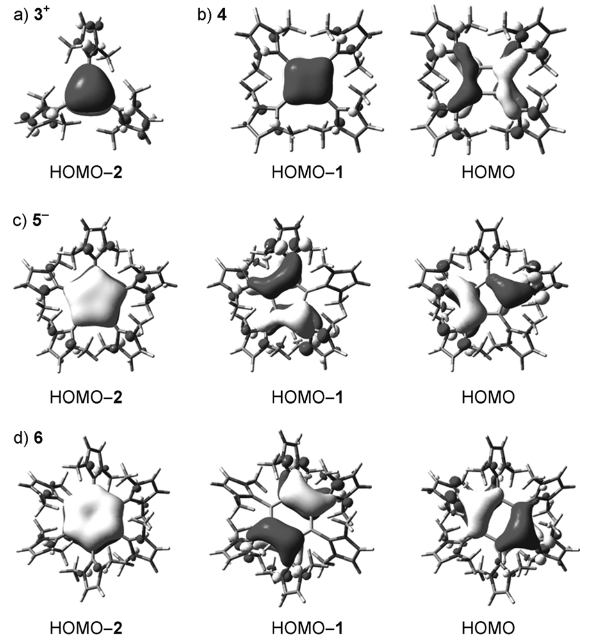

Figure 3. Shapes of selected MOs for a) $\mathbf{3}^+$, b) **4**, c) $\mathbf{5}^-$, and d) **6**.

of $(4N+2)$ electrons and makes $\mathbf{3}^+$ aromatic ($N=0$). Similarly, $\mathbf{5}^-$ and **6** each contain six delocalized π electrons which are distributed in three π MOs. These MOs are responsible for π bonds between B atoms of the inner boron rings and thus make them aromatic ($N=1$). On the contrary, the cyclic species **4** only contains four delocalized π electrons, and is thus antiaromatic. The aromatic features of cycloadducts are also similar to those of $(CH)_n$. Nucleus-independent chemical shifts arising from the *zz* component of the shielding tensors ($NICS_{zz}$)[19,20] of the adducts are calculated at the centers of the B_n frameworks and also at points 0.5, 1.0, 1.5, and 2.0 Å above these centers. The adduct $\mathbf{3}^+$ consistently exhibits a highly negative $NICS_{zz}$ value [NICS(1.0) = −22.4] which indicates its aromaticity. The $NICS_{zz}$ values of both $\mathbf{5}^-$ and **6** are positive at points close to molecular planes, but become negative at 1.0 Å, and reach maximum negative values at 1.5 Å ($NICS_{zz}(1.5) = -6.7$ for $\mathbf{5}^-$ and $NICS_{zz}(1.5) = -8.1$ for **6**). These results point out that both $\mathbf{5}^-$ and **6** are π-aromatic species. The adduct **4** is confirmed to be antiaromatic with highly positive $NICS_{zz}$ values (Table S1).

The ELF plots shown in Figure 2 reveal that there is indeed strong electron delocalization within B_n frameworks. Electron distributions on disynaptic BB basins of $\mathbf{3}^+$, $\mathbf{5}^-$, and **6** are almost the same. For **4**, each of the two disynaptic BB basins has 2.1 electrons, while each of the remaining BB basins contains 2.6 electrons. This electron count is consistent with the fact that the B_4 framework of **4** has a rectangular shape. The population of disynaptic B−C basins varies in a range of 2.6–3.0 electrons, thus indicating a bond order larger than one. These results are in good agreement with the WBI values listed in Table 1. The $WBI_{B\text{-}C}$ values of **3**–**6** vary in the range of 0.97–1.14, and are larger than that of 0.92 for **1** containing a C−B bond. These enhanced electron distributions no doubt arise from π conjugations along the B-B-C and B-C-N chains as observed for the $(BL)_2$ discussed above. Consequently, they further reinforce the strength of B−C bonds, and thereby the high stability of cycloadducts **3**–**6**.

To probe the thermodynamic stability of the designed cyclic compounds, we examine their average dissociation energies (D_e) which are defined by Equation (1).

$$D_e([B(NHC)]_n) = \{(n-1)\,E([B(NHC)]) + E([B(NHC)])^q - E([B(NHC)]_n)\}/n \quad (1)$$

Herein, $E([B(NHC)]_n)$, $E([B(NHC)])$, and $E([B(NHC)])^q$ are total energies of complexes $[B(NHC)]_n$, molecules [B(NHC)], and radicals $[B(NHC)]^q$ ($q=0$ for **2**, **4**, and **6**, $q=+1$ for $\mathbf{3}^+$, and $q=-1$ for $\mathbf{5}^-$), respectively. These energetic parameters are calculated at the B3LYP/6-311++G(d,p)//B3LYP/6-31+G(d,p) level of theory. Our results interestingly show that the designed cycloadducts are highly stable species whose D_e values are considerably larger than the $D_e = 2.95$ eV for **2**, a molecule which has been experimentally isolated.[8] The D_e (in eV) values amount to 4.30 for $\mathbf{3}^+$, 3.18 for **4**, 3.24 for $\mathbf{5}^-$, and 3.42 for **6**. Additionally, the species **4** is characterized by the lowest D_e value among the cyclic compounds designed. This low value can be understood by the fact that **4** is antiaromatic, whereas the others are aromatic.

To further confirm the thermodynamic stability of cycloadducts, the reaction energies are also examined for the fragmentations defined by Equation (2).

$$E_{react}([B(NHC)]_n)^q = \{m\,E([B(NHC)]_2) + k\,E([B(NHC)])^q\} - E([B(NHC)]_n)^q \quad (2)$$

Herein, $m = n/2$ and $k = 0$ for the neutral species **4** and **6** and $m = n/2-1$ and $k = 1$ for the charged species $\mathbf{3}^+$ and $\mathbf{5}^-$.

The reaction energies (E_{react}) also suggest high stability of the relevant cycloadducts. Of the designed compounds, the antiaromatic species **4** has again the lowest E_{react} value, which is consistent with the average dissociation energies (D_e) predicted above ($E_{react} = 0.91$ eV for **4**, 2.82 for **6**, 4.37 for $\mathbf{3}^+$, and 6.99 for $\mathbf{5}^-$).

In conclusion, we found that the π electrons of the dimeric molecules $(BL)_2$ are strongly delocalized over the X-B-B-X chains rather than localized on their central B−B bonds to form B≡B bonds. The high stability of the $[B(NHC)]_2$ molecule can be explained by the π conjugation along B-C-N chains and also a shift of its σ MO into a deeper valence area (the HOMO−6). The cycloadducts $(BL)_n$ with $n = 3$–6 are demonstrated to be stable compounds with π conjugation along B-B-C chains and exhibit aromatic characters similar to those of corresponding $(CH)_n$ hydrocarbons.

Our theoretical results suggest the emergence of a promising type of planar cyclic boron compound. Since the stable dimeric molecules $(BH_nR)_2$ with $n = 0$–2 and R = :C{N(2,6-iPr$_2$C$_6$H$_3$)CH}$_2$ were recently synthesized, experimental studies on the new B rings could be expected in a near future.

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[1] L. C. Ducati, N. Takagi, G. Frenking, *J. Phys. Chem. A* **2009**, *113*, 11693–11698.
[2] M. P. Mitoraj, A. Michalak, *Inorg. Chem.* **2011**, *50*, 2168–2174.
[3] N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517–13525.
[4] a) M. Zhou, Q. Xu, Z.-X. Zhang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2002**, *124*, 14854–14855; b) M. F. Zhou, Z.-X. Wang, P. von R. Schleyer, *ChemPhysChem* **2003**, *4*, 763–766; c) Z.-X. Wang, Z. Chen, H. Jiao, P. von R. Schleyer, *J. Theor. Comput. Chem.* **2005**, *4*, 669–688; d) E. Kaufmann, P. von R. Schleyer, *Inorg. Chem.* **1988**, *27*, 3987–3992; e) A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715–2717.
[5] M. Zhou, N. Tsumori, Z. Li, K, Fan, L. Andrews, Q. Xu, *J. Am. Chem. Soc.* **2002**, *124*, 12936–12937.
[6] M. Zhou, L. Jiang, Q. Xu, *Chem. Eur. J.* **2004**, *10*, 5817–5822.
[7] S.-D. Li, H.-J. Zhai, L.-S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 2573–2579.
[8] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Science* **2012**, *336*, 1420–1422.
[9] Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413.
[10] G. Frenking, N. Holzmann, *Science* **2012**, *336*, 1394–1395.
[11] a) T. B. Tai, A. Ceulemans, M. T. Nguyen, *Chem. Eur. J.* **2012**, *18*, 4510–4512; b) T. B. Tai, N. M. Tam, M. T. Nguyen, *Theor. Chem. Acc.* **2012**, *131*, 1241; c) T. B. Tai, M. T. Nguyen, M. T. Nguyen, *Chem. Phys. Lett.* **2012**, *530*, 71–76; d) T. B. Tai, D. J. Grant, M. T. Nguyen, D. A. Dixon, *J. Phys. Chem. A* **2010**, *114*, 994–1007.
[12] a) A. P. Sergeeva, Z. A. Piazza, C. Romanescu, W.-L. Li, A. I. Boldyrev, L.-S. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 18065–18073; b) W. Huang, A. P. Sergeeva, H.-J. Zhai, B. B. Averkiev, L.-S. Wang, A. I. Boldyrev, *Nat. Chem.* **2010**, *2*, 202–206.
[13] M. L. McKee, Z.-X. Wang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2000**, *122*, 4781–4793.
[14] H. S. Wu, H. Jiao, Z. X. Wang, P. von R. Schleyer, *J. Am. Chem. Soc.* **2003**, *125*, 4428–4429.
[15] S.-D. Li, C.-Q. Miao, J.-C. Gou, G.-M. Ren, *J. Comput. Chem.* **2005**, *26*, 799–802.
[16] A. Becke, K. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5404.
[17] B. Silvi, A. Savin, *Nature* **1994**, *371*, 683–686.
[18] T. B. Tai, M. T. Nguyen, *Chem. Commun.* **2013**, *49*, 913–916.
[19] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
[20] a) P. von R. Schleyer, H. Jiao, H. J. R. van Eikema Hommes, V. G. Malkin, O. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669–12670; b) P. von R. Schleyer, M. Manoharan, Z. X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465–2468; c) H. F. B. Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Org. Lett.* **2006**, *8*, 836–866; d) Z. Chen, C. S. Wannere, C. Corminboeur, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842–3888.