Boron Heterocycles

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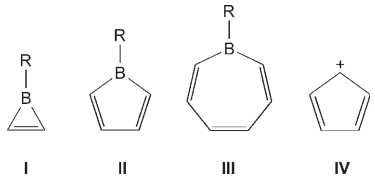
Structural Evidence for Antiaromaticity in Free Boroles**

Holger Braunschweig, Israel Fernández, Gernot Frenking,* and Thomas Kupfer*

Unsaturated boron-containing heterocycles such as borirenes (**I**),[1] boroles (**II**),[2] and borepins (**III**)[3] have attracted fundamental interest owing to their electronic structure. The interaction of the empty p_z orbital at boron in these systems with the unsaturated carbon backbone might result in a stabilization (**I** and **III**) or destabilization (**II**) of the entire π system, depending on the number of available π electrons. In particular, boroles (**II**) are of interest because of their close relationship to the cyclopentadienyl cation (**IV**), which

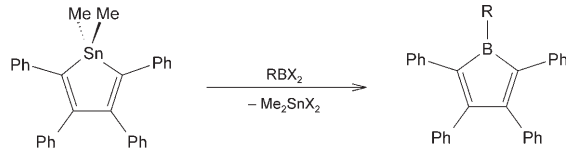


represents one of the prototypical molecules in the theory of aromaticity and antiaromaticity. Both ESR spectroscopic data[4] as well as photoelectron spectroscopic studies[5] have led to the conclusion that the electronic ground state of the cyclopentadienyl cation is a triplet state with almost ideal D_{5h} symmetry, but that several singlet states lie very close in energy.[6] This result has been authenticated by numerous quantum chemical calculations, which predict perfect D_{5h} symmetry for the triplet ground state and a Jahn–Teller distortion for the excited singlet states.[7] In addition, Schleyer and co-workers have demonstrated that the delocalization of the four π electrons in the triplet species results in an aromatic stabilization of the entire molecule, whereas the electronic singlet states are destabilized owing to antiaromaticity.[7f] However, all attempts to isolate or structurally characterize a simple cyclopentadienyl cation have failed so far, as these species are highly reactive.[7g–h,8]

According to ab initio calculations, the isoelectronic borole (**II**) is predicted to have an antiaromatic singlet ground state featuring strongly alternating bond lengths within the BC_4 backbone, which is destabilized by the delocalization of the four π electrons.[9] As a consequence of the antiaromaticity, boroles are regarded as highly reactive species, and the parent molecule **II** has only been generated in the coordination sphere of transition metals.[10] To date, the number of stable and monomeric boroles that have been isolated and spectroscopically characterized is restricted to the pentaphenyl-substituted derivative $PhBC_4Ph_4$ (**1**),[2c] whereby the antiaromatic character was demonstrated both by UV/Vis spectroscopy and by reactivity studies.[2c,e,3a] However, no X-ray diffraction data of any monomeric, non-annulated borole derivative have been reported to date, even though structural data are of interest for determining the consequences of π-electron delocalization in this four-electron, formally antiaromatic system.

Herein, we report on the synthesis and full characterization of **1** and the related ferrocenylborole $FcBC_4Ph_4$ [**2**; $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$], as well as on the elucidation of their electronic structure by quantum chemical methods. The crystal structure analyses of **1** and **2** provide a link between experimental results and the electronic configuration of these borole species.

Compounds **1** and **2** were prepared by boron–tin exchange reactions of the stannole precursor **3** and stoichiometric amounts of the appropriate boron dihalides (Scheme 1).[2c,11]



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1: R = Ph; X = Cl
2: R = Fc; X = Br

Scheme 1. Syntheses of **1** and **2**.

Crystallization of **1** from a saturated CH_2Cl_2 solution at −35 °C yielded deep blue needles that were suitable for X-ray diffraction analysis (Figure 1).[12,13] The solid-state structure of **1** is characterized by a planar BC_4 five-membered ring (root-mean-square deviation: 0.0175 Å) with internal ring dihedral angles of 4.1(1), −3.7(2), 1.7(2), 1.02(2), and −3.1(1)°, as well as a propeller-like arrangement of the five phenyl substituents [for example, C1-B1-C51-C52: −32.9(2)° (*−35.1*°); B1-C4-C41-C46: −51.3(2)° (*−51.3*°), C2-C3-C31-C32: −52.1(2)° (*−49.9*°)].[14] The bond lengths within the central ring moiety are alternating, but the alternations are much less

[*] Prof. Dr. H. Braunschweig, Dr. T. Kupfer
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Dr. I. Fernández, Prof. Dr. G. Frenking
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35043 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de

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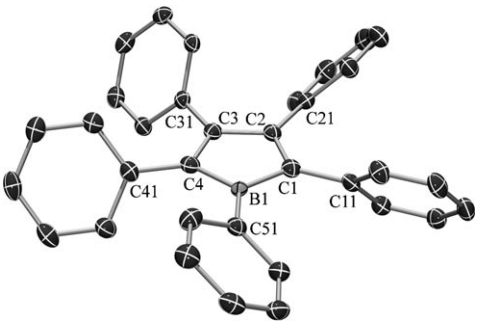

Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°] (calculated values at the BP86/def2-SVP level are given in italics): B1-C1 1.526(2) (*1.595*), B1-C4 1.539(2) (*1.595*), C1-C2 1.428(2) (*1.380*), C2-C3 1.470(2) (*1.533*), C3-C4 1.426(2) (*1.380*); C1-B1-C4 105.4(1) (*105.2*), B1-C1-C2 107.5(1) (*106.1*), C1-C2-C3 109.9(1) (*111.3*), C2-C3-C4 109.8(1) (*111.3*), C3-C4-B1 107.3(1) (*106.1*).

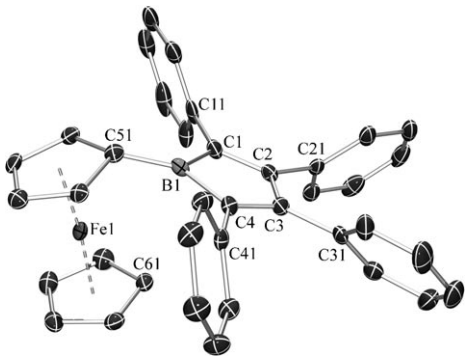

Figure 2. Molecular structure of **2**. Only one molecule of the asymmetric unit is shown for clarity. Selected bond lengths [Å] and angles [°] (calculated values at the BP86/def2-SVP level are given in italics): B1-C1 1.597(3) (*1.600*), B1-C4 1.582(3) (*1.599*), C1-C2 1.358(3) (*1.379*), C2-C3 1.518(3) (*1.525*), C3-C4 1.353(3) (*1.381*), Fe1-C_{Cp} 2.021(2)–2.068(2) (*2.040–2.072*), Fe1-B1 2.664 (*2.825*); C1-B1-C4 103.6(2) (*104.5*), B1-C1-C2 106.4(2) (*106.5*), C1-C2-C3 111.8(2) (*111.2*), C2-C3-C4 110.5(2) (*111.4*), C3-C4-B1 107.8(2) (*106.3*).

pronounced than predicted by theoretical calculations on the parent compound[9] and on **1**. The B–C bond lengths [between 1.516(2) and 1.539(2) (*1.595*) Å] are significantly shortened with respect to the typical value of a boron–carbon single bond (1.61 Å). However, the lengths for the C1–C2 [1.428(2) (*1.380*) Å] and C3–C4 bonds [1.426(2) (*1.380*) Å] are significantly elongated compared to the expected value of a carbon–carbon double bond (1.32 Å), but strongly resemble those found in delocalized ring systems (1.40 Å). Additionally, the formal carbon–carbon single bond [C2–C3 1.470(2) (*1.533*) Å] is somewhat shorter than an isolated single bond (1.54 Å) or a single bond between unconjugated sp^2-hybridized carbon atoms (1.49 Å). The experimental values for the bond lengths suggest a significant p_π–π^* conjugation between the unsaturated sp^2-hybridized boron center and the carbon backbone, which is surprising because the borole is an antiaromatic species with four π electrons. Investigations on the spin multiplicity of **1** by variable-temperature NMR and ESR spectroscopy, as well as magnetic SQUID measurements, revealed no evidence for paramagnetic contributions and, consequently, a significant population of a triplet state can be excluded.

The antiaromaticity in borole systems is manifested by the high Lewis acidity of the boron center that has enabled, for instance, the application of borole derivatives as potent Lewis acids in the polymerization of ethylene.[15] Here, the Lewis acidity of the boron center is convincingly demonstrated by the solid-state structure of ferrocenylborole (**2**, Figure 2),[12,16] which allows for the direct observation of a strong Fe–B interaction. The pronounced bending of the boryl ligand towards the iron center with a dip angle $\alpha^* = 29.4$ (*23.2*)° is significantly increased in comparison to other ferrocenylboranes.[17] As a consequence of this interaction, the p_π–π^* conjugation in the borole subunit is at least partially interrupted in comparison to **1**. Hence, the antiaromatic character of **2** seems to be less pronounced, which is further confirmed by UV/Vis spectroscopy.[11,18] These findings are also supported by the bond lengths within the BC_4 five-membered ring. The B–C bond lengths [B1–C4: 1.582(3) (*1.599*) Å; B1–C1: 1.597(3) (*1.600*) Å] are notably elongated compared to those found in **1** and equal to the value of a typical boron–carbon single bond (1.61 Å). Additionally, the carbon–carbon bond lengths [C1–C2: 1.358(3) (*1.379*) Å; C3–C4: 1.353(3) (*1.381*) Å; C2–C3: 1.518(3) (*1.525*) Å] deviate substantially from the corresponding values for **1**. Whereas the first two bonds are only slightly longer than a typical C–C double bond (1.32 Å), the values for the latter bond lie between those of a single bond between sp^3-hybridized carbon atoms (1.54 Å) and a single bond between unconjugated sp^2-hybridized carbon atoms (1.49 Å). Similiar bond lengths have been observed in *cis*,*cis*-1,2,3,4-tetraphenylbuta-1,3-diene (1.356 and 1.484 Å);[19] thus, the bonding situation is best described as an isolated diene system that is bridged by a boron center.

We calculated the geometries of **1** and **2** in the singlet state at the BP86/def2-SVP level to analyze the structures and bonding situation of the molecules.[20] Relevant geometrical data are given in the captions to Figures 1 and 2. The most striking aspect of the data for **1** is the large difference between the theoretical and experimental values for the bond lengths in the borole ring. The calculations give much longer C–B bonds (1.595 Å) than the experiment (1.526–1.539 Å), and the theoretical C–C bond alternations are much more pronounced (1.380 Å for the short bonds and 1.533 Å for the long bonds) than experimentally determined (1.426–1.428 Å for the short bonds and 1.470 Å for the long bonds). We optimized the geometry of **1** using B3LYP/def2-SVP and RI-MP2/def2-SVP to check whether the discrepancy comes from a failure of the BP86 method. However, all three methods gave very similar bond lengths for the borole ring.[21] We also optimized **1** in the triplet state. The calculated geometry at the BP86/def2-SVP level indicates stronger conjugation in the borole ring, and the calculated bond lengths (B1–C1/C4: 1.595 Å; C1–C2: 1.459 Å; C2–C3: 1.431 Å) appear to be in better agreement with experiment than the theoretical values for the singlet state. However, the calculations predict the opposite order for the C–C bond lengths, that is, C1–C2 > C2–C3 while the experimental data shown in Figure 1 give C1–C2 < C2–C3. Moreover, the triplet state of **1** at the BP86/

def2-SVP level is 14.1 kcal mol^{-1} higher in energy than the singlet state. The theoretical data thus support the experimental results, which suggest that **1** has a singlet state.

Reexamination of the crystal structure helped to solve the puzzling discrepancy between theory and experiment. Inspection of the X-ray data revealed that there are dimeric subunits of **1** with noticeably short B–C and B–H separations between the dimers. The boron phenyl substituent of each borole lies above or below the boron atom of the other borole, which allows for intermolecular phenyl→boron π donation. The shortest intermolecular B–C separation in the dimer is only 3.635 Å, but even the intermolecular B–C separations between the boron atom and a C(phenyl) atom of adjacent dimers of the borole are only 3.855 Å (see the Supporting Information). This finding indicates that the electron-deficient boron atom in free **1** receives electronic charge through intermolecular π donation.

To estimate the effect of the intermolecular interactions on the bond lengths of **1**, we tried to optimize a dimer $(\mathbf{1})_2$ at the MP2 level, which is necessary for an adequate treatment of the intermolecular attraction. A partial optimization showed that the bond lengths in the borole ring change from the values in free **1** to values that approach the X-ray data. We then optimized the geometry of the complex of **1** with the weak electron donor CO to mimic the effect of charge donation to the borole. The optimized complex **1**·CO has a B–CO bond length of 1.550 Å and a bond dissociation energy of $D_o = 17.3$ kcal mol^{-1} (BP86/def2-SVP). These values suggest a slightly longer and weaker bond than in $H_3B{\cdot}CO$ (experimental values: B–CO: 1.534 Å, $D_o =$ 24.6 kcal mol^{-1}).[22] The impact of the B–CO bond on the bond lengths in the borole ring is very large. The calculated bond lengths of **1**·CO are 1.644/1.649 Å for B1–C1/C4, 1.389 Å for C1–C2, and 1.490 Å for C2–C3. The latter bond, which is rather distant from the B-CO moiety, is predicted to be much shorter than the calculated value for the free borole (1.533 Å), while its length is very similar to the experimental value of **1** (1.470 Å).

We also calculated **1** at the BP86/def2-SVP level with fixed C–C and C–B bond lengths for the borole ring (taken from the X-ray data), while the rest of the molecule was completely optimized. The energy difference between the latter species and the completely optimized compound is only 5.2 kcal mol^{-1} at the BP86/def2-SVP level (5.0 kcal mol^{-1} at RI-MP2/def2-SVP). This energy may easily be provided by intermolecular interactions between the phenyl substituents of the borole, which serve as π donors, and the electron-deficient boron atoms. Thus, the discrepancy between theory and experiment is not a sign for a shortcoming of either method. It is rather an interesting finding which shows that already rather weak intermolecular interactions may significantly alter the bond lengths in the borole ring. We predict that the geometry of **1** in the gas phase is quite different from the geometry in the solid state, and that the gas-phase values will exhibit a much larger bond alternation in the borole ring. Large differences between bond lengths in the gas phase and in the solid state have been noted before, but they were confined to bond lengths of donor–acceptor complexes.[23] For example, the nitrogen–boron bond length in $HCN{\cdot}BF_3$ measured in the solid state (1.638 Å) is more than 0.8 Å shorter than in the gas phase (2.473 Å).[24]

Unlike for compound **1**, the theoretical and experimental data for the borole ring of **2** are in very good agreement (Figure 2). The calculations suggest that the B–C and C–C bond lengths in **2** are nearly the same as in **1**, while the experimental data indicate a significant difference. The other calculated data of **2** also agree quite well with experiment except for the Fe–B bond length (2.825 Å), which is clearly longer than the measured value (2.664 Å). The iron–boron donor–acceptor bond should not be very strong, and thus, it may become significantly shorter in the solid state, which is in agreement with a previous study about the length of donor–acceptor bonds in the gas phase and in the condensed phase.[23]

In this contribution we have reported on the determination of the solid-state structure of pentaphenylborole (**1**). The structural parameters of this antiaromatic heterocycle with four π electrons differ significantly from those obtained by quantum chemical calculations and suggest an unexpectedly strong p_π–π* conjugation between the unsaturated sp^2-hybridized boron center and the carbon backbone. Reexamination of the crystal packing revealed distinct borole dimers with short B–C intermolecular contacts. According to quantum chemical studies the discrepancies between the experimentally and theoretically determined bond lengths can be attributed to the increase of electron density at the electron-deficient boron atom in free **1** through intermolecular π donation from adjacent phenyl groups.

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[11] The experimental section including the syntheses, full characterization, and spectroscopic data of all compounds, as well as the UV/Vis spectra can be found in the Supporting Information.

[12] Experimental details of all X-ray crystal structure determinations can be found in the Supporting Information. CCDC-650933 (**1**) and 650934 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] The crystallographic data set was of excellent quality and did not show any evidence for a disorder of **1**, regardless of the high symmetry. Considering the difficulties associated with the crystal structure of trimesitylborirene $MesBC_2Mes_2$ (Mes = 2,4,6-$Me_3C_6H_2$),[1d] in our hands the assignment of boron and carbon atoms of the central ring moiety in the structure of **1** was unambiguously derived from the observed bond lengths and angles, as well as from the thermal ellipsoids, which were found to be almost isotropic.

[14] The values in italics are derived from theoretical calculations, which are discussed below.

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[16] Compound **2** crystallizes in the monoclinic space group $P2_1$ with two independent molecules in the asymmetric unit; one moiety exhibits a weak disorder within a carbon-bound phenyl group. Hence, for simplicity reasons, only the structure of the non-disordered molecule is discussed.

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[18] Whereas the delocalization of the π electrons in **1** is supported by a characteristic visible band at 561 nm ($\varepsilon = 361\ L\,mol^{-1}\,cm^{-1}$), the corresponding absorption in **2** is found significantly blue-shifted at 390 nm ($\varepsilon = 2175\ L\,mol^{-1}\,cm^{-1}$), a region that has been described for the related base adducts.[1c]

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[21] Selected bond lengths [Å]: B3LYP/def2-SVP level: B1-C1/C4 1.588, C1-C2 1.363, C2-C3 1.533; RI-MP2/def2-SVP level: B1-C1/C4 1.587, C1-C2 1.374, C2-C3 1.516. The latter calculation was carried out using the TURBOMOLE (v5.90) program: R. Ahlrichs, M. Baer, M. Haeser, H. Horn, C. Koelmel, *Chem. Phys. Lett.* **1989**, *162*, 165 – 169.

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