Computer Chemistry

Aromatic Boron Wheels with More than One Carbon Atom in the Center: C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^{+}$**

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Dedicated to Professor Reinhardt Ahlrichs on the occasion of his 65th birthday

A large number of molecules with planar tetracoordinated carbon centers have now been characterized, both experimentally and computationally.[1] When the constituent atoms "fit" satisfactorily, both geometrically and electronically, even higher carbon hypercoordination can be achieved.[2] The first example was discovered computationally as a rather stable local minimum: CB_6^{2-} (D_{6h}) has a central planar hexacoordinate carbon center surrounded by a six-membered boron ring as well as six π electrons.[2a] While structures with planar penta- and heptacoordinate carbon centers have also been described, there are limits.[2b] An eight-membered boron ring is too large to bind a carbon atom in the center.[2b] However, planar octacoordination can be achieved with central atoms that are larger than carbon. Newly prepared B_{10} to B_{15} planar clusters are the most recent examples.[3] These neutral and charged boron species B_n^{q+} also exhibit Hückel $(4n+2)\pi$-electron aromaticity.[3] The central atom in planar hypercoordinate compounds may also be a transition metal: Frenking and co-workers predicted theoretically the six-π-electron, aromatic, metal-centered, planar cations $[Fe(Sb_5)]^+$ and $[Fe(Bi_5)]^+$.[4]

Can more than one planar hypercoordinated carbon atom reside inside a binary planar ring system of the type C_nX_m (in which X represents any other atom)? A single carbon enclosed by a B_8 (or a larger boron ring) does not reside in the center and binds to only a few boron atoms at the inner rim.[2b] This positioning leaves space available for a second carbon atom to join the first. Indeed, C_2B_8 is just such a species (Figure 1a). By means of extensive computational exploration of $C_nB_m^{q+}$, possibilities with various compositions and charges, q, we also have located concentric borocarbon minima, with three- ($C_3B_9^{3+}$) and five-membered carbon rings ($C_5B_{11}^{+}$) inside boron circumferences. We searched unsuccessfully for a $C_nB_m^{q+}$ stationary point with a C_4 ring in the center. However, both the planar D_{3h} $C_3B_9^{3+}$ trication (Figure 1c), with a central carbon triangle and six π electrons, as well as the C_{2v} $C_5B_{11}^{+}$ cation (Figure 1e), with central C_5 cycle and ten π electrons are minima.[5] The bonding (σ and π) and the properties of these new aromatic molecules (Figure 1) are intriguing.

Figure 1a, c, and e provide an overview of the geometrical details of the C_2B_8 (D_{2h}), $C_3B_9^{3+}$ (D_{3h}), and $C_5B_{11}^{+}$ (C_{2v}) minima, respectively, calculated at the B3LYP/6-311+G(2df) density functional level by using the Gaussian 03 program.[6,7] These species have structural and bonding features in common. Single bonds more or less normal in length (i.e., 1.53 Å for C–C, 1.60 Å for C–B,[8] and about 1.65 for B–B) are shown with solid lines in Figure 1, whereas dashed lines identify C–B contacts at significantly longer interatomic distances (and imply participation in multicenter bonding). Hence, the carbon atoms of the central C_2, C_3, and C_5 units are more strongly bound to some of the perimeter boron atoms than to others. This influences the B–B distances in the outer rings, which vary over a range of 0.15 Å. In contrast the C–C interatomic distances are all near 1.50 Å (the shortest length is 1.487 Å for the C_2 unit in C_2B_8). While one planar tetracoordinate carbon is clearly present in $C_5B_{11}^{+}$ (Figure 1e), the long C–B distances complicate the assignment of coordination numbers to the carbon atoms. When these long contacts are counted, the carbon atoms in Figure 1a and c are all planar pentacoordinate, while those in Figure 1e are either penta- or tetracoordinate. Note that B_{12}, which is isoelectronic with $C_3B_9^{3+}$, has a quasi-planar equilibrium geometry with lower symmetry (C_{3v}).[3b]

Remarkably, the C_2, C_3, and C_5 units in C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^{+}$, respectively, are highly fluxional and rotate readily inside the perimeters of their boron rings. The behavior of C_2B_8 is much like a compass needle swinging around seeking

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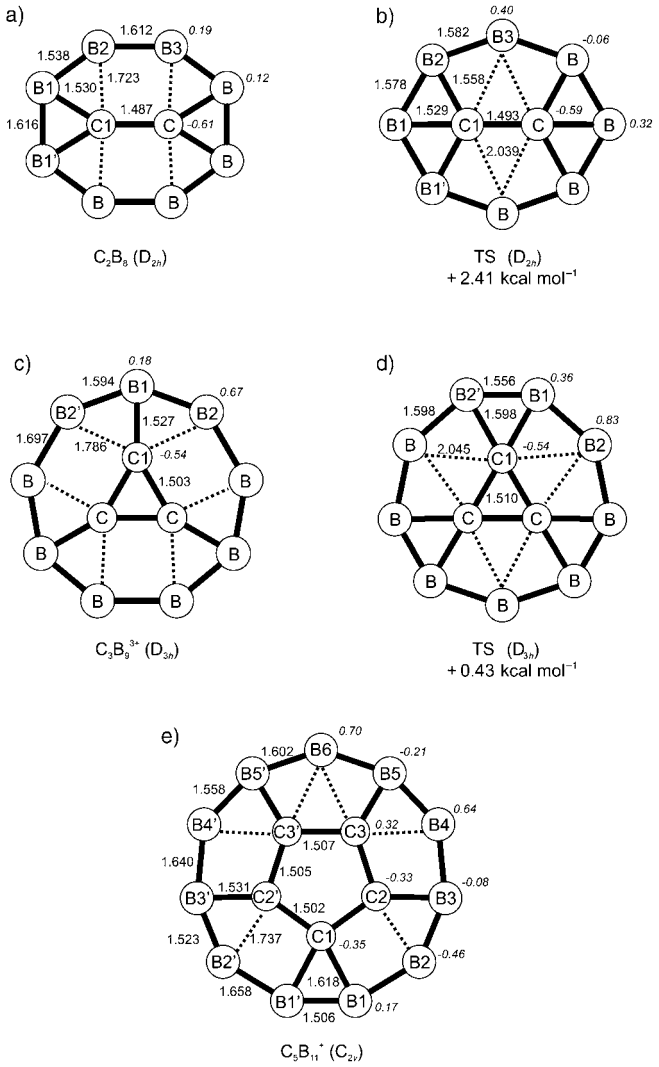

Figure 1. B3LYP/6-311+G(2df) geometries of $C_nB_m^{q+}$ molecules (interatomic distances in Å), natural charges (NBO) are in italics. a) Equilibrium structure of C_2B_8; b) transition structure of C_2B_8 for rotation of the C_2 moiety in the molecular plane; c) equilibrium structure of $C_3B_9^{3+}$; d) transition structure of $C_3B_9^{3+}$ for rotation of the C_3 cycle in the molecular plane; e) equilibrium structure of $C_5B_{11}^{+}$.

its orientation, but the C–C entity remains strongly bound to its perimeter during the rotation. The barrier is only 2.41 kcal mol^{-1} (with zero-point energy (ZPE) corrections) and involves a D_{2h} transition structure (Figure 1b) with planar tetracoordinated carbon centers. Each carbon center is too weakly bound ($r = 2.039$ Å) to the two remaining outer boron atoms to have fully developed planar hexacoordination.

The barrier for the counter rotation of the outer boron ring and the inner C_3 triangle in $C_3B_9^{3+}$ is only 0.43 kcal mol^{-1} with ZPE corrections; the transition structure (Figure 1d) is highly symmetric (D_{3h}). Astonishingly, the rotation of the C_5 cycle within the B_{11} perimeter in $C_5B_{11}^{+}$ is essentially free. We could not locate any transition state for rotation at the B3LYP/6-311+G(2df) level. A C_s transition state was located at the lower B3LYP/6-31G(d) level (harmonic imaginary frequency 6i cm^{-1}), but this only was 0.06 kcal mol^{-1} higher in energy than the C_{2v} equilibrium structure.

The bonding situation in these compounds is peculiar: the total carbon–boron interaction energies are large both in the initial and the rotation transition states. During the rotations that are nearly barrier-less, the multicenter B–C binding interactions transform gradually from one arrangement to the other. Note that more B–C contacts exist in the transition states than in the minima (compare Figure 1b with 1a and 1d with 1c), which helps lower the energy barriers.

The borocarbon systems (Figure 1) all follow the Hückel $4n+2$ electron rule. C_2B_8 and $C_3B_9^{3+}$ have six π electrons, whereas $C_5B_{11}^{+}$ has ten. Figure 2 shows the occupied π molecular orbitals (MOs) and the lowest unoccupied molecular orbital (LUMO) of C_2B_8. The full set of occupied valence MOs and the three lowest-lying vacant orbitals are given in the Supporting Information. The three occupied π orbitals (Figure 2, MOs 17, 23, and 26) are akin to the π MOs of benzene.[9] The $C_3B_9^{3+}$ trication has 18 occupied valence MOs (all are depicted in the Supporting Information). The three occupied π orbitals (also akin to benzene), the degenerate σ highest occupied molecular orbital (HOMO), and the three lowest-lying empty orbitals with π symmetry are shown in Figure 3. $C_5B_{11}^{+}$ has 26 occupied valence MOs (see the

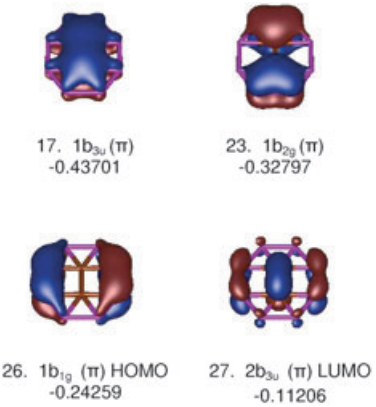

Figure 2. Plot of the occupied π MOs and the LUMO of C_2B_8. Orbital energies are given in Hartrees.

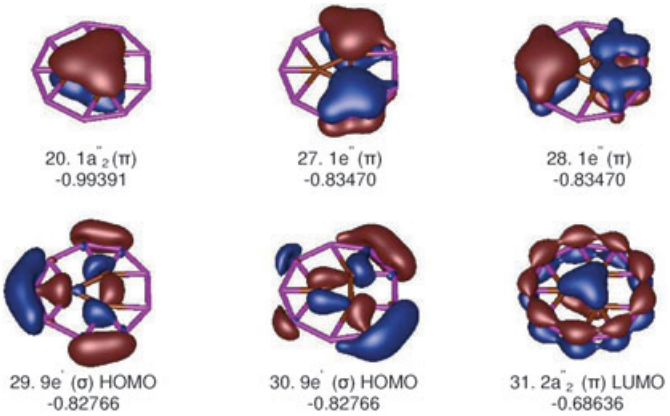

Figure 3. Plot of the occupied π MOs, the degenerate σ HOMO, and the LUMO of $C_3B_9^{3+}$. Orbital energies are given in Hartrees.

Supporting Information), five of which have π symmetry and the typical pattern of a ten-π-electron, Hückel, aromatic system. In addition, Figure 4 depicts the five lowest-lying empty orbitals, which also have π symmetry.

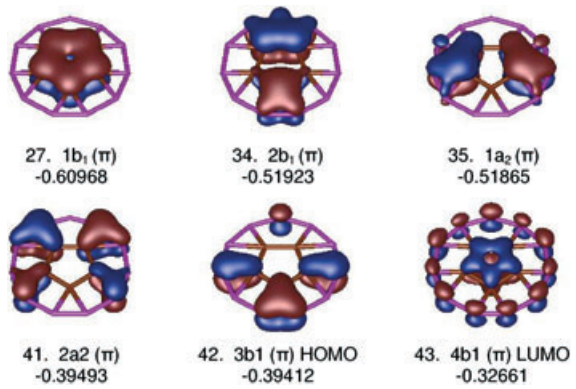

Figure 4. Plot of the occupied π MOs and the LUMO of $C_5B_{11}^+$. Orbital energies are given in Hartrees.

While the lowest-lying π MO of C_2B_8 (Figure 2, MO 17) is centered on the two inner carbon atoms, it also extends over the eight peripheral boron atoms. In contrast, the lowest-energy π MOs of $C_3B_9^{3+}$ (Figure 3, MO 20) and of $C_5B_{11}^+$ (Figure 4, MO 27) only involve the central carbon rings. While these resemble the π MO of the cyclopropenyl cation, $C_3H_3^+$, and the lowest π MO of the cyclopentadienyl anion, the analogy is imperfect because of the higher-lying multinode π MOs of the borocarbons. These MOs are not occupied in the simple carbon rings, which accounts for their shorter C–C bond lengths. The higher-lying borocarbon π MOs (Figure 2, MOs 23 and 24 for C_2B_8,; Figure 3, MOs 27 and 28 for $C_3B_9^{3+}$; Figure 4 MOs 34, 35, 41, and 42 for $C_5B_{11}^+$) have nodal planes through the carbon rings, but contribute to the C–B bonding.

The σ-bonding situations in C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^+$ are similar. C_2B_8 has 13 and $C_3B_9^{3+}$ 15 occupied σ MOs; both correspond to the number of bonds with normal lengths shown in Figure 1. The 21 occupied σ MOs of $C_5B_{11}^+$ also correspond to the solid bonds in Figure 1 if the C1B1B1′ triangle (with the longer C–B bonds) is assigned three-center two-electron character. In addition, the long C–B interactions (1.737 to 2.045 Å) in all minima and transition structures in Figure 1 arise from π and the electron-deficient σ bonding. Note that without such delocalized bonding interactions, a number of the boron atoms in each species would only be bicoordinate.[10] Inspection of the valence orbitals of the rotational transition states of C_2B_8 and $C_3B_9^{3+}$ (depicted in the Supporting Information) show that the σ and π orbitals change only slightly in comparison with the equilibrium forms although there are significant differences between the atomic partial charges and interatomic distances (Figure 1).

If the long contacts are included, all the carbons in these species are planar four- to sixcoordinate, but their total Wiberg bond indices (WBI) range from 3.8 to 3.9. Thus, the octet rule is not violated. If the atomic electronegativity values are used, the natural charges of the carbons are negative and the boron atoms positive. Even in the $C_3B_9^{3+}$ trication, the charge on the carbon atom is negative (−0.54) while that on each boron atom is positive (+0.18 and +0.67), that is, the total charges are −1.62 on the C_3 moiety and +4.62 on the B_9 ring.

As C_2B_8 does not have the requisite higher symmetry, the MOs are not degenerate. The two highest-lying π MOs (Figure 2, MOs 23 and 26) differ significantly in energy. Hence, we also optimized planar $C_2B_8^{2+}$ (in which the HOMO, π MO 26, is empty), but for the resulting cyclic four-π D_{2h} structure one imaginary frequency was obtained, whose vector pointed to out-of-plane deformation. Thus, planar cyclic four-π $C_2B_8^{2+}$ is not a viable species. Although the three lowest-lying empty orbitals of C_2B_8 also have π symmetry, the $C_2B_8^{2-}$ dianion and $C_2B_8^{4-}$ tetraanion (with eight and ten π electrons, respectively) are both transition states with imaginary frequencies pointing out-of-plane.

Similar results were obtained for the eight-π-electron $C_3B_9^+$. The higher lying degenerate 1e″ π MOs (MO 27 and 28) do not constitute the HOMO of 10π $C_3B_9^{3+}$. (The degenerate σ HOMO 17e′, Figure 3, is slightly higher in energy.) The $2a_2''$ LUMO of $C_3B_9^{3+}$ is a nondegenerate π orbital with an aesthetically pleasing concentric antibonding π-MO pattern between the C_5 and B_9 rings. We optimized the geometry of planar $C_3B_9^+$, in which the latter orbital is occupied. Although it has an electronic structure consistent with D_{3h} symmetry, the resulting planar eight-π-electron $C_3B_9^+$ monocation was not a minimum. Its one imaginary frequency corresponds to an out-of-plane C_{3v} distortion.

More details concerning the aromaticity in these intriguing $C_nB_m^{q+}$ compounds were revealed by the total NICS (nucleus independent chemical shifts)[11] and by analyzing their dissected CMO (canonical molecular orbital) contributions (calculated with the NBO 5.0 program).[12] NICS points were calculated in the centers (and above) of all the unique rings. The resulting NICS grids display the diatropic (shielded) points in red and paratropic (deshielded) points in green. NICS plots of C_2B_8 are given in Figure 5 as an example (those for $C_3B_9^{3+}$ and $C_5B_{11}^+$ are given in the Supporting Information). The total NICS plots (Figure 5a), as well as the plots of all the π MO contributions together (Figure 5b), show all the rings to be aromatic. In contrast, the contributions from all the σ orbitals are small and often paratropic (Figure 5c and Supporting Information). Hence, the aromaticity of these borocarbons is dominated by the π, rather than the σ, contributions.

In conclusion, it is possible that more than one directly joined planar hypercoordinated carbon atom can be enclosed by a peripheral ring comprising a suitable number of boron atoms. The C_2B_8, $C_3B_9^{3+}$, and $C_5B_{11}^+$ species described here (Figure 1) are stabilized by substantial Hückel π aromaticity, judging from the NICS behavior (Figure 5). In addition, multicenter σ bonding helps bind the inner carbon units to the boron perimeters. These molecules are highly fluxional. Remarkably, the inner C_2 as well as the C_3 and C_5 units and outer boron rings can rotate quite freely with regard to one another. These unusual planar clusters are stable when the constituent atoms fit nicely, both geometrically and electronically. The original idea[13] for stabilizing such planar clusters

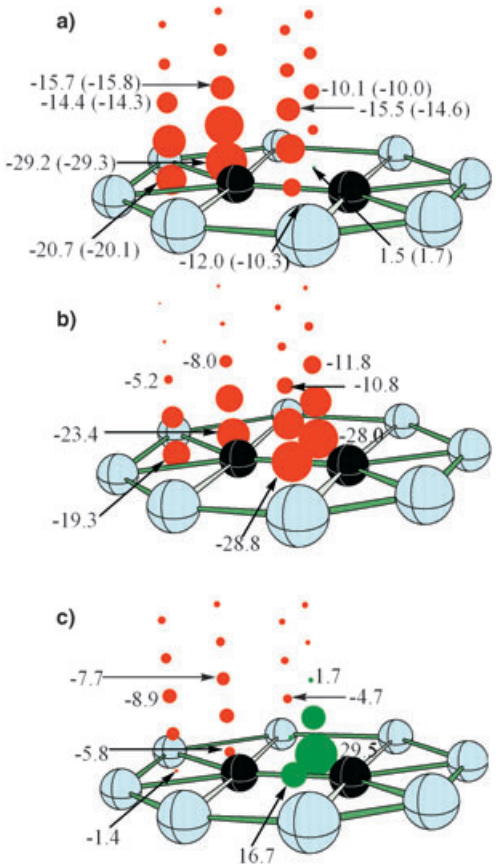

Figure 5. a) Plots of total NICS contributions, b) contributions from all π orbitals, and c) contributions from σ orbitals at the individual ring centers and up to 2 Å above C_2B_8 (D_{2h}) calculated at the GIAO B3LYP/6-31G(d) level. The total NICS values at GIAO-B3LYP/6-311+G(2df) are given in parentheses. The red and green colors denote negative (diatropic) and positive (paratropic) NICS values, respectively.

with hypercoordinate central atoms, which was later experimentally confirmed,[14] should guide the design of additional intriguing structures. While all the structures in Figure 1 are local minima fulfilling both the electronic and geometrical requirement for good bonding, they are not the global minima for the given compositions. Isomers with the carbon atoms on the outside are lower in energy, but they have neither the aesthetic appeal nor the remarkable fluxional characteristics of the structures described here.

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[5] We calculated neutral C_5B_{10} (among other $C_nB_m^{q+}$ species) because the total number of valence electrons (50) and the expected number of π electrons (10) leaves 40 valence electrons for the σ framework. For a cyclic species of C_5B_{10}, one would need 20 electrons for ten B–B bonds and ten electrons for five C–C bonds, thus leaving ten electrons for carbon–boron bonding. The latter ten electrons could be used for five CB_2 moieties, that is, there would be five three-center two-electron bonds for the bonding between the carbon and boron cycles. Planar (D_{5h}) C_5B_{10} is a transition state; the vectors of the imaginary frequency point to an out-of-plane distortion.

[6] The geometries have been optimized at the B3LYP level by using 6-311+G(2df) basis sets. The nature of the stationary points was examined by calculating the Hessian matrices at the B3LYP/6-311+G(2df) level. All the calculations have been carried out with the Gaussian 03 program.[7]

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[10] The work presented herein may be compared with a recent MO analysis of C_5^{2-} and alkaline-metal coordinated analogues that contain a planar tetracoordinate carbon atom at the center: a) G. Merino, M. A. Mendez-Rojas, A. Vela, *J. Am. Chem. Soc.* **2003**, *125*, 6026–6027; b) G. Merino, M. A. Mendez-Rojas, H. I. Beltran, C. Corminboeuf, T. Heine, A. Vela, *J. Am. Chem. Soc.* **2004**, *126*, 16160–16169. We thank one referee for pointing the work out to us.

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