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A Photoelectron Spectroscopic and Theoretical Study of B_{16}^- and B_{16}^{2-}: An All-Boron Naphthalene

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Although boron clusters were experimentally studied shortly after the discovery of the fullerenes,[1] their structural characterization was only possible fairly recently when we combined photoelectron spectroscopy (PES) and theoretical calculations to investigate the structures and bonding of boron clusters.[2–5] Early theoretical studies[6] indicated that small boron clusters do not assume cage-like structures, which are common in bulk boron and compounds; instead, planar or quasi-planar structures were suggested. The combined PES and theoretical studies show indeed boron clusters with up to 15 atoms are planar[2,3,5] and only at B_{20} does a three-dimensional (3D) structure (double ring) become energetically competitive,[4] whereas B_{20}^- still remains planar. A recent ion mobility and theoretical study showed that for B_n^+ the double-ring 3D structure becomes competitive at B_{16}^+.[7]

More interestingly, chemical bonding analyses reveal that π bonding plays an important role in the planar boron clusters.[2,3,5,8] In particular, we have found both aromatic and antiaromatic clusters according to the Hückel rules,[2e,3] analogous to hydrocarbon molecules. In the current work, we focus on B_{16}^- and B_{16}, whose structures and bonding have not been characterized. We show that both B_{16}^- and B_{16} possess quasi-planar structures (C_{2h}). More importantly, we find that addition of an electron to B_{16}^- results in a perfectly planar (D_{2h}) B_{16}^{2-}, which possesses 10 π electrons with a π bonding pattern similar to that in naphthalene. Thus, B_{16}^{2-} can be considered as an "all-boron naphthalene".

Details of the magnetic-bottle PES apparatus used for this study have been described before.[9] Briefly, the B_{16}^- cluster was produced by laser vaporization of a ^{10}B-enriched target and was mass-selected using time-of-flight mass spectrometry. PES spectra were obtained at two photon energies, as shown in Figure 1. The resolution of our PES apparatus was $\Delta E/E \approx 2.5\%$, that is, ~25 meV for 1 eV electrons.

The 266 nm spectrum reveals three broad and well-resolved bands (X, A, B). The broadband widths suggest that there must be significant structural changes between the anion and the neutral final states. The X band defines the ground-state vertical detachment energy (VDE) at 3.39 ± 0.04 eV and an adiabatic detachment energy (ADE) of 3.25 ± 0.05 eV, which also represents the electron affinity of B_{16}. At 193 nm, the relative intensity of the B band is increased and another broadband C, which overlaps with band B, also becomes prominent. The 193 nm spectrum is less well resolved and beyond 4.8 eV there is a series of overlapping spectral transitions, which are labeled for the sake of discussion. The VDEs of all the spectral features are given in Table 1, compared with theoretical calculations, as discussed in the next section.

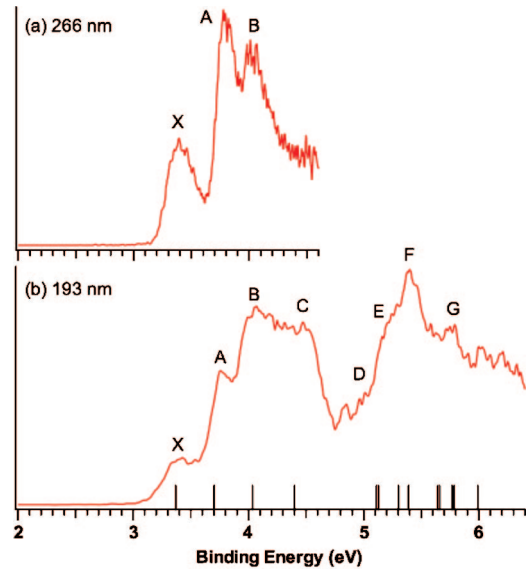

Figure 1. Photoelectron spectra of B_{16}^- at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV). The vertical bars represent the calculated VDEs at the TD-B3LYP level (see Table 1).

Theoretically we first searched for the global minimum of B_{16} using the gradient embedded genetic algorithm (GEGA) program[10] at the B3LYP/3-21G level of theory and then recalculated geometries of the low-lying isomers at the B3LYP/6-311+G* level. The lowest energy structures identified for B_{16} were used as initial structures for B_{16}^- and B_{16}^{2-}. The VDEs of B_{16}^- were calculated using the R(U)CCSD(T)/6-311+G*, the outer valence green function method [UOVGF/6-311+G(2df)] and the time-dependent density functional theory (DFT) method [TD-B3LYP/6-311+G(2df)] at the B3LYP/6-311+G* geometries. All calculations were performed using the Gaussian 03 program.[11a] Molecular orbital (MO) visualization was done using the MOLDEN3.4[11b] and MOLEKEL4.3[11c] programs.

The global minimum of B_{16}^- is shown in Figure 2, **I.1** (C_{2h}, ^2A_u), which is similar to a low-lying isomer found for B_{16}^+.[7] Alternative structures can be found in Figure S1 in the Supporting Information. The second lowest isomer **I.2** (C_s, $^2A''$) is 0.7 kcal/mol (B3LYP/6-311+G*) and 3.7 kcal/mol (CCSD(T)/6-311+G(2df)//B3LYP/6-311+G*) higher in energy. The double-ring structure **I.4** of B_{16}^- (C_s, $^2A'$), analogous to the predicted global minimum structure of B_{20},[4] was found to be 36 kcal/mol higher, very different from B_{16}^+, for which the double-ring structure is a low-lying isomer.[7]

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Table 1. Comparison of the Experimental Vertical Detachment Energies (VDE) with the Calculated Values of B_{16}^- (Structure **I.1**). All Energies Are in eV

			VDE (theoretical)		
feature	VDE (exptl)[a]	final state and electronic configuration	TD-B3LYP[b]	OVGF[c]	ΔCCSD(T)[e]
X	3.39 (4)	^1A_g, $7a_g^2 6b_u^2 4b_g^2 7b_u^2 5b_g^2 5a_u^2 6a_u^0$	3.37	3.57 (0.88)	3.27
A	3.78 (4)	^3A_g, $7a_g^2 6b_u^2 4b_g^2 7b_u^2 5b_g^2 5a_u^1 6a_u^1$	3.70	3.53 (0.88)	3.76
B	4.03 (4)	^1A_g, $7a_g^2 6b_u^2 4b_g^2 7b_u^2 5b_g^2 5a_u^1 6a_u^1$	4.03	*d*	
C	4.4 (1)	^3B_u, $7a_g^2 6b_u^2 4b_g^2 7b_u^2 5b_g^1 5a_u^2 6a_u^1$	4.40	4.44 (0.88)	
D	~5.0	^3B_g, $7a_g^2 6b_u^2 4b_g^2 7b_u^1 5b_g^2 5a_u^2 6a_u^1$	5.11	5.36 (0.88)	
		^1B_u, $7a_g^2 6b_u^2 4b_g^2 7b_u^2 5b_g^1 5a_u^2 6a_u^1$	5.12	*d*	
E	~5.2	^3B_u, $7a_g^2 6b_u^2 4b_g^1 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.30	5.46 (0.83)	
F	5.40 (10)	^1B_g, $7a_g^2 6b_u^2 4b_g^2 7b_u^1 5b_g^2 5a_u^2 6a_u^1$	5.39	*d*	
G	5.6 ~ 6.2	^3B_g, $7a_g^2 6b_u^1 4b_g^2 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.65	5.86 (0.84)	
		^1B_u, $7a_g^2 6b_u^2 4b_g^1 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.66	*d*	
		^1B_g, $7a_g^2 6b_u^1 4b_g^2 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.77	*d*	
		^3A_u, $7a_g^1 6b_u^2 4b_g^2 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.78	6.25 (0.83)	
		^1A_u, $7a_g^1 6b_u^2 4b_g^2 7b_u^2 5b_g^2 5a_u^2 6a_u^1$	5.99	*d*	

[a] Numbers in parentheses represent the uncertainty in the last digit. [b] VDEs were calculated at TD-B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory. [c] VDEs were calculated at UOVGF/6-311+G(2df)//B3LYP/6-311+G* level of theory. Values in parentheses represent the pole strength of the OVGF calculation. [d] This transition cannot be calculated at this level of theory. [e] VDEs were calculated at R(U)CCSD(T)/6-311+G*/B3LYP/6-311+G* level of theory.

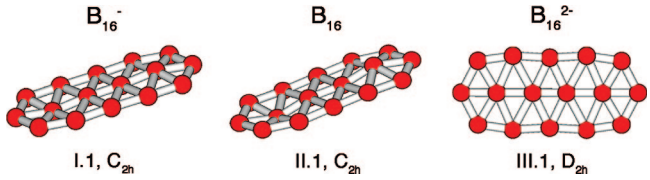

Figure 2. The optimized global minimum structures of B_{16}^- (^2A_u), B_{16} (^1A_g), and B_{16}^{2-} (^1A_g) at B3LYP/6-311+G*.

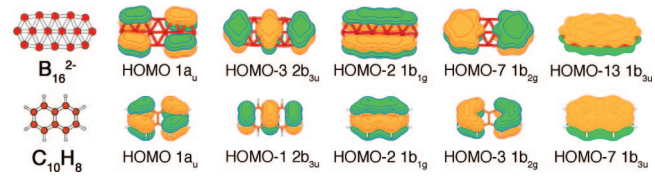

Figure 3. Comparison of the structures and π bonding of B_{16}^{2-} (D_{2h}, ^1A_g) and naphthalene.

The VDEs for the global minimum structure **I.1** of B_{16}^- have been computed using three methods and are compared to the PES data in Table 1. The first two detachment channels are calculated using the ΔCCSD(T) method, which yields VDEs in close agreement with the TD-B3LYP method. The OVGF VDEs appear to be off by as much as 0.3 eV compared to the TD-B3LP values. We have shown previously for smaller B_n^- ($n = 10-15$) clusters that the TD-B3LYP method gives VDEs in very good agreement with PES data with errors in the range of 0.1−0.2 eV.[3] Indeed, as can be seen from Table 1 and Figure 1b, the VDEs from the first four detachment channels, which are well resolved in the PES spectra, are in excellent agreement with the experiment. The first VDE (X) corresponds to detachment from the singly occupied $6a_u$-HOMO with the singlet final state ^1A_g. The second (A) and third (B) VDEs correspond to detachment from the $5a_u$-HOMO-1, leading to the triplet (^3A_g) and singlet (^1A_g) final states, respectively. The forth VDE (C) derives from detachment from the $5b_g$-HOMO-2 leading to the triplet final state (^3B_u). The VDE (5.12 eV) for the corresponding singlet state (^1B_u) is similar to the next detachment channel from the $7b_u$-HOMO-2 with a calculated VDE of 5.11 eV. Higher detachment channels give a series of closely spaced VDEs, consistent with the highly congested PES spectrum in the high binding energy side (Figure 1b). On the other hand, the calculated first VDE (3.69 eV at TD-B3LYP, Table S1) for the second lowest isomer (**I.2** in Figure S1) is significantly higher than the experimental value of 3.39 eV and this isomer can be ruled out as a contributor to the experiment. The good agreement between the calculated and experimental VDEs for structure **I.1** provides considerable credence for its being the global minimum for B_{16}^-.

Structure **I.1** is quasi-planar because two of the four inner B atoms are slightly out of plane by 0.08 Å. We note that the global minimum of B_{16} is similar to that of B_{16}^- but with more severe out-of-plane distortions by 0.24 Å (**II.1** in Figure 2), consistent with the broad ground-state transition in the PES spectrum (Figure 1). However, upon addition of an electron to the $6a_u$-HOMO of B_{16}^- (C_{2h}, ^2A_u), we find that the resulting B_{16}^{2-} dianion becomes a perfect planar (D_{2h}) and closed-shell (^1A_g) species (**III.1**, Figure 2). More interestingly, further analyses of the canonical MOs of B_{16}^{2-} show that it possesses 10 π electrons and its π-system is analogous to that of the well-known aromatic naphthalene (Figure 3). Thus, B_{16}^{2-} can be considered as an "all-boron naphthalene", adding a new member to the hydrocarbon analogues of boron clusters.

It is interesting to note that upon removal of two π electrons from the HOMO of B_{16}^{2-} the neutral B_{16} becomes π-antiaromatic and undergoes out-of-plane deformations, analogous to the out-of-plane distortion in the classical antiaromatic cyclooctatetrene (C_8H_8). In B_{16}, two of the four inner boron atoms (at the terminal positions) distort above and below the molecular plane by 0.24 Å (Figure 2), respectively. The open shell B_{16}^- is in between the π-antiaromatic B_{16} and the π-aromatic B_{16}^{2-} and thus suffers much smaller out-of-plane distortions by only 0.08 Å.

The σ bonding patterns in B_{16}^{2-} are also very interesting and should play important roles in shaping its overall planar structure. It is elucidated using the recently developed adaptive natural density partitioning (AdNDP) method (Zubrev, D. Yu.; Boldyrev, A. I., to be published), which is an extension of the popular natural bond orbital (NBO) analysis. This approach leads to partitioning of the charge density into elements with the highest possible degree of localization of electron pairs. If some part of the density cannot be localized in this manner, it is left "delocalized" (*i.e.*, localized on several atoms in the system), giving rise to *n*-center two electron (nc-2e) bonds. Thus, AdNDP incorporates naturally the idea of delocalized (globally aromatic) bonds and achieves seamless description of chemical bonding in the most general sense.

According to our AdNDP analysis shown in Figure 4, the σ-bonding framework of B_{16}^{2-} consists of 12 peripheral 2c−2e B−B bonds with occupation numbers above 1.89 |e|, six 3c−2e

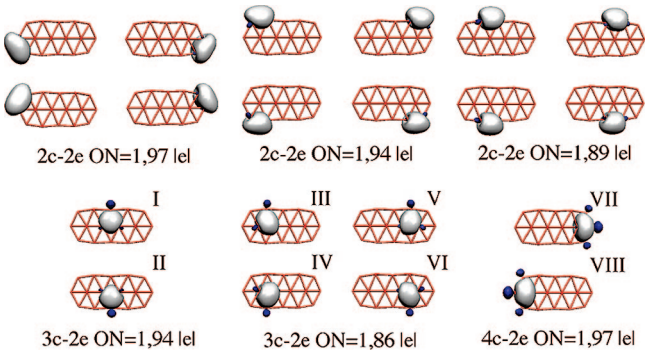

Figure 4. Localized nc-2e σ-bonds and occupation numbers in B_{16}^{2-} obtained by AdNDP analyses.

bonds with occupation number above 1.86 |e|, and two 4c−2e bonds with the occupation number 1.97 |e|. The four inner boron atoms are bonded to the peripheral boron ring via the 3c−2e and 4c−2e bonds. Out of the twenty canonical valence σ-MOs (Figure S2), twelve ($3b_{3g}$, $4b_{1u}$, $3b_{1u}$, $2b_{3g}$, $3a_g$, $2b_{2u}$, $2b_{1u}$, $1b_{3g}$, $1b_{2u}$, $2a_g$, $1b_{1u}$, $1a_g$) are responsible for the formation of the above-mentioned 2c−2e peripheral B−B bonds formed from the sp-hybridized AOs of boron atoms. The other eight valence canonical σ-MOs ($5b_{2u}$, $4b_{3g}$, $5b_{1u}$, $6a_g$, $4b_{2u}$, $3b_{2u}$, $5a_g$, $4a_g$) form delocalized σ-bonds, formally satisfying the $4n$ rule for σ-antiaromaticity. This may be responsible for the globally elongated shape of B_{16}^{2-}, in contrast to the perfectly circular shape of B_8^{2-} and B_9^-, which are both π- and σ-aromatic.[2e]

To assess the viability of using B_{16}^{2-} as building blocks for cluster-assembled nanomaterials, we also optimized structures of B_{16}^{2-} stabilized by two Li^+ cations in Li_2B_{16} (Figure S3). We found that the planar B_{16}^{2-} unit is quite flexible and can be bend or "rippled" upon coordination by Li^+. This flexibility is probably due to the relatively weak delocalized, in-plane B−B σ bonding, in contrast to the strong C−C σ-bond that forms the framework of naphthalene. Other than the bending distortion induced by Li^+, the bonding and structural integrity of B_{16}^{2-} are not altered significantly in Li_2B_{16}, suggesting its stability and viability as a structural and material building blocks.

Boron clusters with 6 π-electrons have been found before, including, B_8^{2-} and B_9^-,[2e] B_{10}, B_{11}^-, and B_{12},[3] as well as B_{13}^+,[8] which can be viewed as all-boron analogues of benzene. Globally π-antiaromatic boron clusters with 8 π-electrons have also been found, including B_{13}^- and B_{14},[3] as well as B_{16}, which can be viewed as analogues of antiaromatic cyclobutadiene or cyclooctatetrene. Here we show that B_{16}^{2-} with 10 π-electrons is an all-boron analogue of naphthalene. A natural question is if we can extend this analogy further to larger all-boron π-aromatic systems and find analogues of anthracene or other polycyclic aromatic hydrocarbons, which are being actively pursued in our laboratories.

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Supporting Information Available: Complete ref 11a, calculated vertical detachment energies for the low-lying B_{16}^- isomer (structure **I.2**, Table S1), alternative optimized structures of B_{16}^-, B_{16}, and B_{16}^{2-} (Figure S1), valence canonical σ-MOs of B_{16}^{2-} (Figure S2), optimized structures of Li_2B_{16} (Figure S3), and total energies and Cartesian coordinates for all the optimized structures of B_{16}^-, B_{16}, B_{16}^{2-} (Table S2) and Li_2B_{16} (Table S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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