

## $\pi$ -Aromatic $B_{16}H_6$ : A Neutral Boron Hydride Analogue of Naphthalene

Qiang Chen · Si-Dian Li

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**Abstract** Systematic ab initio calculations are carried out in this work to investigate the geometrical and electronic structures of  $B_{16}H_6$  neutral and its anion  $B_{16}H_6^-$ . The quasi-planar  $C_{2v}$   $B_{16}H_6(^1A_1)$  with 10 delocalized  $\pi$ -electrons proves to be the neutral boron hydride analogue of naphthalene ( $D_{2h}$   $C_{10}H_8$ ). This  $\pi$ -aromatic neutral may be obtained from the experimentally known  $\pi$ -antiaromatic  $C_{2h}$   $B_{16}$  (Sergeeva et al., J. Am. Chem. Soc. 130:7244, 2008) upon hydrogenation at the six corner positions and is expected to be undistinguishable from a perfect planar  $D_{2h}$   $B_{16}H_6$  in experiments. Detailed adaptive natural density partitioning (AdNDP) analyses clearly reveal the bonding pattern of  $B_{16}H_6$  and the calculated nucleus independent chemical shifts (NICS) strongly support its global  $\pi$ -aromaticity.  $C_{2v}$   $B_{16}H_6(^2B_2)$  anion with one extra electron appears to have a similar quasi-planar structure with even a less severe out-of-plane distortion. Ultraviolet (UV) absorption spectrum of  $B_{16}H_6$  and photoelectron spectroscopy (PES) spectrum of  $B_{16}H_6^-$  are simulated to facilitate their spectroscopic characterizations.

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This paper is dedicated to professor A. I. Boldyrev on the occasion of his 60th birthday.

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Ab initio calculation

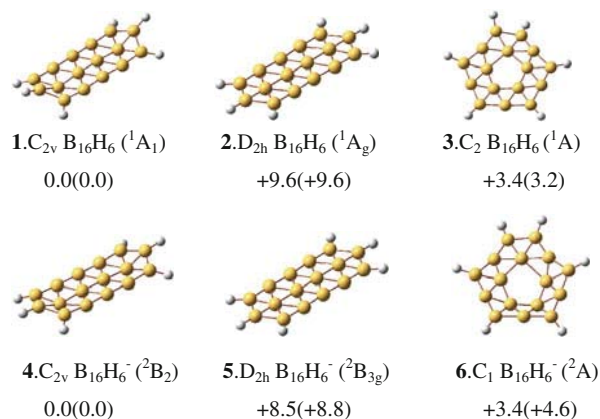
## Introduction

In a series of photoelectron spectroscopy (PES) investigations in combination with ab initio calculations in the past decade, Wang and coworkers [1–4] confirmed that small boron clusters  $B_n$  ( $n = 3–20$ ) possess planar or quasi-planar structures at their ground states in gas phases. The discoveries of all-boron analogues of benzene ( $D_{6h}$   $C_6H_6$ ) with 6  $\pi$ -electrons ( $D_{7h}$   $B_8^{2-}$ ,  $D_{8h}$   $B_9^-$ ,  $C_{2h}$   $B_{10}$ ,  $C_{2v}$   $B_{11}^-$ , and  $C_{3v}$   $B_{12}$ ) [1, 2], naphthalene ( $D_{2h}$   $C_{10}H_8$ ) with 10  $\pi$ -electrons ( $C_1$   $B_{15}^-$  [2] and  $D_{2h}$   $B_{16}^{2-}$  [3]), and coronene ( $D_{6h}$   $C_{24}H_{12}$ ) with two sets of  $\pi$ -aromatic systems ( $C_{2v}$   $B_{19}^-$ ) [4] are remarkable in boron chemistry. Their planarity and aromaticity/antiaromaticity have been interpreted in literature on the basis of the  $4n + 2$  Hückel rule [1–10], the topological resonance energies (TRE) [5], the nucleus independent chemical shifts (NICS) [9, 11, 12], and recently, the newly developed adaptive natural density partitioning (AdNDP) approach [6–8]. These results indicate that both the delocalized  $\pi$  and  $\sigma$  molecular orbitals (MOs) play an important role in determining the structures and stabilities of small boron clusters. However, pure boron clusters  $B_n$  and their cations and anions are known to be highly reactive towards catenation especially at the corner positions of the  $B_n$  sheets which can be partially or fully saturated upon hydrogenation. It remains an active and important area in boron chemistry to investigate the effect of hydrogenation on both the structures and stabilities of small boron clusters [13–15]. A 1:1 hydrogenation of two dimensional (2D) bare  $B_n$  clusters would produce three dimensional (3D)  $B_nH_n$  species analogous to the well-known deltahedral  $B_nH_n^{2-}$  dianions [13]. The partially hydrogenated  $B_nH_m$  with fewer hydrogen atoms than boron atoms ( $m < n$ ) are expected to maintain the 2D structure of the  $B_n$  cores at suitable H:B ratios. Such examples include the perfectly planar  $C_{2v}$   $B_7H_2^-$  [13] with H:B = 1:3.5 and  $C_{2v}$   $B_7Au_2^-$  with Au:B = 1:3.5 [16]. In a highly charged state, a perfectly planar  $D_{6h}$   $B_6H_6^{6-}$  unit with 6 delocalized  $\pi$ -electrons analogous to benzene was also proposed in  $B_6H_6Li_6$  [17]. Recently, Szwacki et al. [14] predicted the possibility of the perfectly planar neutral boron hydride  $D_{3h}$   $B_{12}H_6$ , the so called borozene which can be obtained by hydrogenation of a  $C_{3v}$   $B_{12}$  convex cluster at the six corner positions [2]. Unfortunately, borozene proves to be a local minimum lying considerably higher in energy (about 34.6 kcal/mol) than its icosahedral isomer  $C_2$   $B_{12}H_6$  [15]. Thus, neutral  $B_{12}H_6$  with H:B = 1:2 is expected to exist as a cage-like  $C_2$   $B_{12}H_6$  icosahedron rather than the perfectly planar  $D_{3h}$   $B_{12}H_6$ , similar to the situation in icosahedral  $B_{12}H_6^+$  [18]. Aiming at finding a neutral boron hydride cluster which corresponds to a prototypic  $\pi$ -aromatic hydrocarbon molecule, in this work, we move one step forward to search for a novel boron hydride analogue of naphthalene ( $D_{2h}$   $C_{10}H_8$ ) which possesses 10 delocalized  $\pi$ -electrons to follow the  $4n + 2$  aromatic rule with  $n = 2$ . Extensive ab initio investigations at various theoretical levels indicate that a quasi-planar  $C_{2v}$   $B_{16}H_6$  with H:B  $\approx$  1:2.7 obtained upon hydrogenation of the experimentally known  $C_{2h}$   $B_{16}$  [3] is indeed a neutral

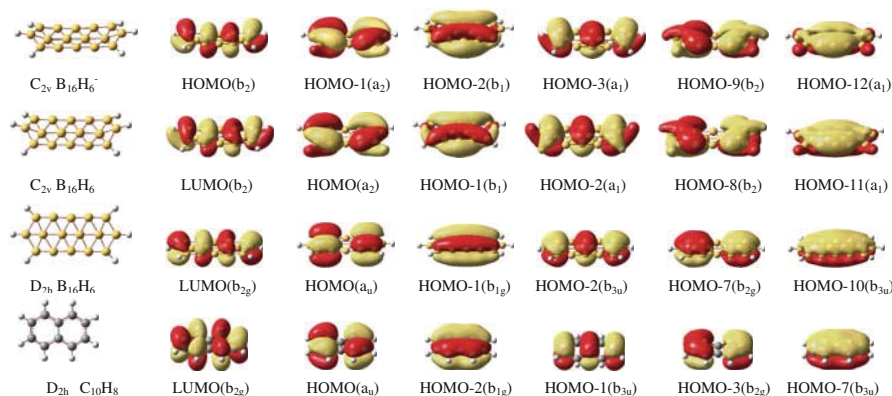
boron hydride analogue of naphthalene with 10 delocalized  $\pi$ -electrons. The  $\pi$ -antiaromatic  $C_{2h} B_{16}$  [3] gains a  $\pi$ -aromatic character upon addition of six hydrogen atoms at the corner positions to produce the  $\pi$ -aromatic  $C_{2v} B_{16}H_6$ . The slightly off-planar  $C_{2v} B_{16}H_6$  is expected to be undistinguishable from a perfectly planar  $D_{2h} B_{16}H_6$  in experiments. With one extra electron attached,  $C_{2v} B_{16}H_6^-$  anion possesses a similar quasi-planar structure with even a less severe out-of-plane distortion. The quasi-planar  $C_{2v} B_{16}H_6^{0/-}$  predicted in this work may be good candidates to be targeted in future experiments. To the best of our knowledge,  $C_{2v} B_{16}H_6$  is the first neutral boron hydride analogue of a prototypic  $\pi$ -aromatic hydrocarbon molecule (naphthalene) proposed so far [1–4, 14–17]. Such boron-rich boron hydrides may have important implications on the chemistry of boron and boron-based materials [13–17].

### Theoretical Procedure

Structural optimizations and vibrational analyses were performed using both the hybrid density functional theory (DFT) methods of B3LYP [19, 20] and X3LYP [21] with the basis sets of 6-311++G(3df,p) implemented in Gaussian 03 program [22]. X3LYP produces essentially the same optimized structures for  $B_{16}H_6^{0/-}$  with B3LYP with only slightly different bond parameters. Low-lying isomers were also optimized using the second-order Møller–Plesset approach (MP2) [23, 24] with the same basis sets. Relative energies were further refined using the coupled cluster method with triple excitations (CCSD(T)) [25–28] with the basis of 6-311+G(d,p) at both B3LYP and MP2 structures. Structural searches based upon various low-lying  $B_{16}$  isomers [3] and arbitrarily or randomly designed structures were performed to locate the low-lying isomers of the boron hydride clusters. An extensive search using the Coalescence Kick [29] program written by Averkiev and coworkers [4] produced no isomers with lower energies than the three lowest-lying isomers shown in Fig. 1. Alternative low-lying isomers obtained for  $B_{16}H_6$  are summarized in Fig. 1S in Supporting Information. The bonding patterns of the concerned systems are demonstrated in both the canonical molecular orbitals (MOs) in Fig. 2 and AdNDP MOs in Fig. 3. The weak  $\pi$ – $\pi$  interaction energies between molecules in  $[B_{16}H_6]_2$  dimers, naphthalene dimers  $[C_{10}H_8]_2$ , and benzene dimers  $[C_6H_6]_2$  are compared in Fig. 4 at MP2/6-311++G(d,p) level with the counterpoise corrections included. The ultraviolet (UV) absorption and PES spectra predicted at the time-dependent DFT level (TD-B3LYP) are shown in Figs. 5 and 6, respectively. To check the  $\pi$ -aromaticity of the  $B_{16}H_6^{0/-}$  clusters, the widely used nucleus independent chemical shifts (NICS) and their perpendicular components NICS<sub>zz</sub> [11, 12] were calculated at points 0.0 and 1.0 Å above the central  $B_3$  triangular units of the concerned molecules using the gauge-independent atomic orbital (GIAO) method [30]. The magnetic susceptibility tensors were obtained employing the continuous set of gauge transformations (CSGT) approach [31–33]. The calculated magnetic properties of the three lowest-lying isomers have been summarized in Table 1 and Table 1S.



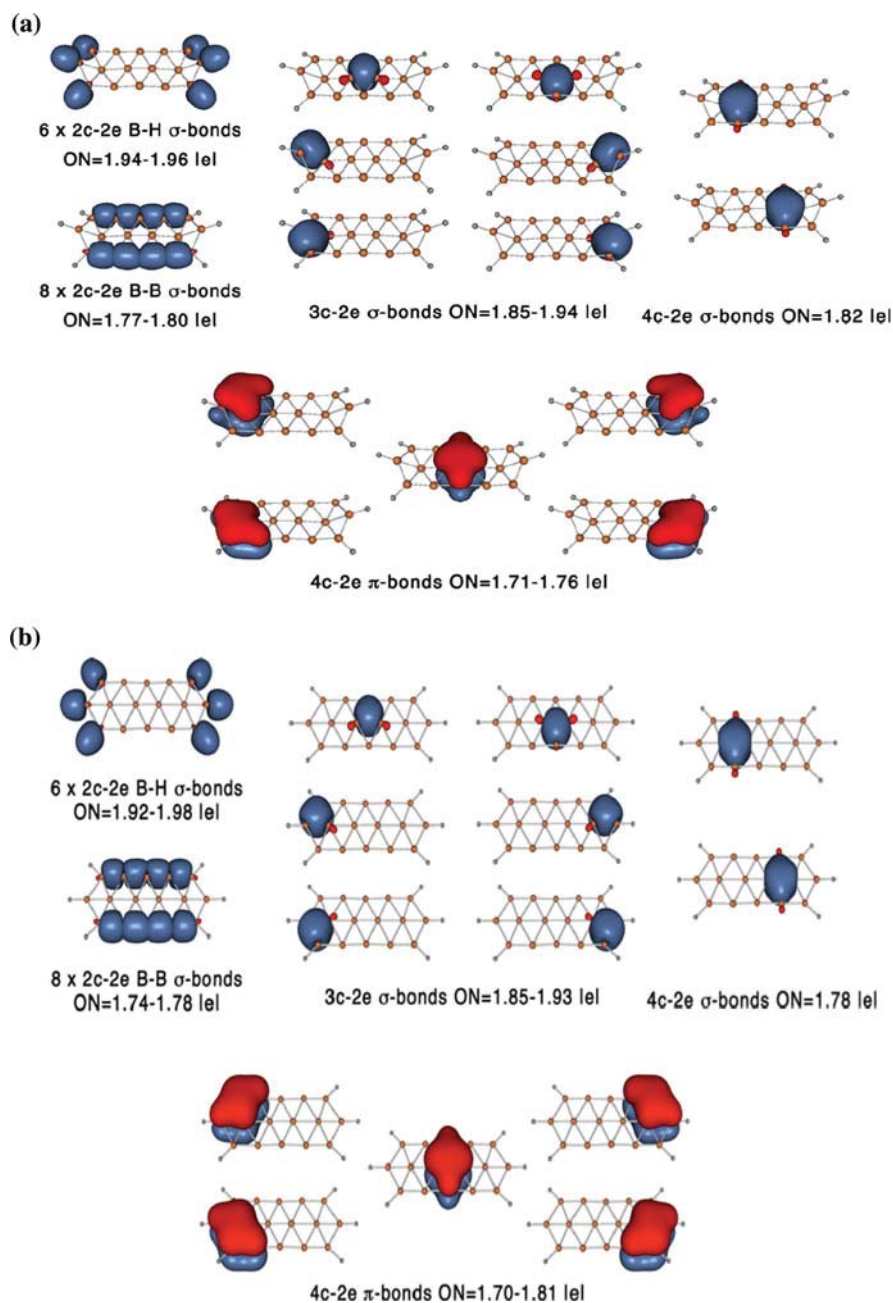
**Fig. 1** Optimized structures of the three lowest-lying isomers of B<sub>16</sub>H<sub>6</sub> neutral (1–3) and B<sub>16</sub>H<sub>6</sub><sup>-</sup> anion (4–6), with their relative energies at CCSDT//B3LYP and CCSD(T)//MP2 (in parentheses) indicated in kcal/mol



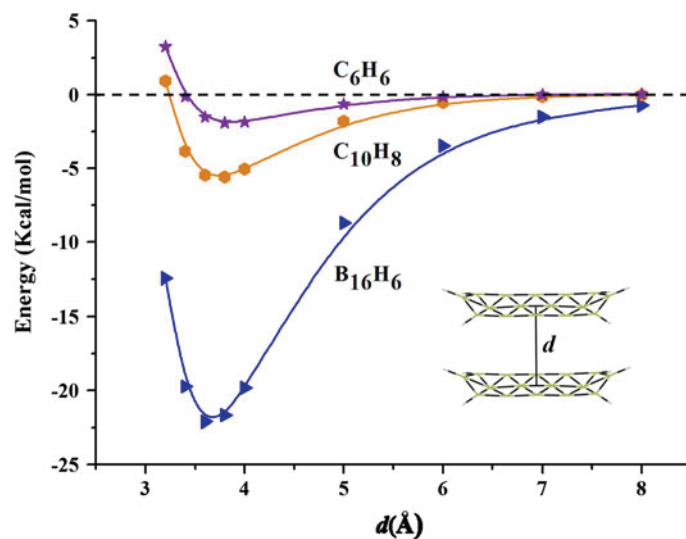
**Fig. 2** Pictures of the  $\pi$ -MOs of D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub>, C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub>, and C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> compared with that of D<sub>2h</sub> C<sub>10</sub>H<sub>8</sub>

## Results and Discussions

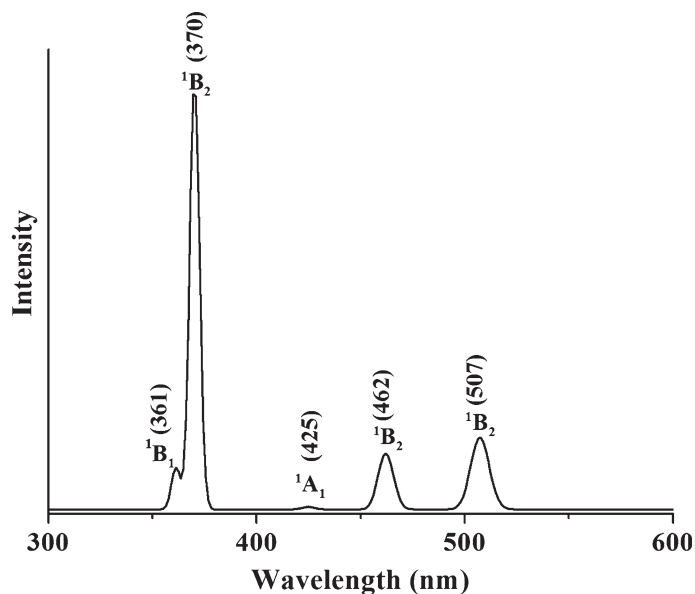
Extensive searches at various ab initio levels indicate that the quasi-planar C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**, <sup>1</sup>A<sub>1</sub>) is the lowest-lying isomer obtained for neutral B<sub>16</sub>H<sub>6</sub> which lies 9.6 and 3.4 kcal/mol lower in energy than the perfectly planar D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub> (**2**, <sup>1</sup>A<sub>g</sub>) and the distorted concentric C<sub>2</sub> B<sub>16</sub>H<sub>6</sub> (**3**, <sup>1</sup>A) at CCSD(T)//B3LYP, respectively. CCSD(T)//MP2 method produces essentially the same relative energies (9.6 and 3.2 kcal/mol) for these isomers. Other low-lying isomers obtained turn out to lie at least 14 kcal/mol higher in energy than C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) (see Fig. 1S). C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) can be obtained upon hydrogenation of the quasi-planar C<sub>2h</sub> B<sub>16</sub> [3] at the six corner positions and appears to be slightly off-planar with the two outmost corner B atoms lying within 0.48 Å above the molecular plane. The perfectly planar D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub> (**2**)



**Fig. 3** Comparison of the bonding elements revealed at AdNDP for  $C_{2v}$   $B_{16}H_6$  (1) (a) and  $D_{2h}$   $B_{16}H_6$  (2) (b). Both isomers contain six 2c-2e B-H  $\sigma$ -bonds superimposed on a single molecular framework, eight 2c-2e B-B  $\sigma$ -bonds superimposed on a single molecular framework, six 3c-2e  $\sigma$ -bonds, two 4c-2e  $\sigma$ -bonds, and five 4c-2e  $\pi$ -bonds, with almost the same occupation numbers for the corresponding bonds

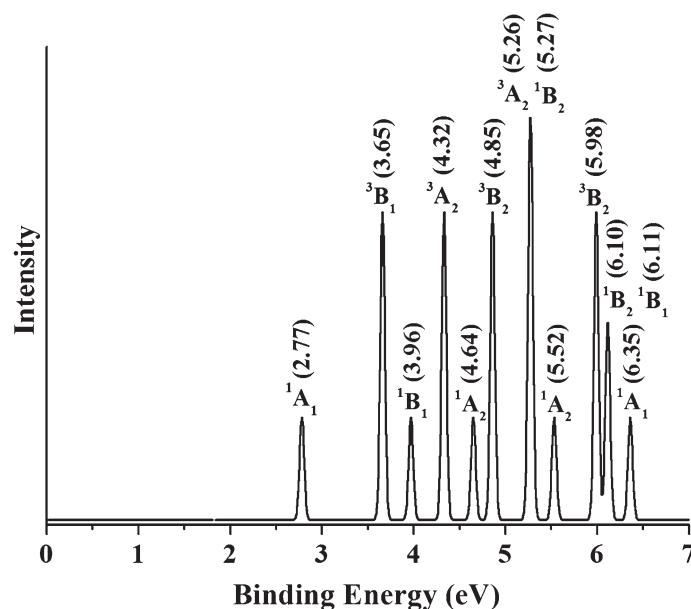


**Fig. 4** Potential energy curves of  $C_{2v}$   $B_{16}H_6$ ,  $D_{2h}$   $C_{10}H_8$ , and  $D_{6h}$   $C_6H_6$  dimers versus the center-to-center distance between the monomers, with the association energies of  $-22.10$ ,  $-5.58$ , and  $-1.92$  kcal/mol at the equilibrium distances of  $3.6$ ,  $3.8$ , and  $3.8$  Å at MP2/6-311++G(d,p), respectively



**Fig. 5** Calculated UV absorption spectrum of  $C_{2v}$   $B_{16}H_6$  (1) neutral at TD-B3LYP in the wavelength range between 300 and 600 nm

is a transition state at B3LYP with an imaginary frequency of  $-450$   $cm^{-1}$  which leads to  $C_{2v}$   $B_{16}H_6$  (1) upon a free structural optimization. However, as demonstrated in Fig. 1 and Fig. 2S, the structural distortion from  $D_{2h}$   $B_{16}H_6$  (2)



**Fig. 6** Calculated PES spectrum of C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**4**) anion obtained at B3LYP/6-311++G(3df,p) in the energy range between 0 and 7 eV

**Table 1** Calculated NICS values (ppm) at the geometrical centers and AMS values of C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) and D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub> (**2**) compared with that of naphthalene (D<sub>6h</sub> C<sub>10</sub>H<sub>8</sub>) and benzene (D<sub>6h</sub> C<sub>6</sub>H<sub>6</sub>) at B3LYP/6-311++G(3df,p)

|  | NICS(0) | NICS <sub>zz</sub> (0) | NICS(1) | NICS <sub>zz</sub> (1) | AMS    | ADE         | VDE         |
|--|---------|------------------------|---------|------------------------|--------|-------------|-------------|
| C <sub>2v</sub> B <sub>16</sub> H <sub>6</sub> | -28.8   | -67.2                  | -21.2   | -49.1                  | -279.1 | 2.52 (2.49) | 2.77 (2.77) |
| D <sub>2h</sub> B <sub>16</sub> H <sub>6</sub> | -29.5   | -66.9                  | -22.0   | -48.6                  | -303.4 | -           | -           |
| D <sub>2h</sub> C <sub>10</sub> H <sub>8</sub> | -40.0   | -82.1                  | -17.6   | -42.2                  | -126.1 | -           | -           |
| D <sub>6h</sub> C <sub>6</sub> H <sub>6</sub>  | -7.7    | -16.3                  | -10.0   | -30.0                  | -65.0  | -           | -           |

The ADE and VDE values of C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**4**) at B3LYP and CCSD(T)//B3LYP (in parentheses) are also tabulated in the last two columns

to C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) is minor in terms of the calculated bond parameters. We notice that D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub> (**2**) is a true minimum at MP2/6-311++G(3df,p). However, it proves to be 9.6 kcal/mol less stable than C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) at the more accurate CCSD(T)//MP2. C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub> (**1**) and D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub> (**2**) are thus expected to be undistinguishable in experiments. They possess essentially the same bonding pattern as detailed in the following parts. C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**4**) anion takes a similar quasi-planar structure which has even a less severe out-of-plane distortion: the two outmost corner B atoms in C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**4**) lie within 0.35 Å above the molecular plane. As shown in Fig. 1, C<sub>2v</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**4**) is about 8.5 and 3.4 kcal/mol more stable than the perfectly planar D<sub>2h</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**5**) and the distorted concentric C<sub>1</sub> B<sub>16</sub>H<sub>6</sub><sup>-</sup> (**6**) at CCSD(T) level, well parallel to the situation in B<sub>16</sub>H<sub>6</sub> neutral.



To evaluate the effect of hydrogenation on the stability of boron hydrides, we calculated the energy of reaction for  $B_{16}(C_{2h})+3H_2 = B_{16}H_6(C_{2v})$  which appears to have the averaged hydrogenation energy of  $\Delta E = 47$  kcal/mol at CCSD(T(T)//B3LYP. This value is slightly higher than the corresponding value of  $\Delta E = 44$  kcal/mol obtained for  $B_{12}(C_{3v})+3H_2 = B_{12}H_6(D_{3h})$  at the same theoretical level (a value of  $\Delta E = 50$  kcal/mol is reported for  $D_{3h} B_{12}H_6$  in Ref. [14]. at the less accurate X3LYP level).

The planarity of  $B_{16}H_6$  originates from its unique  $\pi$ -MO occupation. As clearly shown in Fig. 2, both the quasi-planar  $C_{2v} B_{16}H_6$  (**1**) (HOMO( $a_2$ ), HOMO-1( $b_1$ ), HOMO-2( $a_1$ ), HOMO-8( $b_2$ ), and HOMO-11( $a_1$ )) and the perfectly planar  $D_{2h} B_{16}H_6$  (**2**) (HOMO( $a_u$ ), HOMO-1( $b_{1g}$ ), HOMO-2( $b_{3u}$ ), HOMO-7( $b_{2g}$ ), and HOMO-10( $b_{3u}$ )) possess 5 delocalized  $\pi$ -MOs analogous to that of naphthalene ( $D_{2h} C_{10}H_8$ ) (though certain distortion exists for the low symmetry  $C_{2v} B_{16}H_6$  (**1**)), rendering global  $\pi$ -aromaticity to neutral  $B_{16}H_6$ . The 5 delocalized  $\pi$ -MOs of neutral  $B_{16}H_6$  also appear to be similar with that of the  $D_{2h} B_{16}^{2-}$  dianion, the so-called “all-boron naphthalene” [3]. Thus,  $B_{16}H_6$  can be considered as a neutral boron hydride analogue of naphthalene. We notice here that the experimentally known  $\pi$ -antiaromatic  $C_{2h} B_{16}$  with 8 delocalized  $\pi$ -electrons [3] gains  $\pi$ -aromatic character upon addition of six hydrogen atoms at the corner positions to produce the  $\pi$ -aromatic  $C_{2v} B_{16}H_6$  with 10 delocalized  $\pi$ -electrons: the unoccupied  $\pi$ -LUMO( $a_u$ ) of  $C_{2h} B_{16}$  (corresponding to the HOMO( $a_u$ ) of  $B_{16}^{2-}$ ) [3] becomes the occupied  $\pi$ -HOMO( $a_2$ ) of  $C_{2v} B_{16}H_6$  (see Fig. 2) upon hydrogenation, making  $B_{16}H_6$   $\pi$ -aromatic in nature. Interestingly, with the two  $\pi$ -electrons in the HOMO( $a_2$ ) of  $C_{2v} B_{16}H_6$  removed, a perfectly planar  $D_{2h} B_{16}H_6^{2+}$  ( $^1A_g$ ) dication (similar to  $D_{2h} B_{16}H_6$ (**2**) in geometry with slightly longer bond lengths) is achieved.  $D_{2h} B_{16}H_6^{2+}$  is the lowest-lying isomer obtained for  $B_{16}H_6^{2+}$  at both B3LYP and MP2 levels. This perfect planar dication turns out to be  $\pi$ -antiaromatic in nature with 8 delocalized  $\pi$ -electrons similar to  $C_{2h} B_{16}$  (see Fig. 3S). Figure 2 also indicates that the extra electron of the  $C_{2v} B_{16}H_6^-$  anion occupies a partially antibonding  $\pi$ -HOMO( $b_2$ ) which corresponds to the LUMO( $b_2$ ) of the  $C_{2v} B_{16}H_6$  neutral. The first detachment energy of  $C_{2v} B_{16}H_6^-$  is therefore expected to be low compared to  $C_{2h} B_{16}^-$  anion which has a bonding  $\pi$ -HOMO with a high vertical detachment energy of VDE = 3.39 eV [3].  $C_s B_{16}H_2$ , a neutral boron hydride (isoelectronic with  $D_{2h} B_{16}^{2-}$  [3]) lying 40.9 kcal/mol lower than a perfectly planar  $D_{2h} B_{16}H_2$  with two H terminals at the outmost corner positions, proves to have 8 delocalized  $\pi$ -electrons, similar to  $C_{2h} B_{16}$  [3] and  $D_{2h} B_{16}H_6^{2+}$  (see Fig. 3S).

Detailed AdNDP analyses clearly reveal both the  $\sigma$ - and  $\pi$ -bonding patterns of  $B_{16}H_6$ . As shown in Fig. 3a, the quasi-planar  $C_{2v} B_{16}H_6$  (**1**) possesses 6 localized 2c–2e B–H  $\sigma$  bonds with the occupation numbers of ON = 1.94–1.96|e| at the six corners, 8 localized 2c–2e B–B  $\sigma$  bonds with ON = 1.77–1.80|e| along the periphery, 6 delocalized 3c–2e  $\sigma$  bonds with ON = 1.85–1.94|e| and 2 delocalized 4c–2e  $\sigma$  bonds with ON = 1.82|e| between the twelve periphery boron atoms and the four inner boron atoms, and 5 delocalized out-of-plane 4c–2e  $\pi$  bonds with ON = 1.71–1.76|e| over the  $B_{16}$  sheet. Interestingly, the bonding elements revealed at AdNDP for the perfectly planar  $D_{2h} B_{16}H_6$  (**2**) in Fig. 3b have exactly a one-to-one correspondence relationship with that of  $C_{2v} B_{16}H_6$  (**1**) with almost the same



corresponding occupation numbers. Obviously,  $C_{2v} B_{16}H_6$  (**1**) and  $D_{2h} B_{16}H_6$  (**2**) possess the same bonding pattern at AdNDP and share practically the same chemical structure. Thus,  $B_{16}H_6$  is  $\pi$ -aromatic and  $\sigma$ -antiaromatic in nature according to the  $4n + 2$  Hückel rule in total electron counts. It is the delocalized  $\sigma$ -system with 16 electrons (12  $3c-2e$  electrons plus 4  $4c-2e$  electrons) that accounts for the elongated shape of  $B_{16}H_6$  and the delocalized  $\pi$ -system with 10 electrons that introduces extra  $\pi$ -stability to stabilize the planar geometry of the neutral. It should be noticed that, as indicated in the case of  $D_{2h} Li_4$  reported previously in Ref. [6], an overall  $\sigma$ -antiaromaticity is expected to lead to the formation of islands of  $\sigma$ -aromaticity. AdNDP analysis in Fig. 3 shows the six  $B_3$  triangular regions of  $\sigma$ -aromaticity in  $B_{16}H_6$  as six delocalized  $3c-2e$   $\sigma$ -bonds and the two  $B_4$  rhombus regions of  $\sigma$ -aromaticity as two delocalized  $4c-2e$   $\sigma$ -bonds. Thus,  $B_{16}H_6$  possesses island  $\sigma$ -aromaticity though it is overall  $\sigma$ -antiaromatic in total  $\sigma$ -electron count.

It is interesting to compare the AdNDP bonding pattern of  $B_{16}H_6$  with that of the bare cluster  $C_{2h} B_{16}$  [3] at this stage. Figure 4S clearly shows that  $C_{2h} B_{16}$  contains 12  $2c-2e$  B–B  $\sigma$ -bonds along the periphery, 6  $3c-2e$   $\sigma$ -bonds and 2  $4c-2e$   $\sigma$ -bonds between the twelve periphery B atoms and four inner boron atoms, and 4  $4c-2e$   $\pi$  bonds over the  $C_{2h} B_{16}$  sheet, clearly indicating that  $C_{2h} B_{16}$  is, in overall,  $\sigma + \pi$  doubly antiaromatic [3]. A partial hydrogenation of the doubly antiaromatic  $C_{2h} B_{16}$  at the six corner positions breaks four B–B  $\sigma$ -bonds along the periphery at the two ends and introduces a new  $4c-2e$   $\pi$  bond at the center of the  $B_{16}$  sheet, while the 8 delocalized  $\sigma$ -bonds (6  $3c-2e$  bonds and 2  $4c-2e$  bonds) which are responsible to the elongated shape of  $C_{2h} B_{16}$  have been well inherited in both  $C_{2v} B_{16}H_6$  (**1**) and  $D_{2h} B_{16}H_6$  (**2**) (compare Fig. 3 with Fig. 4S). Consequently, the four B–B  $\sigma$ -bonds along the periphery at the two ends have been elongated from 1.57 Å in  $C_{2h} B_{16}$  to 1.75 Å in  $C_{2v} B_{16}H_6$  (**1**), while the other eight B–B  $\sigma$ -bonds along the periphery are well maintained at about 1.60 Å (see Fig. 2S). Detailed MO analyses in Fig. 3S and AdNDP analyses in Figs. 4S and 5S clearly indicate that, similar to  $C_{2h} B_{16}$  [3], the perfectly planar  $D_{2h} B_{16}H_6^{2+}$  (which has two less  $\pi$ -electrons in HOMO than  $B_{16}H_6$ ) also appears to be overall  $\sigma + \pi$  doubly antiaromatic.

The huge negative NICS(0) and NICS(1) values (between  $-21$  and  $-30$  ppm) and NICS<sub>zz</sub>(0) and NICS<sub>zz</sub>(1) values (between  $-48$  and  $-70$  ppm) obtained for  $C_{2v} B_{16}H_6$  and  $D_{2h} B_{16}H_6$  at their geometrical centers (see Table 1) strongly support the global  $\pi$ -aromaticity of  $C_{2v} B_{16}H_6$  (**1**) and  $D_{2h} B_{16}H_6$  (**2**). These values are even more negative in most cases than the corresponding values of both naphthalene and benzene. An extensive NICS calculation over the  $B_{16}$  sheets in both  $C_{2v} B_{16}H_6$  (**1**) and  $D_{2h} B_{16}H_6$  (**2**) shows that  $B_{16}H_6$  possesses no antiaromatic regions with positive NICS values (see Table 1S), indicating that the molecule is globally  $\pi$ -aromatic (in contrast,  $D_{3h} B_{12}H_6$  possesses an antiaromatic region inside the central  $B_3$  triangle [14]). The negative NICS(0) values at the center of each  $B_3$  triangle in both planar and quasi-planar  $B_{16}H_6$  (see Table 1S) support the formation of islands of  $\sigma$ -aromaticity in  $B_{16}H_6$ . Table 1 also tabulates the calculated anisotropies of magnetic susceptibility (AMS) which have been shown to be important indicators of diatropicity for aromatic systems [34]. The AMS value of  $-279.1$  cgs ppm for  $C_{2v} B_{16}H_6$  (**1**) appears to be over 4 times bigger than for benzene ( $-65.0$  cgs ppm), 2 times bigger than for naphthalene ( $-126.1$  cgs ppm), and 1.5 times bigger than

for  $C_{2h}$   $B_{16}$  ( $-181.4$  cgs ppm) at CSGT level, indicating that neutral  $B_{16}H_6$  possesses a much stronger diatropicity than benzene, naphthalene, and  $C_{2h}$   $B_{16}$ .

Benzene and naphthalene dimers represent prototypic weak  $\pi$ - $\pi$  aromatic interactions in aromatic supramolecular systems. Since a  $C_{2v}$   $B_{16}H_6$  monomer has the same number of  $\pi$ -electrons and similar  $\pi$ -MOs with naphthalene  $D_{2h}$   $C_{10}H_8$ , a  $[B_{16}H_6]_2$  dimer is expected to have similar  $\pi$ - $\pi$  interaction energies with a naphthalene dimer  $[C_{10}H_8]_2$ . We investigate the  $\pi$ - $\pi$  interaction in these dimers in the simplest way with parallel “sandwich” configurations. As shown in Fig. 4, the potential energy curve of the  $[B_{16}H_6]_2$  dimer versus the center-to-center distances  $d$  between  $B_{16}H_6$  monomers is similar with that of both  $[C_{10}H_8]_2$  and  $[C_6H_6]_2$  dimers in general shapes. However, the association energy of  $-22.10$  kcal/mol obtained for  $[B_{16}H_6]_2$  at the equilibrium distance of  $d = 3.6$  Å is over 4 times bigger than for  $[C_{10}H_8]_2$  ( $-5.58$  kcal/mol) at the equilibrium position of  $d = 3.8$  Å and 11 times bigger than for  $[C_6H_6]_2$  ( $-1.92$  kcal/mol) at the equilibrium distance of  $3.8$  Å. These results suggest a much stronger polarization contribution from the 5  $\pi$ -MOs of  $C_{2v}$   $B_{16}H_6$  which originates from the much more delocalized  $\pi$ -MOs in  $B_{16}H_6$  with respect to naphthalene and benzene.

Finally, we simulated the UV spectrum of  $C_{2v}$   $B_{16}H_6$  (**1**) in Fig. 5 and PES spectrum of  $C_{2v}$   $B_{16}H_6^-$  (**4**) in Fig. 6 to facilitate their future spectroscopic characterizations.  $C_{2v}$   $B_{16}H_6$  (**1**) neutral possesses three characteristic UV absorption bands (which all correspond to singlet final states), with the strongest one at  $370$  nm ( $^1B_2$ ) (which is partially overlapped with a weaker shoulder at  $361$  nm ( $^1B_1$ )) and two weak bands at  $462$  ( $^1B_2$ ) and  $507$  nm ( $^1B_2$ ), respectively (see Fig. 5). At B3LYP level,  $C_{2v}$   $B_{16}H_6^-$  (**4**) anion has a relatively low vertical detachment energy of  $VDE = 2.77$  eV corresponding to the first peak  $X(^1A_1)$  in Fig. 6 and an adiabatic detachment energy of  $ADE = 2.52$  eV originated from detaching the extra electron from the partially antibonding HOMO( $b_2$ ) of the anion (see Fig. 2). These values agree well with the CCSD(T)/B3LYP values of  $ADE = 2.49$  eV and  $VDE = 2.77$  eV. With an X-A energy gap of  $0.87$  eV, the second PES band A ( $^3B_1$ ) lies at  $3.65$  eV in Fig. 6. There exists basically a singlet-triplet alternation in the binding energy range between  $3.5$  and  $6.5$  eV where the calculated neighboring VDE peaks are expected to overlap in certain extent in experiments.

## Summary

We have presented in this work an extensive ab initio investigation on 2D  $\pi$ -aromatic  $B_{16}H_6$  which is the boron hydride analogue of naphthalene.  $C_{2v}$   $B_{16}H_6$  may be obtained from the experimentally known  $\pi$ -antiaromatic  $C_{2v}$   $B_{16}$  [3] upon a partial hydrogenation at the six corner boron atoms and is expected to be undistinguishable from  $D_{2h}$   $B_{16}H_6$  in experiments. AdNDP and NICS analyses reveal the  $\pi$ -aromatic and  $\sigma$ -antiaromatic nature of the boron hydride neutral.  $C_{2v}$   $B_{16}H_6^-$  (**4**) anion which may be obtained by a partial hydrogenation of the experimentally known  $C_{2h}$   $B_{16}^-$  anion [3] possesses a similar quasi-planar structure with lower ADE and VDE values than its parent anion  $C_{2h}$   $B_{16}^-$ .  $C_{2v}$   $B_{16}H_6$  (**1**) is the first neutral boron hydride analogue of a prototypic  $\pi$ -aromatic hydrocarbon molecule (naphthalene)

proposed to date which invites experimental syntheses and characterizations to enrich the chemistry of boron hydride clusters [13, 14].

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## References

1. A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang (2006). *Coord. Chem. Rev.* **250**, 2811; and references therein.
2. H. J. Zhai, B. Kiran, J. Li, and L. S. Wang (2003). *Nat. Mater.* **2**, 827.
3. A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang (2008). *J. Am. Chem. Soc.* **130**, 7244.
4. W. Huang, A. P. Sergeeva, H. J. Zhai, B. B. Averkiev, L. S. Wang, and A. I. Boldyrev (2010). *Nat. Chem.* **2**, 202.
5. J. Aihara, H. Kanno, and T. Ishida (2005). *J. Am. Chem. Soc.* **127**, 13324.
6. D. Y. Zubarev and A. I. Boldyrev (2008). *Phys Chem. Chem. Phys.* **10**, 5207.
7. D. Y. Zubarev and A. I. Boldyrev (2008). *J. Org. Chem.* **73**, 9251.
8. D. Y. Zubarev and A. I. Boldyrev (2009). *J. Phys. Chem. A* **113**, 866.
9. D. Y. Zubarev and A. I. Boldyrev (2007). *J. Comput. Chem.* **28**, 251.
10. T. B. Tai, D. J. Grant, M. T. Nguyen, and D. A. Dixon (2010). *J. Phys. Chem. A* **114**, 994.
11. P. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. van Eikema Hommes (1996). *J. Am. Chem. Soc.* **118**, 6317.
12. H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, and P. R. Schleyer (2006). *Org. Lett.* **8**, 863.
13. A. N. Alexandrova, E. Koyle, and A. I. Boldyrev (2006). *J. Mol. Model.* **12**, 569.
14. N. G. Szewacki, V. Weber, and C. J. Tymczak (2009). *Nanoscale Res. Lett.* **4**, 1085.
15. H. Bai and S. D. Li (2011). *Nanoscale Res. Lett.*, submitted.
16. H. J. Zhai, L. S. Wang, D. Yu. Zubarev, and A. I. Boldyrev (2006). *J. Phys. Chem. A* **110**, 1689.
17. A. N. Alexandrova, K. A. Birch, and A. I. Boldyrev (2003). *J. Am. Chem. Soc.* **125**, 10786.
18. Y. J. Ohishi, K. Kimura, M. Yamaguchi, N. Uchida, and T. Kanayama (2008). *J. Chem. Phys.* **128**, 1243054.
19. A. D. Becke (1993). *J. Chem. Phys.* **98**, 5648.
20. C. Lee, W. Yang, and R. G. Parr (1988). *Phys. Rev. B.* **37**, 785.
21. X. Xu and W. A. Goddard (2004). *Proc. Natl Acad. Sci. USA* **101**, 2673.
22. M. J. Frisch, et al. *Gaussian 03, Revision, A. 1* (Gaussian, Inc., Pittsburgh, PA, 2003).
23. M. Head-Gordon, J. A. Pople, and M. Frisch (1988). *Chem. Phys. Lett.* **153**, 503.
24. M. Head-Gordon and T. Head-Gordon (1994). *Chem. Phys. Lett.* **220**, 122.
25. J. A. Pople, M. Head-Gordon, and K. Raghavachari (1987). *J. Chem. Phys.* **87**, 5968.
26. G. E. Scuseria and H. F. Schaefer III (1989). *J. Chem. Phys.* **90**, 3700.
27. G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III (1988). *J. Chem. Phys.* **89**, 7382.
28. J. Cizek (1969). *Adv. Chem. Phys.* **14**, 35.
29. A. P. Sergeeva, B. B. Averkiev, H.-J. Zhai, A. I. Boldyrev, and L.-S. Wang (2011). *J. Chem. Phys.* **134**, 224304.
30. K. Wolinski, J. F. Hinton, and P. Pulay (1990). *J. Am. Chem. Soc.* **112**, 8251.
31. T. A. Keith and R. F. W. Bader (1992). *Chem. Phys. Lett.* **194**, 1.
32. T. A. Keith and R. F. W. Bader (1993). *Chem. Phys. Lett.* **210**, 223.
33. J. R. Cheeseman, M. J. Frisch, G. W. Trucks, and T. A. Keith (1996). *J. Chem. Phys.* **104**, 5497.
34. P. Lazzeretti (2004). *Phys Chem. Chem. Phys.* **6**, 217.