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PAPER

# Perfectly planar concentric $\pi$ -aromatic $B_{18}H_3^-$ , $B_{18}H_4$ , $B_{18}H_5^+$ , and $B_{18}H_6^{2+}$ with [10]annulene character†

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Based upon extensive density functional theory and wave function theory investigations, we predict the existence of the perfectly planar concentric  $\pi$ -aromatic  $D_{3h}$   $B_{18}H_3^-$  (**6**),  $D_{2h}$   $B_{18}H_4$  (**8**),  $C_{2v}$   $B_{18}H_5^+$  (**10**), and  $D_{6h}$   $B_{18}H_6^{2+}$  (**12**) which are the smallest boron hydride clusters composed of a hybrid of the triangular and hexagonal motifs with a hexagonal hole at the center. These partially hydrogenated  $B_{18}$  clusters, tentatively referred to as borannulenes in this work, prove to possess [10]annulene character with 10 delocalized  $\pi$ -electrons. Detailed adaptive natural density partitioning (AdNDP) analyses unravel the bonding patterns of the  $\pi$  plus  $\sigma$  doubly aromatic  $D_{3h}$   $B_{18}H_3^-$  (**6**) and  $C_{2v}$   $B_{18}H_5^+$  (**10**) and the  $\pi$  aromatic and  $\sigma$  antiaromatic  $D_{2h}$   $B_{18}H_4$  (**8**) and  $D_{6h}$   $B_{18}H_6^{2+}$  (**12**). Borannulenes prove to possess negative nucleus-independent chemical shifts (NICS<sub>zz</sub>) comparable with that of [10]annulene and huge negative anisotropies of the magnetic susceptibility (AMS) much bigger than the latter. The slightly non-planar  $C_s$   $B_{18}H_3^-$  (**15**) (which is essentially the same as  $D_{3h}$   $B_{18}H_3^-$ ) with a high first vertical detachment energy of 3.71 eV and the perfectly planar  $D_{2h}$   $B_{18}H_4$  neutral with a huge first excitation energy of 1.89 eV are predicted to be the most possible borannulenes to be targeted in future experiments.

## I. Introduction

As the light neighbor of carbon and the prototype of electron-deficient elements in the periodic table, boron resembles carbon in bonding ability to catenate and form molecular networks and keeps fascinating researchers in both chemistry and materials sciences. Different from boron bulks which are well known to be composed of icosahedral  $B_{12}$  cages,<sup>1</sup> small boron clusters  $B_n^{-/0}$  ( $n = 3-20$ ) have been confirmed to possess planar or quasi-planar structures by joint experimental and theoretical investigations in the past decade,<sup>2-7</sup> with a 2D–3D transition at the double-ring tubular  $B_{20}$ .<sup>4</sup> The discoveries of aromatic 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  $C_{3v}$   $B_{12}$ ),<sup>2,3</sup> naphthalene ( $D_{2h}$   $C_{10}H_8$ ) with 10  $\pi$ -electrons ( $C_1$   $B_{15}^-$ ,<sup>3</sup>  $D_{2h}$   $B_{16}^{2-}$ ,<sup>5</sup> and  $C_{2v}$   $B_{17}^{-7}$ ), and coronene ( $D_{6h}$   $C_{24}H_{12}$ ) with two sets of  $\pi$ -aromatic systems ( $C_{2v}$   $B_{19}^{-6}$  and  $C_{3v}$   $B_{18}^{-7}$ ) are

remarkable in boron chemistry. Both the delocalized  $\pi$  and  $\sigma$  molecular orbitals (MOs) are found to play an important role in determining the structures and stabilities of small boron clusters. However, bare boron clusters  $B_n$  and their cations and anions are known to be highly reactive along the periphery atoms of the  $B_n$  sheets (especially at corner positions) 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.<sup>8-14</sup> A 1 : 1 hydrogenation of two dimensional (2D) bare  $B_n$  clusters would produce three dimensional (3D)  $B_nH_n$  species analogous to deltahedral  $B_nH_n^{2-}$  dianions.<sup>8</sup> 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. Typical hydrogen-poor boron hydride clusters include the perfectly planar  $C_{2v}$   $B_7H_2^{-8}$  which is fundamentally different from the quasi-planar  $C_{6v}$   $B_7^{-2}$  (its isolobal  $C_{2v}$   $B_7Au_2^-$  has been experimentally confirmed<sup>9</sup>), the perfectly planar  $B_4H_n$  series ( $n = 1-3$ ) with a  $B_4$  rhombus core,<sup>10</sup> and the perfectly planar  $D_{6h}$   $B_6H_6^{6-}$ , with 6 delocalized  $\pi$ -electrons, analogous to benzene in  $B_6H_6Li_6$ .<sup>11</sup> Recently, Szwacki and Tymczak<sup>12</sup> predicted the possibility of the perfectly planar neutral boron hydride  $D_{3h}$   $B_{12}H_6$ , with 6 delocalized  $\pi$ -electrons, analogous to benzene, the so called borozene which may be obtained by hydrogenation of the  $C_{3v}$   $B_{12}$  convex<sup>2</sup> at the six corner positions. Borozene has aroused immediate attention since it was proposed in 2009.<sup>13,14</sup>

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† Electronic supplementary information (ESI) available: Alternative low-lying isomers (Fig. 1S), optimized bond parameters and coordinates (Fig. 2S), and AdNDP bond pictures (Fig. 3S) of the concerned borannulenes, ultraviolet absorption spectrum of  $D_{2h}$   $B_{18}H_4$  (**8**) (Fig. 4S), and the NICS<sub>zz</sub> distributions of borannulenes (Table 1S). See DOI: 10.1039/c1cp21927h

Unfortunately, with an H : B ratio of 1 : 2, borozene proves to be only a local minimum lying considerably higher in energy (about 34.6 kcal mol<sup>-1</sup>) than a cage-like C<sub>2</sub> B<sub>12</sub>H<sub>6</sub><sup>15</sup> which is similar to the previously reported cage-like B<sub>12</sub>H<sub>6</sub><sup>+</sup>.<sup>16</sup> Thus, the high-lying borozene will be very hard to be observed in experiments. In this work, we move one step forward to search for bigger boron hydride clusters which have 10 delocalized  $\pi$ -electrons analogous to [10]annulene (D<sub>10h</sub> C<sub>10</sub>H<sub>10</sub>). Extensive theoretical investigations at various *ab initio* levels indicate that, with an H : B ratio of H : B  $\leq$  1 : 3 (lower than the H : B ratio of B<sub>12</sub>H<sub>6</sub>), the perfectly planar concentric  $\pi$ -aromatic D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup> (**6**), D<sub>2h</sub> B<sub>18</sub>H<sub>4</sub>(**8**), C<sub>2v</sub> B<sub>18</sub>H<sub>5</sub><sup>+</sup> (**10**), and D<sub>6h</sub> B<sub>18</sub>H<sub>6</sub><sup>2+</sup> (**12**), tentatively referred to as borannulenes in this work, formally conform to the 4*n* + 2 Hückel rule with 10 delocalized  $\pi$ -electrons (*n* = 2) analogous to [10]annulene (D<sub>10h</sub> C<sub>10</sub>H<sub>10</sub>). Instead of following the triangular motif of the experimentally known C<sub>3v</sub> B<sub>18</sub><sup>-7</sup>, these borannulenes appear to be the smallest boron hydride clusters composed of a hybrid of the triangular and hexagonal motifs with a B<sub>6</sub> hexagon at the center, featuring the structural characteristics of the most stable boron sheet— $\alpha$ -sheet boron.<sup>17,18,19e</sup> The 10  $\pi$ -electrons which grant  $\pi$  aromaticity to the systems are found to be delocalized between the inner B<sub>6</sub> hexagon and outer B<sub>12</sub> ring. Detailed adaptive natural density partitioning (AdNDP)<sup>19</sup> analyses are performed to unravel their  $\pi$  and  $\sigma$  bonding patterns and nucleus-independent chemical shifts (NICS<sub>zz</sub>)<sup>20</sup> are calculated to evidence their global  $\pi$ -aromaticity. The electron detachment energies of the anions and the excitation energies of the neutrals are calculated to facilitate future experiments.

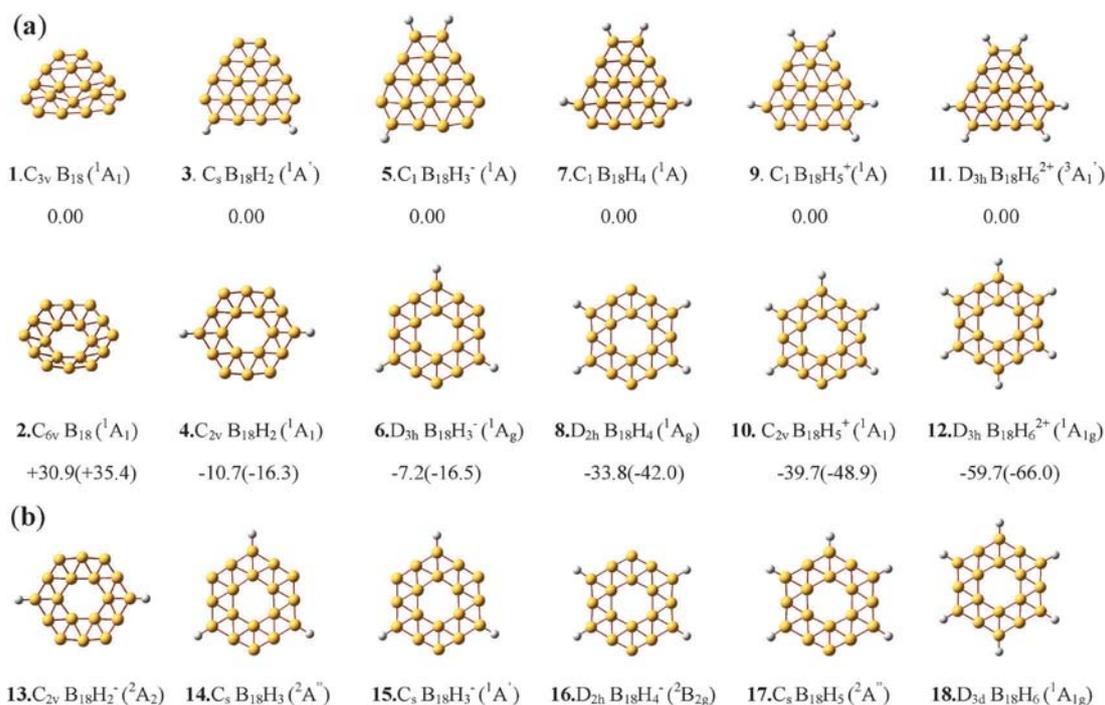
## II. Computational procedures

Structural optimizations and vibrational analyses were performed using the hybrid density functional theory (DFT) method of B3LYP<sup>21</sup> with the basis set of 6-311G(d,p). Relative energies for some important low-lying isomers are further refined using the coupled cluster method with triple excitations (CCSD(T))<sup>22</sup> at the B3LYP geometries. Initial structures for B<sub>18</sub>H<sub>*m*</sub> neutrals and their anions or cations with an H : B ratio of H : B  $\leq$  1 : 3 were either obtained from the low-lying isomers of B<sub>18</sub><sup>-7</sup> and B<sub>18</sub><sup>+23</sup> by adding *m* -H terminals to the periphery B atoms or 2D and 3D structures arbitrarily constructed according to chemical intuition in bonding. Extensive structural searches using the Coalescence Kick (CK) method<sup>24,25</sup> produced no results with lower energies than the low-lying isomers obtained for the concerned clusters depicted in Fig. 1 (alternative structures are summarized in Fig. 1S in the Supplementary Information†). To check the  $\pi$ -aromaticity of the B<sub>18</sub>H<sub>*m*</sub> clusters, the widely used NICS<sub>zz</sub> values<sup>20</sup> were calculated at points 0.0 Å (NICS<sub>zz</sub>(0)) and 1.0 Å (NICS<sub>zz</sub>(1)) above the molecular centers using the gauge-independent atomic orbital (GIAO) method<sup>26</sup> and the magnetic susceptibility tensors were obtained employing the continuous set of gauge transformation (CSGT) approach.<sup>27</sup> The weak  $\pi$ - $\pi$  interaction in the parallel sandwich-like [B<sub>18</sub>H<sub>4</sub>]<sub>2</sub> dimers was evaluated at the MP2 level<sup>28</sup> using the basis set of 6-311++G(d,p) with the counterpoise correction included. The vertical detachment energies (VDEs) of the anions and excitation energies of the neutrals are calculated at the

time-dependent DFT level (TD-B3LYP). All the calculations in this work were carried out using the Gaussian03 program suite<sup>29</sup> and the canonical molecular orbitals (CMOs) and AdNDP bonds were visualized employing the Molekel 5.4 software.<sup>30</sup>

## III. Results and discussions

We start from the parent B<sub>18</sub> first. As shown in Fig. 1S and Fig. 1, B<sub>18</sub> neutral possesses two low-lying quasi-planar isomers (B<sub>18</sub>-**1** and B<sub>18</sub>-**2**) within 2.8 kcal mol<sup>-1</sup> in energy at CCSD(T)//B3LYP, with the triangular C<sub>3v</sub> B<sub>18</sub>(**1**) similar to its anion C<sub>3v</sub> B<sub>18</sub><sup>-7</sup> lying the lowest. The hybridized C<sub>6v</sub> B<sub>18</sub>(**2**) with a central B<sub>6</sub> hexagon lying out of plane by about 0.53 Å proves to lie much higher (30.9 kcal/mole) than C<sub>3v</sub> B<sub>18</sub>(**1**), indicating that a B<sub>12</sub> ring is too small to host a B<sub>6</sub> hexagon at the center. However, as indicated in Fig. 1 and Fig. 1S,† a partial hydrogenation of B<sub>18</sub> at the corner positions leads to a dramatic inversion in relative stabilities in boron hydride clusters. The inversion starts at B<sub>18</sub>H<sub>2</sub> which has two iso-energetic isomers (within 0.4 kcal mol<sup>-1</sup> in energy), with the slightly non-planar C<sub>2v</sub> B<sub>8</sub>H<sub>2</sub>(**4**) originating from the hybridized C<sub>6v</sub> B<sub>18</sub>(**2**) lying 10.7 kcal mol<sup>-1</sup> more stable than C<sub>s</sub> B<sub>18</sub>H<sub>2</sub> (**3**) derived from the triangular C<sub>3v</sub> B<sub>18</sub>(**1**). With one extra electron, the C<sub>2v</sub> B<sub>18</sub>H<sub>2</sub><sup>-</sup>(**13**) anion possesses an even less severe out-of-plane distortion than C<sub>2v</sub> B<sub>18</sub>H<sub>2</sub>(**4**). The lowest-lying isomer obtained for B<sub>18</sub>H<sub>3</sub> neutral appears to be the slightly non-planar C<sub>s</sub> B<sub>18</sub>H<sub>3</sub>(**14**). A perfect planarity is firstly achieved in the highly symmetric D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup> (**6**) with three equivalent -H terminals which lie 7.2 kcal mol<sup>-1</sup> lower than the triangular quasi-planar C<sub>1</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**5**). We notice that D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup> (**6**) is a third-order saddle point with three small imaginary frequencies leading to the quasi-planar C<sub>s</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**15**) in which boron atoms on the hexagon hole are slightly out of plane by less than 0.16 Å. Detailed analyses indicate that D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**6**) and C<sub>s</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**5**) possess essentially the same bond parameters (see Fig. 2S†) and, with zero-point corrections included, the two structures are practically iso-energetic (with the negligible energy difference of -0.04 kcal mol<sup>-1</sup> at B3LYP, -0.96 kcal mol<sup>-1</sup> at MP2, and +0.37 kcal mol<sup>-1</sup> at CCSD(T)//B3LYP), leading to the conclusion that D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**6**) and C<sub>s</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup>(**15**) belong to the same isomer of B<sub>18</sub>H<sub>3</sub><sup>-</sup> and the perfectly planar D<sub>3h</sub> B<sub>18</sub>H<sub>3</sub><sup>-</sup> (**6**) is the vibrationally averaged structure of the anion (possibly with certain fluctuations). The first perfectly planar neutral borannulene is the hybridized D<sub>2h</sub> B<sub>18</sub>H<sub>4</sub>(**8**) with four equivalent -H terminals which lie 33.8 kcal mol<sup>-1</sup> more stable than the slightly non-planar triangular C<sub>1</sub> B<sub>18</sub>H<sub>4</sub>(**7**). With one extra electron, the D<sub>2h</sub> B<sub>18</sub>H<sub>4</sub><sup>-</sup>(**16**) anion keeps the planarity of its neutral D<sub>2h</sub> B<sub>18</sub>H<sub>4</sub>(**8**) with only a minor structural relaxation. The perfect planarity remains in the C<sub>2v</sub> B<sub>18</sub>H<sub>5</sub><sup>+</sup>(**10**) cation which lies 39.7 kcal mol<sup>-1</sup> lower than C<sub>1</sub> B<sub>18</sub>H<sub>5</sub><sup>+</sup>(**9**), while the neutral C<sub>s</sub> B<sub>18</sub>H<sub>5</sub>(**17**) appears to be slightly non-planar. B<sub>18</sub>H<sub>6</sub><sup>2+</sup>(**12**), a beautiful dication which is iso-electronic with B<sub>18</sub>H<sub>4</sub> with six equivalent -H terminals, turns out to have the highest symmetry of D<sub>6h</sub> with a hexagonal hole at the center. Such a hexagonal symmetry represents the structural characteristics of the most stable boron sheet— $\alpha$ -sheet boron.<sup>19e,17,18</sup> With an averaged B-B distance of *r*<sub>B-B</sub> = 1.67 Å (the same B-B distance was reported in  $\alpha$ -sheet boron<sup>19e,17,18</sup>) and a B-H bond length

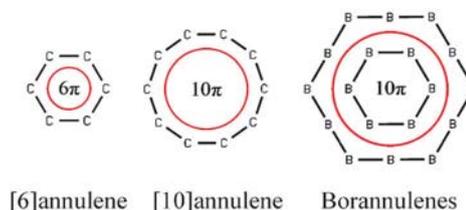


**Fig. 1** (a) Two low-lying isomers of  $B_{18}H_2$ (1,2),  $B_{18}H_2$ (3,4),  $B_{18}H_3^-$ (5,6),  $B_{18}H_4$ (7,8),  $B_{18}H_5^+$ (9,10), and  $B_{18}H_6^{2+}$ (11,12) with relative energies indicated in kcal mol<sup>-1</sup> at CCSD(T)//B3LYP and B3LYP (in parentheses). (b) Optimized  $C_{2v} B_{18}H_2^-$ (13),  $C_s B_{18}H_3$ (14),  $C_s B_{18}H_3^-$ (15),  $D_{2h} B_{18}H_4^-$ (16),  $C_s B_{18}H_5$ (17), and  $D_{3d} B_{18}H_6$ (18) at B3LYP.

of  $r_{B-H} = 1.18 \text{ \AA}$ ,  $D_{6h} B_{18}H_6^{2+}$ (12) proves to be a deep minimum lying at least 51 kcal mol<sup>-1</sup> lower than all the other low-lying isomers obtained (see Fig. 1S<sup>†</sup>). The stability inversion discussed above involves a triangular-hexagonal structural transition in borannulenes which echoes the situation in  $B_7H_2^-$  where the quasi-planar  $C_{6v} B_7^-$  convex was converted to the perfectly planar  $C_{2v} B_7H_2^-$  upon hydrogenation<sup>8</sup> (a similar situation occurs for  $C_{2v} B_7Au_2^-$ <sup>9</sup>). However, for neutral  $B_{18}H_6$ , the quasi-planar  $D_{3d} B_{18}H_6$ (18) proves to be considerably less stable (by 29.5 kcal mol<sup>-1</sup> at CCSD(T)) than the double-ring tubular  $D_3 B_{18}H_6$  ( $B_{18}H_6$ (2)) (see Fig. 1S). Thus, a 2D–3D structural transition occurs at  $B_{18}H_6$  with the H : B ratio of H : B = 1 : 3 in the partially hydrogenated  $B_{18}H_n$  neutral clusters.

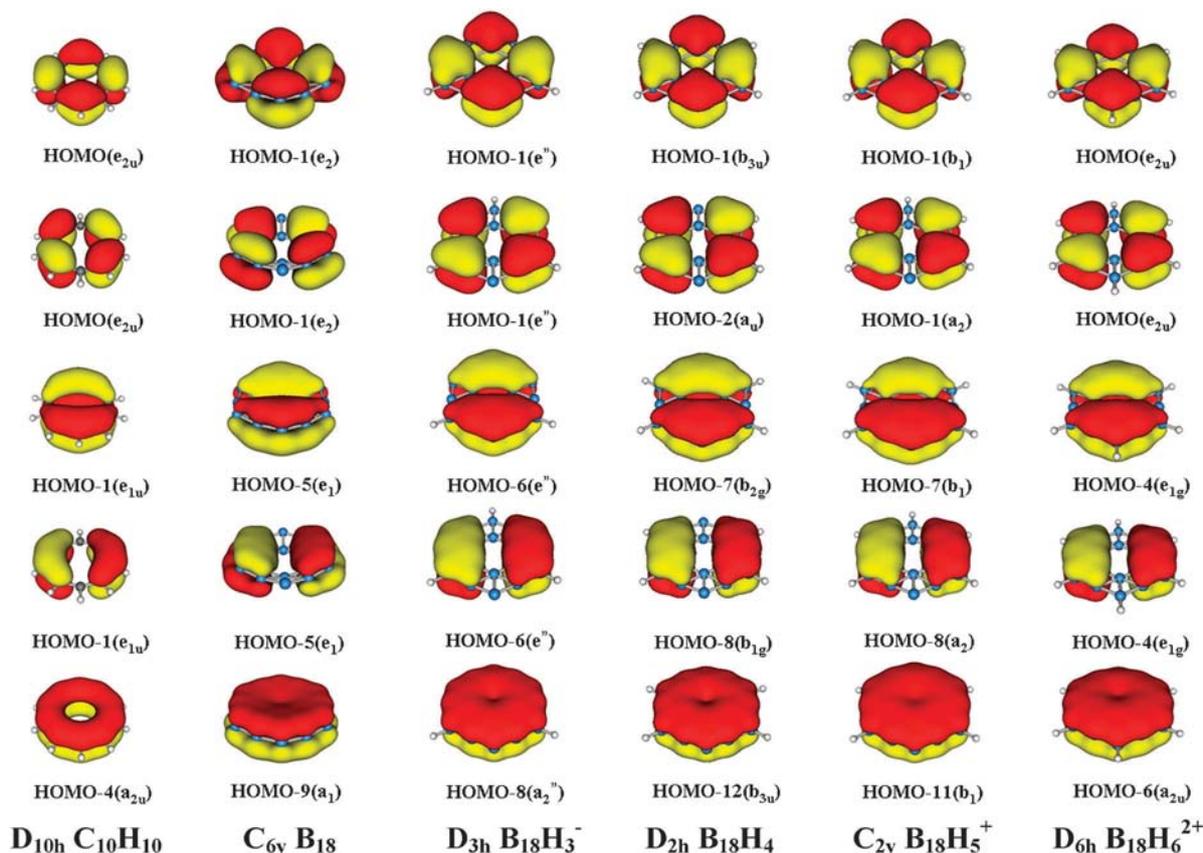
Molecular orbital analyses help to understand the planarity and stability of the borannulenes discussed above. As shown in Fig. 2, the perfectly planar  $D_{3h} B_{18}H_3^-$ (6),  $D_{2h} B_{18}H_4$ (8),  $C_{2v} B_{18}H_5^+$ (10), and  $D_{6h} B_{18}H_6^{2+}$ (12) all possess five delocalized  $\pi$ -CMOs analogous to that of [10]annulene ( $D_{10h} C_{10}H_{10}$ ). For example, the five delocalized  $\pi$ -CMOs of  $D_{3h} B_{18}H_3^-$  (HOMO-1( $e''$ ), HOMO-6( $e''$ ), and HOMO-8( $a_2''$ )) exactly correspond to the five  $\pi$ -CMOs of [10]annulene (HOMO( $e_{2u}$ ), HOMO-1( $e_{1u}$ ), and HOMO-4( $a_{2u}$ )). The delocalized  $\pi$ -CMOs of  $D_{2h} B_{18}H_4$ (8) (HOMO-1( $b_{3u}$ ), HOMO-2( $a_u$ ), HOMO-7( $b_{2g}$ ), HOMO-8( $b_{1g}$ ), and HOMO-12( $b_{3u}$ )) which lose degeneracy due to the lowered symmetry also have a clear one-to-one correspondence relationship with that of [10]annulene. As shown in Fig. 2, a similar  $\pi$ -aromatic system exists in the parent  $C_{6v} B_{18}$ (2) convex. The  $\pi$ -aromatic system in borannulenes between the inner  $B_6$  and outer  $B_{12}$  rings can be schematically represented in the

following pattern which is obviously different from that of both the monocyclic benzene ([6]annulene) and [10]annulene:



With such a fully occupied planar  $\pi$ -aromatic system to provide extra stabilization energies,  $D_{3h} B_{18}H_3^-$ (6) monoanion and  $D_{2h} B_{18}H_4$ (8) neutral are expected to be stable in experiments. It should be pointed out here that, in contrast to the monocyclic [10]annulene which is known to be neither planar nor aromatic,<sup>31–35</sup> the double-ring concentric planar borannulenes obtained in this work are all true minima of the systems as the lowest-lying isomers obtained.

Detailed AdNDP analyses unravel both the  $\pi$  and  $\sigma$  bonding patterns of borannulenes. Fig. 3S<sup>†</sup> clearly indicates that all the borannulenes concerned possess five delocalized 18c–2e  $\pi$ -bonds similar to their delocalized  $\pi$ -CMOs shown in Fig. 2. However, as shown in Fig. 3, their  $\sigma$  bonding patterns change with the number of hydrogen atoms.  $D_{3h} B_{18}H_3^-$ (6) possesses three 2c–2e B–H  $\sigma$  bonds with an occupation number of  $ON = 1.94|e|$ , six 2c–2e B–B  $\sigma$  bonds with  $ON = 1.92|e|$ , twelve 3c–2e B–B  $\sigma$  bonds with  $ON = 1.89–1.97|e|$ , three 4c–2e B–B  $\sigma$  bonds with  $ON = 1.88|e|$ , and five 18c–2e  $\pi$  bonds with  $ON = 2.00|e|$  delocalized between the inner  $B_6$  hexagon and outer  $B_{12}$  ring. The five 18c–2e  $\pi$  bonds of  $D_{3h}$

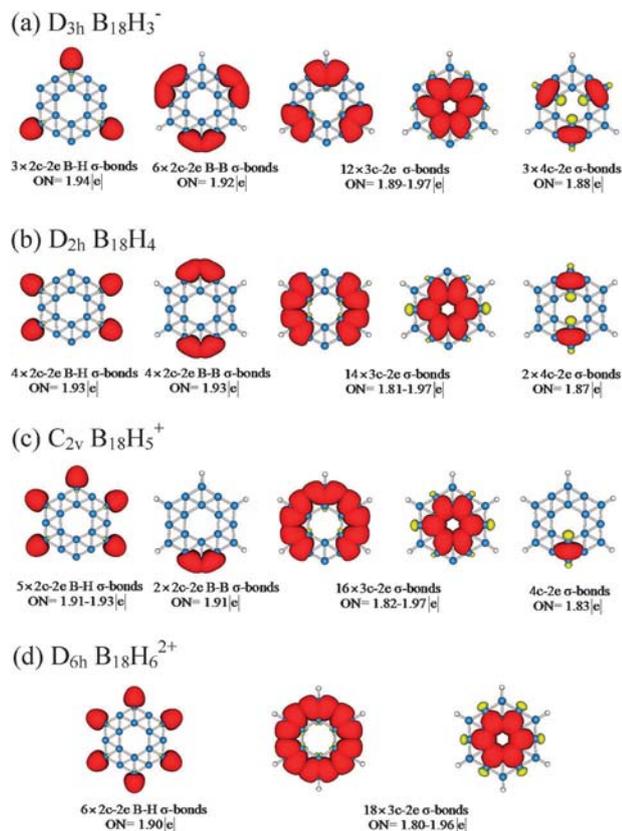


**Fig. 2** Delocalized  $\pi$ -CMOs of the perfectly planar  $D_{3h}$   $B_{18}H_3^-$  (**6**),  $D_{2h}$   $B_{18}H_4$  (**8**),  $C_{2v}$   $B_{18}H_5^+$  (**10**), and  $D_{6h}$   $B_{18}H_6^{2+}$  (**12**) compared with that of  $C_{6v}$   $B_{18}$  (**2**) and [10]annulene ( $D_{10h}$   $C_{10}H_{10}$ ).

$B_{18}H_3^-$  (**6**) appear to be analogous to that of  $D_{10h}$   $C_{10}H_{10}$ .<sup>7</sup> Thus,  $D_{3h}$   $B_{18}H_3^-$  possesses  $\pi$  plus  $\sigma$  double aromaticity in electron count.<sup>36</sup> The slightly non-planar  $C_s$   $B_{18}H_3^-$  (**15**) proves to have the same bonding pattern as  $D_{3h}$   $B_{18}H_3^-$  (**6**) at AdNDP (see Fig. 3S), further indicating that they are essentially the same isomer of  $B_{18}H_3^-$ . The perfectly planar  $C_{2v}$   $B_{18}H_5^+$  (**10**) cation with seventeen delocalized  $\sigma$  bonds and five delocalized  $\pi$  bonds is also  $\pi$  plus  $\sigma$  doubly aromatic (see Fig. 3S<sup>†</sup>). The perfectly planar  $D_{2h}$   $B_{18}H_4$  (**8**) neutral has four 2c–2e B–H  $\sigma$  bonds, four 2c–2e B–B  $\sigma$  bonds, fourteen 3c–2e B–B  $\sigma$  bonds, two 4c–2e B–B  $\sigma$  bonds, and five 18–2e  $\pi$  bonds—it is thus  $\pi$  aromatic and  $\sigma$  antiaromatic. The highly symmetric  $D_{6h}$   $B_{18}H_6^{2+}$  turns out to have six equivalent 2c–2e B–H  $\sigma$  bonds, eighteen 3c–2e B–B  $\sigma$  bonds, and five delocalized 18–2e  $\pi$  bonds. It is therefore overall  $\pi$  aromatic and  $\sigma$  antiaromatic. It is interesting to notice that connecting an –H terminal to a corner boron atom breaks two neighboring 2c–2e B–B periphery bonds and, from  $D_{3h}$   $B_{18}H_3^-$ ,  $D_{2h}$   $B_{18}H_4$ ,  $C_{2v}$   $B_{18}H_5^+$ , to  $D_{6h}$   $B_{18}H_6^{2+}$ , the number of the localized 2c–2e B–B periphery bonds decreases from 6, 4, 2, to 0 (while the number of the delocalized 3c–2e and 4c–2e bonds between the inner  $B_6$  and outer  $B_{12}$  rings increases from 15, 16, 17, to 18). Thus, a partial hydrogenation of  $B_{18}$  gradually enlarges the size of the outer  $B_{12}$  ring to better host the inner  $B_6$  hexagon at the center. It is also interesting to notice that, as previously reported for  $D_{2h}$   $Li_4$ , an overall  $\sigma$ -antiaromaticity is expected to lead to the formation of islands of  $\sigma$ -aromaticity.<sup>19a</sup> In our

cases, as shown in Fig. 3, each  $B_3$  triangle in the borannulenes is covered with a delocalized 3c–2e bond or 4c–2e  $\sigma$  bond and therefore is expected to possess local  $\sigma$ -aromaticity. Thus, the  $\sigma$ -antiaromatic borannulenes discussed above are expected to form islands of  $\sigma$ -aromaticity. The  $4n + 2$  Hückel rule was originally designed for and applied to monocyclic organic molecules. For polycyclic organic or inorganic molecular networks like borannulenes, local aromaticities or islands of  $\sigma$  (or  $\pi$ ) aromaticity require the  $4n + 2$  aromatic rule be applied separately to independent delocalized  $\pi$ - or  $\sigma$ -systems over specific molecular fragments.

The global  $\pi$ -aromaticities of borannulenes get further support from their calculated  $NICS_{zz}$  values and anisotropies of magnetic susceptibility (AMS) listed in Table 1 and detailed in Table 1S.<sup>†</sup> Borannulenes all possess negative  $NICS_{zz}(0)$  values between –6 and –31 ppm and  $NICS_{zz}(1)$  values between –28 and –42 ppm at points 0.0 Å and 1.0 Å above their geometrical centers (similar negative values exist for each  $B_3$  triangle in the molecular planes, see Table 1S). These values compare well with the corresponding  $NICS_{zz}$  values obtained for benzene and [10]annulene, showing that borannulenes are globally  $\pi$ -aromatic in nature. Negative AMS values have been shown to serve as important indicators of diatropicity for aromatic systems.<sup>12,37</sup> As shown in Table 1,  $D_{3h}$   $B_{18}H_3^-$ ,  $D_{2h}$   $B_{18}H_4$ ,  $C_{2v}$   $B_{18}H_5^+$ , and  $D_{6h}$   $B_{18}H_6^{2+}$  have huge negative AMS values of –518.0, –450.5, –433.0, and –403.0 cgs-ppm, respectively, which are at least 5.7 times bigger than for



**Fig. 3**  $\sigma$ -bonding patterns of  $D_{3h}$   $B_{18}H_3^-$  (**6**) (a),  $D_{2h}$   $B_{18}H_4$  (**8**) (b),  $C_{2v}$   $B_{18}H_5^+$  (c), and  $D_{6h}$   $B_{18}H_6^{2+}$  (**12**) (d) at AdNDP.

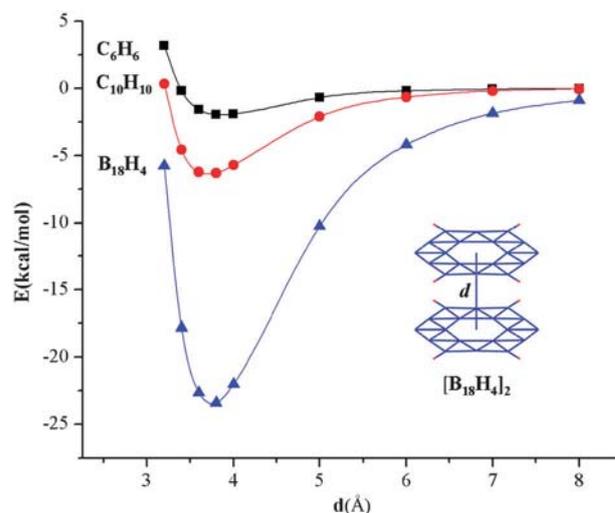
**Table 1** Calculated NICS<sub>zz</sub>/ppm, AMS/cgs-ppm, and HOMO–LUMO energy gaps ( $\Delta E_{\text{gap}}$ /eV) of borannulenes, ionization potentials (IP/eV) and electron affinities (EA/eV) of  $D_{2h}$   $B_{18}H_4$ , and adiabatic (ADE/eV) and vertical detachment energies (VDE/eV) of the concerned anions at B3LYP/6-311G(d,p). The corresponding values calculated for [10]annulene and benzene are tabulated for comparison

	NICS <sub>zz</sub> (0)	NICS <sub>zz</sub> (1)	AMS	$\Delta E_{\text{gap}}$	IP	EA/ADE	VDE
$D_{3h}$ $B_{18}H_3^-$ ( <b>6</b> )	−30.5	−41.4	−518.0	2.42	—	3.53 <sup>a</sup>	3.71 <sup>a</sup>
$D_{2h}$ $B_{18}H_4$ ( <b>8</b> )	−6.6	−28.3	−450.5	3.00	8.27	2.32 <sup>b</sup>	2.36 <sup>b</sup>
$C_{2v}$ $B_{18}H_5^+$ ( <b>10</b> )	−14.1	−30.9	−433.0	2.96	—	—	—
$D_{6h}$ $B_{18}H_6^{2+}$ ( <b>12</b> )	−20.2	−32.5	−403.0	3.08	—	—	—
$D_{10h}$ $C_{10}H_{10}$	−39.1	−37.4	−215.7	4.45	—	—	—
$D_{6h}$ $C_6H_6$	−14.2	−28.8	−69.8	6.72	—	—	—

<sup>a</sup> ADE and VDE values of the slightly off-planed  $C_s$   $B_{18}H_3^-$  (**15**) which is essentially the same as  $D_{3h}$   $B_{18}H_3^-$  (**6**). <sup>b</sup> ADE and VDE values of the perfectly planar  $D_{2h}$   $B_{18}H_4^-$  (**16**).

benzene (−69.8 cgs-ppm), 1.8 times bigger than for [10]annulene (−215.7 cgs-ppm), and 1.9 times bigger than for borozene (−208.2 cgs-ppm).<sup>12</sup>

Now we turn to the weak but characteristic  $\pi$ – $\pi$  interaction between two parallel  $B_{18}H_4$  monomers in the sandwich-like  $[B_{18}H_4]_2$  dimer. As shown in Fig. 4, the potential energy curve of the  $[B_{18}H_4]_2$  dimer versus the center-to-center distances  $d$  between two  $B_{18}H_4$  monomers turns out to be similar to that of both  $[C_{10}H_{10}]_2$  and  $[C_6H_6]_2$  dimers in general shapes. Interestingly, the three potential energy curves approach their minima at the same equilibrium distance of 3.8 Å. More importantly, the  $[B_{18}H_4]_2$



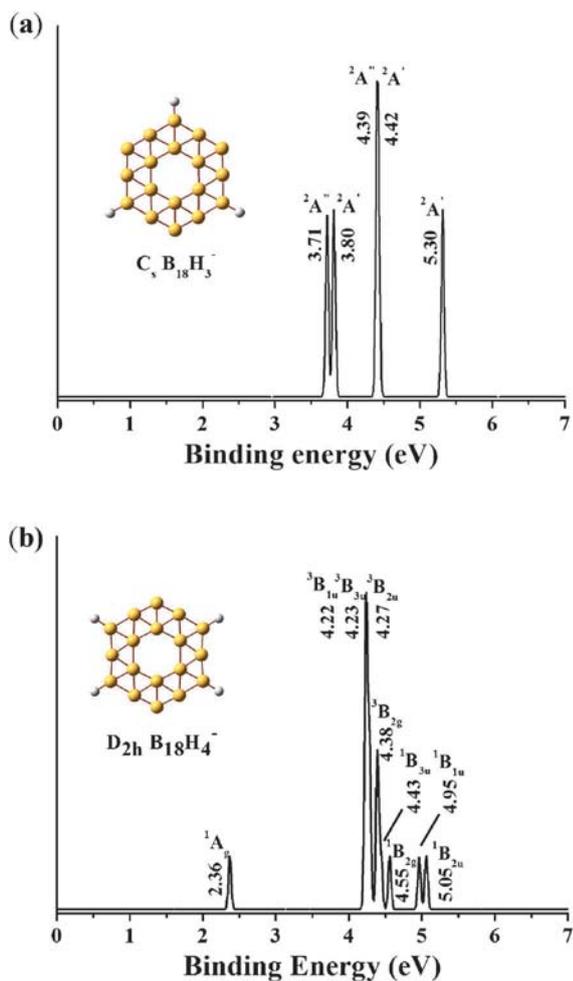
**Fig. 4** Potential energy curves of a  $[B_{18}H_4]_2$  dimer versus the center-to-center distances ( $d$ ) between two parallel  $D_{2h}$   $B_{18}H_4$  monomers compared with that of benzene ( $D_{6h}$   $C_6H_6$ ) and [10]annulene ( $D_{10h}$   $C_{10}H_{10}$ ) dimers.

dimer appears to have a much deeper potential energy well than the latter two: the association energy of  $-23.41$  kcal mol<sup>−1</sup> obtained for  $[B_{18}H_4]_2$  is over 4 times bigger than for  $[C_{10}H_{10}]_2$  ( $-5.58$  kcal mol<sup>−1</sup>) and 12 times bigger than for  $[C_6H_6]_2$  ( $-1.92$  kcal mol<sup>−1</sup>). These results suggest a much stronger polarization contribution from the five  $\pi$ -MOs of  $D_{2h}$   $B_{18}H_4$  which are much more delocalized in  $[B_{18}H_4]_2$  with respect to the [10]annulene and benzene dimers.

Finally, we discuss the electron detachment energies of  $B_{18}H_3^-$  and  $B_{18}H_4^-$  anions and the excitation energy of  $B_{18}H_4$  neutral. As shown in Fig. 5(a), the simulated PES spectrum of the slightly non-planar  $C_s$   $B_{18}H_3^-$  (**15**) (which is, as discussed above, essentially the same as the perfectly planar  $D_{3h}$   $B_{18}H_3^-$  (**6**)) has a high first vertical electron detachment energy of VDE = 3.71 eV, in line with the  $\pi$  plus  $\sigma$  double aromaticity of the anion. The perfectly planar  $D_{2h}$   $B_{18}H_4$  (**8**) neutral appears to have the high ionization potential of 8.27 eV, low electron affinity of 2.32 eV, and a wide HOMO–LUMO gap of 3.00 eV (see Table 1). More importantly, it has a high first excitation energy of 1.89 eV calculated at TD-B3LYP. As shown in Fig. 5(b), its anion  $D_{2h}$   $B_{18}H_4^-$  (**16**) possesses a first PES peak at VDE = 2.36 eV (which is very close to the EA value of 2.32 eV obtained for  $D_{2h}$   $B_{18}H_4$ ) and a huge energy gap of 1.86 eV between the first peak and the second one which is in nice agreement with the high first excitation energy of 1.89 eV obtained above for  $D_{2h}$   $B_{18}H_4$  (**8**). Such a huge energy gap obtained for  $D_{2h}$   $B_{18}H_4^-$  is close to the X–A energy gap of 2.05 eV observed for  $C_s$   $B_{12}^-$  which originates from the highly stable  $C_{3v}$   $B_{12}$  convex.<sup>2,3</sup> We suggest that the  $D_{3h}$   $B_{18}H_3^-$  anion and  $D_{2h}$   $B_{18}H_4$  neutral be the most possible borannulenes to be targeted in experiments through a partial hydrogenation of  $B_{18}^-$  in the gas phase.<sup>7</sup>

## IV. Summary

In summary, we have predicted at *ab initio* levels a series of perfectly planar concentric  $\pi$ -aromatic borannulenes which are the smallest boron hydride clusters with a hexagonal hole at



**Fig. 5** Simulated PES spectra of  $C_5B_{18}H_3^-$  (a) and  $D_{2h}B_{18}H_4^-$  (b) at TD-B3LYP.

the center to feature the structural characteristics of the most stable 2D  $\alpha$ -sheet boron.<sup>19e,17,18</sup> Borannulenes may be generated through partial hydrogenations of the corresponding experimentally known boron clusters through a triangular-hexagonal structural transition in gas phases. The presence of hydrogen atoms on the periphery of the boron ring could help to prevent catenation (which was shown to happen to pure boron clusters) and that makes borannulenes potential building blocks in sandwich-like complexes. Initial investigations indicate that the  $-H$  terminals in borannulenes can be partially or completely substituted with the experimentally known boronyl ( $-BO$ )  $\sigma$ -radicals<sup>38</sup> to form the perfectly planar boron boronyls of  $D_{3h}B_{18}(BO)_3^-$ ,  $D_{2h}B_{18}(BO)_4^{0/-}$ ,  $C_{2v}B_{18}(BO)_5^+$ , and  $D_{6h}B_{18}(BO)_6^{2+}$ . These planar concentric  $\pi$ -aromatic boron hydride and boron oxide clusters deserve more extensive theoretical and experimental investigations to better understand the effects of both hydrogenation and oxidation on small boron clusters and to rationally design boron-based nanomaterials.

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