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# Disk Aromaticity of the Planar and Fluxional Anionic Boron Clusters $B_{20}^{-/2-}$

Truong Ba Tai, Arnout Ceulemans, and Minh Tho Nguyen<sup>\*[a]</sup>

The remarkable features of small boron clusters ( $B_n$ ) have attracted much interest during the past several decades. Their molecular structures were the subject of a large number of experimental and theoretical studies.<sup>[1–7]</sup> The neutral  $B_n$  clusters containing up to  $n=19$  atoms were found to have planar geometry,<sup>[2,8]</sup> whereas  $B_{20}$  exhibits a tubular (double ring) form. For the  $B_n^+$  ions, a transition from two-dimensional (2D) to three-dimensional (3D) structure was demonstrated to occur at  $n=17$ .<sup>[9]</sup> Studies on a series of anionic  $B_n^-$  clusters with  $n \leq 20$ , using photoelectron spectroscopy (PES) in combination with quantum chemical calculations<sup>[2,10,11]</sup> indicated that while the  $B_n^-$  ions with  $n=2–19$  exhibit, similar to the analogous hydrocarbons, either planar or quasi-planar shapes with certain aromatic features, a change in the structural landscape occurs for the  $B_{20}^-$  ion, for which a 3D-tubular structure was calculated to be energetically more favored than the planar counterpart (B3LYP/6-311+G(d) results).<sup>[11]</sup> Nevertheless, the reported experimental PES results did not emphasize any relevant connection to a tubular structure for  $B_{20}^-$ . Thus a legitimate question arises as to whether other lower-lying isomers could exist on the potential energy surface of the  $B_{20}^-$  system.

The fluxional features of boron-based clusters have also long been an intriguing issue. The existence of aromatic boron–carbon wheels,<sup>[12]</sup> such as  $C_2B$ ,  $C_3B_9^{3+}$ , and  $C_5B_{11}^+$ , was proposed with interesting fluxional features. However, these structures were subsequently found to be unstable with respect to those with outer rings of carbon atoms. It was recently shown<sup>[6]</sup> that the  $B_{19}^-$  ion, in which a central hexagonal  $B_6$  ring is located inside an outer  $B_{13}$  ring, exhibits similar fluxionality. Such a feature was also more recently confirmed for the smaller  $B_{13}^+$  ion.<sup>[13]</sup> In this context, another question of interest is as to whether planar fluxional structures exist for larger boron clusters  $B_n$  with  $n > 19$ . This question faces a real challenge, because, as stated above, the neutral  $B_{20}$  cluster was reported to have a 3D-tubular structure.<sup>[11]</sup>

In attempts to obtain some elements of answer to the above questions, we have performed quantum chemical cal-

culations on the negatively charged clusters  $B_{20}^-$  and  $B_{20}^{2-}$ . In contrast to previous reports, our calculated results show that both anionic  $B_{20}^-$  and dianionic  $B_{20}^{2-}$  clusters possess planar and fluxional structures. While the planar structure **I** ( $C_{2v}$ ; Figure 1) in which a central  $B_7$  hexagonal ring is lo-

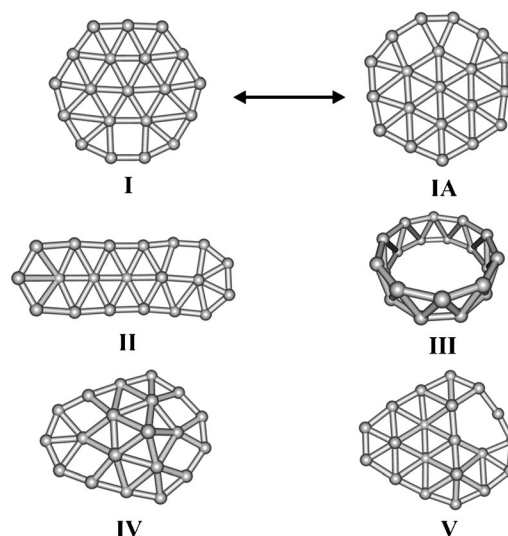


Figure 1. Shapes of the lower-lying isomers of  $B_{20}^-$  and  $B_{20}^{2-}$ .

cated inside an outer  $B_{13}$  ring, is now found to be the global minimum of the dianion  $B_{20}^{2-}$ , both structures **I** and **II** (Figure 1) of the monoanion  $B_{20}^-$  are almost degenerate in energy. More importantly, we find that the global minima **IA**<sup>2-</sup> of  $B_{20}^{2-}$  and **I**<sup>-</sup> of  $B_{20}^-$  are both fluxional species with very small energy barriers for distortion. Our results not only confirm the planarity trend of the anionic boron clusters that is induced by the excess electron, but also point to a new type of compound, that is, planar fluxional polycyclic boron clusters with one B atom located at the centre of the rings. Interestingly, the  $B_{20}^{2-}$  dianion turns out to be a  $\pi$ -aromatic system that can consistently be rationalized by using the model of the particle in a circular box.

In the anionic state, our calculations at the CCSD(T)/6-311G(d)//B3LYP/6-311+G(2df) level (Table 1) indicate that the planar structure **I**<sup>-</sup> ( $C_{2v}$ ,  $^2B_2$ ), which was missed in all earlier reports, turns out the most stable isomer of this system. Another low-spin lower-lying isomer is the elongated form **II**<sup>-</sup> ( $C_s$ ,  $^2A''$ ), which is almost energetically degenerate with **I**<sup>-</sup> (CCSD(T)/6-311G(d)). Although the form **III**<sup>-</sup> ( $C_{2v}$ ,  $^2B_2$ ) is the lowest-lying isomer at the B3LYP/6-311+G-(2df) level, it becomes less stable at the CCSD(T) level. Our

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Table 1. The electronic state (ES), point group, number of imaginary frequencies (NImag), and relative energies [kcal mol<sup>-1</sup>] of lower-lying isomers of B<sub>20</sub>, B<sub>20</sub><sup>-</sup>, and B<sub>20</sub><sup>2-</sup>.

Isomer	ES	NImag	B3LYP <sup>[a]</sup>	CCSDT <sup>[b]</sup>
neutral B <sub>20</sub>				
<b>I</b>	C <sub>s</sub> ( <sup>1</sup> A')	0	33.7	19.1
<b>IA</b>	C <sub>s</sub> ( <sup>1</sup> A')	0	37.2	21.9
<b>II</b>	C <sub>s</sub> ( <sup>1</sup> A')	0	21.1	13.1
<b>III</b>	D <sub>10d</sub> ( <sup>1</sup> A <sub>1</sub> )	0	0.0	0.0
<b>IV</b>	C <sub>s</sub> ( <sup>1</sup> A')	0	21.3	7.3
<b>IV</b>	C <sub>1</sub> ( <sup>1</sup> A')	0	18.3	6.3
anion B <sub>20</sub> <sup>-</sup>				
<b>I</b>	C <sub>2v</sub> ( <sup>2</sup> B <sub>2</sub> )	0	0.0	0.0
<b>IA</b>	C <sub>2v</sub> ( <sup>2</sup> A <sub>1</sub> )	1	-0.1	0.2
<b>II</b>	C <sub>s</sub> ( <sup>2</sup> A')	0	-4.9	0.6
<b>III</b>	C <sub>2v</sub> ( <sup>2</sup> B <sub>2</sub> )	0	-7.3	5.9
<b>IV</b>	C <sub>s</sub> ( <sup>2</sup> A')	0	-1.4	13.4
dianion B <sub>20</sub> <sup>2-</sup>				
<b>I</b>	C <sub>2v</sub> ( <sup>1</sup> A <sub>1</sub> )	1	0.0	0.1
<b>IA</b>	C <sub>2v</sub> ( <sup>1</sup> A <sub>1</sub> )	0	0.0	0.0
<b>II</b>	C <sub>1</sub> ( <sup>1</sup> A')	0	4.0	9.6
<b>III</b>	C <sub>2</sub> ( <sup>1</sup> A)	0	21.7	31.7
<b>IV</b>	C <sub>1</sub> ( <sup>1</sup> A')	0	9.2	2.6
<b>V</b>	C <sub>1</sub> ( <sup>1</sup> A')	0	11.9	10.0

[a] Relative energies include the corrections for zero-point energies (ZPEs) obtained at B3LYP/6-311+G(d) for the neutral B<sub>20</sub> and anion B<sub>20</sub><sup>-</sup> and B3LYP/6-311+G(2df) for the dianion B<sub>20</sub><sup>2-</sup>. [b] CCSD(T) values are based on B3LYP geometries.

theoretical predictions also show that the planar structure **IA**<sup>2-</sup> (C<sub>2v</sub>, <sup>1</sup>A<sub>1</sub>) is the global minimum of the B<sub>20</sub><sup>2-</sup> ion at both levels of theory, B3LYP/6-311+G(2df) and CCSD(T)/6-311G(d)//B3LYP/6-311+G(2df). Details of the computational methods and discussion about structures are given in the Supporting Information.

To confirm the global minima located, the vertical detachment energies (VDEs) of the two anionic global minima **I**<sup>-</sup>

and **II**<sup>-</sup> were computed by using the time-dependent TD-B3LYP method and compared to the available experimental PES results of B<sub>20</sub><sup>-</sup>.<sup>[11]</sup> Our predictions show an excellent agreement between the theoretical and experimental results. While isomer **II**<sup>-</sup> contributes to the band X of the PES spectra, the bands A and B are mainly observed upon detachment channels of **I**<sup>-</sup> (please see the Supporting Information). The remaining VDEs of the **II**<sup>-</sup> ion are found to be almost overlapped with those of **I**<sup>-</sup>. This can explain why the intensities of the experimental bands B, C, and D are high, while that of the band A is relatively weaker. The strong signal of the band X can be understood due to the high stability of **II** at the neutral state as compared to the corresponding neutral **I** (detailed discussion is given in the Supporting Information).

The global minima **I**<sup>-</sup> and **IA**<sup>2-</sup> also possess the fluxional behaviors similar to those of the B<sub>19</sub><sup>-</sup> ion, and the aromatic boron B<sub>n</sub>C<sub>m</sub><sup>q+</sup> wheels.<sup>[12]</sup> The present calculations also point out that the planar isomer **IA**<sup>2-</sup> is a true global minimum for B<sub>20</sub><sup>2-</sup>, while the isomer **I**<sup>2-</sup> is rather a transition structure with one imaginary frequency. The smallest vibrational frequency of **IA**<sup>2-</sup>, which is found to be 58 cm<sup>-1</sup> (B3LYP/6-311+G(2df)), corresponds to that of a rotation of the inner B<sub>7</sub> ring. Following this normal mode, the transition structure **I**<sup>2-</sup> is obtained. The energy barrier for the counter rotation of the inner B<sub>7</sub> ring and the outer B<sub>13</sub> ring amounts to only 0.1 kcal mol<sup>-1</sup> at the CCSD(T)/6-311G(d)//B3LYP/6-311+G(2df) level. Surprisingly, in the anionic state, the isomer **I**<sup>-</sup> is characterized to be a minimum, while the isomer **IA**<sup>-</sup> is a transition structure with an energy barrier of 0.2 kcal mol<sup>-1</sup> (CCSD(T)/6-311G(d)) level. The smallest vibrational frequency of the anion **I**<sup>-</sup> is about 10 cm<sup>-1</sup> and corresponds to a rotation of the inner B<sub>7</sub> ring. Following this vibrational mode, rotation of **I**<sup>-</sup> effectively occurs through the transition structure **IA**<sup>-</sup>.

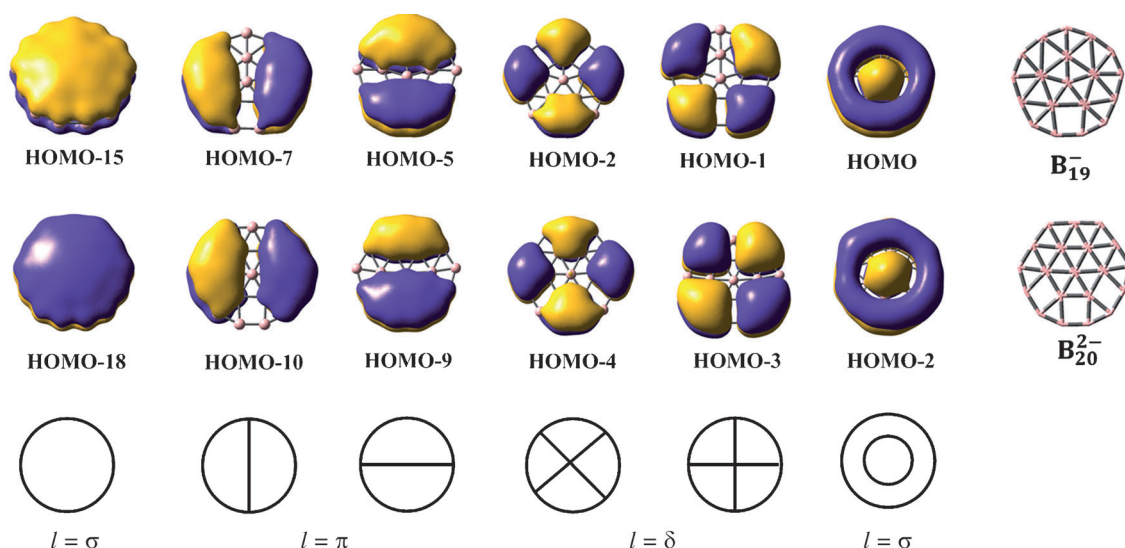


Figure 2. Shapes of the valence  $\pi$ -orbitals of the B<sub>20</sub><sup>2-</sup> (C<sub>2v</sub>), B<sub>19</sub><sup>-</sup> (C<sub>2v</sub>) and the lowest wavefunctions for particle in circular box.

To gain additional insights into the fluxional feature of the anions  $B_{20}^-$  and  $B_{20}^{2-}$ , the Born–Oppenheimer (BOMD) and Car–Parrinello (CPMD) molecular dynamics simulations were performed by using the pure gradient-corrected exchange–correlation energy functional BLYP. The ion–electron interaction was treated by using the Troullier–Martins pseudopotentials. Both CPMD and BOMD simulations show that the inner and outer rings of either  $I^-$  or  $IA^{2-}$  nearly freely rotate with respect to each other in maintaining their planar geometries during the simulating time of 10 ps. The snapshots from a trajectory at 300 K (given in Supplementary Information file) reveal that following a rotation of the rings, the isomers move up to the transition points, and then are converged back to the original ground-state geometries. Both the  $B_{20}^{2-}$  and  $B_{20}^-$  ions can be considered as larger “Wankel engines” similar to the  $B_{19}^-$  and  $B_{13}^+$  clusters.

One of the most intriguing features of small boron clusters is their aromaticity. This aspect was extensively reported in recent literature using various evaluation criteria such as the NICS, resonance energy, electron localization function (ELF), and the Hückel ( $4N+2$ ) rule. More recently, the fluxional  $B_{19}^-$  ion was predicted to be doubly  $\pi$ -aromatic system with two concentric  $\pi$ -electron systems that satisfy the Hückel rule. Although this could explain the aromatic features of  $B_{19}^-$ , the picture is not really clear. For example, while the HOMO of the  $B_{19}^-$  (cf. Figure 2) represents one nodal plane, its HOMO–15 does not. Thus a combination of these two orbitals is not consistent. In this context, we would propose a new type of aromaticity, that is, disk aromaticity, which can be consistently rationalized by using the model of particle in circular box. The simple model of a particle in a circular box<sup>[14,15]</sup> offers an amazingly accurate description of the  $\pi$  states in this triangular boron structure. The eigenstates in the box model are characterized by a radial ( $n=1, 2, \dots$ ) and a rotational ( $l=\sigma, \pi, \delta, \dots$ ) quantum number, and the energies are determined by the zeros of cylindrical Bessel functions. The lowest eigenstates in ascending order are  $1\sigma, 1\pi, 1\delta$ , and  $2\sigma$ . The nodal characteristics of these cylindrical waves exactly match the sequence of the six occupied delocalized  $\pi$  orbitals of the  $B_{20}^{2-}$  ion (cf. Figure 2). Since this sequence closes a circular shell, the dianion reaches an aromatic electron count of 12 electrons, which is valid for a disk, as opposed to the Hückel count of 10 electrons for an aromatic ring. A similar observation can also be found for the  $B_{19}^-$  ion as shown in Figure 2.

The nucleus-independent chemical shifts (NICS) index<sup>[16]</sup> was also considered. Due to the presence of a centered B-atom, we evaluated the NICS values at 1.0 and 1.5 Å on the  $C_2$  axis from the center. The NICS values were also performed at 1 Å on the out-plane  $z$  axis. The present NICS calculations for both isomers  $I^{2-}$  and  $IA^{2-}$  (listed in Table S1 of the Supporting Information) show highly negative values (from –17 to –43 ppm) that confirm well the aromatic feature of both structures.

In conclusion, while a transition from 2D to 3D structure was found at  $n=17$  for the cationic boron  $B_n^+$  clusters, the

neutral boron  $B_n$  counterparts with  $n$  up to 19 are planar. In this work, we demonstrate that the presence of excess electrons modifies the structural landscape and tends to extend the planarity of boron clusters. While the anions  $B_{20}^-$  and  $B_{20}^{2-}$  are planar, the neutral  $B_{20}$  prefers a 3D tubular structure with a 2D to 3D transition energy of 6.3 kcal mol<sup>–1</sup>. More importantly, the geometrical features of the isomers **I** and **IA** suggest the existence of a new type of cluster, which is planar and doubly cyclic with one atom located at the centre, and fluxional. The fluxional double-ring structures with inner rings containing a larger number of B atoms are expected to be stable in larger boron clusters and needs to be further explored in future studies. Additionally, a new concept of aromaticity, that is, disk aromaticity, is proposed and consistently rationalized according to a model of particle in circular box.

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**Keywords:** aromaticity • BOMD simulation • boron • cluster compounds • density functional calculations

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## Boron Clusters

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**Disk Aromaticity of the Planar and Fluxional Anionic Boron Clusters  $B_{20}^{-/2-}$**



**The presence of excess electrons** modifies the structural landscape and tends to extend the planarity of boron clusters. While the neutral  $B_{20}$  is tubular, both the anion and dianion  $B_{20}^{-/2-}$  become planar. Geometrical features of the stable anions suggest the existence of a new type of cluster that is planar and doubly cyclic with one atom located at the center (see figure), as well as being fluxional.