



*Dedicated to the memory of  
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

## STRUCTURES AND STABILITIES $B_9$ , $B_9^+$ and $B_9^-$ CLUSTERS\*\*

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28 isomers of  $B_9$  (**1-10**),  $B_9^+$  (**1<sup>+</sup>-8<sup>+</sup>**) and  $B_9^-$  (**1<sup>-</sup>-10<sup>-</sup>**) clusters, including five isomers reported previously, have been optimized at the B3LYP/6-311+G\* and MP2/6-311+G\* levels of theory. To confirm the global minimum, some low-energy isomers were recalculated with CCSD(T)/AVDZ method. The CCSD(T)/AVDZ results suggest that  $B_9$ ,  $B_9^+$  and  $B_9^-$  clusters have their global minima to be the  $D_{7h}$ -symmetry heptagonal bipyramid structure **2**, the  $C_s$ -symmetry wheel-shaped structure **1<sup>+</sup>** and the  $D_{8h}$ -symmetry planar wheel-shaped structure **1<sup>-</sup>**, respectively. Natural bond orbital analysis suggests that multi-centered  $\sigma$  bonds and delocalized  $\pi$  bonding play an important role in stabilizing the most stable isomers of all the  $B_9/B_9^+/B_9^-$  clusters. The bonding nature and aromaticity of all the clusters are discussed according to their nucleus-independent chemical shifts. Moreover, the adiabatic ionization potentials and electron affinities are also calculated for various  $B_9$  isomers, which express a proof for the clusters' stability.

### INTRODUCTION

Boron is an electron-deficient semimetal element. Because of the  $sp^2$  hybridization of the valence orbitals, boron atom tends to form strong chemical bonds with other atoms. Pure boron clusters have varied polymorphism, including nanostructures<sup>1-8</sup> and complex icosahedral networks.<sup>9-12</sup> Boron compounds

are good candidates for various technological applications.<sup>13-16</sup>

Pure boron clusters have attracted numerous interests. Anderson et al. have produced cationic boron clusters by laser vaporization and investigated their chemical reactivity and fragmentation properties.<sup>17-22</sup> Ray et al. have investigated  $B_n$  and  $B_n^+$  ( $n=2-8$ ) clusters<sup>23</sup> by HF,

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\*\* This paper is dedicated to the memory of our friend Professor Ioan Silaghi-Dumitrescu (1950–2009), in recognition of his contributions to diverse areas of inorganic and computational chemistry as well as his leadership in Roumanian science.

MP2 and MP4 methods, including their fragmentation patterns and ionization potentials. Kato *et al.* have studied  $B_4$ - $B_8$  clusters<sup>24</sup> using ab initio methods. Boustani have calculated  $B_2$ - $B_{14}$  clusters,<sup>25</sup> employing small basis set and a variety of methods (HF-SCF, CI and MP4(SDTQ)). Recently, there are also a lot of theoretical investigations concerning boron clusters, such as  $B_4$ ,<sup>26</sup>  $B_5$ ,<sup>27</sup>  $B_6$ ,<sup>28,29</sup>  $B_7$ ,<sup>30</sup>  $B_n^+$  ( $n < 14$ ),<sup>31</sup>  $B_{12}$  and  $B_{12}^+$ ,<sup>32</sup>  $B_{13}$  and  $B_{13}^+$ ,<sup>33-35</sup> and a series of experimental and theoretical studies on boron clusters, such as  $B_3^-$  and  $B_4^-$ ,<sup>36</sup>  $B_5^-$ ,<sup>37</sup>  $B_6^-$ ,<sup>38</sup>  $B_7^-$ ,<sup>39</sup>  $B_8^-$  and  $B_9^-$ .<sup>40</sup>

For  $B_9$  cluster, Boustani indicated two low-lying isomers: heptagonal bipyramid structure with  $D_{7h}$  symmetry or  $C_s$  symmetry at the HF/DZ level,<sup>25</sup> while Zhai *et al.*<sup>40</sup> claimed that the global minimum of  $B_9$  should have slightly distorted wheel-structure with  $D_{2h}$  symmetry using B3LYP/6-311+G\* and RCCSD(T)/6-311+G\* methods. For  $B_9^-$  cluster, Zhai *et al.*<sup>40</sup> found that the perfect planar  $D_{8h}(^1A_{1g})$  wheel-shape structure with  $D_{8h}$  symmetry has the lowest energy employing B3LYP, CASSCF, and UCCSD(T) methods with 6-311+G\* basis set. In 2007, Drummond *et al.*<sup>41</sup> pointed out that more work is required for  $B_9$  clusters before its ground state can be definitively determined.

In the present paper, both ab initio methods [MP2 and CCSD(T)] and density functional theory [DFT-B3LYP] method are used to predict the structures, energies and stabilities of neutral, cationic and anionic  $B_9^{(\pm)}$  clusters. The natural bond orbital (NBO) analysis and the nucleus-independent chemical shifts (NICS) calculations have also been performed to provide insight into the bonding nature and aromaticity of these clusters.

## COMPUTATIONAL METHODS

Equilibrium geometries of the neutral  $B_9$  clusters and their corresponding ions,  $B_9^-$  and  $B_9^+$ ,

were fully optimized at the B3LYP/6-311+G\* and MP2/6-311+G\* levels where B3LYP method is a hybrid HF/DFT method using a combination of the Becke's three-parameter functional (B3)<sup>42</sup> with the Lee-Yang-Parr (LYP) generalized gradient correlation functional,<sup>43</sup> and MP2 is second-order Møller-plesset perturbation method.<sup>44</sup> In addition to the structural and energetic results, the bonding nature is discussed using the natural bond orbital (NBO) analysis<sup>45</sup> at the B3LYP/6-311+G\* level. The harmonic vibrational frequencies are used to determine whether the optimized structures are genuine minima and to obtain the zero-point vibrational energies (ZPE). The nucleus-independent chemical shifts (NICS)<sup>46</sup> values for some clusters were also calculated at the same level using gauge-including atomic orbital (GIAO) approach. All above calculations were carried out with the Gaussian 03 program package.<sup>47</sup> For some low-energy isomers, CCSD(T) calculations were also performed with the augmented correlation-consistent valence-double- $\zeta$  basis set with polarization functions (AVDZ)<sup>48</sup> using the MOLPRO 2002.6 program package.<sup>49</sup> The CCSD(T) method requests a coupled cluster calculations using both single and double substitutions and including triple excitations.<sup>50</sup>

## RESULTS AND DISCUSSION

The optimized isomers of  $B_9$  (**1-10**),  $B_9^+$  (**1<sup>+</sup>-8<sup>+</sup>**), and  $B_9^-$  (**1<sup>-</sup>-10<sup>-</sup>**) are displayed in Figs. 1-3, respectively, including the Wiberg bond indices (WBIs) between adjacent atoms, while Table 1 lists their total energies, ZPEs, relative energies with ZPE corrections, and the numbers of imaginary frequencies. The molecular orbitals (MOs) of **1**, **1<sup>+</sup>** and **1<sup>-</sup>** are shown in Fig. 4.

Table 1

Total energies (E)<sup>a</sup>, zero-point energies (ZPE)<sup>b</sup> and relative energies (RE)<sup>c</sup> for the B<sub>9</sub>, B<sub>9</sub><sup>+</sup> and B<sub>9</sub><sup>-</sup> isomers

isomer	B3LYP/6-311+G*			MP2/6-311+G*			CCSD(T)/AVDZ		
	E	ZPE	RE	E	ZPE	RE	E	RE	
B <sub>9</sub>	<b>1</b>	-223.41513	19.00(0)	0.00	-222.59920	105.61(1)	0.00	-222.62917	0.00
	<b>2</b>	-223.41003	19.71(0)	3.91	-222.63470	19.80(0)	-108.09	-222.64375	-9.15
	<b>3</b>	-223.40517	20.99(0)	8.24	d			-222.63106	-1.19
	<b>4</b>	-223.36020	26.88(0)	42.35	-222.53803	32.45(0)	-34.78		
	<b>5</b>	-223.37392	20.38(0)	27.24	-222.57649	22.24(1)	-69.12		
	<b>6</b>	-223.36880	21.19(0)	31.26	-222.60778	22.40(0)	-88.60		
	<b>7</b>	-223.36603	20.16(0)	31.97	-222.55211	21.27(0)	-54.79		
	<b>8</b>	-223.36521	20.12(0)	32.45	-222.52444	23.26(1)	-35.44		
	<b>9</b>	-223.30207	19.52(0)	71.47	-222.46524	20.84(0)	-0.71		
	<b>10</b>	-223.28984	19.12(0)	78.74	-222.40953	18.96(0)	32.36		
B <sub>9</sub> <sup>+</sup>	<b>1</b> <sup>+</sup>	-223.11140	21.14(0)	0.00	-222.32461	20.74(0)	0.00	-222.34182	0.00
	<b>2</b> <sup>+</sup>	-223.11014	21.38(0)	1.03	-222.31834	21.10(0)	4.29	-222.33884	1.87
	<b>3</b> <sup>+</sup>	-223.09751	18.45(2)	6.03	-222.28364	18.31(0)	23.28		
	<b>4</b> <sup>+</sup>	-223.08732	21.69(0)	15.66	-222.33425	21.47(0)	-5.32	-222.33410	4.85
	<b>5</b> <sup>+</sup>	-223.08851	20.58(0)	13.80	-222.28190	20.65(0)	26.71		
	<b>6</b> <sup>+</sup>	-223.08526	20.06(0)	15.32	-222.30278	20.32(0)	13.27		
	<b>7</b> <sup>+</sup>	-223.02276	19.37(0)	53.85	-222.17774	18.86(0)	90.28		
	<b>8</b> <sup>+</sup>	-222.98198	19.14(0)	79.21	-222.13899	18.61(1)	114.35		
B <sub>9</sub> <sup>-</sup>	<b>1</b> <sup>-</sup>	-223.53575	20.06(0)	0.00	-222.73819	19.68(0)	0.00	-222.75136	0.00
	<b>2</b> <sup>-</sup>	-223.49916	19.98(0)	22.88	-222.73750	19.68(0)	0.43	-222.73880	7.88
	<b>3</b> <sup>-</sup>	-223.48090	20.88(0)	35.24	-222.69736	20.61(0)	26.55		
	<b>4</b> <sup>-</sup>	-223.44873	22.93(0)	57.48	-222.64088	22.58(0)	63.96		
	<b>5</b> <sup>-</sup>	-223.44467	19.54(0)	54.63	e				
	<b>6</b> <sup>-</sup>	-223.45935	20.89(0)	48.77	-222.68603	20.29(0)	33.34		
	<b>7</b> <sup>-</sup>	-223.44839	19.64(0)	56.40	-222.63487	20.36(0)	65.51		
	<b>8</b> <sup>-</sup>	-223.41613	19.80(0)	74.80	-222.58851	19.28(1)	93.52		
	<b>9</b> <sup>-</sup>	-223.42751	19.29(0)	67.15	-222.60424	18.96(0)	83.34		
	<b>10</b> <sup>-</sup>	-223.29316	17.36(0)	149.53	-222.50819	17.43(0)	142.08		

<sup>a</sup>Total energies in Hartrees.<sup>b</sup>Zero-point energies in kcal/mol. The integers in parentheses are the numbers of imaginary frequencies (NIMAG).<sup>c</sup>The relative energies with ZPE corrections in kcal/mol.<sup>d</sup>At the MP2/6-311+G\* level, structure **3** is the same to structure **2**.<sup>e</sup>At the MP2/6-311+G\* level, structure **5**<sup>-</sup> is the same to structure **7**<sup>-</sup>.

### 1. Neutral B<sub>9</sub> cluster

For neutral B<sub>9</sub> cluster, ten isomers **1-10** are located, as shown in Fig. 1, including two isomers

(**1** and **2**) reported previously.<sup>25,40</sup> Isomer **1** has a slightly distorted wheel-structure with D<sub>2h</sub> symmetry, while isomer **2** has a D<sub>7h</sub> symmetry heptagonal bipyramid structure. With MP2

method, structure **1** is a saddle point with a large imaginary vibrational frequency, but the B3LYP calculations shows structure **1** should be a minimum. Since the MP2 method is deficient in computing systems with high spin-contaminations in their HF reference wave functions, which is common for  $B_n$  clusters,<sup>29,30</sup> the MP2 results are given less weight in discussions below on  $B_9$  cluster. Based on the B3LYP/6-311+G\* results, isomer **1** has lowest energy, while isomer **2** is 3.91 kcal/mol energetically less stable. However, high level CCSD(T)/AVDZ calculations predicted that structure **2** is the most stable isomer of  $B_9$ , which is

in agreement with the result of Boustani by HF, CI and MP4(SDTQ).<sup>25</sup> NBO analyses show that the WBIs of B4-B5 and B5-B6 in structure **1** are 1.248 and 1.390, respectively, indicating that the ring B-B bonds are neither single bonds nor double bonds and the  $\pi$  electrons are highly delocalized, which should be responsible for the stability of structure **1**. In structure **2**, the WBIs of ring bonds are all equal to 1.256, again neither single bonds nor double bonds, indicating that the  $\sigma$  electrons are highly delocalized. Obviously, the multi-centered  $\sigma$  bonds play a significant role in stabilizing structures **2**.

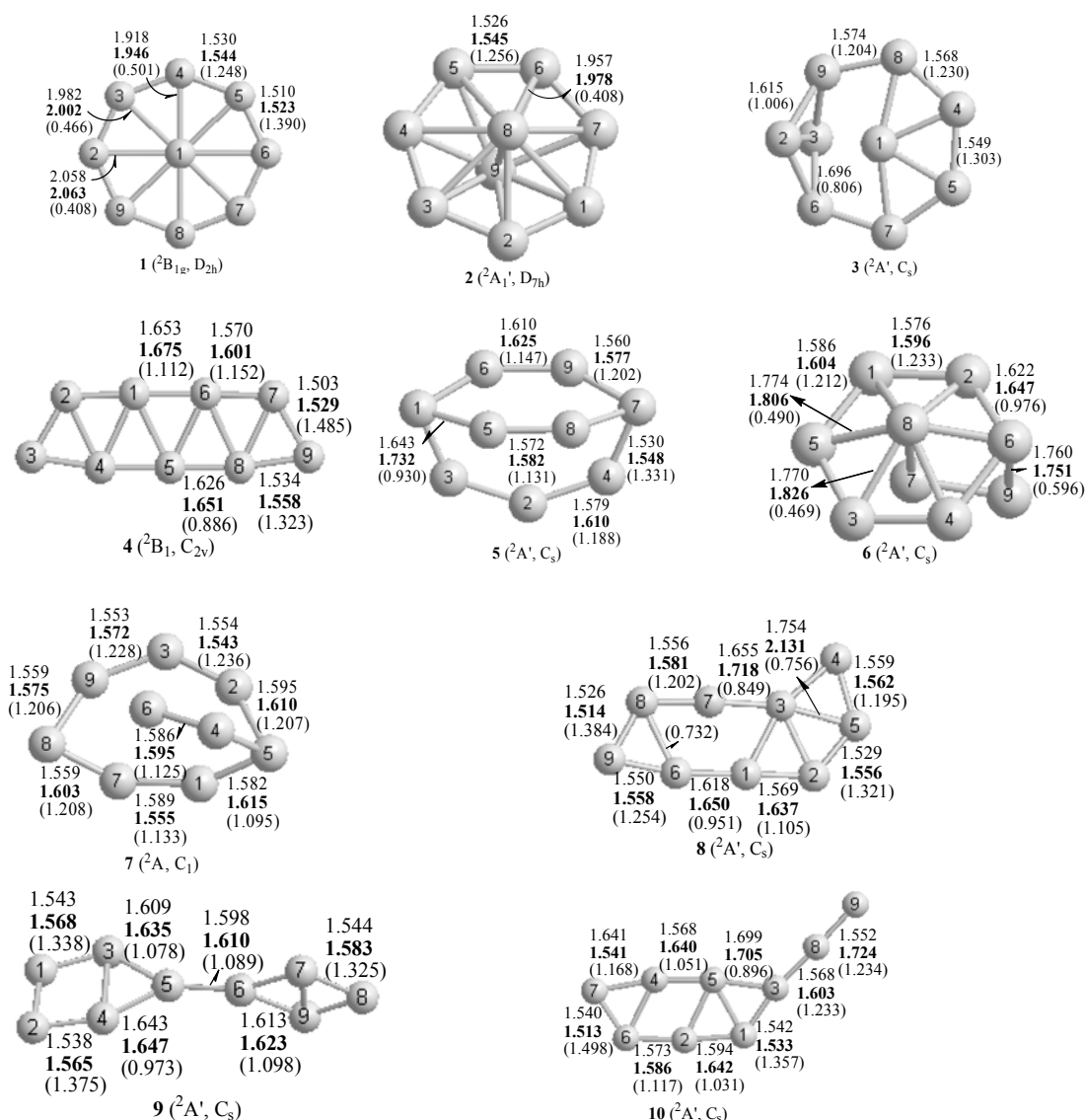


Fig. 1 – Optimized geometries (bond lengths in Å, bond angles in degrees) of  $B_9$  isomers at the B3LYP/6-311+G\* and MP2/6-311+G\* (in bold font) levels and the wiberg bond indices (WBIs, given in parentheses) at the B3LYP/6-311+G\*/B3LYP/6-311+G\* level..

Structure **3** lies 7.96 kcal/mol above structure **2** at the CCSD(T)/AVDZ level. The WBIs of B4-B8, B4-B5 and B5-B7 in structure **3** are 1.230, 1.303 and 1.230, respectively, suggesting the  $\sigma$  electrons are also highly delocalized. Again, the multi-centered  $\sigma$  bonds should play a significant role in stabilizing structures **3**.

Structures **4** (net-like) and **5** (convex-like) lie energetically above structure **1** by 42.35, 27.24 kcal/mol at the B3LYP/6-311+G\* level. Based on our NBO analysis, three-centered bonds exist in these structures, *i.e.*, among B1-B2-B4 and B6-B7-B8 atoms in structure **4**, among B1-B3-B5 and B4-B7-B8 atoms in structure **5**. Local  $\sigma$  bonds also appear in structures **4** and **5**, *i.e.*, B4-B5 (0.886 WBIs) in structure **4**, B1-B5 (0.930 WBIs) in structure **5**, which clearly contribute to their higher energies.

The energies of structure **6** (<sup>2</sup>A' state, C<sub>s</sub> symmetry), **7** (<sup>2</sup>A state, C<sub>1</sub> symmetry) and **8** (<sup>2</sup>A' state, C<sub>s</sub> symmetry) are 31.26, 31.97 and 32.45 kcal/mol higher than **1**, respectively, at the B3LYP/6-311+G\* level. NBO analysis suggests that local  $\sigma$  bonds are common in these structures and heavily destroy their stability, for example, B2-B6 in structure **6**, B1-B5 in structure **7**, B1-B6 in structure **8**.

Structures **9** and **10** lie energetically above structure **1** by 71.47 and 78.74 kcal/mol, respectively, at the B3LYP/6-311+G\* level. They would not be discussed detailedly in this paper because of their much higher energies.

## 2. Cationic B<sub>9</sub><sup>+</sup> clusters

Ten structures of cationic B<sub>9</sub><sup>+</sup> are shown in Fig. 2, in which **1**<sup>+</sup> and **4**<sup>+</sup> have been reported before [51]. The C<sub>s</sub>-symmetry wheel-shaped isomer **1**<sup>+</sup> in its <sup>1</sup>A' state is the global minimum with both B3LYP/6-311+G\* and CCSD(T)/AVDZ methods, which is in agreement with the prediction of Ricca *et al.*<sup>51</sup> NBO analysis suggests that there are six three-centered bonds in structure **1**<sup>+</sup>, *i.e.*, among the B1-B3-B8, B1-B4-B5, B1-B6-B7, B1-B8-B9,

B3-B6-B7 and B3-B8-B9 atoms, which play an important role in its stability. Structure **2**<sup>+</sup> is less stable than structure **1**<sup>+</sup> by only 1.03 (B3LYP/6-311+G\*), 4.29 (MP2/6-311+G\*) or 1.87 (CCSD(T)/AVDZ) kcal/mol. Similarly, three-centered  $\sigma$  bonds are indicated in structure **2**<sup>+</sup> among B1-B4-B5 and B6-B8-B9 atoms. The stability of isomers **1**<sup>+</sup> and **2**<sup>+</sup> should clearly be attributed to their multi-centered  $\sigma$  bonds.

Removing an electron from structure **1** leads to a D<sub>2h</sub>-symmetry planar cation **3**<sup>+</sup>, which is a local minimum at the MP2/6-311+G\* level but a second-order saddle point (imaginary frequencies: 213i and 70i cm<sup>-1</sup>) with the B3LYP/6-311+G\* method. Its energy is higher than isomer **1**<sup>+</sup> by 6.03 kcal/mol with B3LYP/6-311+G\* and 23.28 kcal/mol with MP2/6-311+G\*. Structure **3**<sup>+</sup> has large positive NICS (*vide infra*) values and four  $\pi$  electrons, not obeying (4n+2) rule, which make structure **3**<sup>+</sup> antiaromatic and less stable.

C<sub>2v</sub> symmetrical structure **4**<sup>+</sup> has lowest energy with the MP2 method but lies energetically above structure **1**<sup>+</sup> by 15.66 kcal/mol with the B3LYP method. Refining its energy with CCSD(T)/AVDZ method, structure **4**<sup>+</sup> lies 4.85 kcal/mol above structure **1**<sup>+</sup>. Based on the NBO analysis, structure **4**<sup>+</sup> has six three-centered bonds among B1-B5-B6, B1-B5-B8, B2-B3-B9, B2-B4-B9, B3-B6-B7 and B4-B6-B7 triangular units, respectively. Structure **5**<sup>+</sup> lies energetically above **1**<sup>+</sup> by 13.80 (B3LYP/6-311+G\*) and 26.71 (MP2/6-311+G\*) kcal/mol. NBO analysis suggests that there are two three-centered bonds in structure **5**<sup>+</sup> among B1-B8-B9 and B2-B3-B5 atoms, respectively. Structure **6**<sup>+</sup> is also a local minimum and lies energetically above **1**<sup>+</sup> by 15.32 (B3LYP/6-311+G\*) and 13.27 (MP2/6-311+G\*) kcal/mol. NBO analysis indicates that one three-centered bond among B2-B7-B9 exists in structure **6**<sup>+</sup>. Otherwise, the local  $\sigma$  bonds are common in structures **4**<sup>+</sup>-**6**<sup>+</sup>, for example, B1-B4 in **4**<sup>+</sup>, B1-B4 and B4-B5 in **5**<sup>+</sup>, and B3-B5 in **6**<sup>+</sup>, which may lead the energy of these isomers higher.

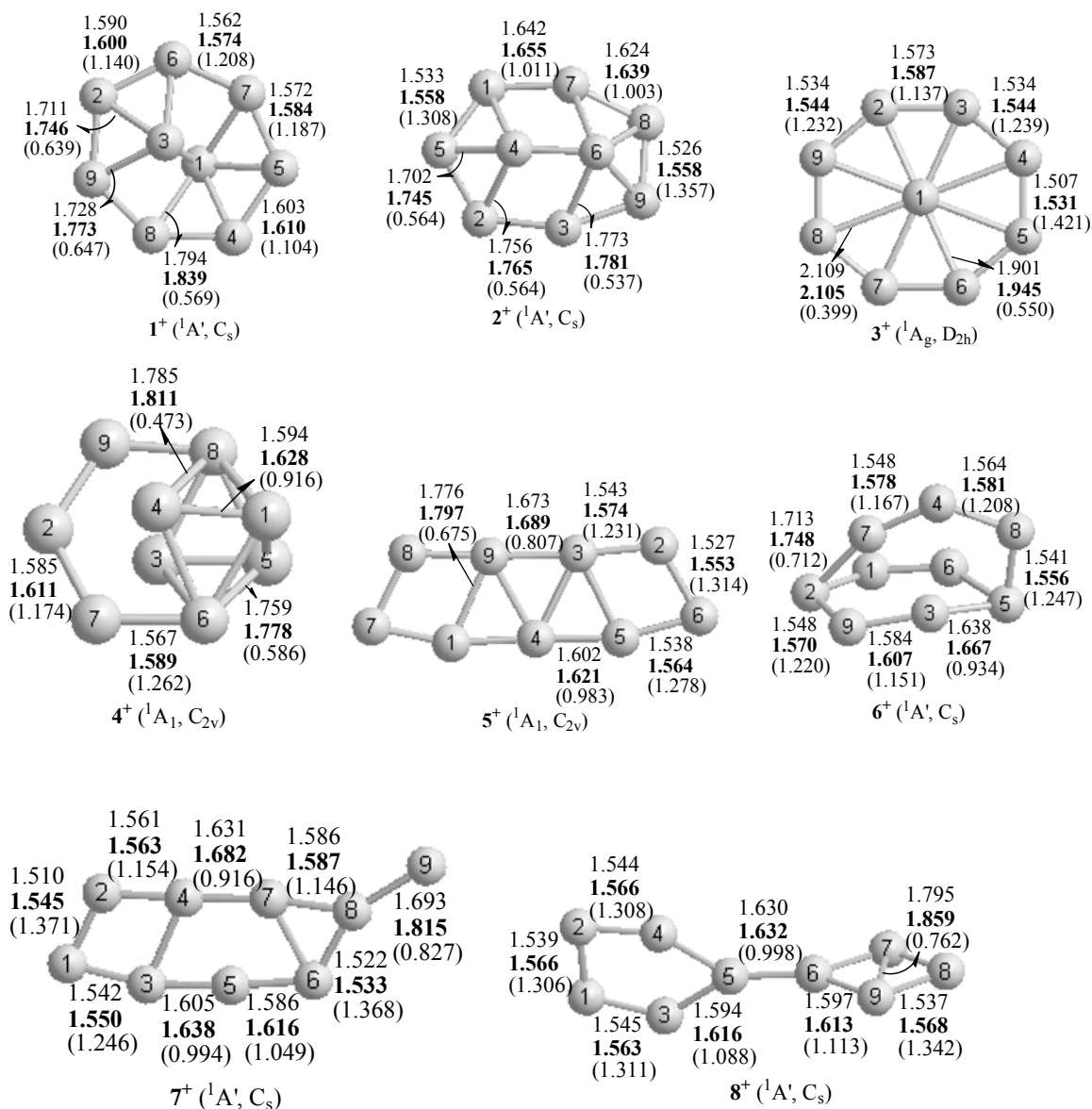


Fig. 2 – Optimized geometries (bond lengths in Å, bond angles in degrees) of  $B_9^+$  isomers at the B3LYP/6-311+G\* and MP2/6-311+G\* (in bold font) levels and the wiberg bond indices (WBIs, given in parentheses) at the B3LYP/6-311+G\*/B3LYP/6-311+G\* level.

Structures 7<sup>+</sup> (<sup>1</sup>A' state, C<sub>s</sub> symmetry) and 8<sup>+</sup> (<sup>1</sup>A' state, C<sub>s</sub> symmetry) are both minima but lie energetically above structure 1<sup>+</sup> by 53.85 and 79.21 kcal/mol, respectively, at the B3LYP/6-311+G\* level. Due to their higher energies, structures 7<sup>+</sup> and 8<sup>+</sup> are not discussed further.

### 3. Anionic B<sub>9</sub><sup>-</sup> clusters

Fig. 3 depicts the structures of ten local minima of B<sub>9</sub><sup>-</sup> cluster (1<sup>-</sup>–10<sup>-</sup>), in which only 1<sup>-</sup> have been investigated before.<sup>40</sup> The most stable isomer of

B<sub>9</sub><sup>-</sup> is the D<sub>8h</sub>-symmetry perfect planar wheel-shaped structure 1<sup>-</sup>, in good agreement with the results of Zhai *et al.*<sup>40</sup> According to our NBO analysis, the ring B-B bonds have WBIs of 1.409 and the radial B-B bonds have WBIs of 0.456, which all are neither single bonds nor double bonds. The strong delocalization among six π electrons plays an important role in stabilizing structure 1<sup>-</sup>.

Structure 2<sup>-</sup> (<sup>1</sup>A', C<sub>s</sub>) lies energetically above 1<sup>-</sup> by 22.88 (B3LYP/6-311+G\*), 0.43 (MP2/6-311+G\*) and 7.88 (CCSD(T)/AVDZ) kcal/mol. NBO

analysis suggests that there are six three-centered bonds in structure  $2^-$ , i.e., among the B1-B7-B8, B2-B3-B9, B2-B8-B9, B4-B5-B8, B6-B7-B9 and B6-B8-B9 atoms. Evidently, the three-centered bonds are responsible for the stabilities of  $2^-$ .

The other isomers are lying energetically above  $1^-$  more than 35 kcal/mol. Cage-like structure  $3^-$ , net-like  $4^-$ ,  $C_s$  symmetrical structure  $5^-$ ,

umbrella-like  $6^-$ , and net-like  $7^-$  are lie energetically above  $1^-$  by 35.24, 57.48, 56.63, 48.77 and 54.40 kcal/mol, respectively, with the B3LYP/6-311+G\* method. NBO analysis suggests that local  $\sigma$  bonds are common in these structures, so we confer that the local  $\sigma$  bonds play an important role in their unstability.

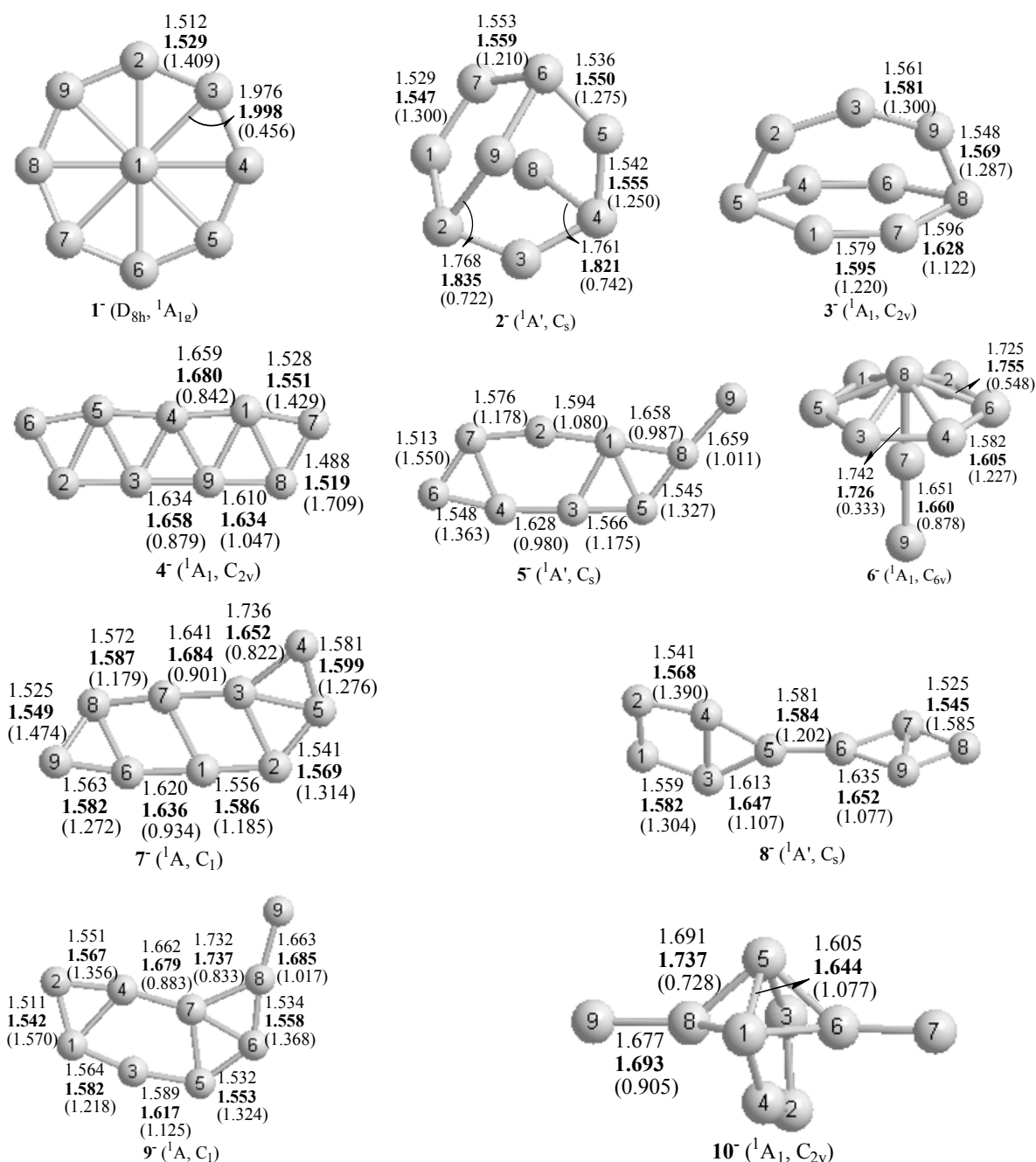


Fig. 3 – Optimized geometries (bond lengths in Å, bond angles in degrees) of  $B_9^-$  isomers at the B3LYP/6-311+G\* and MP2/6-311+G\* (in bold font) levels and the wiberg bond indices (WBIs, given in parentheses) at the B3LYP/6-311+G\*/B3LYP/6-311+G\* level.

For the  $8^-$ - $10^-$ , their energies are much higher than the global minimum  $1^-$ , and they are not discussed further.

#### 4. Adiabatic ionization potentials and electron affinities

Both adiabatic ionization potential (IP) and electron affinity (EA) are important properties of atoms and molecules. The adiabatic IP and EA are determined by,

$$\text{IP} = E(\text{optimized cation}) - E(\text{optimized neutral}),$$

$$\text{EA} = E(\text{optimized neutral}) - E(\text{optimized anion}).$$

Some IPs and EAs of boron clusters have been determined experimentally and theoretically.<sup>18,36,40,52</sup>

In present paper, the adiabatic IPs and EAs of  $B_9$  were calculated for its various isomers with their B3LYP/6-311+G\* energies, as shown in Table 2. It should be noted that cationic  $1^+$ ,  $5^+$ ,  $4^+$ , and  $9^+$  arise from the ionization of neutral  $B_9$  isomers **2**, **4**, **6**, and **9**, respectively. And attaching an electron to **1**, **4**, **8** and **9** would lead to the formation of  $1^-$ ,  $3^-$ ,  $7^-$  and  $8^-$ , respectively. Our EAs of **1** match the experimental result [40] well.

Table 2

Ionization potentials (IPs) and electron affinities (EAs) of the various structures at the B3LYP/6-311+G\* level of theory

isomer	IP		EA	
	Process	$E$ (eV)	Process	$E$ (eV)
<b>1</b>			$1 \rightarrow 1^-$	3.28
<b>2</b>	$2 \rightarrow 1^+$	8.13		
<b>4</b>	$4 \rightarrow 5^+$	7.96	$4 \rightarrow 4^-$	2.45
<b>6</b>	$6 \rightarrow 4^+$	7.58		
<b>8</b>			$8 \rightarrow 7^-$	2.26
<b>9</b>	$9 \rightarrow 8^+$	8.71	$9 \rightarrow 8^-$	3.10

#### 5. Aromaticity and bonding of some isomers of $B_9$ , $B_9^+$ and $B_9^-$ clusters

NICS is a simple and efficient criterion to confirm the aromaticity of some two- and three-dimensional structures. Aromaticity is identified by the negative NICS value, while antiaromaticity by the positive NICS value and non-aromatic system by the NICS value close to zero.

The valence MOs for  $\alpha$  electrons of **1** are collected in Fig. 4. The bonding characters of **1** and  $1^-$  are similar to each other. As discussed by Zhai *et al.*, structure  $1^-$  was not only  $\pi$  aromatic, but also  $\sigma$  aromatic.<sup>40</sup> For the selected orbits of **1**, the HOMO-5 ( $b_{3u}$ ), HOMO ( $b_{2g}$ ) and HOMO-1 ( $b_{1g}$ ) are three delocalized  $\pi$  bonding orbits formed

mainly by out-of-plane boron 2p orbitals. With six  $\pi$  electrons conforming to the  $4n+2$  Hückel rule, **1** is predicted to be  $\pi$  aromatic with negative NICS(1) value. For  $1^-$ , the HOMO-4 ( $b_{2g}$ ) is multi-centered  $\sigma$  bonding MO, with in-planar 2p orbitals pointing to the ring center. The HOMO-5 ( $a_{2u}$ ), HOMO-1 ( $e_{1g}$ ) and HOMO ( $e_{1g}$ ) are delocalized  $\pi$  bonding orbitals formed from out-of-plane boron 2p orbits. The NICS(1) value of -25.63 indicates  $1^-$  is aromatic. Identified by MOs, there is no  $\pi$  orbital in the three-dimensional (3D)  $1^+$  cation. Except for non-aromatic **3**, the 3D isomers exhibited in table 4 are all highly aromatic with very negative NICS(0).



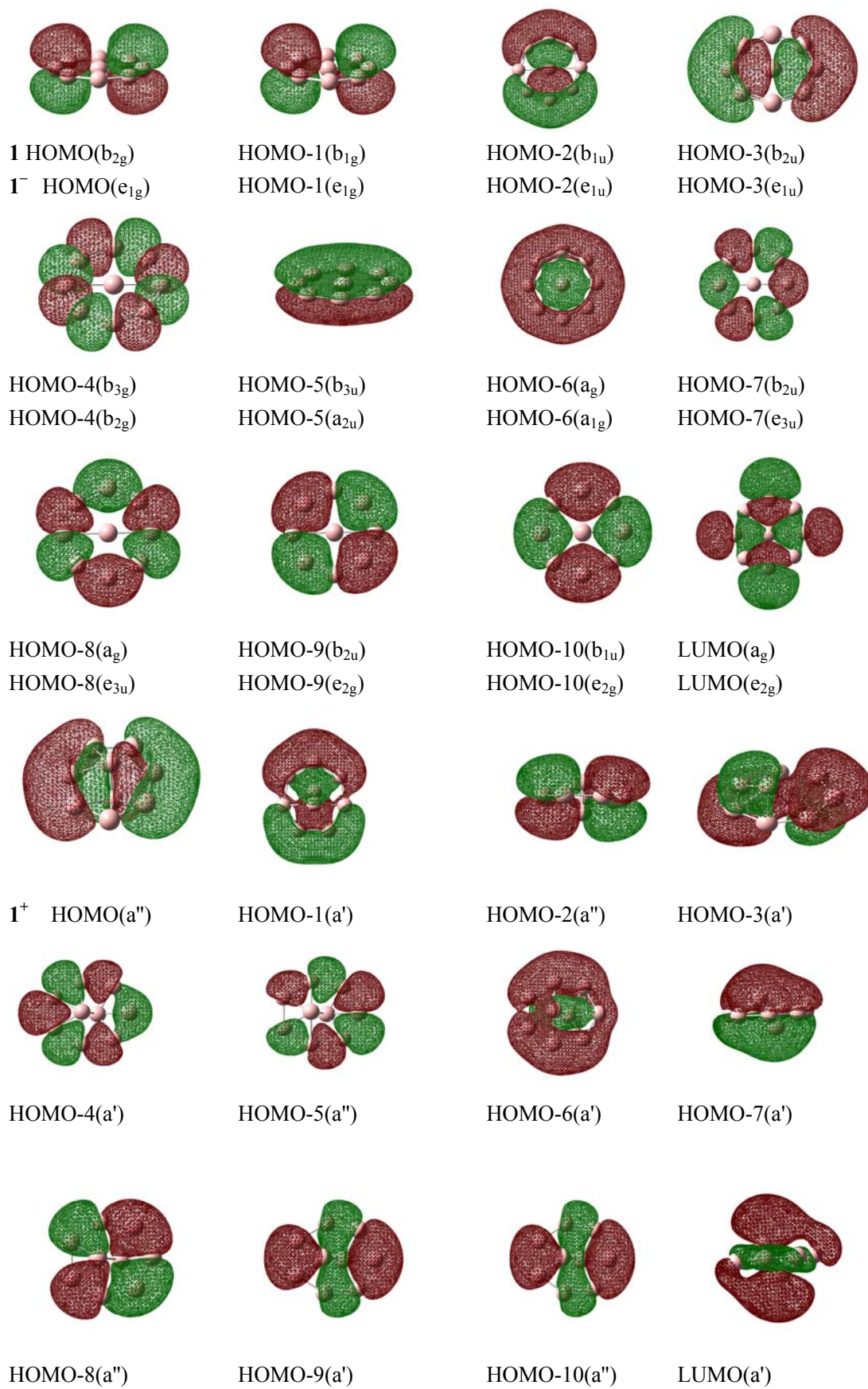
Fig. 4 – MO pictures for the minima of  $B_9$  (1),  $B_9^+$  (1<sup>+</sup>) and  $B_9^-$  (1<sup>-</sup>).

Table 3

NICS for some planar or pseudo-planar B<sub>9</sub>, B<sub>9</sub><sup>+</sup>, and B<sub>9</sub><sup>-</sup> isomers

Isomer	<b>1</b>	<b>4</b>	<b>3<sup>+</sup></b>	<b>4<sup>+</sup></b>	<b>5<sup>+</sup></b>	<b>1<sup>-</sup></b>
Point group	D <sub>2h</sub>	C <sub>2v</sub>	D <sub>2h</sub>	C <sub>2v</sub>	C <sub>2v</sub>	D <sub>8h</sub>
Electronic state	<sup>2</sup> B <sub>1g</sub>	<sup>2</sup> B <sub>1</sub>	<sup>1</sup> A <sub>g</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A <sub>1g</sub>
NICS(0) <sup>a</sup>	-29.21	-9.39	138.71	200.44	-8.95	
NICS(1) <sup>b</sup>	5.62	-8.70	163.25	143.53	-8.26	-25.63

<sup>a,b</sup> NICS (in ppm) is calculated at GIAO-B3LYP/6-311+G\*\*/B3LYP/6-311+G\* level of theory, a ghost atom is placed on the <sup>a</sup>geometric centers or <sup>b</sup>1.0 above.

Table 4

NICS for some 3D structures of B<sub>9</sub>, B<sub>9</sub><sup>+</sup>, and B<sub>9</sub><sup>-</sup> isomers (in ppm)

Isomer	<b>2</b>	<b>3</b>	<b>5</b>	<b>1<sup>+</sup></b>	<b>2<sup>+</sup></b>	<b>4<sup>+</sup></b>	<b>2<sup>-</sup></b>
Point group	D <sub>7h</sub>	C <sub>s</sub>	C <sub>s</sub>	C <sub>s</sub>	C <sub>s</sub>	C <sub>2v</sub>	C <sub>s</sub>
Electronic state	<sup>2</sup> A <sub>1</sub> '	<sup>2</sup> A'	<sup>2</sup> A'	<sup>1</sup> A'	<sup>1</sup> A'	<sup>1</sup> A <sub>1</sub>	<sup>1</sup> A'
NICS(0) <sup>a</sup>	-57.10	0.15	-21.35	-23.64	-5.52	-54.38	-62.44

<sup>a</sup> NICS (in ppm) is calculated at GIAO-B3LYP/6-311+G\*\*/B3LYP/6-311+G\* level of theory, a ghost atom is placed on the geometric centers.

## SUMMARY

28 isomers of B<sub>9</sub> (**1-10**), B<sub>9</sub><sup>+</sup> (**1<sup>+</sup>-8<sup>+</sup>**) and B<sub>9</sub><sup>-</sup> (**1<sup>-</sup>-10<sup>-</sup>**) were optimized at the B3LYP/6-311+G\* and MP2/6-311+G\* levels. Furthermore, low-lying isomers **1-3**, **1<sup>+</sup>-7<sup>+</sup>** and **1<sup>-</sup>-3<sup>-</sup>** were recalculated with CCSD(T)/AVDZ to refine the energies. Except for **9** and **3<sup>+</sup>**, all the isomers are genuine minima on their potential energy surfaces according to the vibrational frequency analysis. Our CCSD(T)/AVDZ calculation suggests that the most stable isomer of B<sub>9</sub> is the heptagonal bipyramid structure **2** with D<sub>7h</sub> symmetry. The C<sub>s</sub>-symmetry wheel-shaped **1<sup>+</sup>** and the D<sub>8h</sub>-symmetry three-dimensional structure **1<sup>-</sup>** are the most stable structures of the B<sub>9</sub><sup>+</sup> and B<sub>9</sub><sup>-</sup> clusters, respectively. Our above results are in agreement with the results reported before. Our NBO analyses show that multi-centered bonds play an important role in stabilizing these structures, and the NICS values confirm that the global minima exhibit evident aromaticity.

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