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Structure and Stability of B_5, B_5^+, and B_5^- Clusters

Qian Shu Li* and Hong Wei Jin

School of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing 100081, P. R. China, and The National Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, P. R. China

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The structure and stability of B_5, B_5^+ and B_5^- clusters have been investigated at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Eight B_5, seven B_5^+, and seven B_5^- isomers are identified. Of these 22 species, 16 have not been reported previously. The planar five-membered ring structures, **1** and **1**$^+$, are found to be the most stable on the neutral and cationic surfaces, respectively, in agreement with the results reported previously. The most stable B_5^- isomer has an arrangement of atoms similar to the neutral **1**. Upon the addition of an electron, the number of bonds increases from five to seven in this anion. Natural bond orbital (NBO) analysis suggests that there are three-centered bonds in both the neutral structure **1** and the anionic structure **1**$^-$, as well as the multicentered σ centripetal bond in the cationic structure **1**$^+$. The calculated nucleus-independent chemical shifts (NICS) of the structures **1**, **1**$^+$, and **1**$^-$ are all negative values, which indicates their aromatic characters. The higher degree of aromaticity and the multicentered σ centripetal bond are responsible for the special stability of the lowest-energy B_5^+ isomer.

1. Introduction

The discovery of the electronic structure of alkali metal clusters,[1] the detection of fullerenes in carbon clusters,[2] and the observation of quantum supershells[3] in sodium clusters have stimulated further interest and developments in the electronic structure and properties of clusters. Boron is an electron-deficient semimetal with short covalent radius. Three-center, two-electron bonding with sp^2 hybridization is a common motif, leading to polyhedral molecules and unusual crystal lattices consisting of stacked and nested icosahedra. Boron has an extremely high melting point, 2300 K, and possesses a hardness similar to that of diamond. Because of these unusual properties, boron compounds are candidates for various technological applications, including high-temperature semiconductors,[4] stable chemical insulators,[5] and high-energy density fuels.[6] Some B-containing materials are of considerable current interest because of their relatively high superconducting temperatures.[7]

In nature, boron occurs in different forms. The α- and the β-rhombohedral boron are the most known crystallines. Both consist of B_{12} icosahedral units. In 1999, Fujimori et al.[8] reported the peculiarity of chemical bonds in α-rhombohedral boron shown by three-dimensional electron density distributions. The results indicate that the characteristic two- and three-center covalent bond network threads through atoms on the cluster surface. Besides, there are two kinds of covalent bonds in intercluster space: a three-center trilaterally formed bond among the three clusters and a two-center bond with a remarkable feature of a bent bond between the clusters.

In 1988, Anderson and co-workers[9] found that the mass distribution of B_n^+ generated by laser ablation showed numerous "magic numbers" in the range $n = 1-20$. Their collision-induced dissociation (CID) results, however, indicated the presence of the noted "magic" clusters; only B_5^+ and B_{13}^+ were especially stable, both showing significant differences in the appearance potentials for B^+ and B_{n-1}^+ when compared to B_n^+ clusters of similar size.

Anomalous experimental results provide a favorite playground for theoreticians. The results of Anderson's group inspired several theoretical studies of small bare boron clusters[10−18] and especially B_5 and B_5^+ clusters.

Anderson and co-workers also performed self-consistent field configuration interaction (SCF-CI) calculations on both neutral and ionic B_5 clusters. They took the linear, symmetric pentagon, square pyramid, and trigonal bipyramid structures as starting geometries for optimization and postulated the trigonal bipyramid structure for B_5 and B_5^+.

In 1992, Kato and co-workers[19] reported a SCF study of neutral and cationic boron clusters, B_n ($n = 2-12$). According to their calculations, the D_{3h} $^2E'$ neutral B_5 and $^1A_1'$ cationic B_5^+ predicted by Anderson et al. are actually equilibrium structures but are higher in energy by 1.57 and 2.38 eV, respectively, at the MP4/6-31G* level than the most stable cyclic pseudoplanar C_2 ^2B B_5 and planar C_{2v} $^1A_1$ B_5^+ structures. Later that year, Ray and co-workers[20] calculated, by means of ab initio technique, the equilibrium geometries, total energies, binding energies, and fragmentation energies for the clusters B_n ($n = 2-8$), in both the neutral and cationic states. Two structures of both B_5 and B_5^+ were studied at the MP4/3-21G* level. The first is a trigonal bipyramid and the second is a planar structure composed of two isosceles triangles with a common apex. They found that the former structure is the most stable. Ihsan Boustani[21] investigated the B_n ($n = 2-14$) neutral clusters using small basis sets and a variety of methods (HF−SCF, direct CI, LSD, and NSD). He predicted a planar ground-state equilibrium geometry for the B_5 neutral cluster, as opposed to the trigonal bipyramid originally postulated by Anderson's group. In 1996, Ricca and Bauschlicher[22] used the B3LYP/6-31G* level of theory to calculate geometries and zero-point energies for B_{2-14}^+ and B_{2-6}. B3LYP accuracy was checked with large CCSD(T)

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* To whom correspondence should be addressed. Telephone: 86-10-68912665. Fax: +86-10-68912665. E-mail: qsli@mh.bit.edu.cn.

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calculations for a few small clusters. Their results showed that B_5^+ is a planar slightly deformed pentagon with C_{2v} symmetry and a $^1A_1$ ground state. The D_{3h} $^1A_1'$ trigonal bipyramid structure, with equatorial bond lengths of 1.810 Å and axial bond lengths of 1.580 Å, is 2.15 eV above the ground state at the B3LYP level. At the CCSD(T) level using a cc-PVTZ basis set, the D_{3h} structure is 2.23 eV above the ground state. The agreement between B3LYP and CCSD(T) confirms the tendency of B_n^+ clusters to prefer two-dimensional over three-dimensional structures. In 1997, Niu et al.[23] calculated the equilibrium geometries of neutral and charged boron clusters containing up to six atoms, as well as their binding energies, ionization potentials, fragmentation patterns, and electronic structures. They found that for the B_5, the triangular bipyramid is the most stable structure at MP4 level. However, the B3LYP predicted the pentagonal structure to be the preferred geometry of B_5.

New stable structures of larger boron clusters can easily be obtained with the help of an "Aufbau Principle".[24] Tang et al.[13] and Lipscomb et al.[25] have also proposed a geometrical conjugation relation of the vertexes and faces between boron and carbon clusters separately. According to the "Aufbau Principle", most of the final structures of the boron clusters ($n > 9$) are composed of two fundamental units: either of hexagonal or of pentagonal pyramids. The combination of only hexagonal pyramids leads either to 2D surfaces of quasi-planar structures or to 3D surfaces of tubular form. The combination of only pentagonal pyramids results in 3D surfaces such as the open 3D structures of refs 21 and 24. However, the combination of pentagonal and hexagonal pyramids transforms the 2D into 3D surfaces and enables cluster formation of convex or spherical clusters. The existence of graphite-like boron surfaces composed of parallel layers in quasi-planar or tubular forms are expected.

In this work, we continue and extend our theoretical study on structure and energetics of cationic, neutral, and anionic B_5 clusters with the MP2 and B3LYP methods. The natural bond orbital (NBO) analysis and the calculations for nucleus-independent chemical shifts (NICS) have also been performed to provide insight into the bonding nature and aromaticity of these clusters, and therein lies the explanation of the curious stability of cationic B_5^+ cluster.

2. Methods

All calculations were performed using the Gaussian 98 program package.[26] Equilibrium geometries of the neutral B_5 clusters and their corresponding ions, B_5^+ and B_5^-, were fully optimized at the B3LYP/6-311+G* and MP2(FC)/6-311+G* levels of theory, where MP2 stands for the second-order Møller−Plesset perturbation theory[27] and B3LYP is a DFT method using Becke's three-parameter nonlocal exchange functional[28] with the nonlocal correlation of Lee, Yang, and Parr.[29] FC denotes "frozen-core". The 6-311+G* is a split-valence triple-ζ plus polarization basis set augmented with diffuse functions.[27] Because the calculation of anion needs a basis set with diffuse functions and to make a better comparison between $B_5^{+/0}$ clusters and B_5^- clusters, we use of the 6-311+G* basis set to calculate all of these clusters in this work, although the diffuse functions are of little significance in $B_5^{+/0}$ clusters' calculations. Vibrational frequencies, calculated at the same levels, were used to determine the nature of the stationary points and give the zero-point vibrational energies. Minima were characterized with zero imaginary frequency and transition states with one imaginary frequency, as well as higher-order saddle points with more than one imaginary frequency. To gain more information of the electronic properties, the natural bond orbital (NBO) analysis[30,31] was performed for the most stable isomers identified at the B3LYP/6-311+G* level of theory using the optimized geometries at the same level.

3. Results and Discussion

The structures and geometric parameters of B_5(**1**−**8**), B_5^+ (**1**$^+$−**7**$^+$), and B_5^-(**1**$^-$−**7**$^-$) isomers optimized at the B3LYP/6-311+G* and MP2/6-311+G* levels are shown in Figures 1−3, respectively. The total and zero-point vibrational energies of these isomers are listed in Table 1, as well as the relative energies (with zero-point vibrational energy corrections) and the number of imaginary frequencies. On the basis of these results, the ionization potentials (IPs) and electron affinities (EAs) can then be easily calculated, and they are tabulated in Table 2.

3.1. Neutral B_5 Clusters. For the neutral B_5 clusters, we have identified eight different stationary structures, that is, one structure with $D_{\infty h}$ symmetry, six structures with C_{2v} symmetry, and one structure with D_{3h} symmetry (see Figure 1). Among them, the planar five-membered ring structure **1**, with C_{2v} symmetry in the $^2B_2$ state, is the lowest in energy at both the B3LYP/6-311+G* and MP2/6-311+G* levels of theory, in agreement with the results obtained by Boustani et al.[21] and Ricca et al.[22] In terms of NBO analysis, except for the five B−B σ bonds in the structure **1**, there is a B2B1B3 three-centered bond, which formed using three hybrid orbitals provided by B1, B2, and B3. That the Wiberg bond indices (WBI) of B1B2 and B1B3 are both 0.68 supports the existence of this three-centered bond. Identified by MO, there are two π orbitals with three π electrons occupied in them. For the structure **1**, the averaged WBI of bonds between adjacent B atoms is 1.24. It indicates that the π electrons are delocalized in the five-membered ring. The three-centered bond and the π-electron delocalization play an important role in stabilizing the planar five-membered ring structure **1**.

The D_{3h} trigonal bipyramid structure **8** is the first minimum of B_5 cluster reported by Anderson et al.[9] According to our calculation, it has one large imaginary frequency of −563.5 cm^{-1} at the B3LYP/6-311+G* level. But at the MP2/6-311+G* level, it is a local minimum with all real vibrational frequencies. It is higher in energy by 3.08 and 2.68 eV at the B3LYP/6-311+G* and MP2/6-311+G* levels, respectively, than the most stable structure **1**. Compared with the two bond lengths (equatorial and axial), 1.750 and 1.430 Å, in Anderson's structure, our optimized bond lengths are 1.816 and 1.624 Å, respectively, at the B3LYP/6-311+G* level. The corresponding MP2 values are 1.817 and 1.647 Å, respectively.

The capped quadrangular structure **2** (C_{2v}), the structure **3** (C_{2v}), and the linear structure **4** ($D_{\infty h}$), as well as structures **5** (C_{2v}) and **6** (C_{2v}), are all characterized as local minima, which have all real vibrational frequencies at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. They are predicted to be 2.30, 3.92, 4.57, 5.01, and 4.17 eV, respectively, higher in energy than **1** at the B3LYP/6-311+G* level. At the MP2/6-311+G* level, these values are 2.33, 4.77, 2.98, 5.91, and 4.91 eV, respectively. For the structure **2**, the bond lengths change greatly from the MP2/6-311+G* level to B3LYP/6-311+G* level, at which the B1−B2 (B4−B5) bond length increases from 1.580 to 1.632 Å, whereas the B2−B3 (B3−B5) bond length decreases from 1.630 to 1.510 Å. Besides the structure **8**, another three-dimensional structure **7** (C_{2v}) is found to be a local minimum on both chosen energy hypersurfaces and to be more stable than **8** by 0.53 eV (B3LYP) and 0.42 eV (MP2).

3.2. Cationic B_5^+ Clusters. As shown in Figure 2, seven isomers of the B_5^+ cluster have been obtained. Similar to the

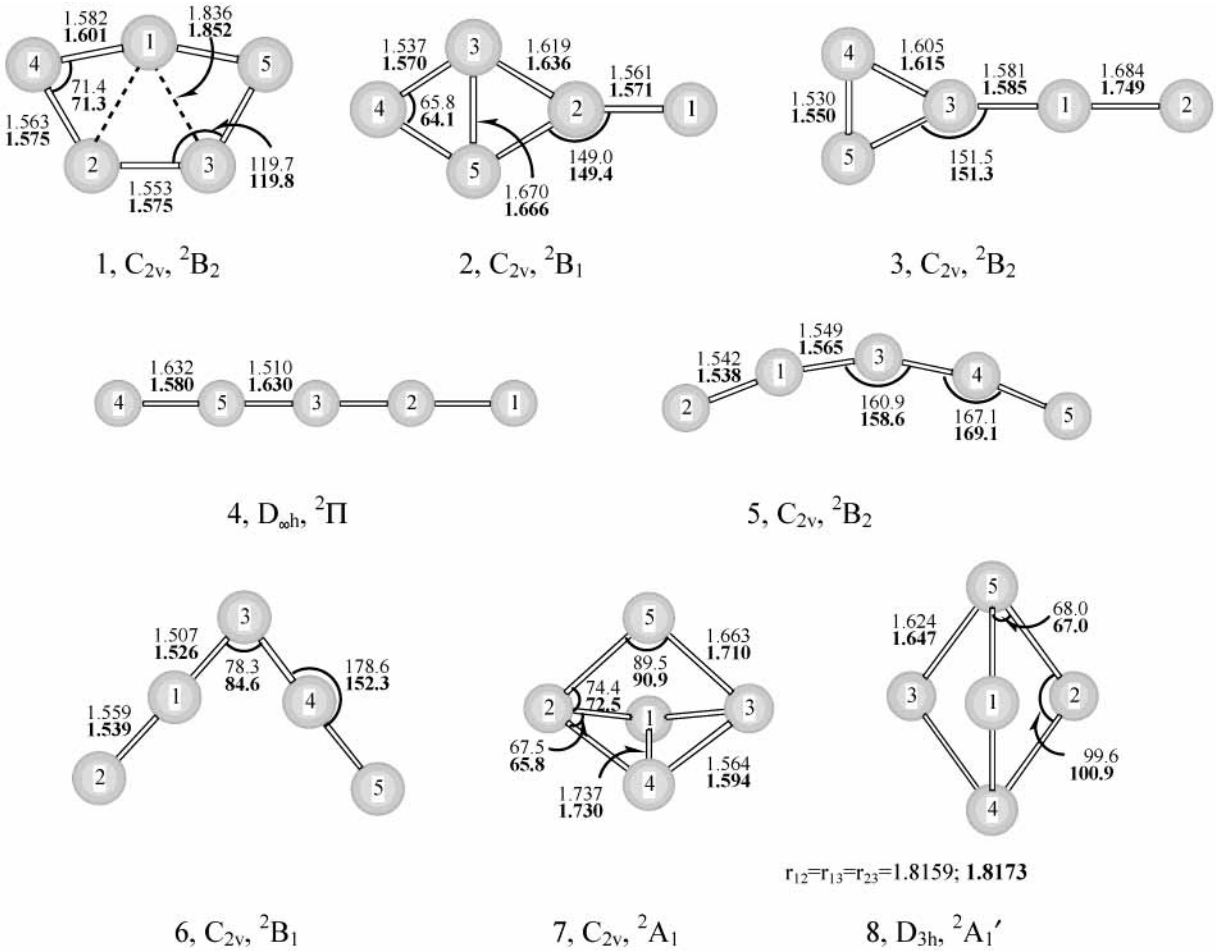


Figure 1. B3LYP/6-311+G* and MP2/6-311+G* (bold font) optimized geometries (bond lengths in Å, bond angles in deg) of various minima characterized on the B_5 potential energy surface.

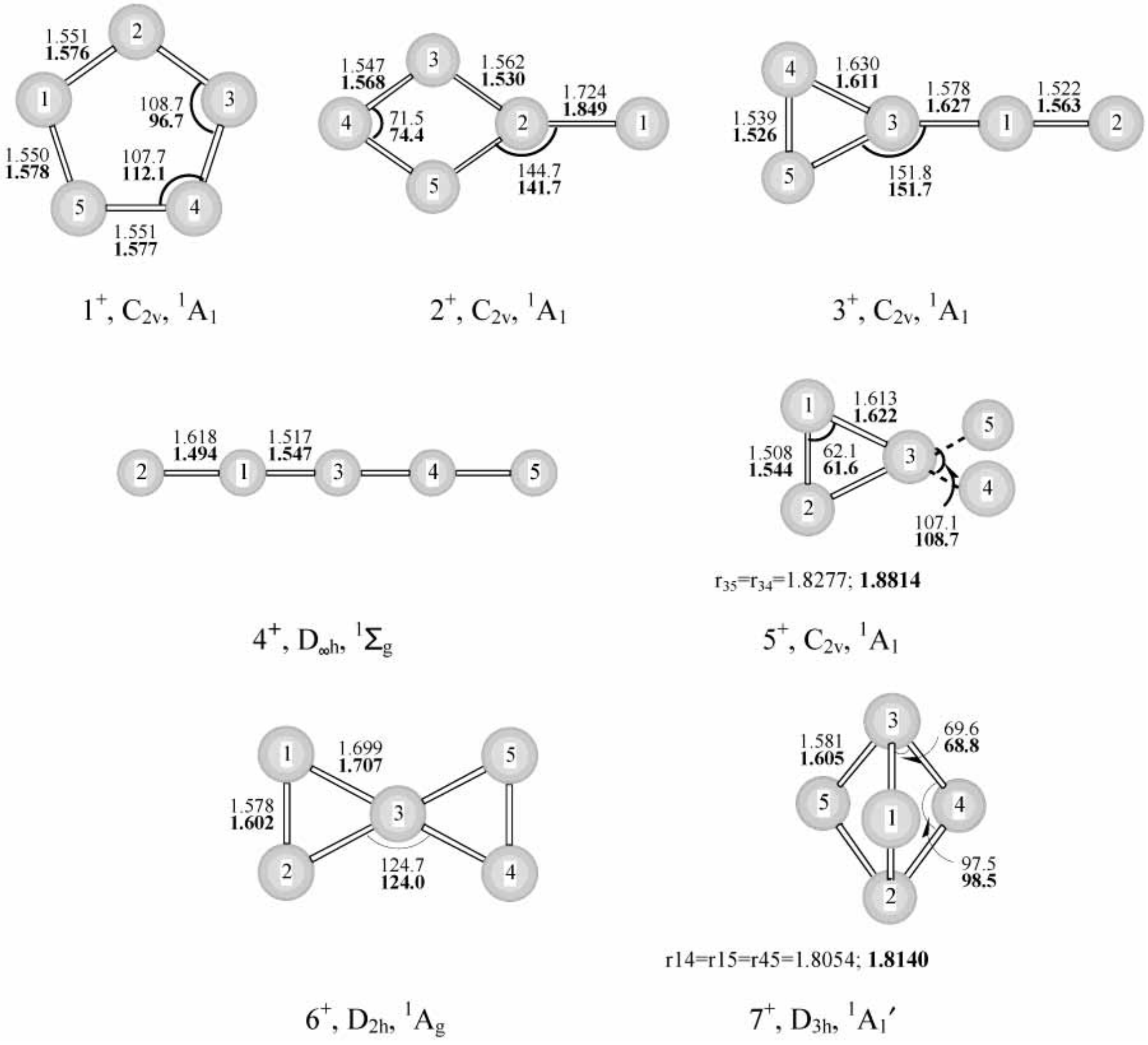
neutral B_5 cluster, the most stable B_5^+ isomer is a planar slightly deformed pentagon with C_{2v} symmetry and a $^1A_1$ state. This result is consistent with the speculation by Kato et al.[19] and Ricca et al.[22] The five bond lengths of optimized structure $\mathbf{1}^+$ differ within 0.001 Å and the averaged bond length is 1.550 Å at the B3LYP/6-311+G* level and 1.570 Å at the MP2/6-311+G* level, similar to that of Ricca et al. (1.560 Å) calculated at the B3LYP/6-31G* level. The NBO results show that there are two π electrons in the structure $\mathbf{1}^+$. The WBI of the five B−B bonds in $\mathbf{1}^+$ are very closed to each other with an averaged value of 1.30, between that of single bond and double bond. So the two π electrons are strongly delocalized in the five-membered ring. The WBI of B2B5 (B2B4), B1B4 (B3B5), and B1B3 are also very closed to each other with a value of 0.35 on average. So there is a multicentered σ centripetal bond in the structure $\mathbf{1}^+$ formed by the five B atoms and two valence electrons participate in the bonding. The strong cyclic π-electron delocalization and the multicentered σ centripetal bond make the planar five-membered ring structure $\mathbf{1}^+$ show special stability.

The D_{3h} $^1A_1'$ trigonal bipyramid structure $\mathbf{7}^+$, with equatorial bond lengths of 1.805 Å and axial bond lengths of 1.581 Å, lies 2.21 eV in energy above the structure $\mathbf{1}^+$ at the B3LYP/6-311+G* level. These results agree well with those of Ricca et al.[22] From the B3LYP/6-311+G* to MP2/6-311+G*, the bond lengths change little, and the corresponding energy difference for the structure $\mathbf{1}^+$ changes to 2.37 eV.

Our structures $\mathbf{2}^+$ (C_{2v}), $\mathbf{3}^+$ (C_{2v}) and $\mathbf{4}^+$ ($D_{\infty h}$) are more similar in arrangement to their neutral counterparts, except for the fact that the bond length of B3−B5 in the structure $\mathbf{2}^+$ becomes larger than that in neutral and the number of bonds decreases from 6 to 5. The isomer $\mathbf{2}^+$ is about 2.25 and 3.10 eV less stable than $\mathbf{1}^+$ at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory, respectively, and is very close in energy to the structure $\mathbf{7}^+$.

The planar structure $\mathbf{6}^+$**,** which is composed of two three-membered rings, has D_{2h} symmetry and a ^1A_g state. It lies 3.85 and 3.79 eV in energy, respectively, above the most stable structure $\mathbf{1}^+$ at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. The three-dimensional structure $\mathbf{5}^+$ has C_{2v} symmetry and a $^1A_1$ state. It is predicted to be a local minimum on both the B3LYP and MP2 potential energy surfaces. Both of the structures $\mathbf{5}^+$ and $\mathbf{6}^+$ contain two three-membered rings, but the different linking modes of boron atoms result in some bond-length changes at the same calculated level. For example, the bond length of B1−B2 in the structure $\mathbf{5}^+$ (C_{2v}) is 1.508 Å (B3LYP/6-311+G*), while the corresponding value in the structure $\mathbf{6}^+$ (D_{2h}) is 1.578 Å (B3LYP/6-311+G*).

3.3. Anionic B_5^- Clusters. Figure 3 depicts the structures of seven minima located on the B_5^- potential energy surface. Seven geometric structures of B_5^- isomers have been optimized at the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. Five structures are determined to be minima on their PES with all real vibrational frequencies. Energetically, the most stable structure among all of the isomers located is the structure $\mathbf{1}^-$ with C_{2v} symmetry. It shows an arrangement of atoms similar to that of the corresponding cationic and neutral structures. There is, however, a consistent trend of lengthed bond lengths. And



1^+, C_{2v}, $^1A_1$ 2^+, C_{2v}, $^1A_1$ 3^+, C_{2v}, $^1A_1$

4^+, $D_{\infty h}$, $^1\Sigma_g$

$r_{35}=r_{34}=1.8277$; **1.8814**

5^+, C_{2v}, $^1A_1$

$r14=r15=r45=1.8054$; **1.8140**

6^+, D_{2h}, ^1A_g 7^+, D_{3h}, $^1A_1'$

Figure 2. B3LYP/6-311+G* and MP2/6-311+G* (bold font) optimized geometries (bond lengths in Å, bond angles in deg) of various minima characterized on the B_5^+ potential energy surface.

upon the addition of an electron, the number of bonds increases from 5 to 7 in this new arrangement. In the structure $\mathbf{1}^-$, there is a three-centered bond formed by atoms B1, B2, and B3. The WBIs of B1B2 and B1B3 are both 0.79, which proves the existence of the three-centered bond. Identified by MO, there are two π orbitals and four π electrons for structure $\mathbf{1}^-$. Similar to the neutral and cationic five-membered ring structures, there are weak cyclic π-electron delocalizations in this anionic five-membered ring structure.

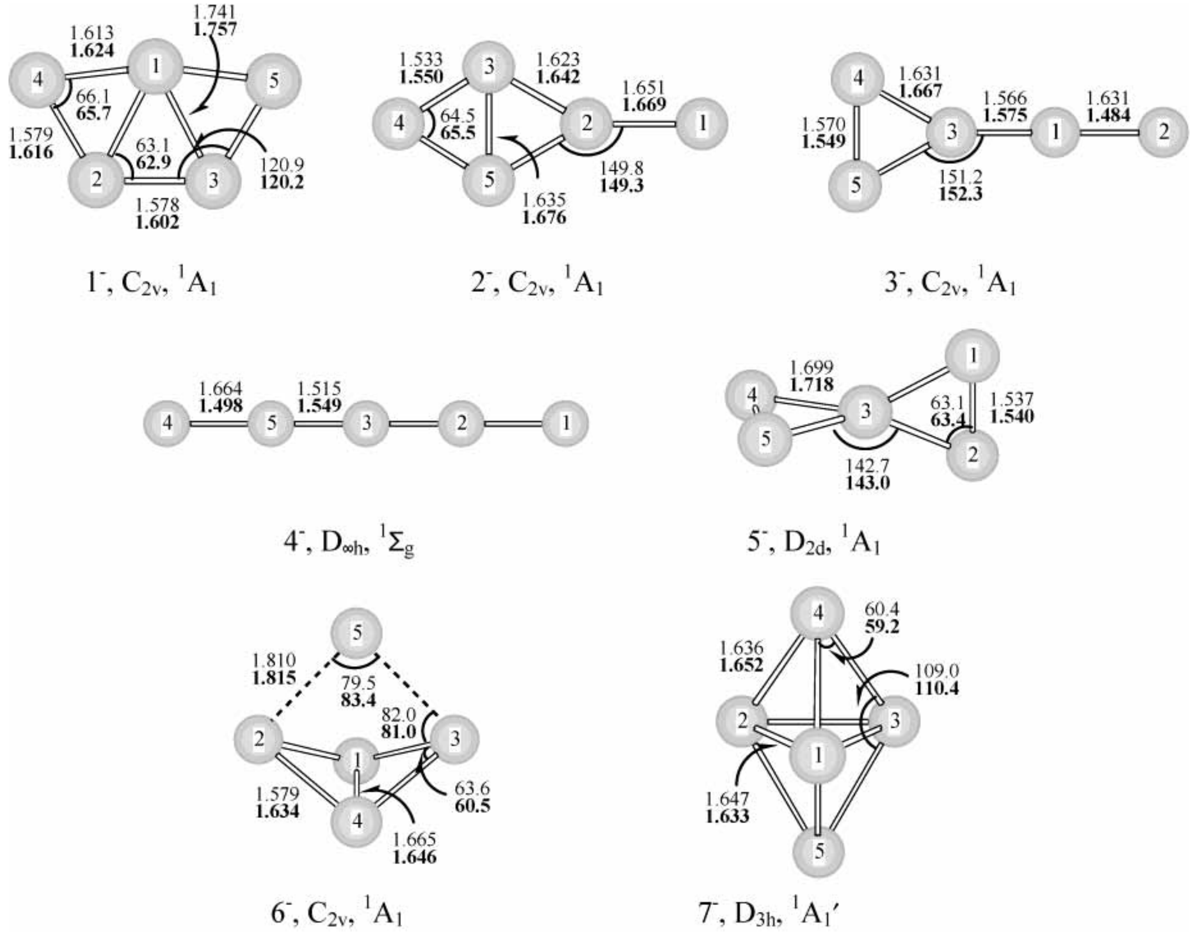
For the planar structures $\mathbf{2}^-$ (C_{2v}) and $\mathbf{3}^-$ (C_{2v}) and the linear structure $\mathbf{4}^-$ ($D_{\infty h}$), they do not differ much from the neutral and anionic isomers in geometric parameters. The structure $\mathbf{2}^-$ is the second stable isomer among the isomers of B_5^-. It lies 1.42 and 1.69 eV in energy above $\mathbf{1}^-$ at the B3LYP and MP2 levels of theory, respectively. For the structure $\mathbf{3}^-$, it has one imaginary frequency at the B3LYP/6-311+G* level, while at the MP2/6-311+G* level, it is a minimum with all real vibrational frequencies. At the B3LYP/6-311+G* level of theory, the linear structure $\mathbf{4}^-$ is the fourth stable isomer among the isomers of B_5^-. But at the MP2/6-311+G* level, it has a higher energy than the other B_5^- isomers.

The trigonal bipyramid structure $\mathbf{7}^-$ with D_{3h} symmetry is found to be a local minimum on both the B3LYP/6-311+G* and MP2/6-311+G* PES. It is noted that, attaching an extra electron to neutral **8** leads to the anion $\mathbf{7}^-$, in which the axial bond lengths increase while the equatorial bond lengths decrease.

Two three-dimensional isomers $\mathbf{5}^-$ and $\mathbf{6}^-$ are local minima with fairly high symmetry at both B3LYP and MP2 levels of theory. The structure $\mathbf{6}^-$, with a $^1A_1$ state, maintains the atomic arrangement of the neutral **7**. The bond lengths of $\mathbf{6}^-$ are only slightly different from those of the neutral **7**, except for the B2−B5 (B3−B5) bond length, which changes from 1.663 Å in **7** to 1.810 Å in $\mathbf{6}^-$ at the B3LYP/6-311+G* level. The five B_5^- isomers, $\mathbf{3}^-$−$\mathbf{7}^-$, are all highly energetic species, about 2.70∼7.60 eV less stable than $\mathbf{1}^-$.

In Table 2 can be found ionization potentials and electron affinities for the various isomers studied in this work. It should be noted that cations $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4}^+$ and $\mathbf{7}^+$ arise from the ionization of neutral B_5 isomers **1**, **2**, **3**, **4**, and **8**, respectively. On the other hand, attaching an electron to **1**, **2**, **3**, **4**, **7**, and **8** would lead to the formation of $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$, $\mathbf{4}^-$, $\mathbf{6}^-$, and $\mathbf{7}^-$, respectively. Their computed IPs and EAs compare reasonably well with those of the boron atom.[32]

3.4. Aromaticity of Some Neutral, Cationic, and Anionic B_5 Isomers. Conventionally, aromaticity is often discussed in term of various criteria such as energetic (resonance and aromatic stabilization energies, ASE), magnetic (^{1}H NMR chemical shifts, magnetic susceptibility anisotropies and their exaltations, and NICS), and geometric (bond length equalization).[33,34,35] NICS (nucleus-independent chemical shift), proposed by Schleyer and co-workers,[35] is based on magnetic shieldings, which have long been calculated by simple methods[36]



1^-, C_{2v}, $^1A_1$ 2^-, C_{2v}, $^1A_1$ 3^-, C_{2v}, $^1A_1$

4^-, $D_{\infty h}$, $^1\Sigma_g$ 5^-, D_{2d}, $^1A_1$

6^-, C_{2v}, $^1A_1$ 7^-, D_{3h}, $^1A_1'$

Figure 3. B3LYP/6-311+G* and MP2/6-311+G* (bold font) optimized geometries (bond lengths in Å, bond angles in deg) of various minima characterized on the B_5^- potential energy surface.

TABLE 1: Total (*E*),[a] Zero-Point (ZPE),[b] and Relative Energies[c] for B_5, B_5^+, and B_5^- Isomers

		B3LYP/6-311+G*			MP2/6-311+G*		
isomer		*E*[a]	ZPE[b]	relative energy[c]	*E*[a]	ZPE[b]	relative energy[c]
B_5	**1**	−124.003 032 5	0.43 (0)	0.0	−123.522 635 5	0.43 (0)	0.0
	2	−123.917 357 4	0.40 (0)	2.30	−123.436 913 5	0.42 (0)	2.33
	3	−123.855 725 0	0.33 (0)	3.92	−123.343 684 5	0.34 (0)	4.77
	4	−123.833 232 6	0.38 (0)	4.57	−123.409 957 3	0.34 (0)	2.98
	5	−123.819 576 5	0.45 (0)	5.01	−123.300 794 8	0.31 (0)	5.91
	6	−123.846 731 3	0.34 (0)	4.17	−123.348 416 2	0.60 (0)	4.91
	7	−123.909 359 8	0.43 (0)	2.55	−123.448 124 0	0.66 (0)	2.26
	8	−123.887 604 9	0.36 (1)	3.08	−123.435 151 9	0.79 (0)	2.68
B_5^+	$\mathbf{1}^+$	−123.692 921 0	0.41 (0)	0.0	−123.241 930 6	0.39 (0)	0.0
	$\mathbf{2}^+$	−123.609 565 0	0.39 (0)	2.25	−123.127 479 6	0.38 (0)	3.10
	$\mathbf{3}^+$	−123.490 566 9	0.36 (0)	5.45	−123.004 248 4	0.37 (0)	6.72
	$\mathbf{4}^+$	−123.488 803 4	0.32 (0)	5.46	−122.917 453 6	0.32 (2)	8.75
	$\mathbf{5}^+$	−123.495 199 3	0.30 (0)	5.27	−123.037 648 9	0.29 (0)	5.45
	$\mathbf{6}^+$	−123.536 478 5	0.31 (0)	3.85	−123.100 872 7	0.35 (1)	3.79
	$\mathbf{7}^+$	−123.613 626 8	0.46 (0)	2.21	−123.156 801 5	0.45 (0)	2.37
B_5^-	$\mathbf{1}^-$	−124.080 872 0	0.42 (0)	0.0	−123.619 034 2	0.42 (0)	0.0
	$\mathbf{2}^-$	−124.027 237 8	0.39 (0)	1.42	−123.555 483 7	0.38 (1)	1.69
	$\mathbf{3}^-$	−123.950 271 4	0.29 (1)	3.84	−123.430 813 2	0.37 (0)	5.07
	$\mathbf{4}^-$	−123.957 642 6	0.32 (0)	3.25	−123.338 390 6	0.34 (0)	7.56
	$\mathbf{5}^-$	−123.945 723 1	0.31 (0)	3.57	−123.515 626 0	0.31 (0)	2.81
	$\mathbf{6}^-$	−123.967 778 6	0.38 (0)	3.03	−123.516 615 2	0.38 (0)	2.74
	$\mathbf{7}^-$	−123.906 320 5	0.42 (0)	4.75	−123.370 101 7	0.65 (0)	7.00

[a] Total energies in hartree. [b] Zero-point energies in eV. The integers in parentheses are the number of imaginary frequencies (NIMAG). [c] The relative energies with ZPE corrections in eV.

TABLE 2: Ionization Potentials and Electron Affinities (in eV) of the Various Structures at the B3LYP/6-311+G* Level of Theory

	ionization potential			electron affinity	
isomer	*E* (eV)	process	exptl[a]	*E* (eV)	process
1	8.42	$\mathbf{1} \rightarrow \mathbf{1}^+$		2.12	$\mathbf{1}^- \rightarrow \mathbf{1}$
2	8.36	$\mathbf{2} \rightarrow \mathbf{2}^+$		2.99	$\mathbf{2}^- \rightarrow \mathbf{2}$
3	9.96	$\mathbf{3} \rightarrow \mathbf{3}^+$		2.62	$\mathbf{3}^- \rightarrow \mathbf{3}$
4	9.31	$\mathbf{4} \rightarrow \mathbf{4}^+$		3.45	$\mathbf{4}^- \rightarrow \mathbf{4}$
5					
6				2.45	$\mathbf{6}^- \rightarrow \mathbf{7}$
7					
8	7.56	$\mathbf{8} \rightarrow \mathbf{7}^+$	7.80	2.90	$\mathbf{7}^- \rightarrow \mathbf{8}$

[a] Reference 9.

and now can be computed with modern ab initio technique.[37] To conform with the usual experimental convention, NICS is the negative value of the shielding evaluated, for example, at or above the geometrical centers of rings or clusters. Aromaticity is characterized by negative NICS values, antiaromaticity by positive NICS, and nonaromatic compounds by values close to zero. The effectiveness of NICS as a simple and efficient criterion to probe two- and three-dimensional delocalization has been demonstrated by studies on the wide-ranging sets of two- and three-dimensional aromatic compounds.[34,35] Therefore, we computed NICS values for the planar five-membered ring structures **1**, $\mathbf{1}^+$, and $\mathbf{1}^-$, as well as the trigonal bipyramid neutral, cationic, and anionic B_5 isomers at the GIAO-B3LYP/6-311+G* level using B3LYP/6-311+G* geometries (Table 3) to study their aromaticity.

According to the NICS criterion, Table 3 shows that the neutral and cationic three-dimensional structures **8** and $\mathbf{7}^+$ are both antiaromatic. The NICS value for the structure **8** is 25.64 ppm, which can be compared to 11.99 ppm for cationic structure $\mathbf{7}^+$. Adding an electron to neutral structure **8** leads to the anionic

TABLE 3: Nucleus-Independent Chemical Shifts (NICS) for Some B_5, B_5^+, and B_5^- Isomers (in ppm)

isomer	**1**	**8**	$\mathbf{1}^+$	$\mathbf{7}^+$	$\mathbf{1}^-$	$\mathbf{7}^-$
PG	C_{2v}	D_{3h}	C_{2v}	D_{3h}	C_{2v}	D_{3h}
ES	$^2B_2$	$^2A_1'$	$^1A_1$	$^1A_1'$	$^1A_1$	$^1A_1'$
NICS[a]	−17.12	25.64	−36.17	11.99	−7.35	2.91

[a] NICS at the geometric centers, calculated at the B3LYP/6-311+G* level.

trigonal bipyramid structure $\mathbf{7}^-$ and makes it become nonaromatic with a small NICS value of 2.91 ppm.

For the planar five-membered ring structures, the NICS value of −17.12 ppm computed at the ring center of structure **1** suggests that this neutral B_5 isomer is aromatic but less so than the corresponding cationic isomer $\mathbf{1}^+$, which has a NICS value of −36.17 ppm. The anionic structure $\mathbf{1}^-$ is also aromatic with a relatively lower NICS value of −7.35 ppm.

As previously reported,[19−23] planar structures are more stable than three-dimensional ones for the neutral and cationic B_5 clusters. This trend holds true for the anionic cluster as well. This is due, at least in part, to the fact that the planar structures are stabilized by π delocalization. According to the NBO analysis above, the structures $\mathbf{1}^+$, **1**, and $\mathbf{1}^-$ have two, three, and four π electrons, respectively. So the structure $\mathbf{1}^+$ has the highest degree of aromaticity. The neutral **1** and anion $\mathbf{1}^-$ have lower NICS values than the cation $\mathbf{1}^+$ because they have a bit more π electrons. The closer the number of π electrons was to that of conjugated boron atoms, the lower the degree of aromaticity would be.

4. Conclusion

We have studied 22 isomers of the B_5, B_5^+, and B_5^- clusters. At the B3LYP/6-311+G* and MP2/6-311+G* levels of theory, eight B_5, seven B_5^+, and seven B_5^- isomers are identified. Among them, sixteen isomers are introduced for the first time.

The most stable isomer among the cationic clusters has a planar five-membered ring structure with C_{2v} symmetry, which was proposed by Kato and Yamashita[19] first. At the B3LYP and MP2 levels, this isomer lies 2.21 and 2.37 eV, respectively, in energy below the second-lowest-energy isomer, the trigonal bipyramid D_{3h} structure $\mathbf{7}^+$. NBO analysis suggests that there are strong cyclic π-electron delocalization and a multicentered σ centripetal bond in this cation. The most stable minimum of the neutrals is the planar five-membered ring structure **1**. According to the NBO results, there is a three-centered bond in this structure that enhances the stability of this neutral together with the π-electron delocalization. The most stable anionic structure $\mathbf{1}^-$ has an arrangement of atoms similar to that of the neutral **1**, while upon the addition of an electron, the number of bonds increases from 5 to 7 in this anion. There are also π-electron delocalization and a three-centered bond in it.

The magnetic criterion, NICS values, has been computed for the structures **1**, $\mathbf{1}^+$, and $\mathbf{1}^-$, as well as the trigonal bipyramid structures **8**, $\mathbf{7}^+$, and $\mathbf{7}^-$ at the B3LYP/6-311+G* level of theory. The results show that the structures $\mathbf{7}^+$ and **8** are both antiaromatic and the structure $\mathbf{7}^-$ is nonaromatic. The negative NICS values of the planar five-membered ring structures **1**, $\mathbf{1}^+$, and $\mathbf{1}^-$ indicate their aromatic characters. Among them, the structure $\mathbf{1}^+$ has the highest degree of aromaticity with a larger NICS value than those of **1** and $\mathbf{1}^-$. The highly aromatic character and the multicentered σ centripetal bond of the lowest-energy B_5^+ isomer are responsible for the special stability of this cation. Therefore, B_5^+ can be proposed as a good candidate for synthesis.

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