3382 J. Phys. Chem. A **2009,** *113,* 3382–3386

Structure and Aromaticity of $B_6H_5^+$ Cation: A Novel Borhydride System Containing Planar Pentacoordinated Boron

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Received: October 30, 2008; Revised Manuscript Received: January 22, 2009

A novel structural pattern: two-dimensional, five-membered ring-like boron hydride system $B_6H_5^+$, which contains both planar tetra- and pentacoordinated boron (ptB and ppB) was designed and investigated at [B3LYP, MP2(Full) and CCSD(T,FC)]/6−311+G(d,p) theoretical levels. The results indicate that both degenerate ppB $B_6H_5^+$ configurations A (D_{5H},$^1A_1'$) and B (C_{2v},$^1A_1$) are energetically favorable, sharing the lowest energy comparison with other isomers considered in this work. The computed considerably large smallest vibrational frequencies [197.5 and 197.4 cm^{-1}, respectively at MP2 (full) level], HOMO−LUMO energy separations [10.99−11.03 eV computed at MP2 (full) level], and fairly large endothermic dissociation reaction energies suggest they are promising candidate molecules for experimental detection. The detailed molecular orbital analysis, natural bond orbital analysis, magnetic susceptibility anisotropy, and NMR chemical shift analyses confirmed that the two low-energy ppB molecules exhibit strong aromaticities.

1. Introduction

Aromaticity,[1−9] one of the most central and useful concepts, was often used to describe cyclic, planar, and conjugated organic molecules, such as benzene (C_6H_6) the cyclopentadienyl anion (C_5H_5-) and the relative compounds possessing $4n + 2\pi$ electrons. On the basis of experimental and theoretical evidence of aromaticity in M_4^{2-} (M = Al, Ga, In)[5,6] dianion and XAl_3^- (X = Si,Ge, Sn, Pb),[7] as found by Wang's group, aromaticity and antiaromaticity were extended to the regime of all-metal clusters,[8] although, the anti/aromatic characters of some molecules are still debated. For example, for the reported "antiaromatic" $Li_3Al_4^-$ anion,[9] Chen et al. claimed that it is net *aromatic* rather than *antiaromatic*! They thought the true antiaromatic all-metal clusters, such as Sn_6^{2-},[10] have long existed experimentally but have escaped recognition. Now, as more and more ring-like inorganic systems[3,5−13] with anti/aromatic characters have been designed and approved, which indeed shows that the anti/aromaticity category can be extended from conventional organic species into inorganic counterparts.

The suggested methods to reduce the strain energies of the ptC molecule were proposed by Hoffmann,[14] Alder, and Wilcox in 1970. Collins and co-workers presented a systematic computational investigation and identified the first molecule with ptC minima[15] in 1976. Later, in 1977, the first experimental example[16] of a ptC was reported by Cotton and Millar. However, the smallest possible (penta-atomic) tetracoordinate planar carbon-containing molecules, with ligands different from carbon, were proposed by Boldyrev and Schleyer (SB)[17] in 1991 and were experimentally realized by Wang and Boldyrev.[18] In 2000, Exner and Schleyer reported a study on the stability of planar hexacoordinate carbon.[19] Recently, substantial efforts and progress have been made in the design and synthesis of systems containing hypercoordinate planar carbon (hpC)[18−47] by overcoming the inherent preference for tetrahedral bonding. Such achievements of novel hpC molecules dramatically inspired the quest for systems[48−55] containing other planar hypercoordinated main group elements. The first molecule containing planar hexacoordinate boron was predicted by Bonacic−Koutecky[56] et al. in 1991. Further examples[57] were subsequently reported. Stable planar structures of the nonclassical compounds $BB_6(CH)_3$ and $BB_6X_2^-$ (X = NH, O)[58] containing a hexacoordinated central boron atom were predicted by Minkin in 2001. In 2003, Zhai et al.[59] presented experimental and theoretical evidence that B_8^- and B_9^- anions clusters are perfectly planar molecular wheels with a hepta- or octa-coordinated central boron atom, respectively. Most recently, Pei et al.[60] theoretically presented a series of planar tetra-, penta-, and hexacoordinate carbon−boron mixed clusters. Some neutral all-boron aromatic clusters with planar hypercoordinate boron[61] were established in terms of topological resonance energy. Hydrogenated small boron clusters were studied. Ricca and Bauschlicher[62] theoretically characterized cationic B_nH^+ clusters. Small systems[63] B_2H^+, $B_2H_2^+$, and $B_3H_2^+$ were presented by Curtiss and Pople. Larger B_nH_n species and the closo-borane dianions, $B_nH_n^{2-}$, were also explored by many groups.[64−72] However, most boron hydrides adopt three-dimensional aromatic structures.[70,71] Two-dimensional species with hypercoordinate planar atoms are considered to be unusual, requiring special explanation. To the best of our knowledge, neither experimental nor theoretical attention has been paid to the planar boron hydride molecule with planar hypercoordinate boron. In this work, the singlet planar pentagonal geometry of $B_6H_5^+$ cation was theoretically validated to be favorable in energy, which contains a central ppB with five surrounding ptBs and exhibits strong aromaticity.

II. Theoretical Calculations

All calculations were carried out using the Gaussian98 program.[73] First, various possible initial structures were designed

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10.1021/jp809599z CCC: $40.75

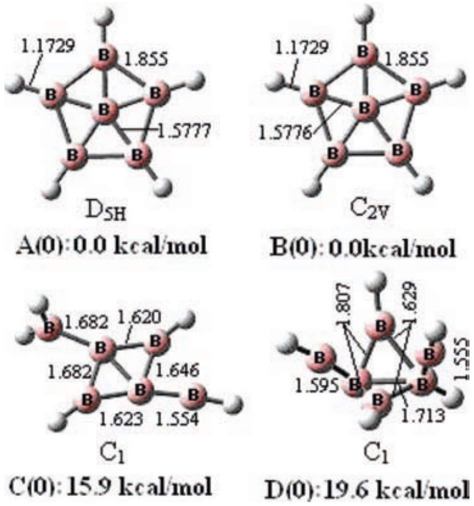

Figure 1. Optimized structures, number of imaginary frequencies (values in parentheses), and relative stability of four singlet lowest-energy $B_6H_5^+$ isomers with important bond parameters (Å) at MP2 (full)/6−311+G(d,p) level.

arbitrarily and fully optimized at B3LYP/6−311+G(d,p) with the imaginary frequencies checked at the same level to characterize stationary points as minima or transition states. Further optimizations were refined at MP2 (full)/6−311+G(d,p) level. Then accurate total energies (single-point calculations) of several lowest-energy MP2 optimized geometries were estimated at CCSD(T, FC)/6−311+G(d,p) levels. The natural bond orbital (NBO)[74] analyses, performed at MP2 (full)/ 6−311+G (d, p) levels, were used to ascertain the electronic structures and bonding properties of molecules. To assess the aromatic character, we performed magnetic susceptibility anisotropy (X_{anis})[2] and NMR (GIAO)[75] chemical shifts calculations to predict magnetic properties. X_{anis} is the difference between the perpendicular and average in-plane component of the magnetic susceptibility tensor. The nucleus independent chemical shifts (NICS),[76−78] proposed by Schleyer and co-workers, defined as the negative of the absolute magnetic shielding computed, were also evaluated at some interesting points of the ppB species. The X_{anis} values were calculated with the CSGT-B3LYP/6−311+G(d,p) approach and NICS values with the GIAO-B3LYP/6−311+G(d,p) method based on the corresponding optimized structures.

III. Results and Discussion

Optimized Structures. Optimization calculations using B3LYP and MP2 (full) methods on more than 40 $B_6H_5^+$ isomers (see Supporting Information) were performed with the 6−311+G(d,p) basis set. Theoretical results show that four isomers (labeled A, B, C, and D, respectively) are the most energetically favorable structures, depicted in Figure 1. The results also show that the planar pentagonal skeleton A (D_{5H},$^1A_1'$) and B (C_{2V},$^1A_1$) share the identical, lowest energy both at aforementioned two levels. We find that the second and third lowest isomers C and D are three-dimensional geometries. They are [15.9 and 19.6 kcal/mol, respectively] higher in energy than A and B at MP2(full)/6−311+G(d,p) level. Further single-point CCSD(T,FC)/6−311+G(d,p) calculations show that C and D are more unstable (17.0 and 23.3 kcal/mol, respectively) than A and B. Isomers A, B, C, and D are all found to be local minima with the corresponding smallest vibrational frequencies (SVFs) [158.6, 159.9, 96.0, and 189.5 cm^{-1} computed at B3LYP level]. The SVFs for A and B were further testified to be 197.5 and 197.4 cm^{-1}, respectively, at the MP2 (full)/6−311+G (d,p) level. They are large enough to guarantee the two minima. Moreover, we did fail to gain the corresponding triplet frames for A, C, and D, and we obtained an unstable triplet for B (C_{2v}, $^3B_1$), which is 52.9 kcal/mol higher in energy than the singlet A or B at MP2 (full)/6−311+G (d, p) level. In order to determine the relative stability of A and B, more theoretical levels were employed to assess the total electronic energies (E_{tot}). All computed E_{tot}'s and their corresponding HOMO−LUMO energy gaps (E_{gap}) were summarized in Table 1. We find that the E_{tot}'s of isomers A and B are always degenerated only with negligible differences by ranging from 0.00 to 0.002 kcal/mol. These minor differences in energy possibly arise from inherent computational errors. This case is obviously different from those for the aluminum-stabilized[79,80] planar pentacoordinated boron cluster: Al_5B. Because we find that the E_{tot} of the C_{2v} Al_5B frame is always lower than that of the D_{5h} counterpart. The mean value of absolute E_{tot} differences between the two Al_5B isomers for eight same levels (see Table 1) is 0.083 kcal/mol with the maximal energy difference $E_{\text{dif}} = 0.138$ kcal/mol at CCSD(T,FU)/6−311+ G(d,p) level. However, the D_{5h} and C_{2v} ppB $B_6H_5^+$ isomers are identical not only structurally but also energetically. Therefore, we carried out various discussions both for A and B coequally.

TABLE 1: Total Electronic Energies (E_{tot} in Hartree) and the HOMO-LUMO Energy Gaps (E_{gap} in eV) for $B_6H_5^+$ Isomer A and B with Eight Theory Levels: (1) B3LYP/6-311+G(d,p), (2)B3PW91/6-311+G(d,p), (3) PW91PW91/6-311+G(d,p), (4)MP2(full)/6-311+G(d,p), (5) MP2(full)/6-311+G(2df,p), (6)MP2(full)/6-311+G(3df,3dp), (7) CCSD(T,FC)/6-311 +G (d,p), and (8)CCSD(T,FU)/6-311+G(d,p)

	A		B	
theory levels	E_{total}	E_{gap}	E_{total}	E_{gap}
1	−151.7780988	4.49	−151.7780991	4.49
2	−151.7009075	4.46	−151.7009083	4.46
3	−151.6603585	2.76	−151.6603588	2.76
4	−151.2865161	10.99	−151.2865159	10.99
5	−151.3621367	11.03	−151.3621367	11.03
6	−151.3877600	11.03	−151.3877601	11.04
7	−151.2555587	10.99	−151.2555540	10.99
8	−151.3708917	10.99	−151.3708885	10.99

Other isomers were also located, but all have higher energies than the above four isomers. They are all provided in the Supporting Information. It is worth noting that, for complicated molecules like $B_6H_5^+$, it is not convincing to claim that the above planar skeletons A ($^1A_1'$, D_{5H}) and B ($^1A_1$, C_{2v}) are global minima, although both have the lowest energy comparison with other isomers considered herein. Although a further global minimum search is important, unfortunately, we are unable to do such a search due to the lack of necessary computational resources.

However, it is interesting to note that both A and B are ppB molecules, which contain five planar tetracoordinate boron atoms (ptB) simultaneously. The computed peripheral B−B lengths (B3LYP:1.844 Å; MP2:1.855 Å) are lying between the reported values of the single B−B bond [1.706(11)−1.859(6) Å],[81] showing that such peripheral B−B interactions are only B−B singlet bonds. But the radial B−B distances [B3LYP: 1.5686−1.569 Å; MP2 (full): 1.5776−1.5777 Å] both for A and B species. They are shorter than those reported for B=B double bonds [1.62−1.64 Å][82] in the "$B_2R_4^{2-}$" dianion. Whereas they are longer than the lengths (1.455−1.481 Å) for B≡B triplet bonds,[83] suggesting the existence of robust interactions and the electron delocalization across these radial bonds.

Emphatically, in the ppB species A and B, the hydrogenated B_5 ring and atomic radii of the central ppB match harmoniously. However, such B_5 ring is too small to accommodate the larger atoms. For example, for optimized D_{5h} symmetry $Li(B_5H_5)^-$ and $Be(B_5H_5)$ structures, each of them has one imaginary frequency [−545.4, −343.1 cm^{-1}, respectively, at B3LYP/6−311+G(d,p) level]: one out-of-plane deformation, following this imaginary mode resulting in pyramidal three-dimensional configuration. This reveals the importance of the geometrical fit for designing stable boron rings with planar hypercoordinate elements.

Chemical Viability.[84] The stability of the ppB $B_6H_5^+$ molecules was also evaluated according to the three criteria proposed by Hoffmann[84] et al. very recently. First, the dissociation reaction energies (DEs) have been estimated at B3LYP/6−311+G(d,p) level according to the following reactions (based on the energies after ZPE correction):

$$B_6H_5^+ \rightarrow BH_2^+ + 5/2B_2 + 3/2H_2 \quad DE = 498.14\ \text{kcal/mol} \tag{1}$$

$$B_6H_5^+ \rightarrow B_2H_2^+ + 2B_2 + 3/2H_2 \quad DE = 434.86\ \text{kcal/mol} \tag{2}$$

$$B_6H_5^+ \rightarrow B_2H_3^+ + 2B_2 + H_2 \quad DE = 451.22\ \text{kcal/mol} \tag{3}$$

$$B_6H_5^+ \rightarrow B_2H_4^+ + 2B_2 + 1/2H_2 \quad DE = 393.14\ \text{kcal/mol} \tag{4}$$

$$B_6H_5^+ \rightarrow B_2H_5^+ + 2B_2 \quad DE = 346.00\ \text{kcal/mol} \tag{5}$$

Here, the most stable states for gaseous positive ions (BH_2^+, $B_2H_2^+$, $B_2H_3^+$, $B_2H_4^+$, $B_2H_5^+$), B_2, and H_2 are considered. As we can see, all of the reactions are considerably endothermic for the dissociation of the ppB $B_6H_5^+$ system since the five DEs are fairly large positive values (≥346.00 kcal/mol). Second, both A and B have no imaginary frequencies. Moreover, the computed smallest vibrational frequencies are reasonably large. They are all larger than 159 cm^{-1} at the MP2 level. Third, for A and B, the fairly large HOMO−LUMO energy gaps [10.99−11.03 eV computed at MP2 (full)/[6−311+G(d,p), 6−311+G (2df,p), 6−311+G(3df,3pd) levels] strongly suggest high stability of the ppB systems. Note that we did not expect both A and B to keep good chemical stability under ambient atmospheric conditions (with H_2O, $^3O_2$ and N_2) because therein most of the borhydride molecules are active.

Molecular Orbital Analysis. In order to better understand the planarity and stability of $B_6H_5^+$, we analyzed the spatial distribution of the valence molecular orbitals. There are 22 valence electrons with the electronic configurations $1a_1'^{(2)}1e_1'^{(2)}$-$1e_1'^{(2)}2a_1'^{(2)}1e_2'^{(2)}1e_2'^{(2)}2e_1'^{(2)}2e_1'^{(2)}1a_2''^{(2)}2e_2'^{(2)}2e_2'^{(2)}$ for A and $1a_1^{(2)}2a_1^{(2)}1b_2^{(2)}3a_1^{(2)}4a_1^{(2)}\ 2b_2^{(2)}\ 5a_1^{(2)}3b_2^{(2)}1b_1^{(2)}4b_2^{(2)}6a_1^{(2)}$ for B. Because the orders and pictures of eleven occupied valence MOs for A and B are found to be very similar, we take the MOs pictures for A as an example, which are displayed in Figure 2 using the MP2(full)/6−311+G(d,p) method. The HOMO-1(a_2''), doubly occupied, is a fully delocalized π orbital formed from the out-of-plane p_z atomic orbitals and renders π aromaticity. However, the doubly occupied HOMO-4 (a_1') is a σ-type MO formed from the in-plane s and $p_{x,y}$ atomic orbitals. Such multicentric occupation of the ligand-ligand bonding HOMO-4 provides enough additional bonding to play the key role in maintaining planarity. The rest of the MOs are either σ-type bonding, antibonding or lone pairs. A significant contribution of the perpendicular $2p_z$ orbital of the central B atom to the π-orbital [HOMO-1] is found, which is consistent with the electronic stabilization mechanism proposed by Hoffmann[14] et al. Orbitals HOMO-1 ($1b_1$) and HOMO-4 ($3a_1$) of B are also similar π, σ MOs, respectively. Emphatically, these very MOs hold the key to understand the planarity and bonding of A and B. On the basis of the above MO analysis, we may initially claim that A and B exhibit π aromaticity.

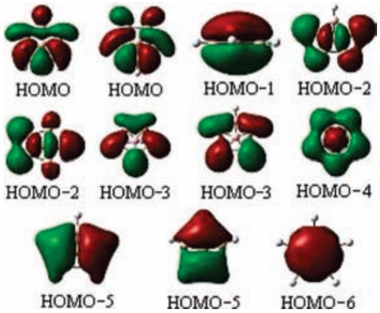

Figure 2. Valence molecular orbitals of isomer A of the $B_6H_5^+$

NBO Analyses. To gain more insights into electronic structure and bonding properties, the natural bond orbital (NBO) analyses were performed at [MP2(full)]/6−311+ G (d, p) level. The natural charges of A and B are $Q = 0.389$ e for each peripheral boron (B_{per}), $Q = 0.011$ e for each Hydrogen, and $Q = -0.998$ e for central boron (B_{cen}). Such charge distributions obviously reveal that ppB atom accepts charges through electron transfer by five peripheral ligand B atoms. Moreover, NBO also reveals significant ppB $2p_z$ orbital occupancies. Because the electronic population of the B_{cen} atom valence shell is $2s^{0.59}2p_x^{1.11}2p_y^{1.11}2p_z^{1.17}$ and the B_{per} is $2s^{0.76}2p_x^{0.81-0.88}2p_y^{0.80-0.88}\ 2p_z^{0.16}$ for A and B. Sum of electrons of p_π for both A and B are equal to two, confirming the existence of doubly occupied delocalized π MOs. The delocalization of the two p_π electrons is more sufficient than those for a number of ptC derivatives,[47] involving beryllium ligand atoms; and such density on the central boron helps to stabilize the ppB arrangement. The NBO analyses also show that there is deviation from the two-center two electron (2c−2e) pictures both for A and B. The occupation numbers (ONs) for A and B are just 1.192−1.334 e for all B_{per}—B_{Cen} radial bonds. In an ideal 2c−2e bond, the ON should be 2.00 e. These profound deviations from the normal 2c−2e bonding pictures are further demonstrations of appreciable electron density delocalization across these radial B—B bonds. At the same time, it also suggests that isomers A and B are aromatic systems. The B_{cen}—B_{per} Wiberg bond indices (WBIs) (0.759 for A and B) and the adjacent B_{per}—B_{per} WBIs (0.585 for A and B) indicate that significant bonding interactions exist not only between the B_{per}—B_{per} bonds but also the B_{cen}—B_{per} ones. These very bonds actually play the key role in maintaining planarity and stability of A and B. The total WBIs of the central ppB atoms (3.804) and the ptBs (3.137) in A and B are close to 4, which shows clearly that the traditional octet rule is not violated despite of the planar pentacoordination.

Magnetic Properties. NICS is an easy and efficient criterion to identify aromatic nature. A large negative NICS at the ring center (or inside and above the molecular plane) implies the presence of diamagnetic ring currents. However, the deshielding effect by the ring current should provide positive NICS values outside the molecular frame. Hereby, we calculated NICS values not only inside [$NICS_{in}$ (0 Å) = −6.3 ppm] or 1 and 2 Å above

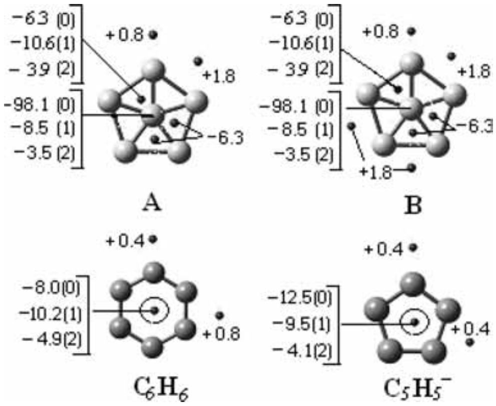

Figure 3. Nucleus-independent chemical shifts (NICS) in ppm for isomer A and B of $B_6H_5^+$ and aromatic organic compounds (C_6H_6 and $C_5H_5^-$) calculated with the GIAO-B3LYP/6−311+G(d,p) level. The values in parentheses represent the distances in Å from the molecular plane. All hydrogen atoms were omitted.

the molecular plane [$\mathrm{NICS_{in}}$ (1 Å) = −10.6 ppm, $\mathrm{NICS_{in}}$ (2 Å) = − 3.9 ppm], but also at 2 Å outside the molecular frame [$\mathrm{NICS_{out}}$ (2 Å) = +1.8 or +0.8 ppm]. All calculated points and the results are shown in Figure 3, together with those for C_6H_6 and $C_5H_5^-$. NICS values for these organic molecules are large negative inside and above the carbon ring and positive outside of the ring, implying that delocalized electrons in both compounds provide diamagnetic ring currents. For A and B, we find that the total NICS values both at inside and above sites are also large negative and its maximum values are at the point 1 Å above the planes, which are similar to those for the C_6H_6.[85] Therefore, the $\mathrm{NICS_{in}}$ (1 Å) values in vertical direction better suite for evaluation of their aromaticities. The negative $\mathrm{NICS_{in}}$ (1 Å) values for A and B are very close to those for C_6H_6 and $C_5H_5^-$ using the same method level. The negative inside and above the rings and positive outside values adequately prove that the diamagnetic ring current effect, characteristic for aromticity, exists both in A and B. Most importantly, we refined the nuclear magnetic resonance (NMR) chemical shifts calculations on these planar molecules at GIAO-B3LYP/6−311++G(3df)//B3LYP/6−311++G(3df) level and found the computed results are in good agreement with those obtained by B3LYP/6−311+G(d,p)//B3LYP/6−311+G(d,p) level used in ref 86. We find that the computed absolute magnetic chemical shifts for B_{per}, B_{cen} atoms are −41.80 and −98.10 ppm, respectively. In ^{11}B NMR, BF_3OEt_2 is customarily used as a reference (0.00 ppm by definition) with its computed value of −101.95 ppm[86] at the aforesaid level of theory. Hereby, we can deduce that the relative chemical shifts of the inner B atom appear at 3.85 ppm and the other surrounding boron atoms at 60.15 ppm. It is obvious that the NMR chemical shift of the central boron atom is largely upfield-shifted as compared to the peripheral boron atoms. Such a great difference in relative chemical shift of the two different kinds of boron atoms should adequately prove the existence of the diamagnetic currents. At the same time, the calculated absolute nuclear shieldings of five outer H atoms are −20.7 ppm. In ^1H NMR, TMS is often used as referenced molecule (the calculated referenced value at −31.97 ppm[86]). Therefore, the relative chemical shifts of these H atoms appear at 11.27 ppm. They are downfield-shifted by 3.7 ppm relative to those of the external protons in classical aromatic benzene (−24.40 ppm) at the same theoretical level. This deshielding of the $B_6H_5^+$ protons may also be a manifestation of the molecular ring current induced by an external magnetic field. Furthermore, magnetic susceptibility anisotropy[87] has been advocated as another criterion of aromaticity early. Planar aromatic compounds often have quite large negative $X_{\mathrm{anis.}}$ Here the calculated X_{anis} values at B3LYP/6−311+G(d,p) for planar A and B are −50.4 and −52.1 (ppm, cgs), respectively. Such large negative values again indicate that A and B have high degree of the aromaticity.

IV. Conclusions

In summary, we first proposed a novel low-energy ppB $B_6H_5^+$ structural pattern theoretically. On the basis of detailed MO, NBO, and NMR analyses, we claimed that both the D_{5h} and C_{2v} planar pentacoordinated boron molecules exhibit aromatic characters. Just like many ring-like hypercoordinated planar systems proposed, the ring and central atomic radii must fit each other harmoniously. In addition, the radial/π electron delocalization dominates the relative stability of the hypercoordinate planar molecule. Both requirements are important factors for the planarity and stability for the ppB minima. Several planar hypercoordinated molecules, such as CAl_3Si^- and CAl_3Ge^-[18], [29]CAl_4^-, [54]B_8^-, and B_9^-, etc. were observed in the gas-phase. Therefore, it is our strong hope that the planar species investigated herein can be verified experimentally in the future. We believe that the above findings are important in fundamental research and may shed new insight into boron chemistry and materials science.

Acknowledgment. H.-L.Yu thanks Professor Si-Dian Li for encouragement and inspiration and is also grateful to Jun-Sheng Hang and Yan Chen for providing excellent research conditions.

Supporting Information Available: Structures, total electronic energies, symmetries, and Cartesian coordinates (in Å) of all isomers considered for $B_6H_5^+$ in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP809599Z