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Articles

Hexa-, Hepta-, and Octacoordinate Boronium Ions:[1] BH$_6^+$, BH$_7^{2+}$, and BH$_8^{3+}$

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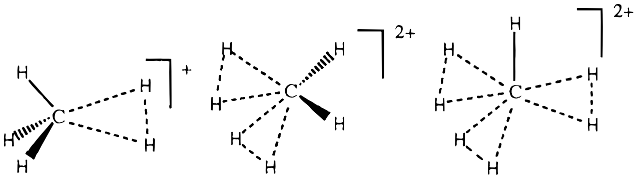
The parent hexa-, hepta-, and octacoordinate boronium ions, BH$_6^+$ (**1**), BH$_7^{2+}$ (**4**), and BH$_8^{3+}$ (**6**), respectively, were found as stable minima by *ab initio* MP2/6-31G** and QCISD(T)/6-311G** level of calculations. The C_{2v} symmetrical structure **1** with two 3c−2e bonds and C_{3v} symmetrical structure **4** with three 3c−2e bonds are isostructural with their isoelectronic carbon analogues CH$_6^{2+}$ and CH$_7^{3+}$, respectively. Eight hydrogen atoms of T_d symmetrical structure **6** are bonded to the boron atom by four 3c−2e bonds. The protonation of BH$_5$ to form BH$_6^+$ was found to be strongly exothermic. The reaction of BH$_4^+$ (**3**) and H$_2$ might be a suitable way to generate BH$_6^+$ (**1**) in the gas phase.

Introduction

There is continued theoretical[2] and experimental[3] interest in higher coordinated[4] main group compounds. Schmidbaur and co-workers have prepared wide variety of gold complexes of higher-coordinated boron,[5] carbon,[6] nitrogen,[7] oxygen,[8] phosphorus,[9] and sulfur[10] and determined their X-ray structures. These include monopositively charged trigonal bipyramidal[6a] {[(C$_6$H$_5$)$_3$PAu]$_5$C}$^+$ and even the dipositively charged octahedral[6b] gold complex {[(C$_6$H$_5$)$_3$PAu]$_6$C}$^{2+}$, which contain five- and six-coordinate carbons, respectively, representing the isolobal analogues of CH$_5^+$ and CH$_6^{2+}$.

Chart 1



CH$_5^+$ C$_s$ CH$_6^{2+}$ C$_{2v}$ CH$_7^{3+}$ C$_{3v}$

The calculated preferred structure[11] of the parent five-coordinate carbocation, i.e protonated methane CH$_5^+$, is C_s symmetrical[12] (Chart 1) with a three-center two-electron (3c−2e) bond. The structure can be viewed as a proton inserted into one of the σ C−H bonds of methane to form a 2e−3c bond between carbon and two hydrogen atoms. At the same time, ready bond to bond (isotopal) proton migration makes it a rather fluxional molecule, the process involving low barriers.[13] The BH$_5$ molecule, which is isoelectronic with CH$_5^+$, is also C_s symmetrical as predicted[14,15] by high-level *ab initio* calculations. The first experimental gas phase observation (by infrared spectroscopy) of BH$_5$ was, however, only recently reported.[16] Olah et al. studied[17] the protonation of BH$_4^-$ to obtain evidence *via* H−D exchange for the intermediacy of BH$_5$ (or its isotopomers). However, calculations show that hydrogen scrambling in BH$_5$ prior to dissociation into BH$_3$ and H$_2$ is very unlikely.[14] The calculated[18] parent six-coordinate carbocation, diprotonated methane (CH$_6^{2+}$), has two 3c−2e bonding interactions in its minimum-energy structure (C_{2v}) (Chart 1). We recently reported[19] that the calculated parent seven coordinate carbocation, triprotonated methane (CH$_7^{3+}$), has three 3c−2e bonding interactions in its minimum-energy structures (C_{3v}). Although the natures of these interactions are different from

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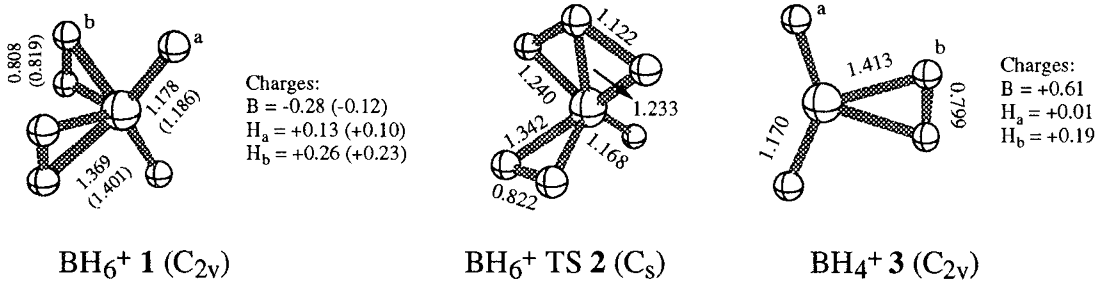
Table 1. Total Energies (−au), ZPE,[a] and Relative Energies (kcal/mol)

	MP2/6-31G**// MP2/6-31G**	G2	QCISD(T)/6-311G**// QCISD(T)/6-311G**	CCSD(T)//cc-pVTZ// QCISD(T)/6-311G**
BH_6^+ (**1**)	27.90408 (33.7)	27.93775	27.95055	27.97525
BH_6^+ TS (**2**)	27.88918 (33.0)	27.92322		
BH_4^+ (**3**)	26.71432 (21.7)	26.74471		
BH_7^{2+} (**4**)	27.87218 (38.6)	27.89774	27.92100	27.94471
BH_7^{2+} TS (**5**)	27.86237 (37.3)	27.89018		
BH_8^{3+} (**6**)	27.54456 (36.4)	27.58341	27.60543	27.62745
BH_3	26.48616 (16.0)	26.52482		
BH_5	27.64712 (27.2)	27.69165		
BH_5^{2+}	26.62656 (25.5)	26.65272		
H_3^+	1.32428 (12.6)	1.32445		

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93.



BH_6^+ **1** (C_{2v}) BH_6^+ TS **2** (C_s) BH_4^+ **3** (C_{2v})

Figure 1. MP2/6-31G** (QCISD(T)/6-311G**) calculated structures of **1**−**3** and NBO charges of **1** and **3**.

one molecule to another, these results indicate the importance 3c−2e interactions in protonated alkanes and other compounds. The parent octacoordinate carbocation, tetraprotonated methane (CH_8^{4+}), is not stable and remains even computationally elusive,[19] as charge−charge repulsions appear to have reached their prohibitive limit. Lithiated penta- and hexacoordinated carbocations, CLi_5^+ and CLi_6^{2+}, respectively, were also calculated to be stable.[20]

We report now our study on elusive isoelectronic boron analogues of higher-coordinate carbocations, i.e. BH_6^+, BH_7^{2+}, and BH_8^{3+}. Because of their structural similarity,[4] we also compared their structures with those of their corresponding carbon analogues.

Calculations

All calculations were performed with the Gaussian 94 program system.[21] The geometry optimizations and frequency calculations were performed at the MP2/6-31G** and QCISD(T)/6-311G** levels. From calculated frequencies, the optimized structures were characterized as minima (NIMAG = 0) or transition structures (NIMAG = 1). For improved energy, the Gaussian-2 (G2) energies[22] and single-point energies at CCSD(T)/cc-pVTZ[23] level on QCISD(T)/6-311G** optimized geometries were computed. MP2/6-31G** geometrical parameters and G2 calculated energies will be discussed throughout, unless stated otherwise. Atomic charges were obtained using the natural bond orbital analysis[24] (NBO) method.

Scheme 1

		ΔH (kcal/mol)[a]
$BH_5 + H^+ \longrightarrow BH_6^+$ (**1**)	(1)	-154.4
$BH_3 + H_3^+ \longrightarrow BH_6^+$ (**1**)	(2)	-55.5
$BH_3 + H^+ \longrightarrow BH_4^+$ (**3**)	(3)	-137.9
BH_4^+ (**3**) + $H_2 \longrightarrow BH_6^+$ (**1**)	(4)	-16.7
BH_6^+ (**1**) + $H^+ \longrightarrow BH_7^{2+}$ (**4**)	(5)	+25.1
BH_4^+ (**3**) + $H_3^+ \longrightarrow BH_7^{2+}$ (**4**)	(6)	+107.5
BH_7^{2+} (**4**) + $H^+ \longrightarrow BH_8^{3+}$ (**6**)	(7)	+197.2
$BH_5^{2+} + H_3^+ \longrightarrow BH_8^{3+}$ (**6**)	(8)	+247.1

[a] *with the G2 method*

Results and Discussion

BH_6^+. The C_{2v} symmetric form **1** is found to be the only stable minimum for BH_6^+. Structure **1** is isostructural with CH_6^{2+}.[18] Six-coordinated BH_6^+ (**1**) contains two 3c−2e bonds and two 2c−2e bonds (Figure 1). The B−H bond distance of 3c−2e interactions is 1.369 Å. This is slightly shorter than that found in the 3c−2e B−H bond (1.427 and 1.444 Å) of the C_s structure of BH_5 at the same MP2/6-31G** level.

Protonation of BH_5 to form **1** is calculated to be remarkably exothermic by 154.4 kcal/mol (eq 1, Scheme 1), which is even 26.4 kcal/mol more exothermic than the protonation of methane and only 8.7 kcal/mol less exothermic than of protonation of water. No transition state for the protonation process could be located. However, we have located a transition structure, **2** (Figure 1), for intramolecular hydrogen transfer in cation **1**. Structure **2** lies 9.1 kcal/mol higher in energy than structure **1**. Thus, hydrogen scambling in cation **1** through transition state **2** has significant kinetic barrier. The dissociation of **1** into BH_3 and H_3^+ (eq 2) is calculated to be endothermic by 55.5 kcal/mol (Scheme 1).

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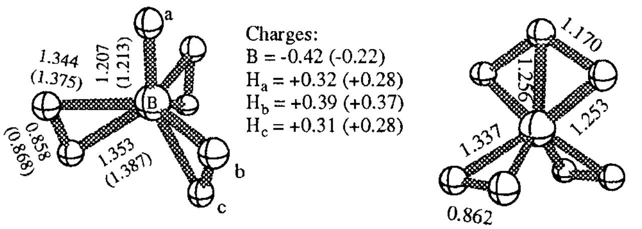
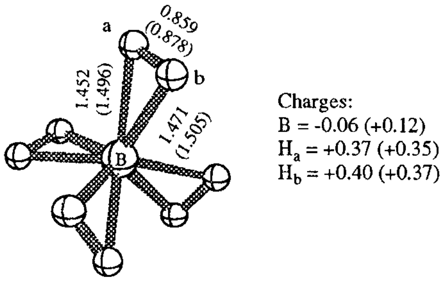


BH_7^{2+} **4** (C_{3v}) BH_7^{2+} TS **5** (C_{2v})

Figure 2. MP2/6-31G** (QCISD(T)/6-311G**) calculated structures of **4** and **5** and NBO charges of **4**.



BH_8^{3+} **6** (T_d)

Figure 3. MP2/6-31G** (QCISD(T)/6-311G**) calculated structures and NBO charges of **6**.

In a previous study Olah et al. investigated[17] the protonation of BH_4^- to obtain evidence *via* H–D exchange for the intermediacy of BH_5 (or its isotopomers). Strong acids such as H_2SO_4 and HF were used in the experiments. However, hydrogen scrambling in BH_5 prior to dissociation into BH_3 and H_2 was shown to be very unlikely.[14] It is now probable that indeed BH_6^+ is formed in the acidic solutions and is in part responsible for the observed scrambling.

We also considered the related reaction of BH_3 with H^+ to give BH_4^+ (**3**). The reaction is calculated to be −137.9 kcal/mol exothermic (eq 3). The calculated structure of **3** (Figure 1) is isostructural with the reported[25] planar C_{2v} structure of CH_4^{2+}. Similar to the carbon atom in CH_4^{2+}, the sp^2-hybridized boron atom of **3** contains a three-center two-electron (3c–2e) bond and an empty p orbital perpendicular to the plane of the molecule. The calculated structure of the BH_4 radical is also C_{2v} symmetrical with a 3c–2e bond, but the 3c–2e unit is perpendicular to the plane of the molecule.[26] We then calculated the reaction of BH_4^+ with H_2 (eq 4), which is calculated to be −16.7 kcal/mol exothermic. In comparison, the enthalpy of complexation of BH_3 and H_2 to give BH_5 is estimated to be exothermic by only 1.4 kcal/mol at 0 K and endothermic by 6.8 kcal/mol at room temperature.[14] This indicates that the reaction of BH_4^+ (**3**) and H_2 might be an alternative way (other than protonation of BH_5) to generate BH_6^+ (**1**) in the gas phase.

BH_7^{2+}. Similar to BH_6^+, the C_{3v} symmetric form **4** is also found to be the only minimum for BH_7^{2+}. Structure **4** is a propeller-shaped molecule resembling a complex between BH^{2+} and three dihydrogen molecules, resulting in the formation of three 3c–2e bonds (Figure 2). Boronium ion **4** is isoelectronic as well as isostructural with the computed[19] carbon analogue CH_7^{3+}. The B–H bond distances of 3c–2e interactions (1.344 and 1.353 Å) are slightly shorter than that found in the 3c–2e B–H bonds (1.369 Å) of BH_6^+. Structure **5** (Figure 2) was identified as the transition state for intramolecular hydrogen transfer in the trication. Structure **5** lies only 4.7 kcal/mol higher in energy than structure **4**. Hydrogen scrambling in **4** therefore is facile. Similar hydrogen scrambling was calculated to be even more facile for CH_7^{3+}.[19] The dissociations of **4** into BH_6^+ and H^+ (eq 5) and into BH_4^+ and H_3^+ (eq 6) are calculated to be exothermic by 25.1 and 107.6 kcal/mol, respectively (Scheme 2).

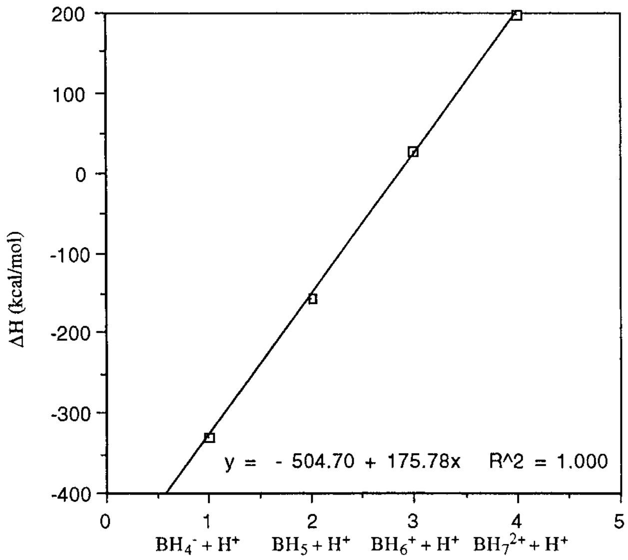


Figure 4. Plot of gas phase protonation energy (G2) vs reaction coordinate.

BH_8^{3+}. We recently reported[19] that tetraprotonated methane, CH_8^{4+}, does not correspond to an energy minimum at the MP2/6-31G** level. This in all probability is due to strong charge-charge repulsions which appear to have reached their prohibitive limit. Our present investigation shows that compared to CH_8^{4+} tetracation, the isoelectronic boron analogue, BH_8^{3+} trication **6**, is a energy minimum at the both MP2/6-31G** and QCISD-(T)/6-311G** levels. The structure **6** can be viewed as four dihydrogens (oriented tetrahedrally) complexed with a tripositively charged boron atom, B^{3+} (Figure 3**)**. The B–H bond distances of 3c–2e interactions (1.452 and 1.471 Å.) are about 0.1 Å longer than those of BH_7^{2+} (**4**) (1.344 and 1.369 Å). The dissociations of the trication into BH_7^{2+} and H^+ (eq 7) and into BH_5^{2+} and H_3^+ (eq 8) are is expectedly highly exothermic by 197.2 and 247.1 kcal/mol, respectively (Scheme 1). The planar C_{2v} symmetric structure of BH_5^{2+} with two 3c–2e bonds was recently reported.[1]

We also calculated (MP2/6-31G**) the NBO charges[24] of the BH_5 and boronium ions **1**, **4**, and **6** (**Figures 1–3**). The average hydrogen charges in each of the ions are 0.056, 0.214, 0.345, and 0.383 au, respectively. This indicates that the hydrogen atoms of the **1**, **4**, and **6** cations bear most of the positive charges. We have plotted ΔH values of the protonation of BH_5, **1**, and **4** as well as related the BH_4^- ion in Figure 4. Interestingly, the ΔH values of BH_4^-, BH_5, **1**, and **4** increase linearly with the increases of positive charge (or decrease of negative charge). To better represent this, we have also plotted the relative energies of BH_5, **1**, **4**, and **6** together with the relative energies of $BH_4^+ + H_2$ and $BH_3 + H_2$ in the Figure 5.

One of the goals of this study is to better understand the chemistry of boron compounds in superacids. Olah et al. reported[27] the hydrogen–deuterium exchange of diborane in superacid solution. The probable mechanism involving an

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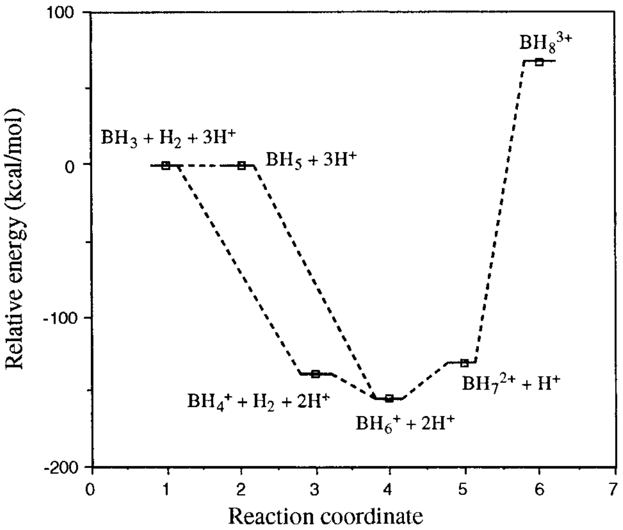

Figure 5. Plot of gas phase relative energy (G2) vs reaction coordinate.

equilibrium with monomeric BH_3 and its deuteriation was considered as unlikely.

$$B_2H_6 \rightleftharpoons 2BH_3 \xrightleftharpoons{FSO_3D\cdot SbF_5} BH_3 + BH_3D^+ \xrightleftharpoons{-H^+} BH_3 + BH_2D \rightleftharpoons B_2H_5D$$

It was concluded "this pathway, however is, unlikely since $[BH_4]^+$ is isoelectronic with the thermodynamically highly unstable $[CH_4]^{2+}$". However, on the basis of our present calculations, hydrogen–deuterium exchange in diborane in superacids can also involve monomeric BH_3 since the protonation of BH_3 is calculated to be strongly exothermic (138 kcal/mol) (Scheme 1).

Conclusions

The present study shows that the parent hexa-, hepta-, and octacoordinated boronium ions BH_6^+ (**1**), BH_7^{2+} (**4**), and BH_8^{3+} (**6**), respectively, are minima on their potential energy surfaces. The calculated structures of **1** and **4** are isostructural with those of their isoelectronic carbon analogues CH_6^{2+} and CH_7^{3+}, respectively. The structures of **1**, **4**, and **6** are stabilized by two, three, and four 3c–2e bonds, respectively. The protonation of BH_5 to form BH_6^+ is calculated to be strongly exothermic. It is suggested that the ion–molecule reaction of BH_4^+ (**3**) and H_2 might be a suitable way to generate BH_6^+ (**1**) in the gas phase. More stabilized analogues, including Schmidbaur-types gold complexes, e.g, $\{[(C_6H_5)_3PAu]_{6-n}BH_n\}^+$, could be also prepared. The possible involvement of the parent boronium ion BH_4^+ in the hydrogen–deuterium exhange of B_2H_6 in superacids was also reconsidered.

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