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Computational study of hydrido boronium dications and comparison with the isoelectronic carbon analogs

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Dedicated to Prof. Kenneth Laali on the occasion of his 65th Birthday and life-long contributions to chemistry

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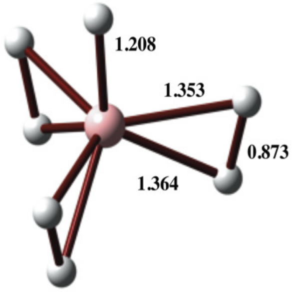
Abstract

Calculations at the CCSD(T)/cc-pVTZ level show that higher coordinate, hydrido boronium dications are viable species despite their charge-charge repulsion. Structure and bonding of the studied boronium dications are discussed and are compared with their isoelectronic carbon analogs. Although the studied boronium dications are thermodynamically unstable towards deprotonation, their computational characterization supports their transient existence.



BH_7^{2+} (C_{3v})

Keywords: Hydrido boronium dications, higher coordinate, two-electron three-center bond, isoelectronic carbon analog

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Introduction

Main group hydrido cations and dications have been a subject of numerous experimental and theoretical investigations.[1-6] A while ago we have reported[7] the calculated structures of parent hexa- and heptacoordinate boronium ions, BH_6^+ and BH_7^{2+}, respectively, with two and three two-electron three-center (2e-3c) bonds. The structures were found to be isostructural with their isoelectronic carbon analogs, CH_6^{2+},[8,9] and CH_7^{3+},[10] respectively. We have also previously investigated the structures and energetics of BH_n^{2+} (n=1-8)[11] and $B_2H_{2n}^{2+}$ (n=1-4)[12] dications at the MP2/aug-cc-pVTZ and QCISD(T)/6-311G** levels, respectively. In continuation of our study of higher coordinate onium ions, we have carried out a study on the structure and bonding of higher coordinate hydrido boronium dications. For comparison, all the structures were calculated at the same CCSD(T)/cc-pVTZ level.

Results and Discussion

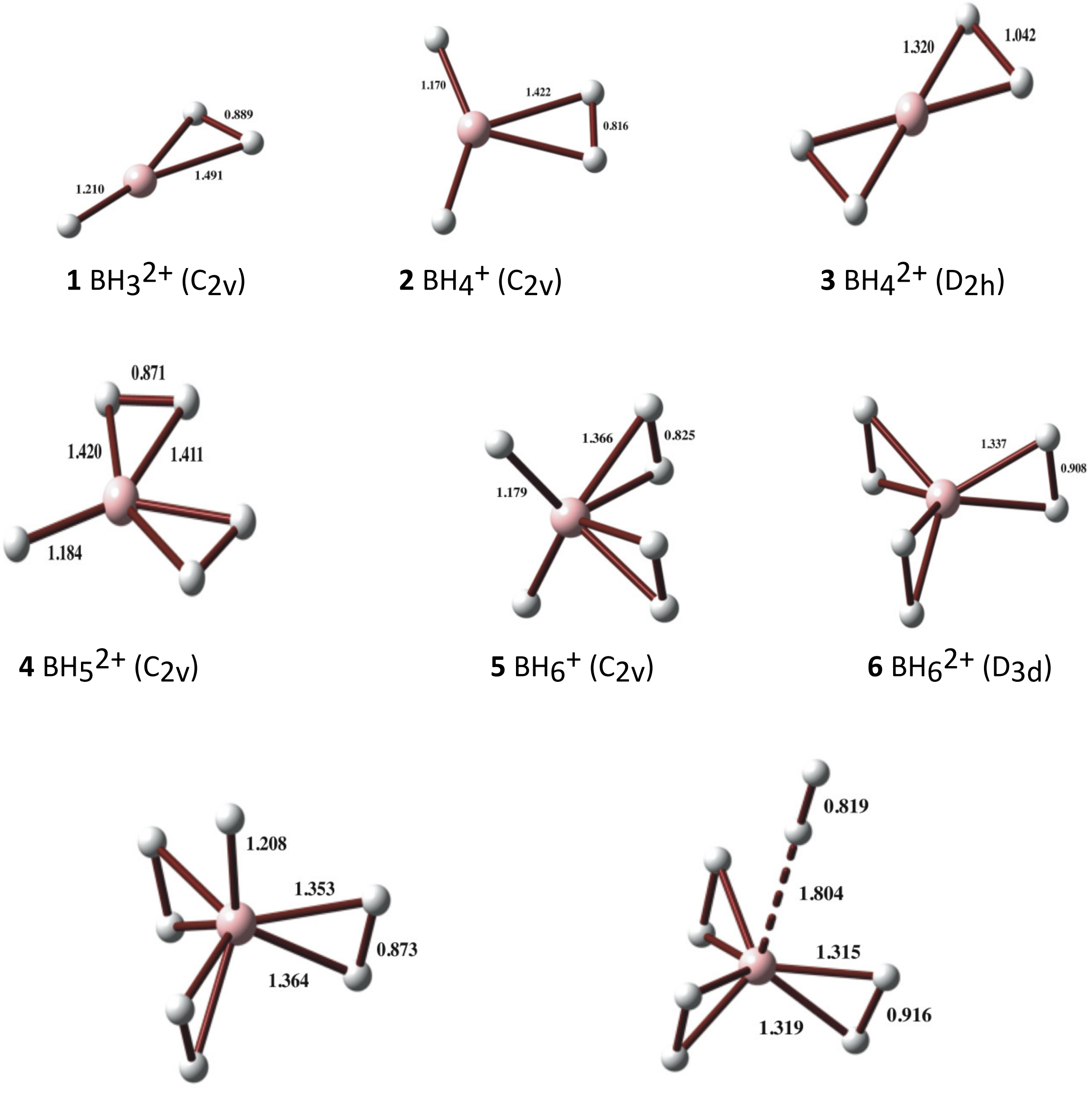
Gaussian 09 program[13] was employed for geometry optimizations and frequency calculations. The geometries were first optimized at the MP2/cc-pVTZ, level. Vibrational frequencies at the MP2/cc-pVTZ//MP2/cc-pVTZ level were used to characterize stationary points as minima (NIMAG (number of imaginary frequency) = 0 or transition state NIMAG = 1) and to compute zero point vibrational energies (ZPE), which were scaled by a factor of 0.96.[14] The MP2/cc-pVTZ geometries were further optimized at the CCSD(T)/cc-pVTZ level. CCSD(T)/cc-pVTZ optimizations have been performed with the CFOUR program.[15] Computed energies are given in Table 1.

BH_n^{2+} (n=3-8) systems

In line with previous calculations at the MP2/aug-cc-pVTZ level,[11] our present calculations at the CCSD(T)/cc-pVTZ level also shows that the C_{2v} symmetric structure **1** is a viable minimum for BH_3^{2+} (Figure 1). The structure **1** is characterized with a two-electron three-center (2e-3c) bond, a two-electron two-center (2e-2c) bond, resembling a complex between BH^{2+} and H_2. The B-H and H-H bond distances of the 2e-3c bond are computed to be 1.491 Å and 0.889 Å, respectively. Expectedly, both thermodynamically and kinetically the dication is unstable due to charge-charge repulsion. The dissociation of **1** into BH_2^+ and H^+ is exothermic by 100.6 kcal/mol and the process has a kinetic barrier of 8.2 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level (Table 2).

Previously we have reported[7] the MP2/6-31G** calculated structure of the boronium ion BH_4^+ **2**. The structure of BH_4^+ was found to be isostructural with the corresponding carbon analog CH_4^{2+}.[16] DePuy et al were able to generate BH_4^+ **2** in the gas phase by the reaction of BH_2^+ and H_2.[17] Removal of an electron from BH_4^+ **2** leads to the dication BH_4^{2+} **3**. The planar D_{2h} symmetric form **3** (Figure 1) is found to be the only minimum on the potential energy surface of BH_4^{2+}. Structure **3** resembles a complex between B^{2+} with two hydrogen molecules resulting in formation of two 2e-3c bonds. Deprotonation of **3** has a substantial kinetic barrier of 24.7 kcal/mol (although exothermic by 68.7 kcal/mol, Table 1). Despite charge-charge repulsion the 2e-3c B-H bond distance of dication **3** (1.320 Å) is considerably shorter than that of monocation **2** (1.422 Å).

Protonation of BH_4^+ **2** leads to the dication BH_5^{2+} **4**. We previously reported[18] the structure of BH_5^{2+} at the QCISD(T)/6-311G** level. CCSD(T)/cc-pVTZ optimized structure of BH_5^{2+} **4** is now computed and displayed in Figure 1. The structure **4** resembles a complex between BH^{2+} and two H_2 molecules resulting in formation of two 2e-3c bonds with an empty p-orbital orthogonal to the plane of the molecule. The dissociation of **4** into BH_4^+ **2** and H^+ was calculated to be exothermic by 56.6 kcal/mol but has a high kinetic barrier of 36.5 kcal/mol (Table 2).



1 BH_3^{2+} (C_{2v}) **2** BH_4^+ (C_{2v}) **3** BH_4^{2+} (D_{2h})

4 BH_5^{2+} (C_{2v}) **5** BH_6^+ (C_{2v}) **6** BH_6^{2+} (D_{3d})

7 BH_7^{2+} (C_{3v}) **8** BH_8^{2+} (C_{3v})

Figure 1. CCSD(T)/cc-pVTZ calculated structures of **1** – **8**.

The parent hexacoordinated boronium ion BH_6^+ **5** is isoelectronic and isostructural with the corresponding carbon analog CH_6^{2+}.[8,9] The ion **5** was studied previously by us.[2] DePuy et al. were able to generate **5** in the gas phase by the reaction of BH_4^+ **2** and H_2.[12] The C_{2v} symmetric form **5** was found to be the only minimum for BH_6^+. **5** contains two 2e-3c bonds and two 2c-2e bonds. Calculated B-H bond distance of 2e-3c interactions is found to be 1.366 Å. Removal of an electron from BH_6^+ **5** leads to dication BH_6^{2+} **6**. The D_{3d} symmetric **6** is a propeller-shaped molecule resembling a complex between B^{2+} with three hydrogen molecules resulting in formation of three 2e-3c bonds. B-H bond distance of 2e-3c interactions of the structure **6** is computed to be 1.337 Å. Deprotonation of **6** has a high kinetic barrier of 52.5 kcal/mol (Table 2).

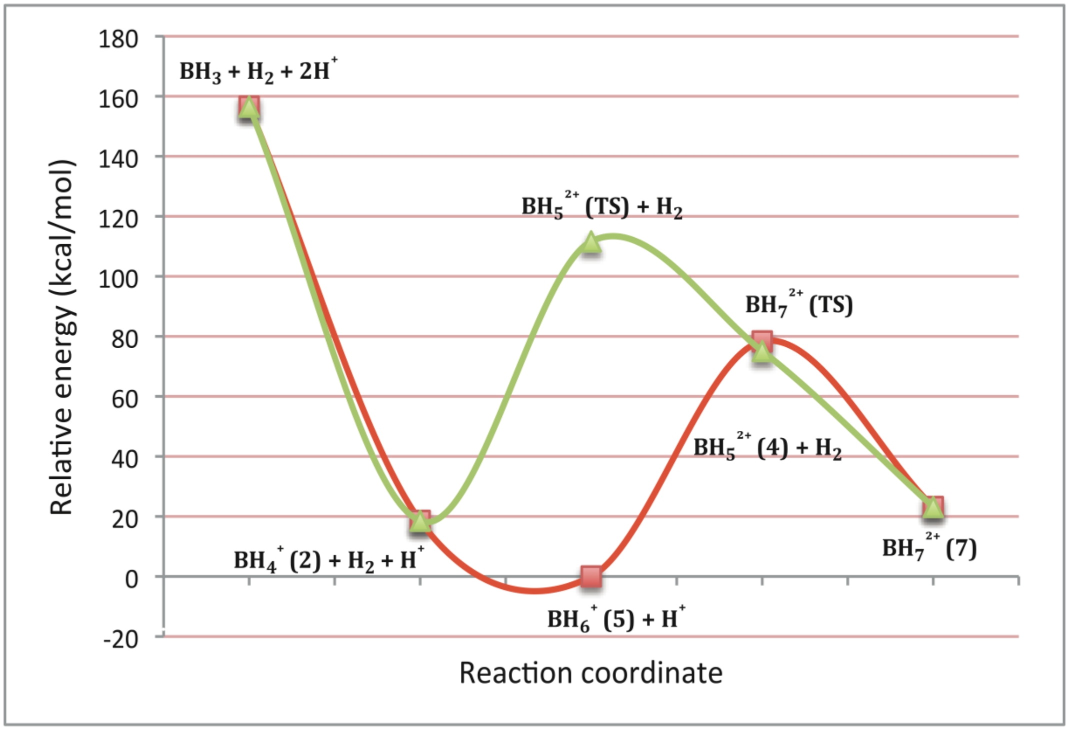


Figure 2. Plot of relative energy of the structures, **2**, **4**, **5** and **7**.

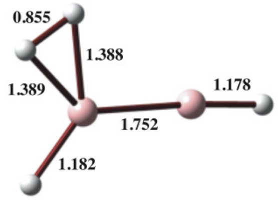
Protonation of BH_6^+ **5** leads to heptacoordinate boronium dication BH_7^{2+} **7**. The C_{3v} symmetric dication **7** is also propeller-shaped resembling a complex between BH^{2+} with three hydrogen molecules resulting in formation of three 2e-3c bonds. Average B-H bond distances of 2e-3c interactions of the structure **7** is found to be 1.359 Å. Deprotonation of **7** into BH_6^+ **5** is exothermic by only 23.2 kcal/mol and the process has a high kinetic barrier of 55.1 kcal/mol at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE level (Table 1). Relative energies of the structures **2**, **4**, **5**, **7** are plotted in Figure 2.

We also searched for any eight coordinate energy-minimum for dication BH_8^{2+}. The structure **8** was found to be a minimum on the potential energy surface of BH_8^{2+} (Figure 1). The C_{3v} symmetrical structure **8** can be considered as a weak complex between BH_6^{2+} **6** and H_2 with a long bond distance of 1.844 Å between boron atom and H_2 moiety.

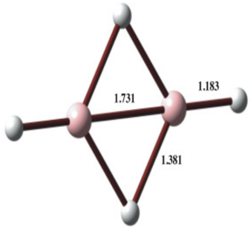
$B_2H_{2n}^{2+}$ (n=2-4) systems

In line with previous calculations at the QCISD(T)/6-311G** level,[12] our present calculations at the CCSD(T)/cc-pVTZ level also shows that the C_s symmetric structure **9** and D_{2h} symmetric structure **10** are the viable minima for $B_2H_4^{2+}$ (Figure 4). Structure **9** resembles a complex between $B_2H_2^{2+}$ and H_2 resulting in the formation of a 2e-3c bond. Structure **10** is characterized as a doubly hydrogen-bridged structure.

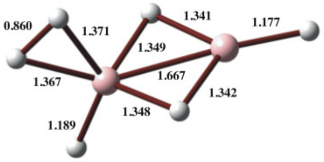
Structure **9** is 9.4 kcal/mol more stable than **10**. The dissociation of **9** into $B_2H_3^+$ and H^+ was computed to be exothermic by 6.7 kcal/mol but has a high kinetic barrier of 61.6 kcal/mol (Table 2).



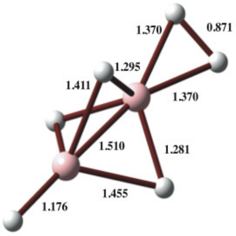
9 $B_2H_4^{2+}$ (C_s)



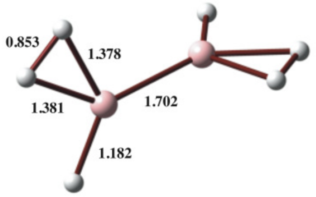
10 $B_2H_4^{2+}$ (D_{2h})



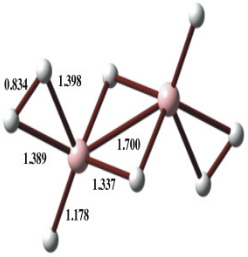
11 $B_2H_6^{2+}$ (C_s)



12 $B_2H_6^{2+}$ (C_s)



13 $B_2H_6^{2+}$ (C_2)



14 $B_2H_8^{2+}$ (C_i)

Figure 3. CCSD(T)/cc-pVTZ calculated structures of **9** – **14**.

Table 1. Total energies (-au), ZPE (kcal/mol) and relative energies (RA in kcal/mol)

No.	MP2/cc-pVTZ	ZPE[a]	CCSD(T)/cc-pVTZ	RA[b]
1	25.39039	12.7	25.41983	
2	26.74205	21.9	26.78047	
3	25.96738	15.9	26.00121	
4	26.65701	25.2	26.69554	
5	27.94345	34.2	27.99208	
6	27.24920	31.5	27.29300	
7	27.91237	38.5	27.96199	
8	28.42359	38.9	28.47827	
9	50.90219	23.3	50.96293	0.0
10	50.88575	22.8	50.94717	9.4
11	52.13230	35.5	52.20481	0.7
12	52.13278	35.3	52.20553	0.0
13	52.12357	34.7	52.19450	6.3
14	53.35921	47.9	53.44053	

[a] ZPE at the MP2/cc-pVTZ//MP2/cc-pVTZ level level scaled by a factor of 0.96;
[b] at the CCSD(T)/cc-pVTZ//CCSD(T)/cc-pVTZ + ZPE (MP2/cc-pVTZ//MP2/cc-pVTZ) level.

Three viable minimum structures (**11**-**13**) were computed for the diboronium dication, $B_2H_6^{2+}$ (Figure 4). Triply hydrogen-bridged structure **12** was found to be the lowest minimum. This structure **12** also contains a 2e-3c bond involving a boron atom and two hydrogen atoms. One of the borons in structure **12** is six-coordinated and the other one is five-coordinated. Dication **11**, on the other hand, is doubly hydrogen-bridged structure. Additionally it also contains a 2e-3c bond involving a boron atom and two hydrogen atoms. Structure **11** is only 0.7 kcal/mol less stable than **12**. Structure **13**, unlike structures **11** and **12**, was characterized to be a non-hydrogen-bridged (involving both boron atoms) structure. Dication **13** with two 2e-3c bonds can be considered as a complex between $B_2H_2^{2+}$ and two hydrogen molecules. Structure **13** is 6.3 kcal/mol less stable than the structure **12**. The dissociation of **12** into $B_2H_5^+$ and H^+ was calculated to be exothermic by 33.9 kcal/mol but has a kinetic barrier of 45.1 kcal/mol (Table 2).

Table 2. Dissociation Energy (ΔE_0) and Respective Kinetic Barrier at 298 K for the Selected Processes[a]

Process	ΔE_0 (kcal/mol)[b]	Barrier (kcal/mol)[b]
BH_3^{2+} (**1**) ---> $BH_2^+ + H^+$	-100.6	8.2
BH_4^{2+} (**3**) ---> $BH_3^+ + H^+$	-68.7	20.2
BH_5^{2+} (**4**) ---> $BH_4^+ + H^+$	-56.6	36.5
BH_6^{2+} (**6**) ---> $BH_5^+ + H^+$	-25.8	52.5
BH_7^{2+} (**7**) ---> $BH_6^+ + H^+$	-23.2	55.1
$B_2H_4^{2+}$ (**9**) ---> $B_2H_3^+ + H^+$	-6.7	61.6
$B_2H_6^{2+}$ (**12**) ---> $B_2H_5^+ + H^+$	-33.9	45.1

[a] at the CCSD(T)/cc-pVTZ// CCSD(T)/cc-pVTZ + ZPE (MP2/cc-pVTZ//MP2/cc-pVTZ level scaled by a factor of 0.96) level.

Structure **14** was computed for diprotonated diborane $B_2H_8^{2+}$. Dication **14** is a doubly hydrogen-bridged structure. It was also characterized to possess two 2e-3c bonds. Structure **14** (Figure 3) contains two six coordinate boron atoms. The structure formally resembles a complex between a $B_2H_4^{2+}$ **10** with two hydrogen molecules resulting in formation of two 2e-3c bonds. Calculated central B-B bond length of **14** is computed to be 1.700 Å.

Conclusions

Structures of higher coordinate hydrido boronium dications were calculated using CCSD(T)/cc-pVTZ level of theory and compared with their isoelectronic carbon analogs. These calculations indicate that higher coordinated doubly charged boronium dications are viable species in the gas phase despite strong charge-charge repulsion. In such small first row highly charged cations, charge-charge repulsions are clearly substantial, but the bonding interactions are strong enough to counter this. Although such hydrido boronium dications are thermodynamically unstable, their computational characterization gives support for their transient existence. Structures, stability and multicenter bonding concept of the intriguing higher coordinate boronium and carbonium (hypercarbon)[19] ions as well characterized compounds have now been calculationally established. By development of new techniques, the characterization of these intriguing species is considered possible.

Acknowledgements

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