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.

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

Main group hydrido cations and dications have been a subject of numerous experimental and theoretical investigations. A while ago we have reported the calculated structures of parent hexa- and heptacoordinate boronium ions, BH₆⁺ and BH₇²⁺, respectively, with two and three two-electron three-center (2e-3c) bonds. The structures were found to be isostructural with their isoelectronic carbon analogs, CH₆²⁺ and CH₇³⁺, respectively. We have also previously investigated the structures and energetics of BHₙ²⁺ (n=1-8) and B₂H₂ₙ²⁺ (n=1-4) dications at the MP2/aug-cc-pVTZ and QCISD(T)/6-31G** 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 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. 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. Computed energies are given in Table 1.

BHₙ²⁺ (n=3-8) systems

In line with previous calculations at the MP2/aug-cc-pVTZ level, our present calculations at the CCSD(T)/cc-pVTZ level also shows that the C₂ᵥ symmetric structure is a viable minimum for BH₃²⁺ (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 BH₂⁺ and H₂. 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 BH₂⁺ 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 the MP2/6-31G** calculated structure of the boronium ion BH₄⁺ 2. The structure of BH₄⁺ was found to be isostructural with the corresponding carbon analog CH₄²⁺. DePuy et al were able to generate BH₄⁺ 2 in the gas phase by the reaction of BH₂⁺ and H₂. Removal of an electron from BH₄⁺ 2 leads to the dication BH₄²⁺ 3. The planar D₂h symmetric form 3 (Figure 1) is found to be the only minimum on the potential energy surface of BH₄²⁺. Structure 3 resembles a complex between B²⁺ 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).

![Figure 1. CCSD(T)/cc-pVTZ calculated structures of 1 – 8.](image)

The parent hexacoordinated boronium ion BH$_6^+$ 5 is isoelectronic and isostructural with the corresponding carbon analog CH$_6^{2+}$. 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$_2$. 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).

![Energy Diagram](image.png)

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

Protonation of BH₆⁺ 5 leads to heptacoordinate boronium dication BH₇^{2+} 7. The C₃ᵥ symmetric dication 7 is also propeller-shaped resembling a complex between BH²⁺ 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 BH₆⁺ 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 BH₈^{2+}. The structure 8 was found to be a minimum on the potential energy surface of BH₈^{2+} (Figure 1). The C₃ᵥ symmetrical structure 8 can be considered as a weak complex between BH₆⁺ 6 and H₂ with a long bond distance of 1.844 Å between boron atom and H₂ moiety.

**B₂Hₙ^{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 C₅ symmetric structure 9 and D₂h symmetric structure 10 are the viable minima for B₂H₄^{2+} (Figure 4). Structure 9 resembles a complex between B₂H₂^{2+} and H₂ 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 \( \text{B}_2\text{H}_3^+ \) and \( \text{H}^+ \) was computed to be exothermic by 6.7 kcal/mol but has a high kinetic barrier of 61.6 kcal/mol (Table 2).

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)

<table>
<thead>
<tr>
<th>No.</th>
<th>MP2/cc-pVTZ</th>
<th>ZPE(^a)</th>
<th>CCSD(T)/cc-pVTZ</th>
<th>RA(^b)</th>
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\(^a\)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 diboron dication, B$_2$H$_6^{2+}$ (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$_2$H$_2^{2+}$ and two hydrogen molecules. Structure 13 is 6.3 kcal/mol less stable than the structure 12. The dissociation of 12 into B$_2$H$_5^+$ 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 ($\Delta E_0$) and Respective Kinetic Barrier at 298 K for the Selected Processes$^a$

<table>
<thead>
<tr>
<th>Process</th>
<th>$\Delta E_0$ (kcal/mol)$^b$</th>
<th>Barrier (kcal/mol)$^b$</th>
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<tr>
<td>BH$_3^{2+}$ (1) ---&gt; BH$_2^+$ + H$^+$</td>
<td>-100.6</td>
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<td>BH$_4^{2+}$ (3) ---&gt; BH$_3^+$ + H$^+$</td>
<td>-68.7</td>
<td>20.2</td>
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<td>BH$_5^{2+}$ (4) ---&gt; BH$_4^+$ + H$^+$</td>
<td>-56.6</td>
<td>36.5</td>
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<td>BH$_6^{2+}$ (6) ---&gt; BH$_5^+$ + H$^+$</td>
<td>-25.8</td>
<td>52.5</td>
</tr>
<tr>
<td>BH$_7^{2+}$ (7) ---&gt; BH$_6^+$ + H$^+$</td>
<td>-23.2</td>
<td>55.1</td>
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<tr>
<td>B$_2$H$_4^{2+}$ (9) ---&gt; B$_2$H$_3^+$ + H$^+$</td>
<td>-6.7</td>
<td>61.6</td>
</tr>
<tr>
<td>B$_2$H$_6^{2+}$ (12) ---&gt; B$_2$H$_5^+$ + H$^+$</td>
<td>-33.9</td>
<td>45.1</td>
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$^a$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$_2$H$_8^{2+}$. 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$_2$H$_4^{2+}$ 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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References


