Octahydrido diborane (B_2H_8) and its protonated cations containing five-, six-, and seven-coordinate boron atoms

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Structures of octahydrido diborane (B_2H_8) **1** and its protonated **3**, diprotonated **5**, triprotonated **6**, and tetraprotonated **7** ions were found to be computationally viable minima at the MP2/cc-pVTZ level of theory. Each structure contains two-electron three-center (2e-3c) bonds. The protonation of **1** to form **3** was found to be strongly exothermic by 176.0 kcal/mol. Subsequent protonation of **3** to form **5** was also found to be exothermic by 28.4 kcal/mol. Further protonation of **5** to form **6** was, however, computed to be endothermic by 122.0 kcal/mol whereas protonation of **6** to form **7** was again highly endothermic by 238.8 kcal/mol. Deprotonation barriers of the ions were also computed.

ab initio | boronium | hypercoordinate | cations | polycations

Higher coordinate (1) main group compounds are of substantial theoretical (2–4) and experimental (5) interest. Schmidbaur et al. have prepared a variety of monopositively charged higher coordinate gold complexes of main group elements (5). They have also prepared dipositively charged carbon $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ (**6**), nitrogen $\{[(C_6H_5)_3PAu]_5N\}^{2+}$ (**7**), phosphorus $\{[(C_6H_5)_3PAu]_5P\}^{2+}$ (**8**), sulfur (9) $\{[(C_6H_5)_3PAu]_4S\}^{2+}$ (**9**) and oxygen $\{[(O-CH_3-C_6H_4)_3PAu]_4O\}^{2+}$ (**10**) and determined their X-ray structures. The structures represent isolobal analogs of CH_6^{2+} , NH_5^{2+} , PH_5^{2+} , SH_4^{2+} and OH_4^{2+} , respectively. They have also prepared a positively charged five-coordinate boron complex of gold (11) $\{[(C_6H_5)_3PAu]_4B[P(C_6H_{11})_3]\}^+$ and determined its X-ray structure, but no dipositively charged gold complexes of boron have been reported to date.

We have previously reported (12) the calculated structures of parent pentacoordinate BH_5 and derived the hexa-, hepta-, and octacoordinate boronium ions BH_6^+ , BH_7^{2+} , and BH_8^{3+} , respectively, with 1–4 two-electron three-center (2e-3c) bonds to be viable energy minima (Fig. 1). The structures were found to be isostructural, with isoelectronic carbon analogs CH_5^+ (13, 14), CH_6^{2+} (15, 16), and CH_7^{3+} (17) respectively.

In continuation of our study of hypercoordinate compounds, we have extended our investigations to the next higher homologue of BH_5 , i.e., B_2H_8 (which can be considered a complex of B_2H_6 and H_2 or BH_5 and BH_3) and its protonated $B_2H_9^+$, $B_2H_{10}^{2+}$, $B_2H_{11}^{3+}$, and $B_2H_{12}^{4+}$ ions at the ab initio MP2/cc-pVTZ level.

Computational Methods

Geometry optimizations, frequency calculations, and natural bond orbital (NBO) analyses were carried out with the Gaussian 09 program (18). The geometry optimizations were performed at the ab initio MP2/cc-pVTZ level. Vibrational frequencies at the MP2/cc-pVTZ//MP2/cc-pVTZ level were used to characterize stationary points as either minima (number of imaginary frequency (NIMAG) = 0) or transition states (NIMAG = 1) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.95 (19). For improved energy, calculations were carried out using the accurate W1BD method (20, 21) as implemented in the Gaussian 09 program (18). Atomic charges

Fig. 1. Higher coordinate boronium ions.

at the MP2/cc-pVTZ//MP2/cc-pVTZ level were obtained using the natural bond orbital analysis (NBO) (22) method. Calculated energies are given in Table 1.

Results and Discussion

Structure **1** was found to be a viable minimum (Fig. 2) on the potential energy surface (PES) of B_2H_8 at the MP2/cc-pVTZ level. Structure **1** contains a 2e-3c bond involving two hydrogen atoms and a boron atom, and a 2e-3c bond involving a hydrogen atom and two boron atoms. The ion can be considered a complex between BH_5 and BH_3 . At the same MP2/cc-pVTZ level, the C_{2h} symmetric form **2** was also found to be a minimum for B_2H_8 . At the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level, structure **1** was computed to be 10.1 kcal/mol more stable than structure **2**. Using W1BD theory (20, 21), this energy difference increases to 10.8 kcal/mol. Structure **2**, resembling a complex between BH_2BH_2 and two hydrogen molecules, results in the formation of two 2e-3c bonds (Fig. 2). Thus, structure **2** contains two five-coordinate boron atoms. We considered the possible dissociation path for **1**. Using W1BD theory, dissociation of **1** into BH_5 and BH_3 is calculated to be endothermic by 4.2 kcal/mol. For comparison, structures of B_2H_6 (diborane), BH_5 , and BH_3 calculated at the same MP2/cc-pVTZ level are also depicted (Fig. 3).

MP2/cc-pVTZ optimizations show that the hydrogen-bridged structure **3** and the non-hydrogen-bridged structure **4** are the minima on the potential energy surface of $B_2H_9^+$ (protonated B_2H_8). Structure **3** (Fig. 2) contains two six-coordinate borons. On the other hand, structure **4** contains five- and six-coordinate boron atoms. Structure **3** was computed to be 16.8 kcal/mol more stable than structure **4**. Protonation of **1** to form **3** was found to be strongly exothermic by 176.0 kcal/mol.

The same level of calculations shows that the C_2 symmetrical structure **5** is the only minimum on the potential energy surface of $B_2H_{10}^{2+}$ (diprotonated B_2H_8). Structure **5** (Fig. 2) contains two six-coordinate boron atoms. The structure formally resembles a complex between a $^+HBBH^+$ with four hydrogen molecules

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

	MP2/cc-pvtz	NIMAG [†]	ZPE	Rel. energy [‡]	W1BD	Rel. energy [§]
1	54.21280	0	47.1	203.8	54.32641	204.4
2	54.19587	0	46.5	213.9	54.30916	215.2
3	54.50277	0	53.5	28.3	54.60696	28.4
4	54.47507	0	52.6	44.8	54.58018	45.2
5	54.55645	0	58.9	0.0	54.65213	0.0
6	54.36557	0	61.2	122.1	54.45774	122.0
7	53.98259	0	59.5	360.7	54.07845	360.0
8	54.40154	1	53.1	91.4	54.50850	90.1
9	54.30641	1	61.2	159.2	54.40500	155.1
10	53.96815	1	56.9	367.2	54.06763	366.8
B ₂ H ₆	53.09722	0	38.4		53.21316	
BH ₅	27.68715	0	27.2		27.74338	
BH ₃	26.51351	0	16.0		26.57641	
H ₂	1.16465	0	6.2		1.16467	

*Zero point vibrational energies (ZPE) at MP2/cc-pvtz//MP2/cc-pvtz scaled by a factor of 0.95;

[†]Number of imaginary frequency;

[‡]Relative energy at MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level;

[§]Relative energy based on computed W1BD energies.

resulting in the formation of four 2e-3c bonds. The calculated central B-B bond length of **5** (1.720 Å) is slightly shorter than the corresponding B-B bond length (1.737 Å) of **4**.

The protonation of **3** to form **5** was also found to be exothermic by 28.4 kcal/mol. Transition structure **8** for the deprotonation in **5** was located. The transition structure **8** lies 90.1 kcal/mol higher in energy than structure **5**. Therefore, it has a high energy barrier for deprotonation. The potential energy surface of protonation of B₂H₈ calculated by W1BD method is also depicted (Fig. 4).

The C_s structure **6** is the only minimum that was located on the potential energy surface of B₂H₁₁³⁺ (triprotonated B₂H₈). The structure **6** is characterized with five 2e-3c bonds and resembles a complex between ²⁺BBH⁺ and five hydrogen molecules (Fig. 2). As a result of strong charge-charge repulsions, the cal-

culated central B-B bond length of **6** (1.845 Å) is considerably longer than the corresponding B-B bond length of **5** (1.720 Å). Dissociation of **6** into **5** and H⁺ was calculated to be highly exothermic by 122.0 kcal/mol. Transition structure **9** for the deprotonation of **6** was also located. The structure **9** lies 33.1 kcal/mol higher in energy than structure **6**. Thus the trication also has considerable barrier for deprotonation.

The C₃ symmetric structure **7** is the only minimum that was located as a energy minimum on the potential energy surface of B₂H₁₂⁴⁺ (tetraprotonated B₂H₈). Structure **7** is a propeller-shaped molecule with six 2e-3c bonds. The calculated central B-B bond length of **7** (2.051 Å) is substantially longer than the corresponding B-B bond length of **6** (1.845 Å) as a result of very strong charge-charge repulsions.

Dissociation of **7** into **6** and H⁺ was calculated to be highly exothermic by 238.8 kcal/mol. The transition structure **10** for this dissociation lies just 6.8 kcal/mol higher in energy than structure **7**. This shows that the tetracation **7**, if formed, will dissociate spontaneously into **6** and H⁺ (Fig. 5).

We also calculated the NBO charges (22) of the boronium ions **5**–**7** (Fig. 6). The average charge of boron atoms in each of the ions **5**, **6** and **7** are −0.36, −0.30, and −0.07 a.u., respectively. This indicates that even in tetracation **7**, the hydrogen atoms bear all of the positive charges.

Conclusions

The present calculational study at the MP2/cc-pVTZ level shows that the neutral B₂H₈ **1**, and its protonated forms B₂H₉⁺ **3**, B₂H₁₀²⁺ **5**, B₂H₁₁³⁺ **6** and B₂H₁₂⁴⁺ **7**, are viable energy minima. Structures **5**, **6**, and **7** were found to be stabilized by four, five, and six 2e-3c bonds, respectively. The protonation of **1** to form **3** was calculated to be strongly exothermic by 176.0 kcal/mol. Structure **7** is a propeller-shaped molecule with two seven-coordinate borons and six 2e-3c bonds. Charge-charge repulsions in these di-, tri- and tetracations are substantial. However, the bonding interac-

Fig. 2. MP2/cc-pVTZ structures of 1–7.

Fig. 3. MP2/cc-pVTZ calculated structures of B_2H_6 , BH_5 , and BH_3 .

Fig. 4. Potential energy surface of protonation of B_2H_8 calculated by W1BD method.

Fig. 5. MP2/cc-pVTZ calculated transition states of 8-10.

Fig. 6. MP2/cc-pVTZ/MP2/cc-pVTZ computed charges of $B_2H_{10}^{2+}$ 5, $B_2H_{11}^{3+}$ 6 and $B_2H_{12}^{4+}$ 7.

tions are strong enough to counter charge-charge repulsions, rendering them remarkably stable.

Materials and Methods

All calculations were performed with the Gaussian 09 program series (18). The geometry optimizations were performed at the MP2/cc-pVTZ level. Final

energies were calculated at the MP2/cc-pVTZ//MP2/cc-pVTZ + ZPE level and by using the W1BD method (20, 21). Cartesian coordinates of the optimized geometries and energies are provided in the [SI Appendix](#).

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