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Calculational Study of the Protonation of BXH_2 and BX_2H (X = F and Cl). Structures of BXH_3^+ and $BX_2H_2^+$ and Their Dihydrogen Complexes BXH_5^+ and $BX_2H_4^+$ [1]

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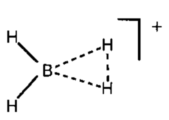
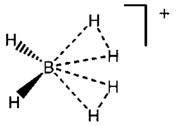
Introduction

We have previously reported[2] the calculated structures of tetracoordinate BH_4^+ and hexacoordinate boronium ion, BH_6^+. The structure of BH_4^+ is planar C_{2v} symmetrical with a three-center two-electron (3c−2e) bond.[2] The structure of BH_6^+ is C_{2v} symmetrical with two 3c−2e bonds.[2] The structures of BH_4^+ and BH_6^+ were found to be isostructural with their isoelectronic carbon analogues CH_4^{2+} [3] and CH_6^{2+},[4] respectively. In our report we suggested that BH_6^+ could be made by the complexation of BH_4^+ and H_2 as the process is exothermic by 16.7 kcal/mol.[2] DePuy et al. were indeed able to prepare and observe the BH_4^+ and BH_6^+ experimentally in the gas phase by reacting BH_2^+ and H_2 and BH_4^+ and H_2, respectively.[5]



BH_4^+



BH_6^+

Higher coordinate compounds involving main group elements are of both theoretical[6] and experimental[7] interest. Schmidbaur and his associates have prepared a variety of higher coordinated boron,[8] carbon,[9] nitrogen,[10] oxygen,[11] phosphorus,[12] and sulfur[13a] gold complexes and determined their X-ray structures. They have prepared trigonal bipyramidal[9a] $\{[(C_6H_5)_3PAu]_5C\}^+$ and octahedral[9b] $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ involving five- and six-coordinate carbon, respectively, representing the isolobal[7] analogues of CH_5^+ and CH_6^{2+}. Lithiated penta- and hexacoordinated carbocations, CLi_5^+ and CLi_6^{2+}, respectively, were also calculated to be stable minima.[13b] In a continuation of our study we have now extended our investigations to the protonated BXH_3^+ and $BX_2H_2^+$ (X = F and Cl) ions as well as their dihydrogen complexes BXH_5^+ and $BX_2H_4^+$, respectively.

Calculations

Calculations were performed with the Gaussian 98 program system.[14] The geometry optimizations were carried out at the MP2/6-311+G** level.[15] Vibrational frequencies at the MP2/6-311+G**//MP2/6-311+G** level were used to characterize stationary points as minima (number of imaginary frequency (NIMAG) = 0) and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.96.[16] For improved energy, single point energies at the MP4(SDTQ)/cc-pVTZ[17] level on MP2/6-311+G** optimized geometries were computed. Final energies were calculated at the MP4(SDTQ)/cc-pVTZ//MP2/6-311+G** + ZPE level. Calculated energies are given in Table 1. Thermodynamics of the selected complexation and protonation processes are given in Table 2. MP2/6-311+G** geometrical parameters and final energies will be discussed throughout, unless stated otherwise.

Results and Discussion

BFH_3^+ and BFH_5^+. Two structures of protonated BFH_2, B−H protonated **1a** and F-protonated **1b** (Figure 1), were found to be the minima on the potential energy surface (PES). Structure **1a** is a planar boronium ion with a 3c−2e bond involving boron and two hydrogens. On the other hand structure **1b** is a fluoronium ion with a relatively long B−F bond (1.552 Å). **1a** is substantially more stable than **1b** by 9.7 kcal/mol. This shows that the B−H bond is a better donor than the fluorine nonbonded electron pair in BFH_2.

Ion **1a** can be considered as a complex between the dicoordinate BFH^+ ion and H_2. The complexation process was computed to be exothermic by 3.0 kcal/mol (Scheme 1, Table 2). Similar complexation of BH_2^+ and H_2 leading to BH_4^+ **1x** (Figure 1) is exothermic by 13.2 kcal/mol. Thus the H_2 unit is

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

	MP2/6-311+G**// MP2/6-311+G**	ZPE	MP4(SDTQ)/ cc-pVTZ// MP2/6-311+G**	rel energy (kcal/mol)
BFH_3^+ **1a**	125.87831	17.6	125.97841	0.0
BFH_3^+ **1b**	125.86878	20.0	125.96684	9.7
BFH_5^+ **2a**	127.04521	27.0	127.15842	0.0
BFH_5^+ **2b**	127.04624	31.3	127.15645	5.5
$BClH_3^+$ **3a**	485.84314	16.5	485.96113	4.3
$BClH_3^+$ **3b**	485.85338	18.6	485.97131	0.0
$BClH_5^+$ **4a**	487.00495	27.2	487.13689	11.0
$BClH_5^+$ **4b**	487.02713	29.9	487.15866	0.0
$BF_2H_2^+$ **5a**	225.02319	15.1	225.18124	2.4
$BF_2H_2^+$ **5b**	225.03119	16.6	225.18740	0.0
$BF_2H_2^+$ **5c**	225.03055	16.7	225.18679	0.5
$BF_2H_4^+$ **6a**	226.18894	23.6	226.36010	
$BCl_2H_2^+$ **7b**	944.96898	14.4		0.3[c]
$BCl_2H_2^+$ **7c**	944.96933	14.3		0.0[c]

[a] Zero point vibrational energies (ZPE) at MP2/6-311+G**//MP2/6-311+G** scaled by a factor of 0.96. [b] At the MP4(SDTQ)/cc-pVTZ//MP2/6-311+G** + ZPE level. [b] At the MP2/6-311+G**//MP2/6-311+G** + ZPE level.

Table 2. Dissociation Energy (ΔE_0), Thermal Contribution to the Enthalpy (ΔH), and Free Energy Change (ΔG) at 298 K for the Selected Processes[a]

process	ΔE_0 (kcal/mol)[a]	ΔH (kcal/mol)[b]	ΔG (kcal/mol)[b]
$BFH^+ + H_2 \rightarrow BFH_3^+$ **1a**	−3.0	1.8	8.1
$BH_2^+ + HF \rightarrow BFH_3^+$ **1b**	−35.7	2.3	10.0
$BFH_2 + H^+ \rightarrow BFH_3^+$ **1a**	−135.3		
BFH_3^+ **1a** $+ H_2 \rightarrow BFH_5^+$ **2a**	−2.0	2.0	9.6
BFH_3^+ **1b** $+ H_2 \rightarrow BFH_5^+$ **2b**	−6.1	3.5	11.6
$BH_4^+ + HF \rightarrow BFH_5^+$ **2b**	−29.4	2.5	11.7
$BH_2^+ + HCl \rightarrow BClH_3^+$ **3b**	−40.8	2.4	10.3
$BClH_3^+$ **3b** $+ H_2 \rightarrow BClH_5^+$ **4b**	−4.7	3.5	11.8
$BH_4^+ + HCl \rightarrow BClH_5^+$ **4b**	−32.4	2.6	12.2
$BF_2^+ + H_2 \rightarrow BF_2H_2^+$ **5a**	−8.0	2.0	8.0
$BFH^+ + HF \rightarrow BF_2H_2^+$ **5b**	−23.6	1.4	9.8
$BF_2H_2^+$ **5a** $+ H_2 \rightarrow BF_2H_4^+$ **6a**	−2.2	1.3	8.8

[a] At the MP4(SDTQ)/cc-pVTZ//MP2/6-311+G** + ZPE level. [b] At the MP2/6-311+G**//MP2/6-311+G** level.

Table 3. MP2/6-311+G** Calculated Frequencies[a] and IR Intensities

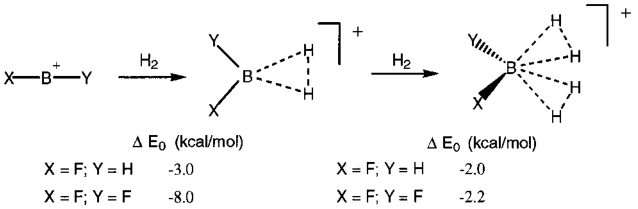
no.	frequencies in cm^{-1} (IR intensities in km/mol)
1a	224 (1), 474 (310), 638 (5), 830 (30), 990 (41), 1049 (21), 1530 (195), 2906 (7), 4154 (216)
1b	469 (200), 622 (100), 767 (207), 1009 (126), 1060 (55), 1204 (51), 2762 (2), 2977 (2), 3722 (530)
3a	251 (0), 296 (304), 585 (2), 773 (5), 955 (79), 1011 (41), 1163 (93), 2877 (3), 4123 (255)
3b	474 (42), 614 (136), 703 (11), 971 (9), 1014 (28), 1205 (84), 2744 (5), 2895 (209), 2927 (0)

[a] Not scaled.

more tightly bound in BH_4^+ than in **1a**. Consequently the 3c−2e B−H bond distances of **1a** (1.674 and 1.718 Å) are considerably longer than that of BH_4^+ (1.448 Å). The parent BH_4^+ **1x** has been prepared[5] in the gas phase by complexing BH_2^+ and H_2. Protonation of BFH_2 to give **1a** was calculated to be exothermic by 135.3 kcal/mol, which is slightly less exothermic than protonation of BH_3 (137.1 kcal/mol). The free energy change ΔG (i.e., including temperature and entropy corrections at 298 K using the rigid-rotor approximation) and thermal contribution to the enthalpy (ΔH) were also calculated and are listed in Table 2. The free energy change for **1a** → $BFH^+ + H_2$ was computed to be 8.1 kcal/mol. These observations indicate that the complex **1a** is expected to be experimentally characterizable at low temperature but not at room temperature in the gas phase. Calculated vibrational frequencies of **1a** and **1b** are given in Table 2.

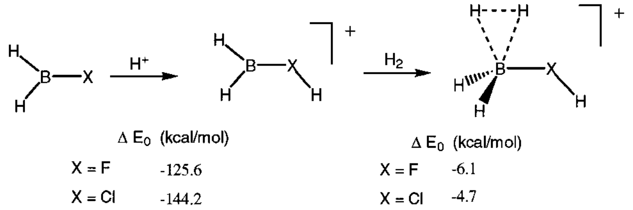
Further complexation of **1a** with H_2 leads to BFH_5^+ **2a**, which was also found to be a stable minimum (Figure 1). The C_s-symmetric **2a** contains a six-coordinate boron and two 3c−2e bonds. Formation of **2a** from complexation of **1a** and H_2 is also an exothermic (by 2.0 kcal/mol) process (Scheme 1). However, the free energy change for **2a** → **1a** + H_2 was computed to be 9.6 kcal/mol. This indicates that the ion **2a** should be unstable at room temperature. In comparison, formation of BH_6^+ from BH_4^+ **1x** and H_2 was calculated to be exothermic by 17.7 kcal/mol. The hexacoordinate parent BH_6^+ has been prepared by DePuy et al. in the gas phase by complexing BH_4^+ with H_2.[5]

Scheme 1



Isomeric **2b** with a five-coordinate boron and a 3c−2e bond is also a stable minimum which can be formed by complexing **1b** with H_2 (Scheme 2, Table 2). The complexation process was found to be exothermic by 6.1 kcal/mol. However, **2b** is 5.5 kcal/mol less stable than **2a** (Table 1). Ion **2b** is in fact a boronium−fluoronium ion and can be considered as a complex between BH_4^+ **1x** and HF. Formation of **2b** from BH_4^+ and HF was calculated to be exothermic by 29.4 kcal/mol (Table 1).

Scheme 2



$BClH_3^+$ and $BClH_5^+$. The B−H and Cl-protonated $BClH_2$, **3a** and **3b** were found to be stable minima. The C_s-symmetric structure **3a** also contains a 3c−2e bond. The structure **3b** is a chloronium ion with a B−Cl bond distance of 1.861 Å. However, unlike fluorinated analogues, **3a** is less stable than **3b** by 4.3 kcal/mol (Table 1). This is expected because the calculated[18] proton affinity (PA) on the chlorine of $BClH_2$ (145.7 kcal/mol) was found to be significantly higher than the PA on the fluorine of BFH_2 (126.1 kcal/mol). Calculated vibrational frequencies of **3a** and **3b** are given in Table 2. Complexations of **3a** and **3b** with H_2 also give stable structures **4a** involving a six-coordinate boron and two 3c−2e bonds and **4b** involving a

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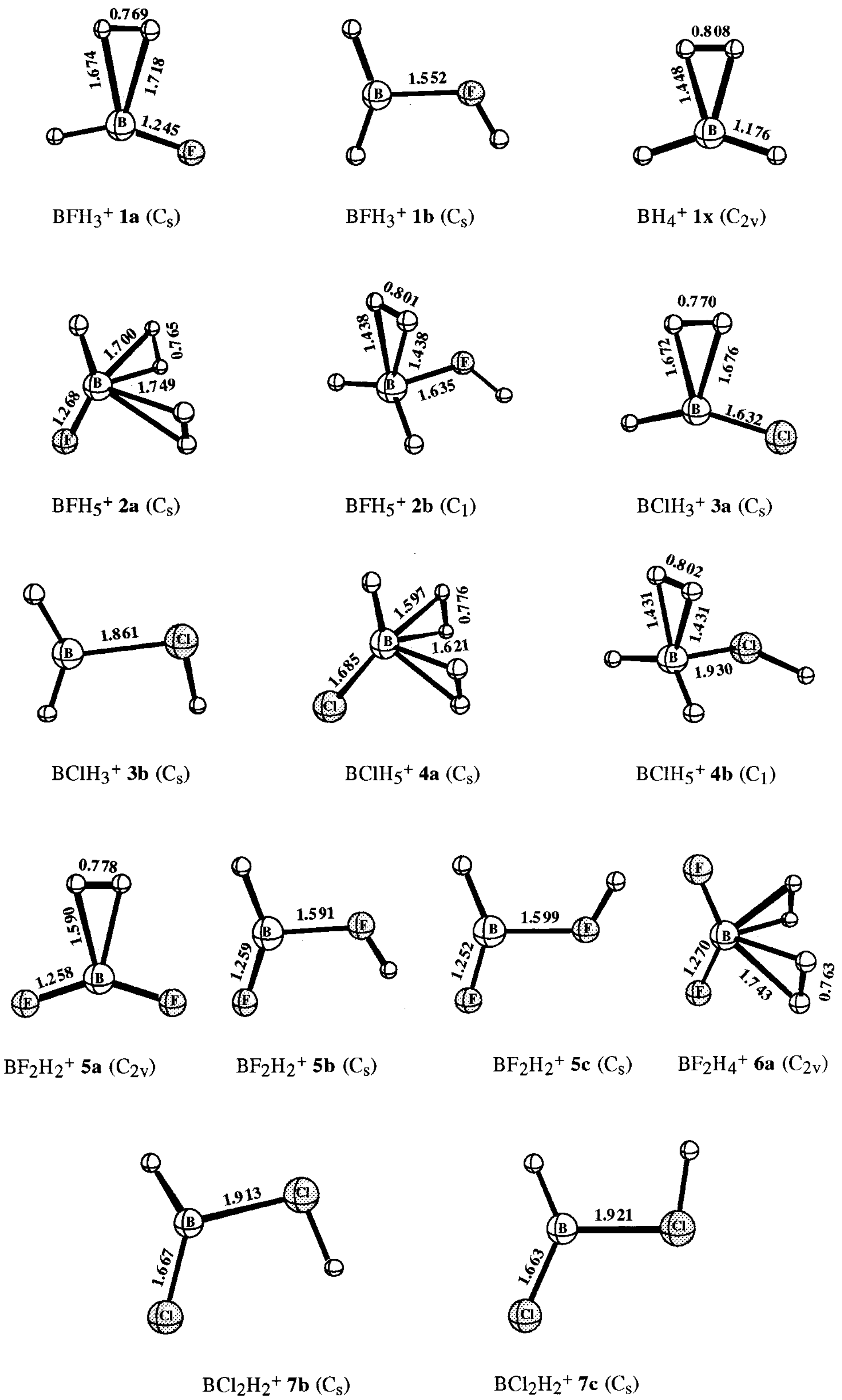
(18) Proton affinities on the halogens at 298 K were calculated at the MP4(SDTQ)/cc-pVTZ//MP2/6-311+G** + ZPE level (PA = 126.1 (BFH_2), = 145.7 ($BClH_2$), and = 124.4 kcal/mol (BF_2H)) and the MP2/6-311+G**Z//MP2/6-311+G** + ZPE level (PA = 146.0 kcal/mol (BCl_2H)); for calculational procedure, see: Hartz, N.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 1277.



BFH_3^+ **1a** (C_s) BFH_3^+ **1b** (C_s) BH_4^+ **1x** (C_{2v})

BFH_5^+ **2a** (C_s) BFH_5^+ **2b** (C_1) $BClH_3^+$ **3a** (C_s)

$BClH_3^+$ **3b** (C_s) $BClH_5^+$ **4a** (C_s) $BClH_5^+$ **4b** (C_1)

$BF_2H_2^+$ **5a** (C_{2v}) $BF_2H_2^+$ **5b** (C_s) $BF_2H_2^+$ **5c** (C_s) $BF_2H_4^+$ **6a** (C_{2v})

$BCl_2H_2^+$ **7b** (C_s) $BCl_2H_2^+$ **7c** (C_s)

Figure 1. MP2/6-311+G** structures of **1**−**7**.

five-coordinate boron and a 3c−2e bond, respectively. However, **4a** is substantially less stable than **4b** by 11.0 kcal/mol (Table 1). Ion **4b** can also be considered as a complex between BH_4^+ and HCl. Formation of **4b** from BH_4^+ and HCl was calculated to be exothermic by 32.4 kcal/mol (Table 1).

$BF_2H_2^+$ and $BF_2H_4^+$. B−H protonated form **5a** with a 3c−2e bond and two F-protonated forms **5b** and **5c** (Figure 1) were found to be the minima. Between the two F-protonated forms, **5b** is slightly more stable than **5c** by 0.5 kcal/mol. However, unlike protonated BFH_2, the F-protonated **5b** is more more stable than the B−H protonated **5a** form by 2.4 kcal/mol. Thus the fluorine nonbonded electron pairs are better donors than the B−H bond in BF_2H. Complexation of BF_2^+ with H_2 to give **5a** (Scheme 1) and complexation of BFH^+ with HF to give **5b** (Scheme 2) were both calculated to be exothermic by 8.0 and 23.6 kcal/mol, respectively.

Further complexation of **5a** with H_2 leads to $BF_2H_4^+$ **6a**. Similar to **2a**, the C_{2v}-symmetric structure **5a** also contains a hexacoordinate boron and two 3c−2e bonds (Figure 1). Formation of **6a** from **5a** and H_2 is also exothermic by 2.2 kcal/mol (Scheme 1). No minimum could be located for the complex of **5b** with H_2.

Unlike BF_2H, protonation on BCl_2H seems to occur primarily on the chlorine atom to give **7b** and **7c** (Figure 1) since on PES the B−H protonated structure is not a minimum. This is also consistent with the calculated[18] PA on the chlorine of BCl_2H (146.0 kcal/mol), which was found to be significantly higher than PA on the fluorine of BF_2H (124.4 kcal/mol). The structure **7c** is slightly more stable than **7b** by 0.3 kcal/mol. No minimum for the complex of **7b** or **7c** with H_2, however, could be located.

Conclusion

The structures and stabilities of protonated BXH_2 and BX_2H (X = F and Cl), BXH_3^+ and $BX_2H_2^+$, as well as their dihydrogen complexes BXH_5^+ and $BX_2H_4^+$, respectively, were calculated at the MP2/6-311+G** level. Global minimum structures for the BFH_3^+ and $BClH_3^+$ were found to be B−H protonated **1a** with a 3c−2e bond and Cl-protonated **3b**, respectively. Complexation of **1a** with H_2 leads to BFH_5^+ **2a** with a hexacoordinate boron atom and two 3c−2e bonds. On the other hand complexation of **3b** with H_2 leads to boronium-chloronium structure **4b** with a 3c−2e bond. Thermodynamics of the various complexation processes were computed. Structures of $BH_2F_2^+$ and $BF_2H_4^+$ were also calculated and discussed.

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