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Structure, Nature of Bonding, and Charge Distribution in Hydridoborane Dications BH_n^{2+} ($n = 1-8$)[1a]

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Structures and stabilities of hydridoborane dications BH_n^{2+} ($n = 1-8$; **1−8a**) were calculated at the ab initio MP2/aug-cc-pVTZ and DFT B3LYP/aug-cc-pVTZ levels of theory. The dications BH^{2+} (**1a**) and BH_2^{2+} (**2a**) were characterized as being unstable, both kinetically and thermodynamically. However, dications BH_n^{2+} ($n = 3-8$; **3−8a**) have a considerable kinetic barrier for deprotonation. Each of the structures **3−8a** contains one or more two-electron, three-center (2e−3c) bonds. In the BH_n^{2+} ($n = 1-8$) series, the calculated energies and kinetic barriers of protodissociation indicate an increasing stability of the dications toward protodissociation with the increase in the number of hydrogen substituents.

Introduction

The structures of main group hydrido dications are of fundamental importance and have been a topic of numerous experimental and theoretical studies.[2] Structures and bondings of such highly electron deficient dications are of substantial significance. We have previously reported calculated structures of CH_3^{2+}, CH_5^{2+}, and CH_6^{2+} carbodications.[3−5] The structure of CH_4^{2+} dication was reported by Wong and Radom.[6] We have also recently reported structures and energetics of hydrido onium dications XH_4^{2+} and XH_5^{2+} (X = N, P, and As),[7,8] boronium BH_5^{2+} and BH_7^{2+} dications,[4,9] and their corresponding alonium analogues, AlH_5^{2+} and AlH_7^{2+} dications.[10] In continuation of our study of the main group hydrido dications, we have now extended our investigations to the structures and energetics of hydridoborane dications BH_n^{2+} ($n = 1-8$) by ab initio and density functional theory (DFT) calculations.

Calculations

Calculations were performed by using the Gaussian 98 program system.[11] Geometry optimizations were performed at the ab initio MP2/aug-cc-pVTZ level. For comparison optimizations were also carried out at the DFT B3LYP/aug-cc-pVTZ level of theory.[12] Vibrational frequencies at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level were used to characterize stationary points as minima (number of imaginary frequencies (NIMAG) = 0) or transition-state structures (NIMAG = 1) and to evaluate zero-point vibrational energies (ZPE), which were scaled by a factor of 0.98.[13] Final energies were calculated at the MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ+ZPE level. Atomic charges and Wiberg bond index[14] (bond order) were obtained using the natural bond orbital analysis (NBO) method.[15]

Results and Discussion

Structure **1a** was found to be a minimum (Figure 1) on the potential energy surface (PES) of singlet BH^{2+} at the MP2/aug-cc-pVTZ level of theory. In diatomic **1a** there are only two valence electrons which are involved in the B−H bond. The computed distance for B−H bond is 1.423 Å. This is 0.235 Å longer than the B−H bond of neutral BH_3 (Figure 1) calculated at the same MP2/aug-cc-pVTZ level. For comparison, the structure **1a** was also calculated at the DFT B3LYP/aug-cc-pVTZ level (Figure 1). DFT, however, predicts a slightly longer B−H bond length of 1.470 Å. The relative bond strength of the B−H bond of **1a** was estimated using the Wiberg bond index[13] analysis (Figure 2). The computed bond index of the B−H bond was found to be 0.79 (MP2/aug-cc-pVTZ). This is 0.16 units less than the calculated B−H bond index of BH_3. NBO charge calculations show that in dication **1a** the boron carries a charge of 1.59 and the hydrogen carries 0.41 (Figure 2). Expectedly, the dication was found to be highly unstable both kinetically and thermodynamically. The dissociation of **1a** into B^+ and H^+ is calculated to be exothermic by 133.6 kcal/mol (Table 1). The transition structure **1ats** for the dissociation lies only 1.0 kcal/mol higher in energy than structure **1a** at the MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level (Table 2). Including the zero-point vibrational energy (i.e., at the MP4(SDTQ)/aug-cc-pVTZ//MP2/aug-cc-pVTZ+ZPE level), the transition structure **1ats** in fact lies 0.4 kcal/mol lower in energy than structure **1a**. This is due to the large imaginary frequency of **1ats** (693*i*) that is a major contributor to the large differences in the zero-point vibrational energies of **1a** and **1ats**. These results indicate that the dication **1a**, if formed, will dissociate spontaneously.

The linear $C_{\infty v}$ symmetric structure **2a** and the bent C_{2v} symmetric structure **2b** were located as minima on the PES of BH_2^{2+} (Figure 1). The structure **2a** is characterized with a two-electron, two-center (2e−2c) B−H bond with a length of 1.272 Å and a two-center, one-electron (2c−1e) B−H bond with a length of 1.756 Å. The structure resembles a complex between BH^{2+} **1a** and a hydrogen atom. The electron deficient longer B−H bond is expectedly very weak, as indicated by a calculated bond index of only 0.25 (Figure 2). On the other hand, structure **2b** is characterized with a two-electron, three-center (2e−3c) bond involving the boron and two hydrogen atoms. However, structure **2a** is 4.2 kcal/mol more stable than **2b**. The linear

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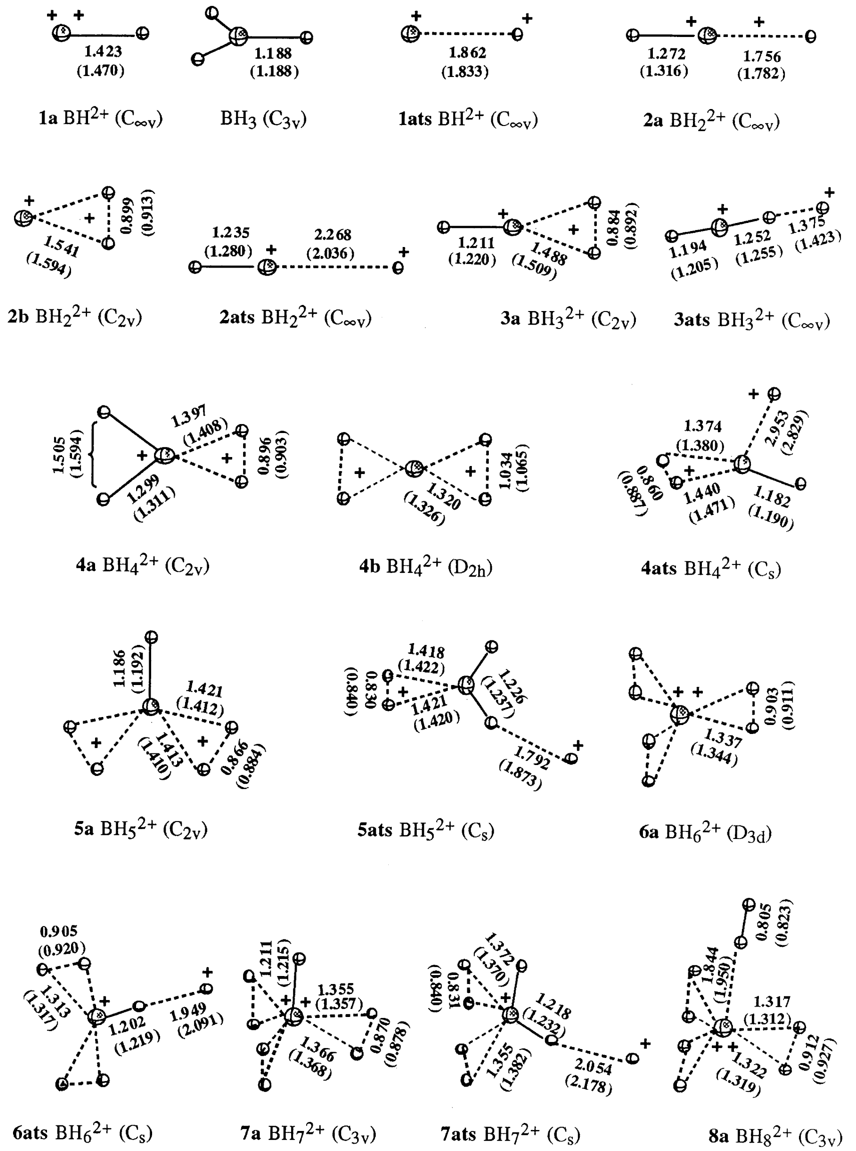

1a BH^{2+} ($C_{\infty v}$) BH_3 (C_{3v}) **1ats** BH^{2+} ($C_{\infty v}$) **2a** BH_2^{2+} ($C_{\infty v}$)

2b BH_2^{2+} (C_{2v}) **2ats** BH_2^{2+} ($C_{\infty v}$) **3a** BH_3^{2+} (C_{2v}) **3ats** BH_3^{2+} ($C_{\infty v}$)

4a BH_4^{2+} (C_{2v}) **4b** BH_4^{2+} (D_{2h}) **4ats** BH_4^{2+} (C_s)

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

6ats BH_6^{2+} (C_s) **7a** BH_7^{2+} (C_{3v}) **7ats** BH_7^{2+} (C_s) **8a** BH_8^{2+} (C_{3v})

Figure 1. MP2/aug-cc-pVTZ (B3LYP/aug-cc-pVTZ values are given in parentheses) structures of **1**−**8**.

$D_{\infty h}$ symmetric structure was not found to be a minimum on the PES of BH_2^{2+}. In dication **2a** boron carries 1.21 of charges and the two hydrogens carry 0.79 (Figure 2). The dication **2a** was also characterized to be highly unstable. Deprotonation of **2a** is exothermic by 105.5 kcal/mol (Table 1), and the process has a kinetic barrier of only 1.8 kcal/mol through transition state **2ats** (Figure 1). This indicates that if the dication **2a** is formed, it will also dissociate spontaneously.

The C_{2v} symmetric structure **3a** is the only minimum that was located on the PES of singlet borane dication BH_3^{2+} (Figure 1). The structure **3a** is characterized with a 2e−3c bond and a 2e−2c bond, resembling a complex between BH^{2+} **1a** and dihydrogen. The B−H and H−H bond distances of the 2e−3c interaction are 1.488 and 0.884 Å, respectively. The deprotonation of **3a** is exothermic by 99.8 kcal/mol, but the process has a kinetic barrier of 8.2 kcal/mol through transition state **3ats** (Figure 1).The dissociation of **3a** into **1a** and H_2 is, however, highly endothermic by 93.3 kcal/mol (Table 1).

The both planar C_{2v} symmetric form **4a** and D_{2h} symmetric form **4b** were located as minima for the doublet BH_4^{2+} (Figure 1). The structure **4a** is characterized with a 2e−3c bond. On the other hand, the structure **4b** is characterized with two 2e−3c bonds. Energetically they are very similar with **4b** only 0.3 kcal/mol more stable than **4a**. Structure **4b** resembles a complex between $B^{2+\bullet}$ and two hydrogen molecules resulting in the formation of two 2e−3c bonds. The sp^2-hybridized boron atom of **4b** possesses two formal orthogonal p-orbitals (containing a single electron), i.e., one planar and the other perpendicular to the plane of the molecule. The calculated charges of boron and each of the hydrogen of **4b** are +0.64 and +0.34, respectively (Figure 2). We have located transition structure **4ats** (Figure 1) for deprotonation in **4a**. No tansition state, however, could be located for deprotonation in more stable **4b**. The deprotonation of **4a** has a substantial kinetic barrier of 24.7 kcal/mol through transition state **4ats**.

Olah and Rasul previously reported[4] the structure and energy of BH_5^{2+} at the QCISD(T)/6-311G** level of theory. The optimized structure of BH_5^{2+} (**5a**) is displayed in Figure 1 for comparison. Structure **5a** resembles a complex between BH^{2+} with two hydrogen molecules resulting in formation of two 2e−3c bonds with an empty p-orbital orthogonal to the plane of the molecule.

The six-coordinate propeller-shaped D_{3d} symmetrical structure **6a** with three 2e−3c bonds is the only minimum on the PES of doublet BH_6^{2+} (Figure 1). The B−H bond distance of **6a** is 1.337 Å, slightly longer than that found in the 2e−3c B−H

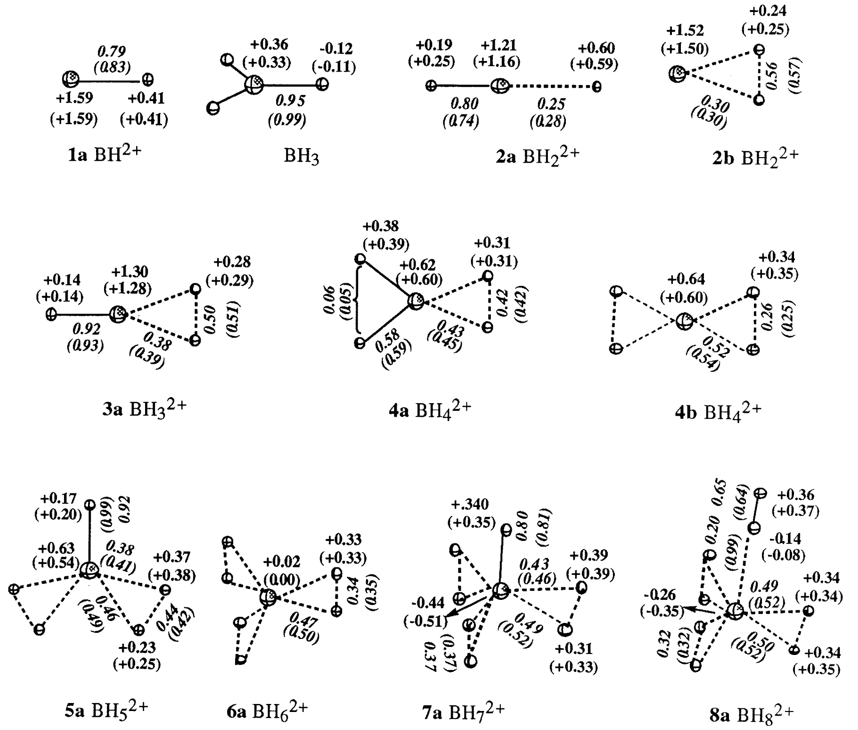

Figure 2. MP2/aug-cc-pVTZ calculated NBO charges, (in italics) Wiberg bond indices, and (in parentheses) B3LYP/aug-cc-pVTZ values of structures **1**−**8**.

TABLE 1: Dissociation Energy (ΔE_0) and Respective Kinetic Barrier at 298 K for the Selected Processes[a]

process	ΔE_0[a] (kcal/mol)	barrier (kcal/mol)
BH^{2+} (**1a**) → $B^+ + H^+$	−133.6	0.0
BH_2^{2+} (**2a**) → $BH^+ + H^+$	−105.5	1.8
BH_3^{2+} (**3a**) → $BH_2^+ + H^+$	−99.8	8.2
BH_4^{2+} (**4b**) → $BH_3^+ + H^+$	−67.0	24.7
BH_5^{2+} (**5a**) → $BH_4^+ + H^+$	−57.0	31.8
BH_6^{2+} (**6a**) → $BH_5^+ + H^+$	−25.9	51.5
BH_7^{2+} (**7a**) → $BH_6^+ + H^+$	−23.4	54.2
BH_2^{2+} (**2b**) → $B^{2+} + H_2$	+92.6	
BH_3^{2+} (**3a**) → BH^{2+} (**1a**) + H_2	+93.3	
BH_4^{2+} (**4b**) → BH_2^{2+} (**2b**) + H_2	+70.1	
BH_5^{2+} (**5a**) → BH_3^{2+} (**3a**) + H_2	+57.3	
BH_6^{2+} (**6a**) → BH_4^{2+} (**4b**) + H_2	+66.5	
BH_7^{2+} (**7a**) → BH_5^{2+} (**5a**) + H_2	+56.0	
BH_8^{2+} (**8a**) → BH_6^{2+} (**6a**) + H_2	−0.2	

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

TABLE 2: Total Energies (au), ZPE,[a] and Relative Energies (kcal/mol)[b]

	B3LYP/ aug-cc-pvtz	ZPE	MP2/ aug-cc-pvtz	MP4(SDTQ)/ aug-cc-pvtz// MP2/aug-cc-pvtz	rel energy (kcal/mol)
1a	24.140 95	1.4	24.068 15	24.079 84	0.4
1ats	24.139 07	0.0	24.064 41	24.078 27	0.0
2a	24.783 50	3.9	24.691 80	24.703 26	0.0
2b	24.773 33	5.6	24.688 25	24.699 28	4.2
2ats	24.783 37	3.8	24.689 07	24.700 31	1.8
3a	25.483 06	12.5	25.391 38	25.408 20	0.0
3ats	25.447 068	9.1	25.373 03	25.389 760	8.2
4a	26.080 05	16.1	25.969 13	25.989 29	0.3
4b	26.078 83	15.3	25.968 64	25.988 47	0.0
4ats	26.054 61	14.2	25.928 59	25.947 44	24.7
5a	26.769 65	24.9	26.658 49	26.681 25	0.0
5ats	26.716 09	21.1	26.601 14	26.624 53	31.8
6a	27.372 06	30.8	27.250 90	27.277 93	0.0
6ats	27.285 58	25.1	27.160 31	27.186 73	51.5
7a	28.041 16	38.1	27.914 45	27.945 27	0.0
7ats	27.951 00	33.3	27.821 06	27.851 18	54.2
8a	28.574 17	39.2	28.425 99		

[a] Zero-point vibrational energies (ZPE) at B3LYP/aug-cc-pvtz//B3LYP/aug-cc-pvtz scaled by a factor of 0.98. [b] At MP4(SDTQ)/aug-cc-pvtz//MP2/aug-cc-pvtz+ZPE level.

bond (1.320 Å) of BH_4^{2+} (**4b**). The six hydrogen atoms bear almost all of the charges (1.98). The dication was found to have a high kinetic barrier of deprotonation (51.5 kcal/mol through the transition state **6ats**), although the process is exothermic by 25.9 kcal/mol. Even the trication BH_6^{3+} was found to be a minimum, as shown by Olah and Rasul.[4] Interestingly, the monocationic BH_6^+, as predicted, was experimentally observed in the gas phase by DePuy et al.[16]

Rasul and Olah previously reported[9] the structure of BH_7^{2+} at the QCISD(T)/6-311G** level. The optimized structure of BH_7^{2+} (**7a**) with three 2e−3c bonds and a 2e−2c bond is displayed in Figure 1 for comparison. Structure **7a** is isostructural with that of carbon analogue CH_7^{3+}.[17]

We also searched for any eight-coordinate minimum-energy structure for BH_8^{2+}. The propeller-shaped six-coordinate C_{3v} symmetrical structure **8a** was found to be the only minimum on the PES of doublet BH_8^{2+} (Figure 1). Structure **8a** can be considered as a weak complex between BH_6^{2+} (**6a**) and H_2. Accordingly, the distance between the H_2 moiety and the boron atom was found to be long with a distance of 1.844 Å. The loss of H_2 from structure **8a** was calculated to be slightly exothermic by 0.2 kcal/mol.

Conclusions

Structures and stabilities of BH_n^{2+} ($n = 1-8$) dications were calculated at the ab initio MP2/aug-cc-pVTZ and DFT B3LYP/aug-cc-pVTZ levels of theory. Structures **1**−**8a** were found to be the minima for the dications. The dications BH^{2+} (**1a**) and BH_2^{2+} (**2a**) were found to be highly unstable both kinetically and thermodynamically. However, dications BH_n^{2+} ($n = 3-8$; **3**−**8a**) have considerable kinetic barrier for deprotonation. Each of the structures **3**−**8a** contains at least one 2e−3c bond. The calculated energies and kinetic barriers of protodissociation indicate an increase in the stability of the dications toward protodissociation with the increase in the number of hydrogens. The Wiberg bond indices and charge distributions of the structures by the NBO method were also computed.

A significant implication of our work is to understand the nature of bonding of highly electron-deficient higher coordinate main group ions (superelectrophiles).[18] Although such hydrido dications are thermodynamically unstable, their computational characterization gives additional support for their transient existence and probable involvement in superacid-catalyzed processes and gas-phase ion molecule reactions. Better stabilization of some of these dications by Schmidbaur type auration[19] with $(C_6H_5)_3PAu$, an isolobal analogue of H^+, should also be possible.

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