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Competition between Hydrogen and Dihydrogen Bonding: Interaction of B_2H_6 with HF and LiH

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Ab initio calculations were used to analyze the interactions between a molecule of B_2H_6 with HF and LiH at the MP2/aug-cc-pvdz computational level. B_2H_6 could interact with HF and LiH through both its terminal (H_t) and bridged (H_b) hydrogens. Interaction of H_b of B_2H_6 with HF and LiH result in formation of H_b···F hydrogen and H_b···H dihydrogen bonds, respectively. In contrast, H_t of B_2H_6 leads to formation of H_t···H and H_t···Li bonds in the interaction with HF and LiH. The B_2H_6–LiH complexes are more stable than B_2H_6–HF counterparts. The structures obtained have been analyzed with the atoms in molecules (AIMs) methodology.

Diborane (B_2H_6) is a colorless gas with a repulsive and sweet odor. The major uses of diborane are in the chemical industry, electronics industry, rubber vulcanization, hard boron coatings on metals and ceramics, doping agents for p-type semiconductors, and as an additive for high-energy fuels.[1–6]

Borane complexes have been studied extensively and even been the subject of Nobel Prize work by Brown.[7,8] It has been the subject of proton affinity experiments in chemical ionization mass spectrometers.[9] Borane compounds are an important class which contain dihydrogen bonding.[10–25]

Diborane as the simplest member of borane complexes is an unusual compound that exhibits four terminals (H_t–B) and two bridging (B–H_b–B) hydrogen atoms which are different in their nature and characteristics.[26] The bridged hydrogen atoms (H_b) are incorporated in so-called "three-center, two-electron" 3c–2e bonds, thus hydrogen bonding with HX ($B–H_b^{\delta+}\cdots{}^{\delta-}X–H$) or DHB with metal hydrides ($B–H_b^{\delta+}\cdots{}^{\delta-}H–M$) is expectable for them. Oppositely, H_t atoms of B_2H_6 due to bearing negative charges are favorable for dihydrogen bond (DHB) interaction with HX ($B–H_t^{\delta-}\cdots{}^{\delta+}H–X$), inverse hydrogen bonding (IHB) or metal bonding with metal hydrides ($B–H_t^{\delta-}\cdots{}^{\delta+}M–H$). Apparently, former interactions have been less studied for 3c–2e bonds. Here the ability of B_2H_6 to form H_b···F or LiH···H_b is aim of our investigation. Results of this work on characteristics of H_b atoms could be tried for other 3c–2e bonds in heavier coordination and organometallic complexes. From a fundamental point of view, the present work aims to extend the knowledge of the intrinsic activity of H_t and H_b atoms of B_2H_6 as hydrogen bond acceptor or hydrogen bond donor toward other molecules.

Computational Methods

Calculations were performed using the Gaussian 03 system of codes.[27] The geometries of the isolated B_2H_6, HF and LiH moieties as well as B_2H_6–HF and B_2H_6–LiH complexes were fully optimized at the MP2/aug-cc-pvdz computational level. Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of zero point energy (ZPE). The counterpoise procedure was used to correct the interaction energy for basis set superposition error.[28]

Results and Discussion

B_2H_6–HF Complexes. Association of one molecule of B_2H_6 with one molecule of HF leads to the formation of S1-B_2H_6–HF, S2-B_2H_6–HF, and S3-B_2H_6–HF complexes illustrated in Figure 1. In S1-B_2H_6–HF a weak hydrogen bond has been predicted between a bridging proton of the B_2H_6 as a proton donor and fluorine atom of HF as a proton acceptor (B–H_b···F–H). This type of interaction recently has been predicted for diborane.[26] On the other hand, S2-B_2H_6–HF and S3-B_2H_6–HF are usual DHB complexes, in which terminal protons of B_2H_6 act as proton acceptor and HF acts as proton donor (B–H_t···H–F). In the S2-B_2H_6–HF the HF molecule lies in plane with terminal hydrogens of B_2H_6, while in the S3-B_2H_6–HF the HF is approximately perpendicular to the plane of H_ts of diborane. Also structures with imaginary frequencies S4-B_2H_6–HF and S5-B_2H_6–HF have been optimized. Table 1 gives the stabilization energies (SE) of B_2H_6–HF complexes. According to these results stability of complexes are in the order: S2-B_2H_6–HF > S1-B_2H_6–HF > S3-B_2H_6–HF.

Results of intermolecular bond lengths are given in Figure 1. The H–F bond is 0.925 Å in free HF and slightly elongated in the H_t···HF dihydrogen bond complexes. On the other hand, B–H_t is 1.198 Å in the free B_2H_6 molecule which increases to 1.203–1.205 Å in DHB complexes. Therefore dihydrogen bond formation is accompanied by weakness of both H–F and B–H_t bonds in these systems. Also, B–B distance is 1.782 Å in free B_2H_6 which decreased to 1.776–1.778 in studied complexes.

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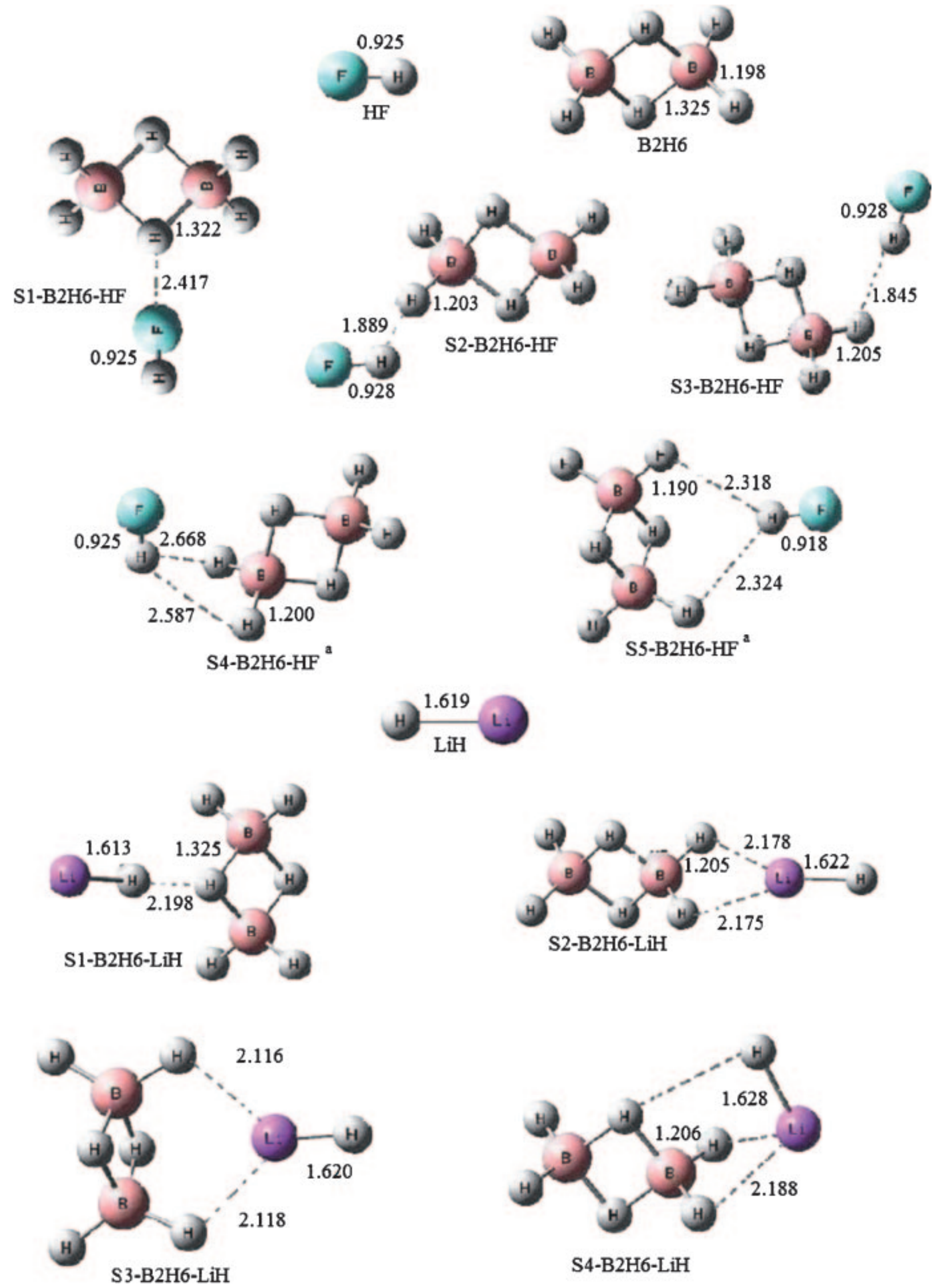

Figure 1. Schematic representation of B_2H_6–HF complexes. ^{a}Structures with imaginary frequencies.

In S1-B_2H_6–HF hydrogen bond complex the H–F bond remained constant but B–H_b bond decreased from 1.325 Å in free B_2H_6 to 1.322 in HB complex.

The selected vibrational stretching frequencies (cm^{-1}) with corresponding intensities ($km\,mol^{-1}$) for complexes are listed in Table 2. In both HB and DHB complexes the HF molecule shows red shift upon complex formation. This red shift is accompanied by lengthening of HF bond and in DHB complexes it is greater than the HB complex.

B_2H_6–LiH Complexes. Association of a molecule of B_2H_6 with a molecule of LiH leads to the formation of a dihydrogen bond complex S1-B_2H_6–LiH, two lithium bond complexes S2-B_2H_6–LiH, S3-B_2H_6–LiH, and another complex which is stabilized via interaction of B with two atoms of interacting LiH molecule as depicted in Figure. In S1-B_2H_6–LiH a dihydrogen bond has been predicted between a bridging proton of the B_2H_6 as a proton donor and hydrogen atom of LiH as a proton acceptor (B–H_b···H–Li). Two different kinds of bifurcated lithium bonds have been predicted in S2-B_2H_6–LiH, and S3-B_2H_6–LiH dimers which formed between terminal hydrogens of the B_2H_6 as electron donor and lithium atom of LiH as an electron acceptor. These kinds of interactions rarely have been reported for boranes previously. Stabilization energies of these complexes with their basis set superposition error (BSSE) is given in Table 1 and has been predicted in the order: S2-B_2H_6–LiH > S4-B_2H_6–LiH > S3-B_2H_6–LiH > S1-B_2H_6–LiH.

Intermolecular bond lengths are presented in Figure 1. The Li–H bond is 1.619 Å in the free LiH molecule and elongated to 1.622–1.628 in the B_2H_6–LiH inverse hydrogen bond (lithium bond) complexes.[29,30] On the other hand, B–H_t is 1.198 in the free B_2H_6 molecule which is increased to 1.204–1.206 in lithium bond complexes. Therefore inverse hydrogen bond formation is acompany with weakness of both LiH and B–H_t bonds in this system. In S1-B_2H_6–LiH dihydrogen bond complex the LiH bond is reduced to 1.613 which means that DHB formation leads to strengthening of LiH bond. The B–H_b bond remained constant.

The LiH$\cdots H_b$ distance in DHB complex is 2.198 and for lithium bond complex the $H_t\cdots$Li distance is 2.116–2.188. These distances could be considered as moderate bonding interactions between two components. For lithium bond complexes comparison of the $H_t\cdots$Li distances shows that this bond in S3-B_2H_6–LiH is shorter than S2-B_2H_6–LiH and S4-B_2H_6–LiH which are in contrast with stability of these complexes. For interpretation of this observation it might be mentioned that in S3-B_2H_6–LiH and S4-B_2H_6–LiH complexes bonding interaction occurred between Li with H_t atoms as electron donor.

The selected vibrational stretching frequencies (cm^{-1}) with corresponding intensities ($km\,mol^{-1}$) for complexes are detailed in Table 2. In DHB complex S1-B_2H_6–LiH the LiH bond shows blue shift upon complex formation. This blue shift is in agreement with shortening of the LiH bond. In lithium bond complexes different behaviors have been predicted. S3-B_2H_6–LiH stretching frequency of LiH remained constant in S2-B_2H_6–LiH and S4-B_2H_6–LiH shows red shift upon complex formation. These red shifts are in agreement with changes predicted for Li–H distance. Two other important parameters are vibrational stretching frequencies of LiH$\cdots H_b$ and $H_t\cdots$Li. Data given in Table 2 show that $H_t\cdots$Li in lithium bond complexes appeared at higher frequencies relative to LiH$\cdots H_b$ in DHB. This relates to greater stabilities of lithium bonds with respect to DHB complex.

Table 1. The BSSE, SE_{corr} (Corrected with ZPE), SE_{unc} (Uncorrected with ZPE) in $kcal\,mol^{-1}$ Calculated at MP2/aug-cc-pvdz

Complex	BSSE	SE_{corr}	SE_{unc}
S1-B_2H_6–HF	0.71	−1.20	−1.73
S2-B_2H_6–HF	0.78	−1.21	−2.39
S3-B_2H_6–HF	0.84	−0.93	−2.09
S4-B_2H_6–HF[a)]	—	—	−1.82
S5-B_2H_6–HF[a)]	—	—	−1.72
S1-B_2H_6–LiH	1.04	−2.84	−3.91
S2-B_2H_6–LiH	1.31	−4.99	−6.19
S3-B_2H_6–LiH	1.44	−3.98	−5.20
S4-B_2H_6–LiH	1.26	−4.80	−6.21

a) Structures with imaginary frequencies.

The atoms in molecules (AIM) theory[31,32] is applied here to analyze the characteristics of the H$\cdots H_t$, F$\cdots H_b$, Li$\cdots H_t$, and H$\cdots H_b$ bond critical points (BCP) in studied complexes. The parameters ($\nabla^2_{\rho\mathrm{BCP}}$ is Laplacian of electron density at BCP and H_C is the electron density at BCP and is the sum of the kinetic electron energy density (G_C) and the potential electron density (V_C), $H_C = G_C + V_C$) derived from the Bader theory also indicate the type of interaction. The negative value of the Laplacian of the electron density at BCP ($\nabla^2_{\rho\mathrm{BCP}} < 0$) designates the concentration of the electron charge in the region between the nuclei of the interacting atoms and is typical of covalent bonds-shared interactions. In the case of the $\nabla^2_{\rho\mathrm{BCP}} > 0$, there is a depletion of the electron charge between atoms, indicating that there is an interaction of closed-shell systems like ions, van der Waals interactions, or H-bonds. Hence one can see that the Bader theory arbitrarily provides the characteristics of BCPs based on whether the interaction is covalent in nature. For a negative value of a Laplacian, there is no doubt about its covalency (from the AIM theory point of view). When $H_C < 0$, we have an H-bond or van der Waals interaction while $H_C > 0$ returns to bonds with covalent in character.

The analysis of the electron density within the AIM methodology shows the presence of bond critical points (Table 3 and Figure 2) between the atoms involved in the interactions. All kinds of interactions have $\nabla^2_{\rho\mathrm{BCP}} > 0$ and $H_C < 0$ which they are noncovalent in nature and they could be considered as HB, DHB, or IHB interaction.

Table 2. Unscaled Vibrational Frequencies (cm^{-1}) with Corresponding Intensities (Values Given in Parenthesis, $km\,mol^{-1}$) Calculated at MP2/aug-cc-pvdz Level

Complex	νX–H (X = Li and F)	νB–H_b	νB–H_t
B_2H_6	—	1756(535), 2016(11)	2629(150), 2742(178)
HF	4082(116)	—	—
S1-B_2H_6–HF	4072(136)	1755(515), 2032(5)	2625(156), 2737(186)
S2-B_2H_6–HF	3993(426)	1748(563), 2033(7)	2613(157), 2649(34)
	—	—	2714(38), 2750(106)
S3-B_2H_6–HF	3996(293)	1748(515), 2029(7)	2608(146), 2647(36)
	—	—	2719(59), 2749(124)
LiH	1378(217)	—	—
S1-B_2H_6–LiH	1427(339)	1731(457), 2158(48)	2615(165), 2725(196)
	—	1737(563), 2033(7)	—
S2-B_2H_6–LiH	1373(395)	1737(508), 2206(8)	2590(151), 2662(38)
	—	—	2674(42), 2770(65)
S3-B_2H_6–LiH	1378(371)	1737(430)	2610(58), 2627(74)
	—	—	2735(18), 2749(134)
S4-B_2H_6–LiH	1353(263)	1713(573), 2182(23)	2585(160), 2648(43)
	—	—	2660(49), 2750(82)

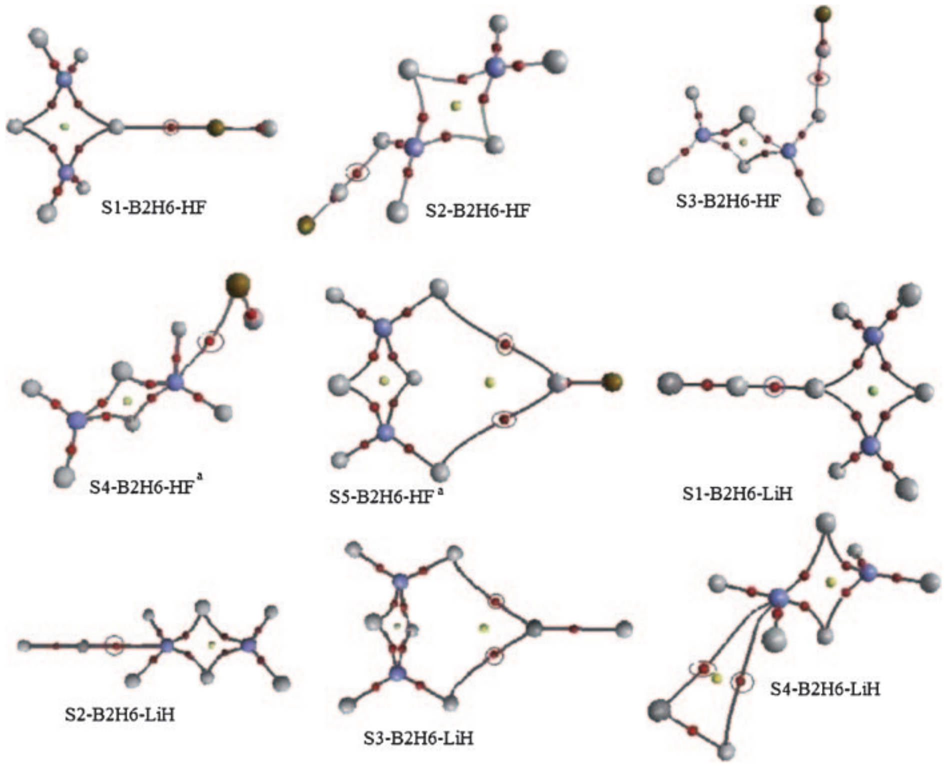

Figure 2. Molecular graphs of B_2H_6–HF and B_2H_6–LiH complexes at MP2/aug-cc-pvdz level. [a]Structures with imaginary frequencies.

Table 3. Topological Parameters for the Fully Optimized Complexes

Complex	H-bond	ρ_{BCP}	$\nabla^2\rho_{BCP}$	$-H_C$
S1-B_2H_6–HF	F···H	0.0076	0.0324	0.0010
S2-B_2H_6–HF	H···H	0.0127	0.0431	0.0024
S3-B_2H_6–HF	H···H	0.0133	0.0424	0.0010
S1-B_2H_6–LiH	LiH···H	0.0100	0.0223	0.0003
S2-B_2H_6–LiH	Li···B	0.0094	0.0587	0.0039
S3-B_2H_6–LiH	Li···H	0.0072	0.0484	0.0033
	Li···H	0.0072	0.0482	0.0033
S4-B_2H_6–LiH	Li···B	0.0103	0.0666	0.0089
	Li···B	0.0107	0.0184	0.0046

Conclusion

B_2H_6 might form weak hydrogen bond as well as dihydrogen bond complexes with HF. For interaction of B_2H_6 with LiH both DHB and lithium bond complexes have been predicted. According to our results B_2H_6–LiH dimers are more stable than B_2H_6–HF.

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