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Unusual Hydrogen Bonds with a Hydride Atom in Boron Hydrides Acting as Proton Acceptor. Spectroscopic and Theoretical Studies

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The interaction of different proton donors with ionic (Bu_4NBH_4) and neutral (BH_3NEt_3, $BH_3P(OEt)_3$) boron hydrides was studied by IR and NMR spectroscopy in solution (CH_2Cl_2, C_6H_14, and C_6D_{12}). A close similarity was observed between the spectral and thermodynamic properties of these unusual $BH\cdots HX$ and those of classical H bonds. The typical characteristics of hydrogen bonding, such as linearity of the fragment $H\cdots HX$, lengthening of X−H and H−B bonds, and strong electron redistribution, were confirmed by ab initio calculations.

Introduction

Classical hydrogen bonds between proton donors and organic bases containing heteroatoms with an *sp*-type lone electron pair or π bonds play a substantial role in chemical and biochemical processes. They have long been under extensive investigation both experimentally and theoretically. In recent years a new and unusual type of hydrogen bond was found where the hydride atom of a transition metal hydride plays the role of proton acceptor: $MH\cdots HX$. Intramolecular H bonds $IrH\cdots HX$ (X = N, O) were studied by NMR, X-ray, and IR spectroscopy (the latter was used only in the case of solid samples).[2] We recently provided the first spectral and thermodynamic data for intermolecular H bonds $MH\cdots HO$ (M = W, Re) in nonpolar media obtained by IR and NMR spectroscopy.[3] A neutron diffraction study of the $[ReH_5(PPh_3)\cdot indole]$ adduct proved the existence of such an H bond in a crystal.[4] The first theoretical studies of these unusual H complexes were presented.[2e,3b,5]

The ability of main group hydrides to form the same hydrogen−hydrogen bonding mode ("dihydrogen" bond) was discussed by Crabtree with reference to aminoboranes.[6] The analysis of structures from The Cambridge Crystallographic Database (CSD) showed that the $H\cdots H$ distances are in many cases comparable with those found for H bonds of the $MH\cdots HX$ type (1.7−2.2 Å), $B-H\cdots H(N)$ angles being variable over a wide interval from 170 to 95°. On this basis the author made a conclusion about the bent character of such a bond. Theoretical calculations on the dimer $(BH_3NH_3)_2$ confirmed the unusual character of $B-H\cdots H-N$ bond.[6]

The first experimental data on intermolecular interactions of BH_3 and BH_2 groups with proton donors were obtained in the 1970s and were unfairly forgotten.[7] Recently we published a short communication about the spectral investigation of $BH\cdots HX$ bonds in solution.[8]

The aims of this work were to determine the spectral and thermodynamic characteristics of H bonds with the hydride atom of boron hydride as proton acceptor and to correlate the properties of such unusual H bonds found experimentally and theoretically with those of classical hydrogen bonds. The salt Bu_4NBH_4 and neutral hydrides BH_3NEt_3 and $BH_3P(OEt)_3$ were selected for investigation of the interactions with proton donors of different strengths: $(CF_3)_3COH$ (PFTB), $(CF_3)_2CHOH$ (HFIP), CF_3CH_2OH (TFE), Pr^iOH, MeOH, and indole. We studied these interactions in CH_2Cl_2, C_6H_{14}, and C_6D_{12} by IR and NMR spectroscopy. The structure and the $H\cdots H$ interaction energy of the model H complexes (BH_4^- and NH_3BH_3 with

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(2) (a) Lough, A. J.; Park, S.; Ramashandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356. (b) Park, S.; Ramashandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (c) Lee, J. C.; Peris, E.; Rheingold, A.; Crabtree, R. H. *J. Am. Chem. Soc.*, **1994**, *116*, 11014. (d) Lee, J. C.; Rheingold, A.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun* **1994**, 1021. (e) Peris, E.; Lee, J. C.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485.

(3) (a) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105. (b) Belkova, N. V.; Shubina, E. S.; Ionidis, A. V.; Epstein, L. M.; Jacobson, H.; Niedermann, M.; Berke, H. *Inorg. Chem.* **1997**, *36*, 1522. (c) Shubina, E. S.; Belkova, N. V.; Ionidis, A. V.; Golubev, N. S.; Smirnov, S. N.; Epstein, L. M. *Izv. Akad. Nauk, Ser. Khim.* **1997**, 1405; *Russ. Chem. Bull.* **1997**, *44*, 1349 (English transl.).

(4) (a) Peris, E.; Wessel, J.; Lee, J. C.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem.* **1995**, *107*, 2711; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507.

(5) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*, 10108.

(6) (a) Richardson, T. B.; de Gala, S.; Crabtree R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875. (b) Crabtree, R. H.; Siegbahn, R. E. M.; Eisenstein, O.; Rheingold, A.; Koetzle, S. A. T. L. *Acc. Chem. Res.* **1996**, *29*, 348.

(7) (a) Brown, M. P.; Heseltine, R. W. *Chem. Commun.* **1968**, 1551. (b) Brown, M. P.; Heseltine, R. W.; Smith, P. A.; Walker, P. J. *J. Chem. Soc. A* **1970,** 410. (c) Brown, M. P.; Walker, P. J. *Spectrochim. Acta* **1974**, 30A, 1125.

(8) Shubina, E. S.; Bakhmutova, E. V.; Saitkulova, L. N.; Epstein, L. M. *Mendeleev Commun.* **1997**, 83.

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Table 1. Spectral Characteristics in the ν(XH) Range for H Complexes (BH···HX)

base	HX	$\nu(XH)_{bonded}$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu$(XH) (cm^{-1})	$A(XH)_{bonded} \times 10^4$ L/(cm^2 mol)
Bu_4NBH_4[a]	HFIP	3177	185	402	11.8
	TFE	3310	171	290	8.0
	MeOH	3410	91	214	3.8
	Pr^iOH	3416	89	192	
	indole	3254	88	219	6.0
BH_3NEt_3[a]	HFIP	3390	112	185	
BH_3NEt_3[b]	HFIP	3443	121	178	3.8
	TFE	3498	102	128	2.9
	MeOH	3566	58	86	
	Pr^iOH	3556	55	75	
	indole	3401	51	96	4.5
$BH_3P(OEt)_3$[b]	PFTB	3405	107	184	3.1
	HFIP	3493	98	116	2.2
	TFE	3544	76	83	1.7
	Pr^iOH	3586	35	47	

[a] In CH_2Cl_2. [b] In hexane.

H_2O and MeOH as well as the dimer ($(NH_3BH_3)_2$) were studied by ab initio methods.

Experimental Section

Tetrabutylammonium tetrahydroborate (Fluka) was dried under vacuum. The absence of water was controlled by IR spectroscopy in the range of ν(OH). BH_3NEt_3 was purchased from Fluka and $BH_3P(OEt)_3$ was prepared at the Institute of New Chemical Problems of Russian Academy of Sciences. Fluorinated alcohols were donated by P&M (Moscow, Russia). Solutions for IR and NMR studies were prepared in an argon atmosphere, and all solvents were freshly distilled in an argon atmosphere.

IR spectra of hexane and dichloromethane solutions (cells CaF_2, $d = 0.012-0.120$ cm) were measured with the "Specord M-80" and "Specord M-82" instruments (Carl Zeiss, Jena) with the resolution 2 cm^{-1}. Low-temperature IR studies were carried out in the XH and BH stretching region with a Carl Zeiss Jena cryostat in the temperature range 200−300 K, with an accuracy in the temperature setting of ±0.5 K.

The NMR data were collected with AMX-400 and WP-200 spectrometers. The ^1H chemical shifts were taken from the resonance of C_6D_{12} as internal standard and recalculated from TMS. The BH_3NEt_3 solution concentrations was 8×10^{-2} mol/L and HFIP concentration varied in the range 8×10^{-2} to 2×10^{-1} mol/L.

Quantum-chemical calculations were carried out by Hartree−Fock method with a 6-31G basis.

Results and Discussion

IR and NMR Evidence for BH···HX Hydrogen Bonding. Hydrogen bond formation of the proton donors with boron hydrides under investigation was detected in the usual range of stretching vibrations ν(XH) of proton donors. The intensity decrease of the free XH groups ($\nu(XH)_{free}$) bands and the appearance of broad intense low-frequency bands of bonded XH groups ($\nu(XH)_{bonded}$) leave no doubt about the formation of hydrogen bonds (Table 1).

The IR spectra of different proton donors (in concentration of 0.005−0.01 mol/L in order to exclude self-association) were measured in hexane in the presence of $BH_3NEt_3/BH_3P(OEt)_3$ and in methylene chloride for the salt Bu_4NBH_4 which is insoluble in hexane. The data in the Table 1 show that all the spectral parameters, such as frequency shifts ($\Delta\nu(XH) = \nu(XH)_{free} - \nu(XH)_{bonded}$), half-widths of the ν(XH) bands ($\Delta\nu_{1/2}$), and integral intensities ($A(XH)_{bonded}$), increase with the proton donating ability of XH acids (P_i, vide infra).[9] The considerable increase of the ν(NH) band intensity on H bonding was explained earlier by the inclusion of the nitrogen atom into the conjugated system of the ring.[9d] For any proton donor, spectral parameters of the $\nu(XH)_{bonded}$ bands decrease on going from a charged boron hydride to neutral ones in the following order: $BH_4^- > BH_3NEt_3 > BH_3P(OEt)_3$. Thus, in the interaction with HFIP, $\Delta\nu_{1/2}$ changes from 185 cm^{-1} (BH_4^-) to 121 (BH_3NEt_3) and 98 cm^{-1} ($BH_3P(OEt)_3$), $\Delta\nu$(OH) are 402, 178, and 116 cm^{-1}, and $A(OH)_{bonded}$ are 11.8, 3.8, and 2.2 L/(cm^2 mol), respectively.

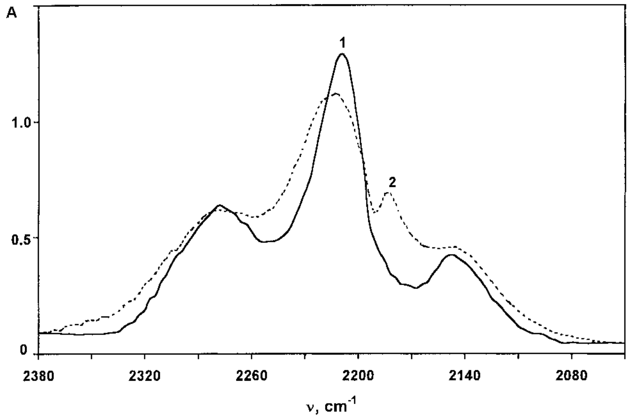

Figure 1. IR spectra in the ν(BH) range in CH_2Cl_2: (1) Bu_4NBH_4 and (2) Bu_4NBH_4 (0.08 mol/L) in the presence of HFIP (0.08 mol/L).

Changes in the range of B−H stretching vibrations $\nu(BH)_{as}$ correspond to the coordination of proton donors with hydride atom as proton acceptor site. As it is known the IR absorptions of ligands being the sites of coordination in H bonding are shifted to lower frequency and the bands of unbound ligands are shifted to higher frequency. That was previously demonstrated for MH···HX, MCO···HX, and MNO···HX bonds in compounds containing two or more ligands.[3,10−12] Therefore the formation of BH···HX hydrogen bonds with boron hydrides including three or four B−H bonds should cause the appearance of both low-frequency bands assigned to H-bonded groups ($\nu(BH)_{bonded}$) and high-frequency bands of free B−H groups in the H complex ($\nu(BH)_{free}$). In fact, in the case of the BH_4^- anion ($\nu(BH)_{as} = 2200$ cm^{-1}) shoulders shifted by 25 cm^{-1} to low frequency and by 10 cm^{-1} to high-frequency both appear in the proton donors presence (Figure 1). Similar changes were observed for the $\nu(BH)_{as}$ (2392 cm^{-1}) band of BH_3NEt_3·HOR complexes with shifts of 20 cm^{-1} to low frequency and 9 cm^{-1} to high frequency. Moreover the band $\nu(BH)_s$ (2283 cm^{-1}) was simultaneously shifted to lower frequency.

The existence of BH···HX bonding can also be firmly deduced from the room-temperature ^1H NMR spectra. For example, addition of BH_3NEt_3 to a C_6D_{12} solution of HFIP (an 1:1 ratio) leads to a downfield shift of the OH group from $\delta = 2.726$ to $\delta = 4.690$ ppm ($\Delta\delta \sim 2$ ppm). In full accordance

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(9) (a) Iogansen, A. V. *Teor. Eksp. Khim.* **1971**, *7*, 302. (b) Iogansen A. V. *Theor. Eksp. Khim.* **1971**, *7*, 314. (c) Iogansen, A. V. *The Hydrogen Bond*; Nauka: Moscow, 1981. (d) Kurkchi, G. A. *Zh. Prikl. Spectrosc.* **1967**, *6*, 829.

(10) (a) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986,** *11*, 2605. (b) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, *4*, 948. (c) Lokshin, B. V.; Kazarian, S. G.; Ginzburg, A. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, *2*, 333.

(11) Hamley, P. A.; Kazarian, S. G.; Poliakoff, M. *Organometallics* **1994**, *13*, 1767.

(12) Shubina, E. S.; Belkova, N. V.; Epstein, L. M. *J. Organomet. Chem.* **1997**, *17*, 536.

Table 2. Thermodynamic Parameters of H Complexes (BH···HX)

base	HX	$-\Delta H^\circ$ [a] (kcal/mol)	$-\Delta H^\circ$ [b] (kcal/mol)	K_f (L/mol)
Bu_4NBH_4[c]	HFIP	6.5	6.0	
	TFE	5.2	5.0	50
	MeOH	4.1	3.9	44
	Pr^{i}OH	3.8 (3,2)[d]		2
	indole	2.5	2.3	7
BH_3NEt_3[c]	HFIP	3.7		8
BH_3NEt_3[e]	HFIP	3.5 (3.4)[d]	3.3	21
	TFE	2.7	2.9	10
	MeOH	1.9		3
	Pr^{i}OH	1.7		2
	indole	1.3	1.4	4
$BH_3P(OEt)_3$[e]	PFTB	3.6	3.1	13
	HFIP	2.5	2.5	12
	TFE	1.9	2.0	7
	Pr^{i}OH	1.1		2

[a] From eq 1. [b] From eq 2. [c] In CH_2Cl_2. [d] From eq 3. [e] In hexane

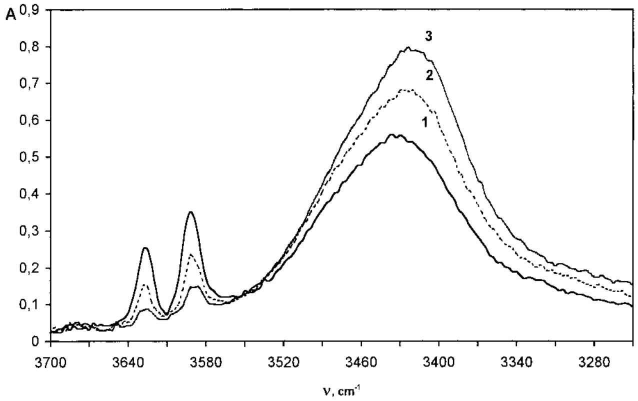

Figure 2. IR spectra in the ν(OH) absorption range of HFIP (0.05 mol/L) in the presence of BH_3NEt_3 (0.09 mol/L) in hexane: (1) 300 K, (2) 280 K, (3) 260 K.

with this proposal, addition of an excess of HFIP to the solution results in high-field displacement of the OH resonance to 4.11 ppm. The $^1H\{^{11}B\}$ NMR spectrum of a C_6D_{12} solution of BH_3NEt_3 shows a quite narrow BH_3 resonance at 1.532 ppm. Addition of excess HFIP is accompanied by transformation of these lines to a strongly broadened resonance at 1.490 ppm (the broadening effect could be attributed to more rapid quadrupole relaxation of ^{11}B). Thus we observe for the BH_3 group some high-field shift due to BH···HX interaction similar to MH···HX bonding.[3]

Strength of the BH···HX Hydrogen Bond. The H-bonding enthalpy values ($-\Delta H^\circ$) of the BH···HX bond were estimated from empirical correlations: $-\Delta H^\circ$ vs $\Delta\nu$(XH) and $-\Delta H^\circ$ vs ΔA(XH) proposed by Iogansen initially for organic systems:[9]

$$-\Delta H^\circ = 18\Delta\nu(\mathrm{OH})/(\Delta\nu(\mathrm{OH}) + 720) \tag{1}$$

$$-\Delta H^\circ = 2.9(\Delta A(\mathrm{OH}))^{1/2} \tag{2}$$

Data from Table 2 indicate that both equations provide similar results. The applicability of these correlations to the unusual hydrogen bonding was shown by the comparison of the $-\Delta H^\circ$ values (Table 2) with those obtained from the temperature dependence of the formation constants (K_f) (Figure 2) as given by the van't Hoff (eq 3) (values in parentheses in Table 2).

$$\Delta H^\circ = \mathrm{d}\ln K_f/\mathrm{d}T\cdot RT^2 \tag{3}$$

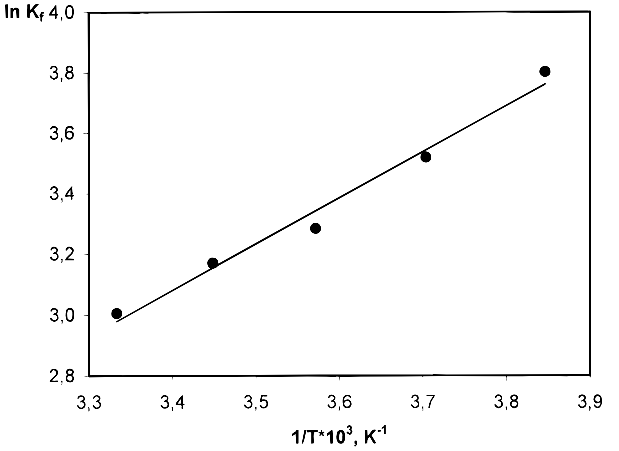

Figure 3. A plot of the ln K_f vs $1/T$ for HFIP·BH_3NEt_3 in hexane (0.05/0.09 mol/L) in the range 250–300 K.

Formation constants K_f were determined for an equilibrium [B]H + HX $\rightleftarrows$ [B]H···HX from eq 4:

$$K_f = [C_{XH} - D/(\epsilon l)]/[(C_{base} - (C_{XH} - D/(\epsilon l)))D/(\epsilon l)] \tag{4}$$

C_{XH} and C_{base} are the initial concentrations of alcohol and the substance respectively, D is the optical density of a $\nu(XH)_{free}$ band of the H complex, ϵ is extinction coefficient, and ls the cell width.

Thus the $-\Delta H^\circ$ values obtained from temperature dependence ln K_f vs $1/T$ (3) and from eq 1 for the system Pr^{i}OH·H_4B^- provide consistent results: 3.2 ± 0.2 and 3.8 ± 0.2 kcal/mol, respectively. The enthalpy in the case of H complex of BH_3NEt_3·HFIP is 3.5 kcal/mol from eq 1 and 3.3 kcal/mol from eq 2 (Table 2). These values are in agreement with that obtained from the van't Hoff equation, eq 3: 3.4 ± 0.2 kcal/mol. The value of entropy, $\Delta S^\circ = -4.6$ eu, was determined from the plot in Figure 3 and normally lies in the range 4–20 eu for H bonds in known organic systems.

As seen from the ΔH° values in Table 2, BH···HX hydrogen bonding is of medium strength (6.5–2.5 kcal/mol) for BH_4^- anion and becomes rather weak for neutral boron hydrides (3.6–1.1 kcal/mol). The strength of H-complexes for any proton donor decreases in the order $BH_4^- \rightarrow BH_3NEt_3 > BH_3P(OEt)_3$. It should be noted that formation constants K_f change in parallel with the H bond strength (Table 2). This indicates the absence of significant steric hindrance for proton donors to approach the boron hydrides under investigation. Only the sterically hindered Pr^{i}OH causes anomalously low K_f values for all three boron hydrides.

Comparison of Properties of BH···HX and Classical Hydrogen Bonds. A thorough analysis of the spectroscopic and thermodynamic characteristics (Tables 1 and 2) enabled us to show the unusual BH···HX interaction to be similar to that of MH···HX[3] as well as M···HX[12] and to be governed by basic laws established for classical hydrogen bonds with bases containing lone electron pairs or π density.

The temperature dependence of the IR spectrum is as expected: the intensity of the bonded XH groups bands increases reversibly with a decrease in temperature (Figure 2).

The isotopic effect of the frequencies quantitatively coincides with that of common medium strength H bonds: $\nu(OH)/\nu(OD) = 1.35$ (Table 1). The data were obtained on the example of MeOH/MeOD interaction with BH_3NEt_3.

The enthalpy values ($-\Delta H^\circ$) determined from the temperature dependence of the formation constants (ln K_f vs $1/T$) and from

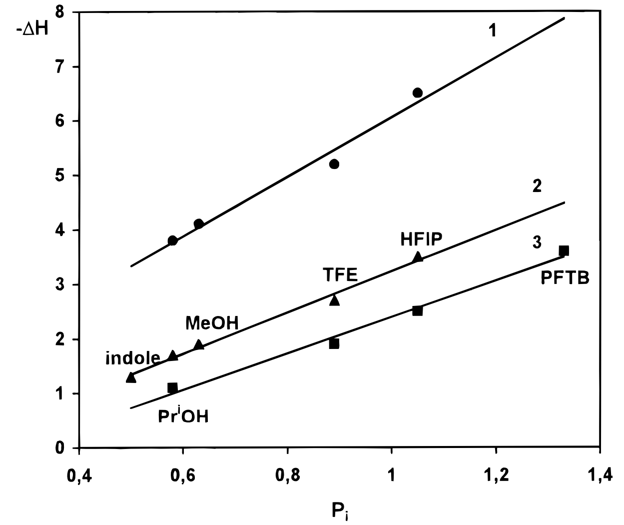

Figure 4. A plot of the $\Delta H°$ vs P_i (the strength of hydrogen bond donors) for boron hydrides: (1) Bu_4NBH_4 in CH_2Cl_2, (2) BH_3NEt_3 in hexane, (3) $BH_3P(OEt)_3$ in hexane.

correlation eqs 1 and 2 proposed by Iogansen initially for organic systems[9] are close to each other (Table 2).

The linear dependencies between $-\Delta H°$ values of H complexes and the proton donor ability of XH acids (P_i) are similar to those determined earlier for different classes of organic bases[9] (Figure 4). The linear character of this dependence shows the applicability of the "rule of factors" introduced by Iogansen to a new and unusual type of H bond.[9a,b] Equation 5

$$E_j = \Delta H_{ij}/(\Delta H_{00}P_i),\ \Delta H_{ij} = -\Delta H° \qquad (5)$$

based on the constancy of acidic and basic properties of partners in a hydrogen bond allows us to estimate the proton accepting properties of the hydride ligand independent of the proton donor used (Table 1). The basicity factors (E_j) of the hydride atom for neutral boron hydrides (0.53 ± 0.02 for BH_3NEt_3 and 0.41 ± 0.02 for $BH_3P(OEt)_3$) appeared to be smaller than those for tungsten hydrides[3] ($E_j = 0.70-0.92$) and to be close to those for organic bases such as nitromethane[9] ($E_j = 0.53$) or Ph_2O[9] ($E_j = 0.42$). The basicity factor for the hydride atom of BH_4^- ($E_j = 1.25 \pm 0.05$) is close to E_j of such a strong proton acceptor as DMSO[9] ($E_j = 1.27$). Notably, the thermodynamically based scale connecting Abraham's parameter of acidity in H bonding ($\alpha^H{}_2$) with formation constants of H complexes of various organic bases[13] is applicable to the new hydrogen bond of BH···HX type. Figure 5 shows the excellent linear dependence of $\alpha^H{}_2$ vs K_f for the H complexes of BH_3NEt_3.

Theoretical Data on the Structure and Energy of the BH···HX Hydrogen Bond. The theoretical studies of complexes $BH_4^-\cdot H_2O$ (**1**), $BH_4^-\cdot HOCH_3$ (**2**), $H_3NBH_3\cdot HOCH_3$ (**3**), and $(H_3NBH_3)_2$ (**4**) revealed the existence of local minima on the potential energy surfaces corresponding to structures presented in Figure 6. In all cases these minima are achieved for monodentate coordination of one hydride atom of boron hydride with a hydrogen atom of alcohol or water.

A partially negatively charged hydrogen atom of $B-H^{\delta-}$ bond ($q^- = -0.27-0.15$) and positively charged hydrogen atom of $X^{\delta-}-H^{\delta+}$ ($q^+ = 0.43-0.47$) take part in the interaction $B-H^{\delta-}\cdots{}^{\delta+}H-X$ (Table 3). The H···H distances vary in the range from 1.836 to 2.209 Å, that is, the H···H distances are smaller than the sum of van der Waals radii (2.4 Å) and are close to those obtained earlier for M−H···H−X bonds.[2,3] A very small but positive overlap population present between $H^{\delta+}$ and $H^{\delta-}$ atoms, for example 0.005 for complex **3** and 0.021 for complex **4**. The arrangement of atoms participating in H bond is linear. Angles X−H···H are close to 180° similar to classical H bonds, and they are 172.3−179.7° in complexes **2**−**4**.[14] Only in the complex $BH_4^-\cdot H_2O$ (**1**) are there certain deviations from linearity. The O−H···H angle value 154.5° is determined by energetic gain of additional interaction of free hydrogen atoms of BH_4^- and the free hydrogen atom in the water molecule (Figure 6-**1**). Note that this interaction should not be regarded as an additional hydrogen bond, as the H···H distance is 2.691 Å.

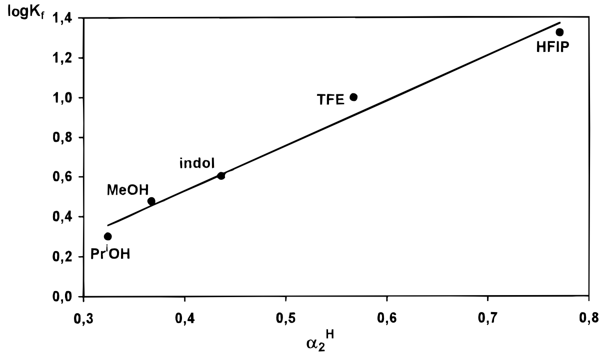

Figure 5. Plot of log K_f vs $\alpha_2{}^H$ for H complexes of BH_3NEt_3 with a variety of hydrogen bond donors.

The calculated energies by which the H complexes with BH_4^- are stabilized relative to the separated molecules are larger than those obtained experimentally in solution (Tables 2 and 3). Previously we showed the great decrease of $XH\cdots A^-$ energy on going from the gas phase to solution. This decrease is due to the substantial excess solvation energy for anions (A^-) over H complexes.[15] These solvation effects explain the discrepancy between the experimental and calculated values of the energies of the H complexes (for $BH_4^-\cdot HOCH_3$ (**2**), $\Delta E_{calc} = 12.9$ kcal/mol and $\Delta H°_{exp} = 4.1$ kcal/mol). This explanation is confirmed by close values of ΔE_{calc} and $\Delta H°_{exp}$ for the neutral H complex for which the solvation effects are not large (for $H_3NBH_3\cdots HOMe$ (**3**) $\Delta E_{calc} = 3.4$ kcal/mol, and $\Delta H°_{exp} = 2.5$ kcal/mol).

It is interesting that the similarity of BH···HX and classical H bonds also appears in the changes of bond lengths and redistribution of electron density in partner molecules. The X−H and H−B bonds become longer ($\Delta r = 0.003-0.017$ Å in complexes **1**−**3**, 0.004 and 0.007 Å in the dimer **4**). The negative charge on the hydride atom taking part in H bonding and positive charge on the hydrogen of OH/NH groups increase ($\Delta qH(\text{OH}) = 0.04-0.07$ for complexes **1**−**3**, and $\Delta qH(\text{NH}) = 0.04$, $\Delta qH(\text{BH}) = 0.07$ for the dimer **4**). It is necessary to note that changes of charges and Mulliken overlap population (o.p.) of bonds are not limited by the BH···HX fragment and

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[13] Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Duce, P. P.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans.* **1989**, *2*, 699.

[14] Theoretical calculations carried out recently (Alkorta, I.; Elguero, J.; Foces-Foces, C. *Chem. Commun.* **1996**, 1633) showed that the most energetically preferable structure of the complex of BH_4^- with HC≡N is nonlinear. We carried out the calculation of this complex by our method and also obtained the most profound minimum corresponding to the tridentate coordination of HC≡N ($\Delta E = 17.93$ kcal/mol). However, features of hydrogen bonds are characteristic not to this complex but to a linear one though its formation energy is smaller for 2.5 kcal/mol. It is characterized by positive population of H···H (0.079 Å), by considerably smaller H···H distance (1.7 Å instead of 2.2 Å), and by the more substantial repolarization of partner molecules.

[15] Epstein, L. M.; Saitkulova, L. N.; Shubina, E. S. *J. Mol. Struct.* **1992**, *270*, 325.

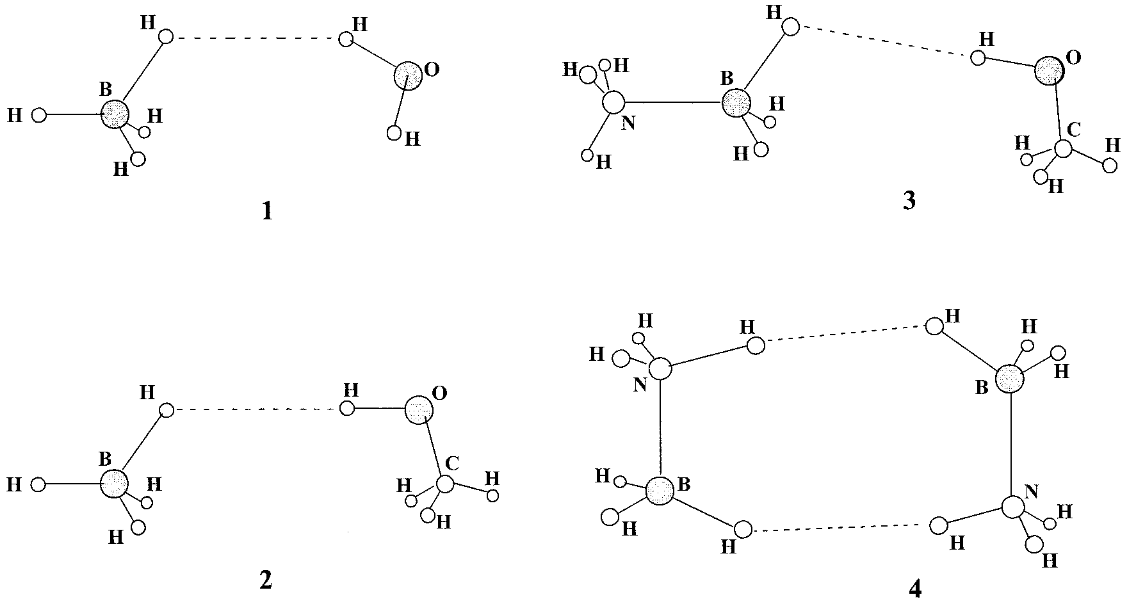

Figure 6. Structure of model complexes: (**1**) $BH_4^-\cdot HOH$, (**2**) $BH_4^-\cdot HOCH_3$, (**3**) $BH_3NEt_3\cdot HOCH_3$, (**4**) $(BH_3NH_3)_2$.

Table 3. Calculated Values of Energy of Complexes **1**−**4**, Bond Lengths, Overlap Population (o.p.), and Charges of Fragments BH···HX

	model complexes	$E_{tot.}$ (a.e.)	Δ*E* (kcal/mol)	$r_{H\cdots H}$ (Å)	*r*(BH) (Å, o.p.)	*r*(XH) (Å, o.p.)	*qH*(BH)	*qH*(XH)
	H_2O	−75.9854				0.950 (0.792)		0.41
	BH_4^-	−26.9519			1.231 (0.928)		−0.26	
1	$BH_4^-\cdot H_2O$	−102.9603	14.4	2.028	1.248 (0.892)	0.956 (0.730)	−0.27	0.45
	$HOCH_3$	−114.9882				0.950 (0.789)	0.40	
2	$BH_4^-\cdot HOCH_3$	−141.9607	12.9	1.917	1.247 (0.887)	0.960 (0.688)	−0.26	0.47
	H_3NBH_3	−82.5817			1.202 (0.986)	1.001 (0.828)	−0.14	0.39
3	$H_3NBH_3\cdot HOCH_3$	−197.5752	3.4	2.209	1.209 (0.974)	0.951 (0.745)	−0.15	0.44
4	$(H_3NBH_3)_2$	−163.1723	5.6	1.836	1.214 (0.936)	1.005 (0.758)	−0.21	0.43

include the other parts of partner molecules. For example, the negative charge on the carbon atom in the molecule of alcohol changes for 0.04 and even positive charge on H atoms of CH_3 group decreases for 0.01−0.07 (complex **2**). If the overlap population of the B−H bond taking part in H bonding of the complex **3** decreases for 0.012, the increase of this value for B−N bond is 0.005, and the change of bond length is 0.023 Å.

These results indicate that the driving force of this unusual H bonding derives from electrostatic interactions just as is the case for classical H bonds. In this case we are dealing with the electrostatic attraction between hydride atom of boron hydrides and hydrogen atom of proton-donating XH groups, $B^{\delta+}{-}H^{\delta-}\cdots{}^{\delta+}H{-}X^{\delta-}$. It is complemented by mutual polarization of the electron clouds of partner molecules in which the redistribution of electron density has the same character as in classical H bonds.

Thus, the spectral and thermodynamic characteristics of H···H hydrogen bonding of proton donors with main group hydrides, namely boron hydrides, were determined. It was established that the properties of the unusual BH···HX bonds are similar to those of previously studied MH···HX bonds[3,12] and of classical H bonds. The geometry, energy, and electron redistribution were theoretically analyzed on model H complexes including boron hydrides.

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