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Journal of Organometallic Chemistry 657 (2002) 155–162

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Dihydrogen bonding of decahydro-*closo*-decaborate(2−) and dodecahydro-*closo*-dodecaborate(2−) anions with proton donors: experimental and theoretical investigation

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Received 18 October 2001; accepted 12 March 2002

Abstract

The interactions of $[Bu_4N]_2[B_{10}H_{10}]$ and $[Bu_4N]_2[B_{12}H_{12}]$ with various proton donors (MeOH, EtOH, Pr^iOH, PhOH, $4\text{-}FC_6H_4OH$, $4\text{-}NO_2C_6H_4OH$, CF_3CH_2OH, $(CF_3)_2CHOH$, $(CF_3)_3COH$) in low polarity media were investigated. The site of coordination for $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ was found to be hydride hydrogen. Spectral (IR, NMR) evidences for the BH···HO hydrogen bonding between the boron hydrides and the OH proton donors in solution are presented. Spectral ($\Delta\nu$, $\Delta\nu_{1/2}$, ΔA) and thermodynamic (ΔH°, ΔS°) characteristics of the H-complexes were determined. The BH···HO bonding strength increases from $[B_{12}H_{12}]^{2-}$ to $[B_{10}H_{10}]^{2-}$. The geometry, energy, as well as electron distribution in the $[B_{10}H_{10}]^{2-}\cdot HOCH_3$, $[B_{10}H_{10}]^{2-}\cdot HOCF_3$, $[B_{10}H_{10}]^{2-}\cdot HCN$, and $[B_{12}H_{12}]^{2-}\cdot HOCH_3$ complexes were studied using ab initio HF/6-31G approximation. It was shown that increase of the proton donor ability of acids leads to formation of bifurcate H-bonds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Decahydro-*closo*-decaborate(2−) anion; Dodecahydro-*closo*-dodeca-borate(2−) anion; Hydrogen bond; IR spectroscopy; NMR spectroscopy; Quantum chemistry calculation

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1. Introduction

The proton-hydride ($H^{\delta+}\cdots{}^{-\delta}H$) interactions have attracted great attention from chemists during the past decade. It was established that hydride atoms in hydride complexes of transition metals (M = Ir, Os, Re, Ru, W) [1,2] as well as simple boron and gallium hydrides [3,4] can play the role of proton acceptors to give the unconventional hydrogen bonds (dihydrogen bonds as proposed by Crabtree). Detailed structural and energetic characteristics of such unconventional hydrogen bonds were determined by IR and NMR spectroscopy in solution, X-ray and neutron diffraction in the solid state and theoretical calculations in the gas phase [1–5]. It was demonstrated that even weak proton–hydride interactions can play a significant role in the stabilization of conformational molecular states [4c]. It has been shown that these H···H complexes are important intermediates in proton transfer reactions leading to the formation of transition metal dihydrogen compounds [6–8].

Earlier we studied formation of the dihydrogen complexes of various proton donors with ionic (Bu_4NBH_4) and neutral (BH_3NEt_3, $BH_3P(OEt)_3$) boron hydrides by methods of IR and NMR spectroscopy in solution and ab initio calculations. Similarity of the nature, geometric parameters, as well as spectral and thermodynamic properties of these unusual BH···HX bonds and classical H-bonds were established. It has been shown that proton accepting ability of the hydrogen atom in the tetrahydroborate anion is considerably larger than in neutral boron hydrides [4a,4b].

An ability of *closo*-borate anions $[B_{10}H_{10}]^{2-}$ (**I**) and $[B_{12}H_{12}]^{2-}$ (**II**) to form ionic dihydrogen bonds with

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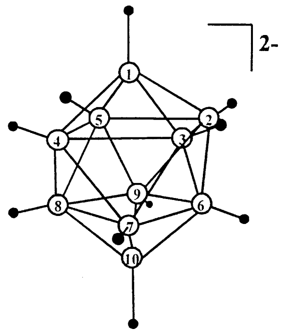
PII: S0022-328X(02)01380-3

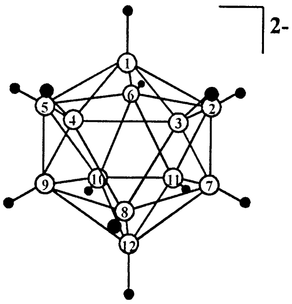
protonated nitrogen bases (as counter ions) is discussed in numerous works [9]. However the discussions are mainly based on the X-ray and IR data collected in the solid state and there is no evidence for the existence of these interactions in solutions. Note additionally that the studies in solutions could establish the coordination mode, determine the proton-accepting ability of the anions and reveal a role of dihydrogen bonds in the formation of the so-called “super-electron-deficient” structures $[B_nH_{n+1}]^-$ appearing at proton transfer from a proton-donor molecule to boron cage.

In this work we report the spectral (IR, NMR) and thermodynamic characteristics of intermolecular dihydrogen bonds between $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$ and proton donors of different strength—$(CF_3)_2CHOH$ (HFIP), CF_3CH_2OH (TFE), Pr^iOH, MeOH, PhOH, 4-FC_6H_4OH, and 4-$NO_2C_6H_4OH$, $(CF_3)_3COH$ (PFTB) formed in solutions.

The complexes formed between $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$, from one side, and MeOH, CF_3OH, and HCN, from the other side, were used as model systems for ab initio calculations.



$[B_{10}H_{10}]^{2-}$



$[B_{12}H_{12}]^{2-}$

2. Experimental

$[Bu_4N]_2[B_{10}H_{10}]$ (**I**) [9a], $[Bu_4N]_2[B_{12}H_{12}]$ (**II**) [10a], and $[Bu_4N]_2[1,10\text{-}B_{10}H_8D_2]$ (**III**) [10b] were prepared as described in the literature. Fluorinated alcohols were donated by P&M (Moscow, Russia). The solutions for IR and NMR studies were prepared under Ar atmosphere. All solvents were freshly distilled under Ar atmosphere.

The IR spectra of hexane and CH_2Cl_2 solutions (cells CaF_2, $d = 0.012$–0.120 cm) were measured on Specord M-82 (Carl Zeiss Jena) spectrometer with resolution of 2 cm^{-1}. The low temperature IR studies were carried out in the OH and BH stretching region using Carl Zeiss Jena cryostat in the temperature range 200–300 K with the accuracy of the temperature setting ±0.5 K. ^1H-, ^{11}B-, and ^{19}F-NMR spectra were obtained on Bruker WP-200 and AMX-400 spectrometers using CD_2Cl_2 as solvent. The chemical shifts were referred to Me_4Si, $BF_3 \cdot OEt_2$, and CF_3COOH, respectively. Standard Bruker software was used for measuring the longitudinal relaxation times, T_1, using the inversion-recovery method. Concentrations of $[Bu_4N]_2[B_nH_n]$ and proton donors were varied in the range 0.01–0.2 M.

3. Results

3.1. Spectroscopic evidences for hydrogen bonding in solution

The IR spectra of different proton donors (in concentration range of 0.01–0.02 M in order to exclude self-association) were measured in dichloromethane in the presence of excess **I** or **II**. The IR pattern of the $\nu(OH)$ stretching vibrations of proton donors demonstrates formation of dihydrogen bonds between the proton donors and *closo*-borate anions **I** and **II**, that manifests in the decrease of band intensities of the free OH groups ($\nu(OH)_{free}$) and the appearance of broad intensive low-frequency bands (3327–3529 cm^{-1}) of bonded OH groups ($\nu(OH)_{bonded}$) (Table 1).

According to Table 1, frequency shifts ($\Delta\nu(OH) = \nu(OH)_{free} - \nu(OH)_{bonded}$), half-widths of the $\nu(OH)$ bands ($\Delta\nu_{1/2}$) and integral intensities ($A(OH)_{bonded}$) grow with the increase of the proton-donating ability of the OH-acids [11]. Note however that these parameters are smaller for PFTB than for 4-$NO_2C_6H_4OH$. Nevertheless, for all the proton donors studied, the spectral changes decrease from **I** to **II**. For example, the IR spectra of HFIP show $\Delta\nu_{1/2} = 126$ and 83 cm^{-1}, $\Delta\nu(OH) = 212$ and 158 cm^{-1}, $A(OH)_{bonded} = 8.8 \times 10^4$ and 5.6×10^4 l cm^{-2} mol^{-1} in the presence of **I** and **II**, respectively.

The changes in the range of B–H stretching $\nu(BH)$ correspond to coordination of the proton donors via hydride atom as proton acceptor site. It was shown earlier that formation of dihydrogen bond results in low-frequency shift of the B(M)–H stretching for groups participating in H-bonding, whereas the bands corresponding to groups that do not participate in H-bonding shift to the high-frequency region [4b]. Therefore the formation of the BH···HO hydrogen bonds with boron hydrides should cause the appearance of both low-frequency bands assigned to the H-bonded groups ($(BH)_{bonded}$) and high-frequency bands of free B–H groups in the H-complex formed ($(BH)_{free}$). In the case of **II**, however, $\nu(BH)$ (2474 cm^{-1}) is shifted by 10 cm^{-1} to high frequency range (2484 cm^{-1}) in the presence of proton donors, whereas the $\nu(BH)_{bonded}$ band is not observed. At the same time, the broadening $\nu(BH)$ band ($\Delta\nu_{1/2}$ changes from 34 to 44 cm^{-1}) and low frequency asymmetry indicates the formation of the

Table 1
Spectral characteristics of H-complexes between proton donors and **I** and **II** in the ν(XH) range

Hydride	Proton donors	$\nu(OH)^{free}$ (cm^{-1})	$\nu(OH)^{bonded}$ (cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu(OH)$ (cm^{-1})	$A(OH)^{free} \times 10^4$ ($l\ cm^{-2}\ M^{-1}$)	$A(OH)^{bonded} \times 10^4$ ($l\ cm^{-2}\ M^{-1}$)
I	Pr^iOH	3607	3501	–	106	–	–
	EtOH	3611	3498	68	113	–	–
	MeOH	3624	3500	70	124	0.8	–
	TFE	3601	3440	101	161	1.29	4.8
	HFIP	3580	3368	126	212	1.95	8.8
	PhOH	3586	3405	106	181	1.72	6.0
	$4\text{-}FC_6H_4OH$	3586	3398	108	188	1.73	6.4
	$4\text{-}NO_2\text{-}C_6H_4OH$	3562	3327	130	235	2.63	10.1
	PFTB	3520	3300	128	220	–	–
II	Pr^iOH	3607	3529	–	78	–	–
	EtOH	3611	3528	–	83	–	–
	TFE	3601	3490	66	111	1.29	3.2
	HFIP	3580	3422	83	158	1.95	5.6
	PhOH	3586	3450	76	136	1.72	5.1
	$4\text{-}FC_6H_4OH$	3586	3448	73	137	1.73	5.0
	$4\text{-}NO_2\text{-}C_6H_4OH$	3562	3394	87	168	2.63	7.4
	PFTB	3520	3357	85	163	–	–

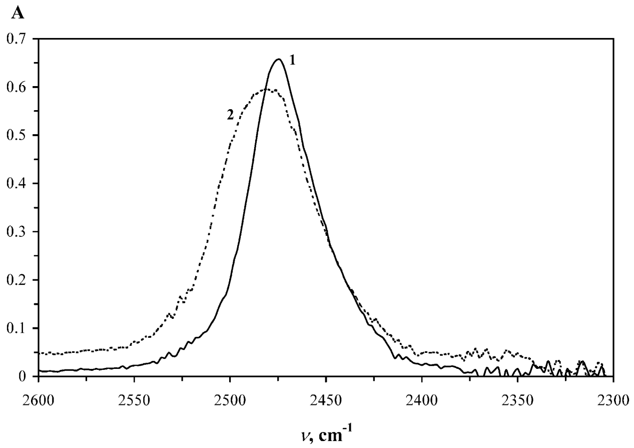


Fig. 1. IR spectra in the ν(BH) range in CH_2Cl_2: (1) **I** (0.0029 mol l^{-1}), (2) **I** (0.0029 mol l^{-1}) in the presence of HFIP (0.058 mol l^{-1}), $T = 200$ K, $d = 0.12$ cm.

dihydrogen-bonded complex BH···HX (Fig. 1). It is not surprising if we assume that the number of free BH groups are larger than the number of the bonded BH groups.

The band at 2448 cm^{-1} and the shoulder at 2487 cm^{-1} in the spectrum of **I** were assigned to equatorial and apical BH groups, respectively [12]. In the presence of HFIP new high frequency ν(BH) band at 2474 cm^{-1} and shoulder at 2556 cm^{-1} appear. These spectral changes are accompanied by a broadening effect of 20 cm^{-1}. To determine contribution of the axial and equatorial hydrogen atoms in the dihydrogen bonding we studied the interaction between the selectively deuterated *closo*-decaborate $[1,10\text{-}B_{10}H_8D_2]^{2-}$ anion (**III**) with proton donors (CH_3OH, PhOH, HFIP, PFTB and $4\text{-}NO_2C_6H_4OH$) by low-temperature measurement (200–250 K) to prevent possible H–D-exchange. The spectrum of **III** in dichloromethane contains ν(BH) band at 2450 cm^{-1} and ν(BD) band at 1887 cm^{-1} relating the equatorial BH and apical BD groups, respectively (Fig. 2). The isotope ratio ν(BH)/ν(BD) has the usual value—1.32 [11c]. The addition of the proton donors results in decrease of ν(BD) intensity and appearance of broad low-frequency $\nu(BD)_{bonded}$ band ($\Delta\nu = 20$–40 cm^{-1}) (f.e. Fig. 2b). It is obvious that only the apical deuterium atoms accept the protons and hence the high-frequency bands, ν(BD), (1892 cm^{-1}) and ν(BH) (2467 cm^{-1}) can be well attributed to stretching vibrations of the terminal B–D and B–H bonds in the BD(H)···HOR complexes.

On cooling, the intensity of the $\nu(BD)_{bonded}$ band increases (Fig. 2a), reflecting the shift of equilibrium (1) towards the dihydrogen-bonded complexes.

$$B_{10}H_8D_2 + (CF_3)_2CHOH \rightleftharpoons (CF_3)CHOH \cdots DB_{10}H_8D \quad (1)$$

The other pattern was observed for interaction of **I** with stronger proton donors. Thus, in the presence of PFTB low frequency bands appear not only for ν(BD) at 1860 cm^{-1}, but also for ν(BH) at 2420 cm^{-1} (200 K). They are assigned to the axial $\nu(BD)_{bonded}$ and equatorial $\nu(BH)_{bonded}$ bands. The similar pattern was observed in the presence of $4\text{-}NO_2C_6H_4OH$. It means that strong proton donors such as PFTB and $4\text{-}NO_2C_6H_4OH$ interact with both the equatorial and the apical BH groups.

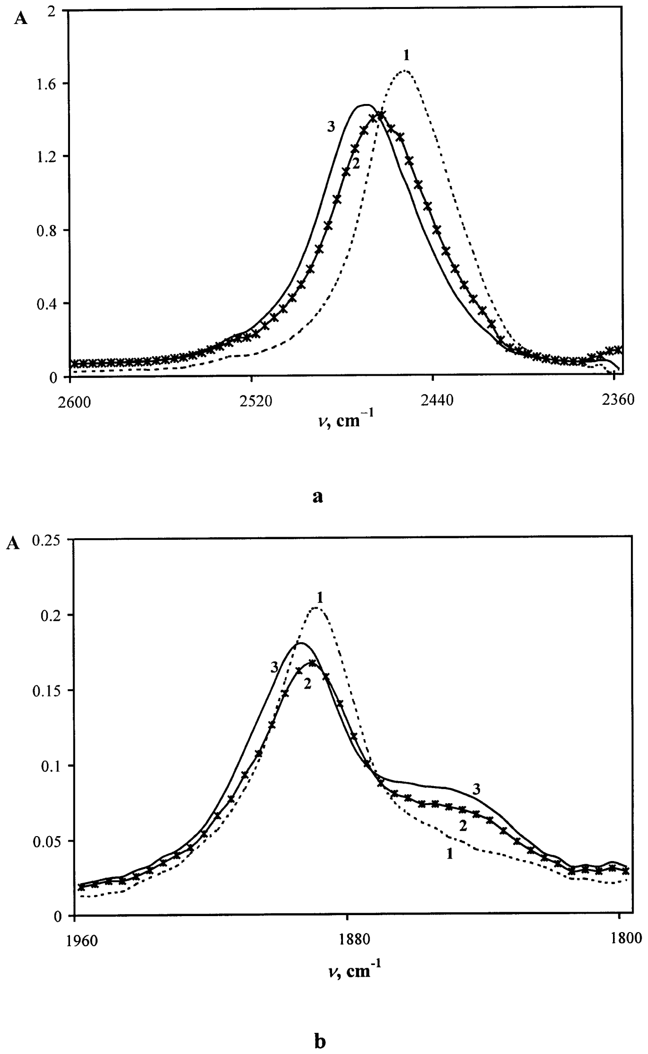


Fig. 2. IR spectra in the ν(BH) (a) and ν(BD) (b) range in CH_2Cl_2: (1) $(Bu_4N)_2[1,10\text{-}B_{10}H_8D_2]$ (0.01 mol l^{-1}); (2) $(Bu_4N)_2[1,10\text{-}B_{10}H_8D_2]$ (0.01 mol l^{-1}) in the presence of HFIP (0.1 mol l^{-1}) $T = 200$ K, (3) $(Bu_4N)_2[1,10\text{-}B_{10}H_8D_2]$ (0.01 mol l^{-1}) in the presence of HFIP (0.1 mol l^{-1}) $T = 250$ K.

The ^{1}H-NMR spectra also support the formation of H-bonds between the proton donors and anions **I**, **II**. The addition of **II** to solution of HFIP in CD_2Cl_2 (**II**/HFIP = 2.4) results in a low-field shift of the OH resonance in the ^{1}H-NMR spectrum from 3.55 to 5.16 ppm, as well as in significant decrease of the longitudinal relaxation times T_1(OH), T_1(CH), and T_1(^{19}F) from 5.4, 7.5, and 6.3 s to 1.9, 1.9, and 3.1 s, respectively. These results can be interpreted easily in terms of an increase of the molecular inertia moment of HFIP due to its hydrogen binding with bulky *closo*-dodecaborate anion **II** [7a]. Similarly, the addition of HFIP to the solution of **II** in CD_2Cl_2 decreases the relaxation time T_1(^{11}B) from 21.5 to 17.9 ms.

For objective reasons (see Section 3.2), the ^{1}H-NMR spectra of **I**, **II** did not allow us to establish the proton-accepting sites. For example, the ^{1}H{^{11}B}-NMR spectrum of a CD_2Cl_2 solution of **I** shows a very broad signal and sharp resonance at 0.06 ppm. The ^{11}B-NMR spectrum of the solution exhibits two strongly-broadened doublets of the apical (−0.9 ppm) and the equatorial (−29.2 ppm) boron atoms [13]. Selective ^{11}B-irradiation experiments provided to attribute a sharper ^{1}H resonance to apical hydride atoms of **I**. An addition of an excess of HFIP leads to an additional broadening of both hydride lines and for this reason the ^{1}H{^{11}B}-NMR spectrum becomes quite uninformative. Note that both ^{11}B signals of **I** even in the presence of a 20-fold excess of HFIP undergo insignificant and practically identical up-field shifts, observing at −1.4 and −30.1 ppm. The latter, in our opinion, does not provide correct conclusions but formally corresponds to the formation of H-bonds with the apical and equatorial BH groups of **I** (see the IR data).

3.2. Strength of the BH···HO hydrogen bond

The H-bonding enthalpy ($-\Delta H^\circ$) of the BH···HO bond was determined from empirical correlations $-\Delta H^\circ$ versus $\Delta\nu$(XH) and $-\Delta H^\circ$ versus ΔA(XH) proposed by Iogansen for organic systems [11].

$$-\Delta H^\circ = 18\Delta\nu(\mathrm{OH})/(\Delta\nu(\mathrm{OH}) + 720) \qquad (2)$$

$$-\Delta H^\circ = 2.9(\Delta\mathrm{A}(\mathrm{OH}))^{1/2} \qquad (3)$$

The data in Table 2 indicate that both equations provide similar results. The applicability of these correlations to unconventional hydrogen bonding of proton donors with transition metal hydrides and a series of the boron hydrides was shown earlier in our work [4b] by the comparison of the $-\Delta H^\circ$ values obtained from Eqs. (2) and (3) with those obtained from the temperature dependence of the formation constants (K_f) as given by the van't Hoff equation (Eq. (4)).

$$\ln K_f = -\Delta H^\circ/RT + \Delta S/R \qquad (4)$$

In the case of the *closo*-borate anions, the formation constants K_f for equilibrium 5

$$[\mathrm{B}]\mathrm{H} + \mathrm{HX} \rightleftharpoons [\mathrm{B}]\mathrm{H}\cdots\mathrm{HX} \qquad (5)$$

$$[\mathrm{B}]\mathrm{H} = [\mathrm{B}_{10}\mathrm{H}_{10}]^{2-},\ [\mathrm{B}_{12}\mathrm{H}_{12}]^{2-},\ \mathrm{HX} = \mathrm{CF}_3\mathrm{CH}_2\mathrm{OH}$$

were determined from Eq. (6):

$$K_f = (C_{\mathrm{OH}} - D/(\varepsilon l))/((C_{\mathrm{base}} - (C_{\mathrm{OH}} - D/(\varepsilon l)))D/(\varepsilon l)) \qquad (6)$$

where C_{OH} and C_{base} are initial concentrations of alcohol and boron hydride, respectively, D is optical density of the $(\mathrm{OH})_{\mathrm{free}}$ band of the H-complex, ε is the extinction coefficient, and l is the cell width.

The $-\Delta H^\circ$ values were obtained from the ln K_f versus $1/T$ dependence (4) (Fig. 3) and from Eqs. (2) and (3) for two H-complexes: **I**/TFE and **II**/TFE provide

Table 2
Thermodynamic parameters of H-complexes (BH···HX)

Hydride	Proton donors	$-\Delta H^\circ$ [a] (kcal mol^{-1})	$-\Delta H^\circ$ [b] (kcal mol^{-1})	K_f (kcal mol^{-1})	E_j
I	Pr^{i}OH	2.3	–	–	0.86
	EtOH	2.4	–	–	0.87
	MeOH	2.6	–	2.3	0.89
	TFE	3.3 (3.2) [c]	3.1	27	0.81
	HFIP	4.1	3.9	106	0.85
	PhOH	3.6	3.3	30	0.78
	4-FC$_6$H$_4$OH	3.7	3.7	49	0.78
	4-NO$_2$C$_6$H$_4$OH	4.4	4.4	215	0.75
	PFTB	4.2	–	–	0.70
II	Pr^{i}OH	1.8	–	–	0.67
	EtOH	1.9	–	–	0.68
	TFE	2.4 (2.3) [c]	2.0	17	0.59
	HFIP	3.2	3.1	69	0.66
	PhOH	2.8	2.6	21	0.61
	4-FC$_6$H$_4$OH	2.9	2.7	27	0.6
	4-NO$_2$C$_6$H$_4$OH	3.4	3.2	183	0.58

[a] From Eq. (1).
[b] From Eq. (2).
[c] From Eq. (3).

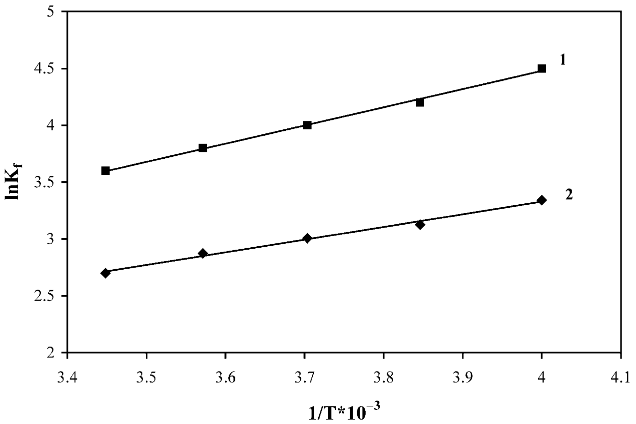


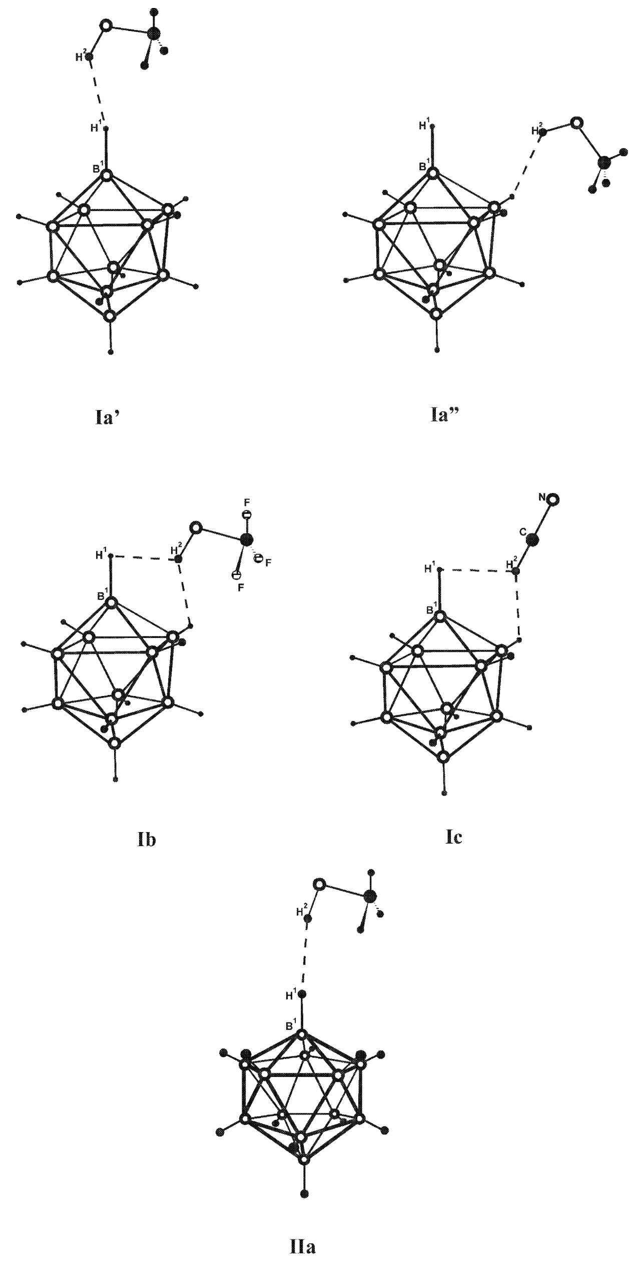
Fig. 3. A plot of the ln K_f vs. $1/T$ for **I**·TFE (1) and **II**·TFE (2) in CH_2Cl_2 (0.02/0.04 mol l^{-1}) in the range 250–300 K.

consistent results -3.2 ± 0.2 and 2.2 ± 0.2 kcal mol^{-1}, respectively. The entropy value, $\Delta S^\circ = 3.8$–3.6 eu, was determined from the plot in Fig. 3 and lies at the low limit of the range 3–20 of eu that is typical for hydrogen bonds in organic systems. This indicates the absence of significant steric hindrance for proton donors to approach the boron hydrides. It should be noted that the formation constants K_f change in parallel with the H-bond strength (Table 2).

3.3. *Ab initio Hartree–Fock calculation of the BH···HX hydrogen-bonded complexes*

The theoretical study of the $[B_nH_n]^{2-}$·HX model complexes ($n = 10, 12$, X = OMe, OCF$_3$, CN) in gaseous state was performed in the frameworks of the HF/6-31G method using the GAMESS (USA) program package [14].

For the $[B_{10}H_{10}]^{2-}$·HOMe (**Ia**) and $[B_{12}H_{12}]^{2-}$·HOMe (**IIa**) complexes, local minima correspond the structures with monodentate coordination involving H···H bonding of alcohol to anions. The less symmetrical anion **I** (symmetry D_{4d}) in contrast to **II** (symmetry I_h where all H atoms are equivalent) forms two types of dihydrogen-bonded complexes ascribed above. The structures with coordination through an axial (**Ia′**) or an equatorial (**Ia″**) hydride atom are considered (Fig. 4). The energies of the complex formation for the three complexes **Ia′**, **Ia″**, **IIa** are very close ($\Delta E_{calc} = 10.8$–11.0 kcal mol^{-1}) and less than that for the earlier studied $[BH_4]^-$·HOMe complex ($\Delta E_{calc} = 12.9$ kcal mol^{-1}) [4]. The H···H distance appears to be a more sensitive and informative parameter. These distances were found to be 1.926 Å (**IIa**) and 1.899 or 1.955 Å for **Ia′** and **Ia″**, respectively, i.e. they are less than the sum of van der Waals radii (2.4 Å) and close to the value calculated for the $[BH_4]^-$·HOMe complex [4]. As one can see, the short distance for **Ia′** demonstrates significant preference of the apical H-bonded complex in comparison with the equatorial H-bonded one—the bonding in **Ia″** is even weaker than in the complex **IIa** (r(H···H) for **Ia″** has the maximum value). Thus, the strength of hydrogen bonding decreases in the series **Ia′** > **IIa** > **Ia″**. The OHH angle (172°) demonstrates the small deviations from linearity as in the case of the complexes with $[BH_4]^-$ and BH_3NMe_3. The B–H and H–O distances are increased insignificantly by 0.003 and 0.007 Å, respectively. The hydrogen-bonded complex formation is accompanied by considerable polarization of both partners. The charges of the atoms taking part in the $XH^{\delta+}\cdots{}^{\delta-}HB$ interaction increase by +0.06 and −0.07 a.u. and the bond order decreases by 0.062 and



Ia' **Ia"** **Ib** **Ic** **IIa**

Fig. 4. The structure of model complexes: **Ia′**—**I**·HOMe, **Ia″**—**I**·HOMe, **Ib**—**I**·$HOCF_3$, **Ic**—**I**·HCN, **IIa**—**II**·HOMe.

● – C ○ – B • – H ◉ – O ⊖ – F ◎ – N

0.048 a.u., respectively for XH and HB (Table 3). The weak binding between $H^{\delta+}$ and $^{\delta-}H$ appears (bond order is equal 0.018–0.026).

In the case of the stronger proton donors, CF_3OH and HCN, local minima on the potential energy surface corresponds to the structures **Ib** and **Ic**, respectively, with bidentate coordination of the **I** through apical and equatorial hydride atoms to the hydrogen proton donors atom. It should be noted that the monodentate coordination was used as initial approximation for optimization of the **Ib** and **Ic** complexes. The values of dihydrogen bond energy $-\Delta E_{\text{calc}}$ for complexes **Ib** and **Ic** are about two times as much as those for the complexes with CH_3OH. But the H···H distances in the structures **Ib** and **Ic** (2.021–2.197 Å) were found to be larger than those for monodentate complexes with weak proton donor **Ia′** and **Ia″**. The dihydrogen bonds became far from linearity; the angles XHH are equal to 125–135°.

The dihydrogen-bonded complexes with bidentate coordination **Ib**, **Ic** differ from the monodentate coordinated (**Ia**, **IIa**) not only in the structure but also in electron distribution. The increase of the positive charge on the hydrogen atom of the HX groups by 0.10 as well as the reduction of the corresponding bond order by 0.206–0.139 are much more than ones for complexes **Ia′** and **Ia″** (Table 3). At the same time the changes in the charge distribution in the polyhedral anions are significantly smaller than in the complexes with monodentate coordination.

The results of calculations indicate that the driving force of this BH···HX-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 the 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. The particularity of the structure of H-bonding with rather strong proton donors are bidentate coordination.

4. Discussion

The experimental results show that the *closo*-decaborate and *closo*-dodecaborate anions form dihydrogen bonds with proton donors in solution. The calculations demonstrate a practically linear structure of the H-bonded complexes with weak proton donors such as MeOH. It should be noted that the similar parameters of the dihydrogen bond were found recently in the crystal structure of $[Bu_4N]_2\{[(o\text{-}C_6F_4Hg)_3][B_{10}H_{10}]\}\cdot MeOH$, where the methanol molecule is binding to one of the apical vertex of the *closo*-decaborate anion in a linear manner [15]. The H···H distance is less than the sum of van der Waals radii—r(H···H) = 2.2(2) Å and the fragment H···HO is practically linear (the angle: 171(18)°).

The BH···HO dihydrogen bonds in solution can be classified as weak or medium strength bonds. The $-\Delta H$ values of the H-bonded complexes vary from 1.8 to 4.4 kcal mol^{-1} (Table 2). The bonding strength of the H-complexes for any proton donor studied decreases from **I** to **II**. The enthalpies of the H-bonding for **I** and **II** with the proton donors studied are less than that found for $[BH_4]^-$ anion. For example the enthalpies of **I** and **II**

Table 3
Values of total energy (E_t, a.u.), destruction energy on fragments $B_nH_n^{2-}$ and HX (ΔE_{calc}, kcal mol^{-1}), bond lengths (r, Å), bond orders (b.o., in clammers, a.u.) and effective atomic charges (q, a.u.) of complexes **1**–**4** and their fragments (HF/6-31G-calculations)

Complex or fragment	No.	$-E_t$	ΔE_{calc}	$H\cdots H^1$ [$H\cdots H^2$]	$r(BH^1)$ (b.o.)	$r(BH^2)$ (b.o.)	r(XH) (b.o.)	qH^1	qH^2	qH_X
$[B_{12}H_{12}]^{2-}$	**II**	303.1361	–	–	1.197 (0.933)	1.197 (0.933)	–	−0.17	−0.17	–
HOMe		114.9882	–	–	–	–	0.950 (0.789)	–	–	0.40
$HOMe\cdot[B_{12}H_{12}]^{2-}$	**IIa**	418.1416	10.8	1.926	1.199 (0.885)	1.196 (0.931)	0.956 (0.727)	−0.24	−0.17	0.46
$[B_{10}H_{10}]^{2-}$	**I**	252.5019	–	–	1.199 (0.919)	1.201 (0.923)	–	−0.18	−0.18	–
$HOMe\cdot[B_{10}H_{10}]^{2-}$	**Ia**′	367.5073	10.8	1.899	1.200 (0.870)	1.200 (0.925)	0.957 (0.721)	−0.23	−0.17	0.46
$HOMe\cdot[B_{10}H_{10}]^{2-}$	**Ia**″	367.5075	11.0	1.955	1.198 (0.926)	1.202 (0.882)	0.957 (0.721)	−0.16	−0.23	0.46
$HOCF_3$		411.4941	–	–	–	–	0.954 (0.735)	–	–	0.46
$HOCF_3\cdot[B_{10}H_{10}]^{2-}$	**Ib**	664.0375	25.8	2.027 [2.021]	1.199 (0.916)	1.201 (0.923)	0.978 (0.529)	−0.16	−0.14	0.56
HCN		92.8283	–	–	–	–	1.053 (0.851)	–	–	0.33
$HCN\cdot[B_{10}H_{10}]^{2-}$	**Ic**	345.3609	19.2	2.197 [2.176]	1.200 (0.917)	1.203 (0.913)	1.069 (0.714)	−0.17	−0.18	0.43

with HFIP H-bonding are 3.4 and 4.1 kcal mol^{-1}, respectively, whereas the $-\Delta H$ values of $[BH_4]^-$/HFIP bonding reaches 6.5 kcal mol^{-1} [4b]. It should be noted that the calculated dihydrogen bond energies ΔE_{calc} for the polyhedral boron hydride anions (**I**, **II**, and $[BH_4]^-$ [4b]) are much higher than ones determined experimentally in solution (f.e., for **I**·HOMe $\Delta E_{calc} = 10.8$ kcal mol^{-1}, $-\Delta H^\circ_{exp} = 2.6$ kcal mol^{-1}). This difference can be explained by the substantial excess solvation energy for anions over energy of the H-complexes.

The enthalpy values were analyzed and linear correlations between the enthalpy ($-\Delta H^\circ_{exp}$) of formation of H-complexes of **I** and **II** and the proton-donor ability (P_i) of the OH acids were found (Fig. 5). The dependencies between the $-\Delta H^\circ$ values of the H-complexes and the P_i values of the OH acids are very similar to those determined earlier for different transition metal and boron hydrides [2d,4a,7d] (Fig. 5). The linear character of these dependencies shows applicability of the “rule of factors” introduced by Iogansen for hydrogen bonds [11] to dihydrogen bonding of the *closo*-borate anions (Eq. (7)).

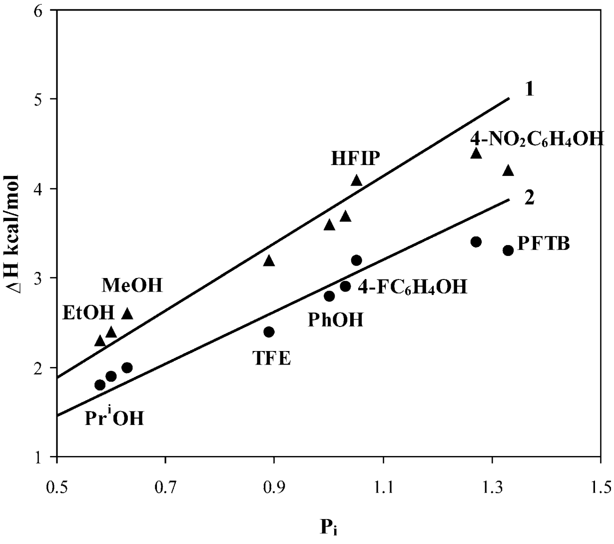


Fig. 5. A plot of the ΔH° vs. P_i (the strength of hydrogen bond donors) for boron hydrides in CH_2Cl_2: (1) **I**, (2) **II**.

$$E_j = \Delta H_{ij}/(\Delta H_{00}P_j),\ \Delta H_{ij} = -\Delta H^\circ \tag{7}$$

The proton accepting ability (E_j) of the **I** and **II** anions (0.83 ± 0.5 and 0.63 ± 0.4, respectively) is greater than that for neutral boron hydrides (0.53 for BH_3NEt_3 and 0.41 for $BH_3P(OEt)_3$) and significantly smaller than E_j for tetrahydroborate anion ($E_j = 1.25$) [4b]. The ability of anionic boron hydrides to form dihydrogen bonds decreases in the order $[BH_4]^- > [B_{10}H_{10}]^{2-} > [B_{12}H_{12}]^{2-}$.

The deviations from linearity are significant only for the quite strong proton donors, such as $4\text{-}NO_2C_6H_4OH$ and PFTB. Enthalpy values of the H-complexes of $[B_nH_n]^{2-}$ with these strong proton donors are less than should be expected. In the case of **I** it could be explained by formation of two types of hydrogen-bonded complexes formed through apical and equatorial hydrogen atoms. The second type is less energetically preferable and its contribution can decrease the summary enthalpy. However this explanation is not acceptable for $[B_{12}H_{12}]^{2-}$, where all the hydride atoms are equivalent. The theoretical calculations, carried out for **I**, revealed that the more strong proton donors can form the bifurcated H-bonds. This exotic type of weak interactions, studied mainly in solids [16], result in the so-called non-linear H-bonds. According to the theoretical studies [2b,16], such bonds are less energetically preferable than linear ones. However if the bifurcated hydrogen bonds form six- or five-membered ring structures (as in the case of **Ib**,**c**) they become favored [17]. Add also that the bifurcate intramolecular H-bonds were detected in solutions of 2,6-disubstituted phenol derivatives [18]. Therefore we believe that namely the bifurcated hydrogen bonds, really existing in CH_2Cl_2 solutions of *closo*-borate anions **I**, **II** and $4\text{-}NO_2C_6H_4OH$ or PFTB, are responsible for the above deviations.

5. Conclusion

The spectral studies provided evidence for the BH···HO bonding between *closo*-borate anions $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$ and the proton donors in solution. The thermodynamic characteristics of H···H hydrogen bonding of proton donors with *closo*-borate anion hydrides were determined. Their proton accepting ability is less than that of $[BH_4]^-$ anion and decreases from $[B_{10}H_{10}]^{2-}$ to $[B_{12}H_{12}]^{2-}$.

The geometry, energy, and electron distribution in the H-complexes were analyzed by the ab initio method on the model complexes including the *closo*-borate anion hydrides. In contrast to "classical" boron hydrides, such as the tetrahydroborate anion and BH_3NMe_3 complex, the increase of the proton donor strength in the case of the *closo*-borate anions results in formation of bifurcate hydrogen bonds that can have great importance for reactivity of these compounds in whole and for formation of the super-electron deficient structures at proton transfer to the boron cage in particular.

Acknowledgements

The authors thank P&M (Moscow, Russia) for the gift of the fluorinated alcohols and Russian Foundation for Basic Research (Grant N 98-03-33037, N 01-03-32068, N 02-03-06243) for financial support.

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