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# Competition between non-classical and classical hydrogen bonded sites in [BH<sub>3</sub>CN]<sup>-</sup>: Spectral, energetic, structural and electronic features

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#### Abstract

Interaction of the salt ( $Ph_3P=N=PPh_3$ ) $BH_3CN$  with the various OH and NH proton donors in low polar media was studied by variable temperature (200–290 K) IR spectroscopy and theoretically by DFT calculations. The formation of two types of complexes containing nonclassical dihydrogen bond to the hydride hydrogen (DHB) and classical hydrogen bond (HB) to nitrogen lone pair was shown in solution. The 1:1 complexes of both types (XH···H and XH···N) coexist in the presence of equimolar amount of proton donor. The addition of excess XH-acid leads to the increase of the classical HB content and appearance of the 1:2 complexes, where two basic sites work simultaneously. The structure, spectral characteristics, energy and electron redistribution were studied by DFT (B3LYP) method. The comparison DHB parameters of [BH<sub>3</sub>CN]<sup>-</sup> with those of the unsubstituted analogue [BH<sub>4</sub>]<sup>-</sup> allowed analyzing the electronic effects of the CN group on the basic properties of boron hydride moiety. The electronic influence of the BH<sub>3</sub> group on CN<sup>-</sup>···HX hydrogen bond was also established by comparison with the corresponding classical HB to the CN<sup>-</sup> anion.

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## 1. Introduction

The spectral, structural and energetic properties of the most unusual unconventional hydrogen bonds (HB) to a hydride hydrogen as a proton acceptor were actively investigated in the recent years for the transition metal (XH···HM) or main group (XH···HE) hydride complexes (see, for example reviews [1–3]). This type of HB is usually named dihydrogen bond (DHB). The one of the first aims of investigations was to prove that these interactions are really HB's. Significant similarity of the nature, geometry and spectral features of both new and classical HB was demonstrated for numerous hydride complexes [1]. For main group hydrides the experimental studies in the solid state [3] and in solution [4] as well as the theoretical calculations were devoted initially to boron hydrides [3,4]. Later the theoretical studies of the different simple hydrides [5] appeared where DHB nature and structure were analyzed. Our spectral study of closo-borate anions  $[B_{10}H_{10}]^{2-}$  and  $[B_{12}H_{12}]^{2-}$  showed that they form rather weak DHB, whose structure, energy and electron distributions have been calculated [6]. Recently the spectral investigation of DHB complexes to GaH<sub>4</sub><sup>-</sup> in solution was combined with DFT calculations of model DHB complexes of GaH<sub>4</sub><sup>-</sup>, BH<sub>4</sub><sup>-</sup>, [7] and, for the first time, the discussion about the mechanism of proton transfer reaction to main group hydrides. However, the problem of competition between DHB and classical HB was practically not studied. Only in our recent paper the coexistence of both types of hydrogen bonds was determined at the example of the substituted polyhedral boron hydride  $[B_{12}H_{11}SCN]^{2-}$  [8].

Continuing our work in this field we present in this paper the spectral, energetic, structural and electronic features of HB's of the cyanoborohydride  $[BH_3CN]^-$  with different strength XH proton donors (X=O, N). The competition between DHB and HB to nitrogen lone pair and possibility of the classical and DHB bonds coexistence in one hydride molecule was studied theoretically and by IR spectroscopy, comparing with DHB of the unsubstituted analogue  $[BH_4]^-$  and HB of CN<sup>-</sup> anion.

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# 2. Experimental part

## 2.1. Computational details

Full geometry optimization for  $BH_3CN^-$ ,  $BH_4^-$  and their HB complexes with  $CH_3OH$  and  $CF_3CH_2OH$  were carried out with GAUSSIAN 98 [9] package at DFT level using the hybrid B3LYP functional [10]. The 6-311<sup>++</sup>G(d,p) basis set was used for all the atoms. The nature of all the stationary points on the potential energy surfaces was confirmed by a vibrational analysis. Natural bond orbital (NBO) analysis was performed on all optimized structures.

### 2.2. Spectroscopic studies

All manipulations were carried out under an argon atmosphere by standard Schlenk techniques.  $[Ph_{3-}P=N=PPh_{3}][BH_{3}CN]$  was prepared by precipitation with  $[Ph_{3}P=N=PPh_{3}]Cl$  from aqueous solution of Na[BH\_{3}CN] (Merck) followed by drying of the precipitate formed over phosphorus pentoxide. All solvents used were dried using appropriate agents and freshly distilled prior to use. The fluorinated alcohols were from P&M company, Moscow.

The IR spectra of dichloromethane or tetrahydrofuran solutions (CaF<sub>2</sub> cells, d=0.012-0.120 cm) were measured on Specord M-82 (Carl Zeiss Jena) spectrometer with 2–4 cm<sup>-1</sup> resolution and Infralum FT-801 (Lumex) FTIR spectrometer. Low temperature IR studies were carried out in the OH, BH and CN stretching regions using Carl Zeiss Jena cryostat in the temperature range 200–300 K with the accuracy of the temperature setting  $\pm 0.5$  K. To examine spectra in the region of  $v_{\rm XH}$  the concentration of BH<sub>3</sub>CN<sup>-</sup> was equal to  $10^{-1}-10^{-2}$  M, and was  $10^{-2}-10^{-3}$  M in the region of  $v_{\rm BH}$  and  $v_{\rm CN}$ . The concentration of XH-acids in the first region was equal to  $10^{-2}-10^{-3}$  M to avoid self-association and was taken in 1:1 ratio or in excess (from 2 to 14 fold) in the region  $v_{\rm BH}$  and  $v_{\rm CN}$ .

Both experimental and theoretical  $\Delta v_{BH}$  band shifts are calculated from the position of A<sub>1</sub> band as  $\Delta v_{BH} = v_{BH}^{free} - v_{BH}^{init}(A_1)$  or  $\Delta v_{BH} = v_{BH}^{bond} - v_{BH}^{init}(A_1)$ .

# 3. Results and discussion

#### 3.1. Theoretical study

The  $BH_3CN^-$  anion possesses two potential proton accepting sites: the non-classical one is hydride hydrogen of the  $BH_3$  group and classical one is the lone pair of CN group nitrogen atom. These two sites could compete for the hydrogen bonding with XH-acids leading to the DHB ( $BH\cdots HX$ ) and/or classical HB ( $CN\cdots HX$ ) formation. To address this problem the theoretical study of the interaction between  $BH_3CN$  with rather weak XH-acids was carried out, the structures of the complexes formed as well as electronic redistributions and vibrational frequencies were obtained.

The theoretical study show the real competition of the two proton-accepting sites in  $BH_3CN^-$ —hydride ligand and nitrogen lone pair. Three minima are found for

 $BH_3CN^-$  with  $CH_3OH$ —classical hydrogen bonded complex (1), DHB complex (2) and, in presence of two proton donor molecules, 1:2 complex with both classical and non classical H-bonds, (3) (Fig. 1). The same results were obtained for  $BH_3CN^- \cdot CF_3CH_2OH$  system (complexes 5–7, correspondingly). Structural characteristics of these complexes are collected in Table 1.

The linear arrangement of OH…L (L=H, N) moiety was found for all the HB complexes, OH···L angles being 168.2-178.3°. The L···H distances are rather short (1.625–1.839 Å) and substantially less than the sum of van der Waals radii  $(2.4 \text{ Å for } H \cdots H \text{ and } 2.7 \text{ Å for } N \cdots H)$  for both types of HB complexes. As expected they shorten with the increase of the proton donor strength. The elongation of the H···H distances in the complexes 2 and 6 of  $BH_3CN^-$  anion in comparison with analogous complexes of the unsubstituted  $BH_4^-$  anion (4 and 8) is induced by the electronic influence of CN group decreasing proton accepting ability of the hydride hydrogen (the  $E_i$  factors decrease will be discussed later). It is interesting that both H···H and N···H distances in the 1:2 complexes with CH<sub>3</sub>OH and CF<sub>3</sub>CH<sub>2</sub>OH (3 and 7) are 0.020–0.042 Å longer, than in the corresponding complexes 1:1 due to the electron density redistribution upon HB formation to the second centre.

The hydrogen bond formation leads to the elongation of O– H bonds from their values in the isolated molecules which is larger in hydrogen bonded complexes on N atom lone pair  $(\Delta r(O-H)=0.024-0.034 \text{ Å})$  than in DHB complexes  $(\Delta r(O-H)=0.014-0.018 \text{ Å})$ . The length of B–H bond implicated in dihydrogen bonding increases, while the non-bonded B–H bonds shorten in all DHB as well as classical HB complexes. The C–N bond shortens in the same extent (by 0.001–0.002 Å) in HB complexes on N atom lone pair and in DHB complexes.

The electrostatic attraction between the partial negative charge of the hydrogen and/or nitrogen lone pair of BH<sub>3</sub>CN<sup>-</sup> and the partial positive charge of the acidic hydrogen is the driving force for both DHB (BH<sup> $\delta$ -</sup>...H<sup> $\delta$ +</sup>O) and classical HB (N<sup> $\delta$ -</sup>...H<sup> $\delta$ +</sup>O). The HB formation leads to an increase of an absolute values of both the positive charge on the acidic hydrogen and the negative charge on the nitrogen or the hydride atom (Table 2). The value of  $\Delta q$ (OH) increase is slightly larger for the classical HB. In the same time the negative charge on the non-bonded (B)H and (C)N atoms decreases in absolute value (-0.008 for BH in the complex 1 and -0.023 for CN in the complex 2). Notably, that polarization in the 1:2 complex 3 seems to be a superposition of these two changes ( $\Delta q$ (BH)= 0.009 and  $\Delta q$ (CN)=0.021) (Table 2).

Notably, all structural and electronic changes observed in the HB complexes studied here are in agreement with general trends established for hydrogen bonds to classical bases as well as to the boron hydrides studied previously. The calculations allow us to assume coexistence of both classical and nonclassical hydrogen bonds in one molecule.

# 3.2. Spectroscopic features of hydrogen bonds

The theoretical approaches help us in IR assignments and appear to able predicting different HB complexes



Fig. 1. The optimized geometries (distances in Å) of the model hydrogen bonded complexes between BH<sub>3</sub>CN<sup>-</sup> and CH<sub>3</sub>OH.

Table 1

The structural characteristics (angles in degrees, bond lengths and elongations in Å) of HB complexes to boron hydride hydrogen or to nitrogen atom (in italics) calculated by the DFT method

	Complex	L…HO	$r(L\cdots H)$	$\Delta r(BH)$	$\Delta r(CN)$	$\Delta r(OH)$
1	BH <sub>3</sub> CN <sup>-</sup> ·HOCH <sub>3</sub>	178.3	1.839	-0.003	-0.001	0.024
2	NCBH <sub>3</sub> <sup>-</sup> ·HOCH <sub>3</sub>	169.7	1.751	0.006	-0.001	0.014
•		171.3	1.859	0.002	0.002	0.022
3	$BH_3CN \rightarrow 2CH_3OH$	168.2	1.788	0.002	-0.003	0.012
4	$BH_4^- \cdot HOCH_3$	172.8	1.654	0.005		0.021
5	$BH_3CN^- \cdot HOCH_2CF_3$	176.4	1.727	-0.004	-0.002	0.034
6	NCBH <sub>3</sub> · HOCH <sub>2</sub> CF <sub>3</sub>	177.4	1.625	0.009	-0.002	0.018
-		175.7	1.761	0.004	0.004	0.029
7	$BH_3CN \rightarrow 2HOCH_2CF_3$	174.4	1.668	0.004	-0.004	0.015
8	$BH_4^- \cdot HOCH_2CF_3$	176.4	1.553	0.007		0.028

Table 2

The electronic characteristics (L···H bond orbital populations, o.p.; changes of the NBO charges,  $\Delta q$ ) of HB complexes to boron hydride hydrogen or to nitrogen atom (in italics) calculated by the DFT method

	Complex	o.p. (L…H)	$\Delta q(\mathrm{BH})$	$\Delta q(\text{CN})$	$\Delta q(\text{OH})$
1	BH <sub>3</sub> CN <sup>-</sup> ·HOCH <sub>3</sub>	0.092	-0.008	0.045	0.055
2	NCBH <sub>3</sub> ·HOCH <sub>3</sub>	0.078	0.019	-0.023	0.052
3	BH <sub>3</sub> CN <sup>-</sup> ·2CH <sub>3</sub> OH	0.088 0.062	0.009	0.021	0.054 0.049
4	$BH_4^- \cdot HOCH_3$	0.174	0.021		0.062

 $\Delta q = |q^{\text{complex}}| - |q^{\text{free}}|.$ 

Table 3 Spectral features (in cm<sup>-1</sup>) in the  $v_{XH}$  range of proton donors and their hydrogen bonded complexes to BH<sub>3</sub>CN<sup>-</sup>

RXH $v_{\rm XH}^{\rm init}$		BH····H	ВН⋯НХ		CN···HX	
		$\nu_{\rm XH}^{\rm bond}$	$\Delta { u_{ m XH}}^{ m a}$	$\nu_{\rm XH}^{\rm bond}$	$\Delta \nu_{\rm XH}{}^{\rm a}$	
CH <sub>3</sub> OH	3630	3523	-107	3398	-232	
FCH <sub>2</sub> CH <sub>2</sub> OH	3609	3456	-153	3344	-265	
CF <sub>3</sub> CH <sub>2</sub> OH	3600	3416	-184	3231	-369	
(CF <sub>3</sub> ) <sub>2</sub> CHOH	3576	3383	-193	3128	-448	
Pyrrole	3472	3370	-102	3244	-228	
2-Phenyl-pyrrole	3459	3355	-104	3227	-232	
Imidazole	3458	3326	-132	3155	-303	

<sup>a</sup> Band shift  $\Delta v_{\rm XH} = v_{\rm XH}^{\rm bond} - v_{\rm XH}^{\rm init}$ .

formation. Interaction of the salt [Ph<sub>3</sub>P=N=PPh<sub>3</sub>][BH<sub>3</sub>CN] with different strength proton donors: CH<sub>3</sub>OH, FCH<sub>2</sub>CH<sub>2</sub>OH (MFE), CF<sub>3</sub>CH<sub>2</sub>OH (TFE), (CF<sub>3</sub>)<sub>2</sub>CHOH (HFIP), imidazole, pyrrole, 2-phenyl-pyrrole, was investigated by IR spectroscopy in low polar solvents (methylene chloride and tetrahydrofuran, THF) in the temperature range 190–290 K. The two sites competing for the hydrogen bonding with XH-acids in agreement with computational results were found and characterized by the studies in the ranges of the stretching vibrations of the XH-acid bonds ( $v_{\rm XH}$  = 3700–3100 cm<sup>-1</sup>) as well as BH and CN bonds of cyanoborohydride anion (2500- $2100 \text{ cm}^{-1}$ ) were conducted according to our established protocol [1a,4]. In this section we discuss the observed spectral changes (Tables 3–5) in conjunction with results of frequency calculations (Table 6) while the structural and electronic features of the complexes calculated are discussed in the separate section.

# 3.2.1. Range of $v_{XH}$

The observed intensity decrease of the unbonded  $\nu_{XH}^{\text{init}}$  bands was accompanied by the appearance of two new broad lowfrequency bands of hydrogen bonded XH groups ( $\nu_{XH}^{\text{bond}}$ ) (Fig. 2).

These two bonded bands could be assigned to hydrogen bonding to two possible proton accepting sites (XH···HB and XH···NC). Comparison of the data in Table 3 with the spectral changes observed for the interaction of the same proton donors with the unsubstituted hydride anion  $BH_4^-$  [4b] and  $CN^-$  anion [11] allows to validate this suggestion.

The higher frequency  $\nu_{XH}^{bond}$  bands of BH····HX complexes appear in the range 3523–3326 cm<sup>-1</sup>. The frequency shifts Table 4

Spectral features (in cm  $^{-1})$  of classical HB complexes BH\_3CN…HX in the range of  $\nu_{\rm CN}$ 

RXH	$ u_{ m CN}^{ m bond}$	$\Delta { u_{ m CN}}^{ m a}$
CH <sub>3</sub> OH	2174	6
FCH <sub>2</sub> CH <sub>2</sub> OH	2176	8
CF <sub>3</sub> CH <sub>2</sub> OH	2178	10
(CF <sub>3</sub> ) <sub>2</sub> CHOH	2182	14
Imidazole	2173	5
Pyrrole	2174	6
2-Phenyl-pyrrole	2174	6

<sup>a</sup> Band shift  $\Delta v_{\rm CN} = v_{\rm CN}^{\rm bond} - v_{\rm CN}^{\rm init}$ .

Table 5

The  $\nu_{BH}$  bands in IR spectra of 1:1 and 1:2 hydrogen bonded complexes of BH<sub>3</sub>CN<sup>-</sup> with HFIP

Complex	$v_{\rm BH}^{\rm free}~(\Delta v_{\rm BH})$	$\nu_{\rm BH}^{\rm bond}~(\Delta\nu_{\rm BH})$
BH <sub>3</sub> CN <sup>-</sup> · HFIP BH <sub>3</sub> CN <sup>-</sup> · 2HFIP	2330 (+12) 2330 (+12) 2348 (+30)	2278 (-38)

Band shifts are calculated as  $\Delta \nu_{BH} = \nu_{BH}^{free} - \nu_{BH}^{init}(A_1)$  or  $\Delta \nu_{BH} = \nu_{BH}^{bond} - \nu_{BH}^{init}(A_1)$ , where  $\nu_{BH}(A_1) = 2318 \text{ cm}^{-1}$ .

Table 6 Calculated frequency shifts (in cm<sup>-1</sup>) of the model hydrogen bonded complexes of BH<sub>3</sub>CN<sup>-</sup> or BH<sub>4</sub><sup>-</sup> with CH<sub>3</sub>OH

	Complex	$\Delta  u_{ m BH}^{ m free}$			$\Delta \nu_{ m BH}^{ m bond}$	$\Delta \nu_{\rm CN}$	
1	BH <sub>3</sub> CN <sup>−</sup> ·CH <sub>3</sub> OH	25	24	17		11	
2	NCBH <sub>3</sub> <sup>-</sup> ·CH <sub>3</sub> OH	31	22		-29	13	
3	BH <sub>3</sub> CN <sup>-</sup> ·2CH <sub>3</sub> OH	53	38		-6	24	
4	$BH_4^- \cdot CH_3OH$	56	49	37	-14		

 $\Delta v_{\rm XH} = v_{\rm XH}^{\rm init} - v_{\rm XH}^{\rm bond}$  increase with the strength of the proton donors (from 102 cm<sup>-1</sup> for pyrrole to 193 cm<sup>-1</sup> for HFIP). Notably, that the positions of the  $v_{\rm XH}^{\rm bond}$  bands for the different proton donors interacting with BH<sub>3</sub>CN<sup>-</sup> are higher and, consequently, the band shifts  $\Delta v_{\rm XH}$  are smaller than those for the parent BH<sub>4</sub><sup>-</sup> anion [4a,b,7] (for example  $\Delta v_{\rm OH}$  184 cm<sup>-1</sup> for BH<sub>3</sub>CN<sup>-</sup>/TFE and 290 cm<sup>-1</sup> for BH<sub>4</sub><sup>-</sup>/TFE). The difference between  $\Delta v_{\rm OH}$  for BH<sub>3</sub>CN<sup>-</sup> and BH<sub>4</sub><sup>-</sup> increases with the increase of the proton donor strength. Thus, the presence of electron accepting CN ligand weakens the proton accepting strength of the hydride hydrogen, decreasing spectral shifts. Similar effect of  $\Delta v_{\rm OH}$  decrease was observed by us for DHB in the system [B<sub>12</sub>H<sub>11</sub>SCN]<sup>2-</sup>/HOR in comparison with DHB's of unsubstituted [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> [8].

The second  $v_{XH}^{bond}$  band assigned to the BH<sub>3</sub>CN···HX complexes is characterized by larger shift values ( $\Delta v_{XH} = 232-448 \text{ cm}^{-1}$ ) (Table 3) and greater intensity than those of DHB. An overlap of two  $v_{XH}^{bond}$  bands can mask the first band of



Fig. 2. Variable temperature IR spectra in the  $v_{\rm NH}$  range of 2-phenyl-pyrrole (0.023 M) in the presence of (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN (0.15 M). CH<sub>2</sub>Cl<sub>2</sub>, d= 0.12 cm.



Fig. 3. Variable temperature IR spectra in the  $\nu_{OH}$  range of MFE (0.023 M) in the presence of (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN (0.15 M). CH<sub>2</sub>Cl<sub>2</sub>, d=0.12 cm.

OH····HB at low temperatures as indeed was observed in the case of the  $BH_3CN^-/MFE$  system (Fig. 3).

The  $\Delta \nu_{OH}^{bond}$  value for BH<sub>3</sub>CN···HOCH<sub>3</sub> hydrogen bonded complex is less than that in the case of HB with CN anion [11] (232 and 345 cm<sup>-1</sup>, respectively). The decrease of the CN group proton accepting ability is due to the electron withdrawing effect of the BH<sub>3</sub> group analogous to the strong electron accepting effect of the boron cage found by us previously for [B<sub>12</sub>H<sub>11</sub>SCN]<sup>2-</sup> [8]. Significant decrease of SCN group proton accepting ability was found in [B<sub>12</sub>H<sub>11</sub>SCN]<sup>2-</sup>/HOCH<sub>3</sub> systems in comparison with SCN<sup>-</sup> anion hydrogen bonded to CH<sub>3</sub>OH [8,12].

The frequency calculations for the system  $BH_3CN^-/CH_3$ . OH give two  $\nu_{XH}^{bond}$  bands with low frequency shifts of 242 and 433 cm<sup>-1</sup> for DHB (2) and classical HB (1) complexes, respectively. Although the band shifts are overestimated in comparison with experimental values for the complexes with CH<sub>3</sub>OH (Table 3) due to carrying out the calculations in the gas phase, they are in agreement with the experimental trend.

#### 3.2.2. Range of $v_{BH}$ and $v_{CN}$

The data in the  $\nu_{\rm XH}$  region show the formation of HB complexes of two types, but do not provide any information about the centres of coordination. So, the study of concentration and temperature dependences of  $\nu_{\rm BH}$  and  $\nu_{\rm CN}$  bands of the BH<sub>3</sub>CN in the presence of different proton donors in THF was performed in order to elucidate the types of coordination in the different HB complexes.

The stretching vibration of  $\nu_{CN}^{init}$  of BH<sub>3</sub>CN<sup>-</sup> appears at 2168 cm<sup>-1</sup> in THF. The decrease of the intensity of this band and the appearance of the high frequency broad intense  $\nu_{CN}^{bond}$  band were observed in the presence of XH proton donors. The band shift values  $\Delta \nu_{CN}$  increase with the proton donor strength growing up from 6 to 14 cm<sup>-1</sup> in the case of OH proton donors (Table 4). The intensity of the broad bonded bands of complicated shape increases on cooling from 290 to 210 K (Fig. 4).

The high frequency shift of  $\nu_{CN}$  band was assigned to the coordination of proton donor on the nitrogen lone pair [11,13].



Fig. 4. Variable temperature IR spectra in the  $v_{CN}$  range of (Ph<sub>3</sub>P=N= PPh<sub>3</sub>)BH<sub>3</sub>CN (0.01 M) in the presence of TFE (0.01 M) in THF, d=0.04 cm.

But according to our calculations the proton donor coordination both to the nitrogen and to the hydride sites leads to the high frequency shifts of  $v_{\rm CN}$  band of close values (Table 5). This is due to the same shortening of CN bond in both HB complexes (Table 1).

The spectral picture in the range of  $\nu_{BH}$  stretching vibrations of the BH<sub>3</sub>CN<sup>-</sup> anion as well as its changes upon the interaction with XH-acids are more complicated than these for BH<sub>4</sub><sup>-</sup> [4a,b,7] according to the  $C_{3\nu}$  symmetry of BH<sub>3</sub>CN<sup>-</sup> there should be two  $\nu_{BH}$  bands in the IR spectra belonging to A<sub>1</sub> and two degenerate E<sub>1</sub> modes. However, the band decomposition analysis for  $\nu_{BH}^{init}$  band shows the presence of three overlapped bands at 2318 (s), 2284 (m) and 2268 (m) cm<sup>-1</sup>. This could be due to removing of E<sub>1</sub> mode degeneracy as the result of the cation and solvent effects. In addition to three  $\nu_{BH}$  bands two weak bands of the overtones of BH deformation modes are observed at 2230 and 2215 cm<sup>-1</sup>.

Analysis of all the spectra shows that the DHB and CN···HO complexes coexist in the presence of one equivalent of proton donor. Under these conditions the high frequency shifted single band of complex shape is observed in the range of  $v_{BH}$  stretching vibrations with maximum at 2330 cm<sup>-1</sup> ( $\Delta v_{BH} = +12 \text{ cm}^{-1}$ ). The band decomposition shows the decrease of the intensity of  $v_{BH}^{init}$  band and appearance of new low and high frequency shifted  $v_{BH}$  bands (Fig. 5, Table 5). We assign the high frequency band to  $v_{BH}^{free}$  modes of the both complexes 1 and 2 on the basis of close values  $\Delta v_{BH}^{free}$  calculated for these complexes (20–30 cm<sup>-1</sup>, Table 6). The calculated low frequency shift of  $v_{BH}$  stretching vibration of B–H bond implicated in the dihydrogen bond ( $\Delta v_{BH}^{bond} = -29 \text{ cm}^{-1}$ , 2) is in agreement with the band shift ( $\Delta v_{BH}^{bond} = -38 \text{ cm}^{-1}$ ) obtained by decomposition of the observed  $v_{BH}$  band (Fig. 5).

Twofold excess of proton donors leads to the intensity decrease of the  $\nu_{BH}^{bond} = 2278 \text{ cm}^{-1}$  and the intensity increase of the  $\nu_{BH}^{free} = 2330 \text{ cm}^{-1}$ , while the  $\nu_{CN}^{bond}$  band grows up in parallel with the intensity decrease of the  $\nu_{CN}^{init}$  band (Figs. 6 and 7).

This suggests that the hydrogen bonding equilibrium (Eq. (1)) shifts to the right in the presence of excess proton donors



Fig. 5. IR spectra in the  $\nu_{BH}$  range of (a) (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN (0.015 M, bold dashed) and (b) in the presence of HFIP (0.015, bold solid). Bands decomposition of the last spectra (thin dashed lines are assigned to BH<sub>3</sub>CN<sup>-</sup> anion bands and thin solid lines to HB complex). 290 K, THF, d=0.04 cm.

and the content of the classical HB complexes increases.

$$RXH + BH_3CN^{-} \rightleftharpoons [RXH \cdots H_3BCN]^{-}$$
$$+ [BH_3CN \cdots HXR]^{-}$$
(1)

Upon cooling the equilibrium (1) shifts also to the right, that becomes apparent from a decrease of the  $\nu_{CN}^{init}$  and  $\nu_{OH}^{init}$  bands as well as an increase of the bonded bands (Figs. 4 and 3). Temperature dependences indicate that the classical (BH<sub>3</sub>CN···HX) complexes are thermodynamically more stable. Really, the intensity increase of  $\nu_{XH}^{bond}$  of the classical HB complexes (H<sub>3</sub>BCN···HXR) at low temperatures is larger than this for DHB (for example, Figs. 2 and 3). Thus, the shift of the equilibrium is mainly due to an increase of the classical HB content.

It is interesting that the single high frequency shifted band  $\nu_{\rm CN}$  is observed at the BH<sub>3</sub>CN<sup>-</sup>/HFIP ratios from 1:1 to 1:4. A great excess of the proton donor (1:4, 1:8, 1:14) induces appearance of the additional weak broad high frequency shoulder in the  $\nu_{\rm CN}$  range ( $\Delta \nu_{\rm CN} = 24$  cm<sup>-1</sup>, Fig. 6), which we assign to the complex of 1:2 composition. Computational



Fig. 6. IR spectra in the  $\nu_{CN}$  range of (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN (0.015 M) (1) and in the presence of HFIP. (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN/HFIP concentration ratios: 1:1 (2), 1:2 (3), 1:8 (4), 1:14 (5). 290 K, THF, d=0.04 cm.



Fig. 7. IR spectrum in the  $\nu_{BH}$  range of (Ph<sub>3</sub>P=N=PPh<sub>3</sub>)BH<sub>3</sub>CN (0.015 M) in the presence of excess of HFIP (0.03 M) and band decomposition. 290 K, THF, d=0.04 cm. Thin dashed— $\nu_{BH}$  bands of free BH<sub>3</sub>CN<sup>-</sup>; thin solid— $\nu_{BH}$  bands of hydrogen bonded BH<sub>3</sub>CN<sup>-</sup>.

results give additional support to this assignment:  $\Delta \nu_{CN}^{bond}$  of the HB complex **3** is equal to 24 cm<sup>-1</sup>, i.e. increases about twice in comparison to complex 1:1 (Table 6). Calculated value of  $\Delta \nu_{BH}^{bond} = -6 \text{ cm}^{-1}$  in the complex 1:2 (**3**) is so small that its experimental observation is impossible in the presence of much stronger  $\nu_{BH}^{init}$  band. On the other hand the new high frequency band at 2348 cm<sup>-1</sup> appears in the  $\nu_{BH}^{free}$  range at the BH<sub>3</sub>CN<sup>-/</sup> HFIP concentration ratio being 1:2 and increases upon further addition of proton donor (Fig. 7). We assign this new band to the  $\nu_{BH}^{free}$  vibration in the complex with two proton donor molecules using calculation results indicating larger shift  $\Delta \nu_{BH}^{free} = 38-53 \text{ cm}^{-1}$  for the complex **3**. Thus this range is more sensitive to the coordination of the second proton donor molecule.

Thus, we can suggest that in the case of proton donor excess the complex 1:2 with two HB's: classical and non-classical coexists in the equilibrium with HB complexes 1:1 (Eq. (2)).

$$RXH + BH_{3}CN \rightleftharpoons [RXH \cdots H_{3}BCN]^{-}$$
$$+ [BH_{3}CN \cdots HXR]^{-} \rightleftharpoons [RXH \cdots H_{3}BCN \cdots HXR]^{-} \qquad (2)$$

Table 7

The formation enthalpy values  $(-\Delta H^\circ, \text{ in kcal/mol})$  for hydrogen bonded complexes of BH<sub>3</sub>CN<sup>-</sup> or BH<sub>4</sub><sup>-</sup> with RXH proton donors

RXH	$P_{i}^{a}$	BH <sub>3</sub> CN <sup>-</sup> ·H	H <sub>3</sub> BH…	
		BH···HX	CN···HX	HXR <sup>b</sup>
CH <sub>3</sub> OH	0.63	2.3	4.4	4.1
FCH <sub>2</sub> CH <sub>2</sub> OH	0.74	3.2	4.8	
CF <sub>3</sub> CH <sub>2</sub> OH	0.89	3.6	6.1	5.2
(CF <sub>3</sub> ) <sub>2</sub> CHOH	1.05	3.8	6.9	6.5
Pyrrole	0.65	2.2	4.3	
2-Phenyl-pyrrole	0.67	2.3	4.4	
Imidazole	0.78	2.8	5.3	

<sup>a</sup> The acidity factors of proton donors. Values from Ref. [14] and our own measurements.

<sup>b</sup> Data from Ref. [4b].

	Complex	$-\Delta E_{\text{calc}}$ , kcal/mol	$-\Delta H_{\text{calc}}(\Delta \nu)^{\text{a}}$ , kcal/mol
1	BH <sub>3</sub> CN <sup>-</sup> ·HOCH <sub>3</sub>	12.09	6.76
2	NCBH <sub>3</sub> ·HOCH <sub>3</sub>	8.23	4.53
3	BH <sub>3</sub> CN <sup>-</sup> ·2CH <sub>3</sub> OH	19.47	4.12 (N···HO)
			6.33 (BH····HO)
4	$BH_4^- \cdot HOCH_3$	11.13	6.29
5	BH <sub>3</sub> CN <sup>-</sup> ·HOCH <sub>2</sub> CF <sub>3</sub>	18.81	8.29
6	NCBH <sub>3</sub> <sup>-</sup> ·HOCH <sub>2</sub> CF <sub>3</sub>	13.91	5.49
7	BH <sub>3</sub> CN <sup>-</sup> ·2HOCH <sub>2</sub> CF <sub>3</sub>	30.47	4.69 (N···HO)
			7.51 (BH····HO)
8	$BH_4^- \cdot HOCH_2CF_3$	19.00	7.64

Table 8 Energies of model HB complexes with ZPE correction and those enthalpies obtained from the Iogansen's correlation

<sup>a</sup>  $-\Delta H^{\circ} = 18\Delta \nu_{\text{OHcalc}}/(720 + \Delta \nu_{\text{OHcalc}}).$ 

### 3.3. Hydrogen bond formation enthalpy

The formation enthalpies  $(-\Delta H^{\circ}, \text{ in kcal mol}^{-1})$  of DHB and classical HB complexes for all the proton donors were obtained from bands displacement  $\Delta \nu_{\text{XH}}$  using the Iogansen's correlation Eq. (3) proposed for organic systems [14]. Its applicability for unconventional HB was proved previously by us [1].

$$-\Delta H^{\circ} = \frac{18\Delta\nu_{\rm OH}}{\Delta\nu_{\rm OH} + 720} \tag{3}$$

The classical HB's to the CN group of  $BH_3CN^-$  are of medium strength varying from 4.3 to 6.9 kcal mol<sup>-1</sup> (Table 7). Thus they are stronger than the NCH<sub>2</sub>BH···HX hydrogen bonds, which enthalpy values are in the range 2.2–3.8 kcal mol<sup>-1</sup> (Table 7). The magnitudes of DHB complexes of BH<sub>3</sub>CN<sup>-</sup> enthalpy are in all cases two thirds less than these of DHBs of the unsubstituted BH<sub>4</sub><sup>-</sup> complexes with same proton donors, quantitatively characterizing the strength of electron accepting effect of CN<sup>-</sup> group.

Theoretically calculated  $-\Delta E$  values were obtained as difference of energies of HB complex and free reactants (Table 8). The  $-\Delta E_{\text{calc}}$  values are higher than experimentally obtained because the calculations were carried out in gas phase in the absence of counterion. Such overestimation of HB energies was observed previously for other main group hydride systems [4b,6,7]. Energy values of HB complexes depend on proton donating ability (for example  $-\Delta E = 8.23$  for 2 and 13.91 for 6). Comparison of DHBs formed by cyanoborohydride and tetraborohydride anions shows that introduction of CN group greatly decreases  $-\Delta E$  values as was obtained in IR experiment. The hydrogen bond formation enthalpies,  $-\Delta H_{\text{calc}}(\Delta \nu)$ , reported in Table 8 are calculated by means of the logansen's empirical rule (3) using the computed OH frequency shifts. There is rather good agreement between the computed hydrogen bonding enthalpies and those obtained from the IR experiments.

The linear dependences between experimentally obtained  $-\Delta H^{\circ}$  of both BH····HX and CN···HX complexes and the characteristics of the proton donating ability of XH-acids  $P_i$  [14a] (Fig. 8) were found. Analogous dependences were

established previously for different classes of organic bases as well as for transition metal hydrides [1].

Using these dependences we calculated proton accepting ability named as the basicity factor  $(E_j)$  of the both basic sites from the Eq. (4), where  $-\Delta H_{11}$  is the enthalpy of HB formation for a 'standard' pair (phenol-diethylether) for which  $P_i = E_j = 1.0, -\Delta H_{ij}$ . is experimentally obtained enthalpy and  $P_i$  is known acidity factor of proton donor [14a]. The  $E_j$  values are independent of the partners and media and therefore are more convenient for comparison of the basicity of different proton accepting sites [1,4b,c].

$$E_j = \frac{\Delta H_{ij}}{\Delta H_{11} P_i} \tag{4}$$

The  $E_j$  value of the hydride hydrogen of BH<sub>3</sub>CN<sup>-</sup> obtained in this work is equal 0.80. Thus, the substitution of one hydride by CN group (BH<sub>4</sub>/BH<sub>3</sub>CN<sup>-</sup>) induced the greater decrease of  $E_j$  in comparison with the analogous changes produced by SCN substitution in the hydride pair B<sub>12</sub>H<sub>12</sub>/B<sub>12</sub>H<sub>11</sub>SCN<sup>2-</sup>. Introduction of CN group decreases the basicity of BH<sub>4</sub><sup>-</sup> anion by a factor of 1.56, while the basicity of B<sub>12</sub>H<sub>11</sub>SCN<sup>2-</sup> is 1.11 times lower than that in B<sub>12</sub>H<sub>12</sub><sup>2-</sup> [8]. The scale of factors shows position of  $E_j$  of hydride hydrogen for BH<sub>3</sub>CN<sup>-</sup> relative to the



Fig. 8. Dependence of the formation enthalpy values  $(-\Delta H^\circ)$  for BH···HX (circles) and CN···HX (triangles) bonds on the acidity factors  $(P_i)$  of the proton donors.



Fig. 9. Basicity factors  $(E_i)$  for boron hydrides and related organic bases.

values reported up to date for the other neutral and anionic boron hydrides (Fig. 9), which vary from 0.62 to 1.25.

We can also consider the relative decrease of the basicity of classical HB sites in the pairs BH<sub>3</sub>CN<sup>-</sup>/CN ( $E_j = 1.42/2.0$ ) and  $[B_{12}H_{11}SCN]^2$ -/SCN<sup>-</sup> ( $E_j = 0.54/1.67$ ). Thus, the decrease of proton accepting ability of CN group in  $[BH_3CN]^-$  in comparison with CN<sup>-</sup> anion is greater than that of SCN in  $[B_{12}H_{11}SCN]^{2-}$  (1.50 and 1.41 times, respectively) showing that the electronic effect of BH<sub>3</sub> group is less than that of the boron cage.

## 4. Conclusions

The cyanoborohydride BH<sub>3</sub>CN<sup>-</sup>, possessing two HB sites: the hydride hydrogen and the nitrogen lone pair, appeared to be very convenient model for the investigation of the competition between non-classical and classical sites of hydrogen bonding. The combination of the IR spectroscopy and DFT calculations allowed elucidating many aspects of this problem. The assignment of all characteristic stretching vibration bands in the IR spectra was made in conjunction with frequency calculations. The formation of HB complexes of different types was shown in dependence on the acid-base concentration ratio. The thermodynamic characteristics and proton accepting ability of the two sites were determined. Classical H-bonds are stronger and more stable; therefore the equilibrium between free anion and the HB complexes of two types shifts to the right on cooling (200-290 K) mainly due to the increase of the classical HB complexes content. The coexistence of the classical and DHB bonds in one hydride molecule was established for the first time. Structural and electronic changes in the interacting molecules upon HB formation were studied theoretically. The elongations of OH and BH bonds as well as the small contraction of CN bond found are in agreement with previous studies of parent anions and the present experimental data. The strong electronic effects of the CN ligand and the boron framework on proton accepting properties of each other are demonstrated.

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