Intermolecular hydrogen bonds BH···HX in solution

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The interaction of proton donors with Bu_4NBH_4 and BH_3NEt_3 in hexane and dichloromethane was studied by IR and NMR spectroscopy and it was found for the first time that the proton-accepting centre of interaction of charged and neutral borohydrides with proton donors in solution is the hydrogen atom; the spectral and thermodynamic characteristics of the BH···HX hydrogen bond in solution were obtained and found, from enthalpy values, to be of medium strength.

Transition metal hydrides are known to form unusual intra- and inter-molecular hydrogen bonds MH···HX, the main coordination site being the hydridic hydrogen.[1–7] The H···H distance was determined by X-ray and NMR spectroscopy to be 1.7–2.0 Å. Experimentally determined enthalpy values (2.9–7.0 kcal mol^{-1}, 1 cal = 4.184 J) are typical for hydrogen bonds of medium strength.

Data from the Cambridge Crystallographic Data Centre (CCDC) for nitrogen containing borohydrides[8] showed that H···H distances are comparable with those found for hydrogen bonds with transition metal hydrides. This resulted in the conclusion that the interaction BH···HN existed. The N–H···HB angles vary between 117 and 171° indicating a bent BH···HN bond. Calculations[8] for the dimer $(BH_3NH_3)_2$ confirmed the possibility of the existence of such an unconventional hydrogen bond. The first IR spectral data about the proton accepting role of coordinated BH_3 and BH_2 groups of self-associated boranes and the interaction with proton donors was obtained in 1968–1974.[9] Thermodynamic characteristics of these bonds in CCl_4 were determined by IR spectroscopy.

Here we report the comparative study of the proton accepting ability of the anion (BH_4^-) and neutral borane (BH_3NEt_3) by IR and NMR spectroscopy. The interaction of proton donors of different strength [indole, Pr^iOH, MeOH, CF_3CH_2OH (TFE), $(CF_3)_2CHOH$ (HFIP)] with Bu_4NBH_4 in dichloromethane and neutral BH_3NEt_3 with HFIP in dichloromethane and hexane was studied.

Typical hydrogen bonds are observed in the stretching vibrations of alcoholic OH groups in the presence of the borohydride. The intensity of the free hydroxy groups decreases and broad bands of bonded OH groups (3177–3416 cm^{-1}) appear (Table 1). The shift values ($\Delta\nu$)[†] and half-width values ($\Delta\nu_{1/2}$) of bands increase with the increase of proton donor ability of the alcohol. Comparison of the IR spectra of the complex of Bu_4NBH_4 with indole in solution and of the film precipitated from solution shows that a hydrogen bond also exists in the solid state. The band of bonded NH groups in the IR spectra of the film is shifted downfield to 26 cm^{-1} in comparison with that in solution (Figure 1). Such a shift is characteristic for hydrogen bonded complexes when comparing solution and solid states. Enthalpies ($-\Delta H$)[‡] and formation constants (K_{form})[§] were calculated basing on the spectral characteristics obtained. This hydrogen bonding is of medium strength. Values of $-\Delta H$ (3.8–6.5kcal mol^{-1}) are comparable with enthalpies obtained for H-complexes with WH···HO tungsten hydrides in solution.[4]

The hydrogen bonding for the interaction of the neutral compound BH_3NEt_3 with HFIP was studied. Bands of bonded OH groups appear in the range 3390–3433 cm^{-1} (Table 1). The $-\Delta H$ values (3.6–3.7kcal mol^{-1}) are similar to those in phenols–BH_3NMe_3.[9c] This H-bond is weaker than with the BH_4^- anion ($-\Delta H$ = 6.5 kcal mol^{-1}). The formation constant for neutral borohydride is considerably smaller than that for the anion (8 and 217 dm^3 mol^{-1} respectively). The magnitude of K_{form} in hexane is appreciably higher than in CH_2Cl_2 in accordance with the decrease of medium polarity (Table 1).

The existence of the interaction of HFIP with BH_3NEt_3 in C_6D_{12} inevitably follows from ^1H NMR data. For example, addition of BH_3NEt_3 to HFIP in the ratio 1 : 1 caused the hydroxy group proton shift upfield by 2 ppm {^1H NMR, 200 MHz, C_6D_{12}: δ 2.7269 [$(CF_3)_2CHOH$]; δ 4.6902 [$(CF_3)_2CHOH$ in the presence of BH_3NEt_3]}.

The range of ν_{BH} stretching vibrations was studied in order to elucidate whether the hydride atom is a proton accepting centre. The ν_{WH} band was found to shift to low frequency during bond formation with the hydride ligand (WH···HOR),[4] similar to shifts of ν_{CO} in the case of carbonyl hydrogen bonding (MCO···HOR).[11] At the same time if a compound has more than one CO group, an additional high frequency band (or shoulder) assigned to free CO ligands in the hydrogen bonded complex is observed. Therefore we assumed, that BH···HOR H-complex formation for compounds containing three or four BH bonds should result in both high and low frequency shifts of the ν_{BH} bands. As a matter of fact both low frequency ($\Delta\nu$ = 26cm^{-1}) and high frequency ($\Delta\nu$ = 10cm^{-1}) shoulders are seen on the band ν_{asBH} of BH_4^- anion (2200 cm^{-1})[12] in the presence of proton donors. Similar changes of ν_{asBH} (2392 cm^{-1})[13] took place, $\Delta\nu$ values being 20 and 9 cm^{-1} respectively in the case of BH_3NEt_3 in the presence of HFIP, and the band ν_{sBH} (2283 cm^{-1})[13] underwent a low frequency shift.

Thus, we found that the proton accepting site in hydrogen bonding in solution is the hydride atom of charged and neutral borohydrides. Enthalpy values are characteristic for hydrogen bonds of medium strength and decrease on going from charged to neutral base. For a better understanding of the nature and

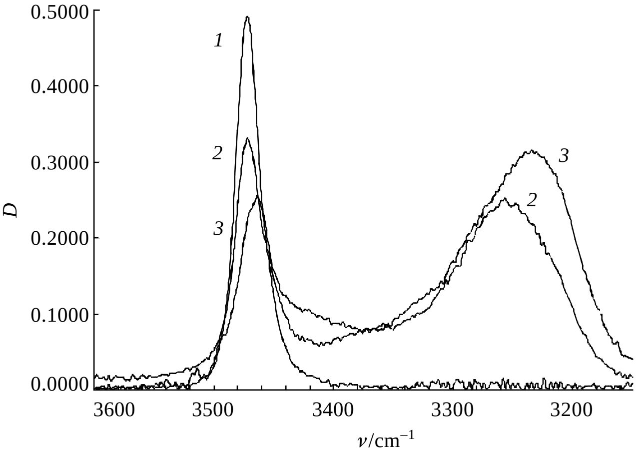

Figure 1 IR spectra in the ν_{NH} range of (*1*) indole (C = 0.03M), (*2*) indole (C = 0.03M) with Bu_4NBH_4 (C = 0.08 M) in CH_2Cl_2, and (*3*) indole with Bu_4NBH_4 in the solid state.

[†] $\Delta\nu = \nu_{OH_{free}} - \nu_{OH_{bond}}$.

[‡] $\Delta H = 18\Delta\nu/(720 + \Delta\nu)$.[10]

[§] $K_{form} = [C_{HX} - D/(\varepsilon l)]/\{C_{base} - [C_{HX} - D/(\varepsilon l)]D/(\varepsilon l)\}$; C_{HX}, C_{base} = initial concentrations of alcohol and base respectively, D = optical density of $\nu_{OH_{free}}$ band in the presence of a base, ε =extinction of $\nu_{OH_{free}}$ alcohol band in the solvent, l = size of the cell.

Table 1 Spectral and thermodynamic data of H-complexes of the proton donors with Bu_4NBH_4 and BH_3NEt_3.

Base	Solvent	HX	$\nu_{OH_{free}}$/cm^{-1}	$\nu_{OH_{bond}}$/cm^{-1}	$\Delta\nu^{\dagger}_{OH}$ /cm^{-1}	$\Delta\nu_{1/2}$/cm^{-1}	$-\Delta H^{\ddagger}$/kcalmol^{-1}	$K^{\S}_{form}$/dm^3 mol^{-1}
Bu_4NBH_4	CH_2Cl_2	HFIP	3579	3177	402	185	6.5	217
	CH_2Cl_2	TFE	3600	3310	290	171	5.2	46
	CH_2Cl_2	MeOH	3625	3410	214	91	4.1	44
	CH_2Cl_2	Pr^iOH	3608	3416	192	89	3.8	2
	CH_2Cl_2	indole	3473	3254	219	88	4.2	7
BH_3NEt_3	CH_2Cl_2	HFIP	3575	3390	185	112	3.7	8
	C_6H_{14}	HFIP	3630 3593	3443	178	121	3.6	21

structure of those unusual hydrogen bonds, both quantum mechanical and structural calculations as well as further spectral studies are in progress.

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