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Dihydrogen Bond Intermediated Alcoholysis of Dimethylamine-Borane in Non-Aqueous Media

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ABSTRACT

Dimethylamine-borane (DMAB) acid/base properties, its dihydrogen-bonded (DHB) complexes and proton transfer reaction in non-aqueous media were investigated both experimentally (IR, UV/vis, NMR and X-ray) and theoretically (DFT, NBO, QTAIM and NCI). The effects of DMAB concentration, solvents polarity and temperature on the degree of DMAB selfassociation are shown and the enthalpy of association is determined experimentally for the first time ($-\Delta H^{\circ}_{assoc} = 1.5-2.3$ kcal/mol). The first case of "improper" (blue-shifting) NH···F hydrogen bonds was observed in fluorobenzene and perfluorobenzene solutions. It was shown, that hydrogen-bonded complexes are the intermediates of proton transfer from alcohols and phenols to DMAB. The reaction mechanism was examined computationally taking into account the coordinating properties of the reaction media. The values of the rate constants of proton transfer from HFIP to DMAB in acetone were determined experimentally [(7.9 ± 0.1)×10⁻⁴ to (1.6 ± 0.1)×10⁻³ mol⁻¹·s⁻¹] at 270–310 K. Computed activation barrier of this reaction $\Delta G^{\partitude{theor}}_{298K}$ (acetone) = 23.8 kcal/mol is in good agreement with the experimental value of the activation free energy $\Delta G^{\partitude{texp}}_{270K} = 21.1$ kcal/mol.

KEYWORDS: amine-boranes; boron hydrides; DFT; IR spectroscopy

INTRODUCTION

The amine-boranes ($R_x^1 NH_{(3-x)}BH_{(3-y)}R_y^2$, where x,y ≤ 3) are well known as hydroborating agents and selective reducing agents, (for example, chiral amine-borane complexes can be used in enantioselective syntheses).¹⁻⁴ These compounds find many interesting applications⁵⁻⁸ and are considered as prospective materials for reversible hydrogen storage systems due to their high H₂ volumetric and gravimetric density.⁹⁻¹² Amine-boranes as well as related bifunctional compounds (metal borohydride ammonia borane complexes,¹³ metal tetrahydroborate ammoniates,¹⁴⁻¹⁷ metal amidoborane borohydrides¹⁸⁻¹⁹ and amidoborane ammoniates²⁰, metal hydrazine-boranes²¹⁻²²

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etc.) containing both acidic and basic groups are of particular interest for these purposes, as these compounds are capable to evolve hydrogen at heating.²³ Definitely, this reactivity relies on the existence dihydrogen bonds between acidic and basic functional groups.²⁴⁻²⁶

Widely recognized nowadays,²⁷ dihydrogen bond to borohydrides was suggested almost 50 years ago, but proved only in late 1990's^{24-25, 28} after reports on MH^{δ-...+δ}HX hydrogen bond formed by hydrides of transition metals.²⁹⁻³³ Thus, in 1964 Burg observed by IR-spectroscopy that the stretching vibration of NH-group of dimethylamine-borane (DMAB) appears in CS₂ and CCl₄ solutions at lower frequency than v_{NH} of gaseous (CH₃)₂NH.³⁴ On the basis of perturbation analysis of stretching vibrations it was suggested that NH···H₃B interaction similar to hydrogen bond exists in DMAB solution. In 1967 Rudolph and Parry, analyzing the high lattice energy of solid PH₃BH₃, suggested that "possible source of this lattice energy is the interaction of the acidic phosphine hydrogens and the hydridic borane hydrogens in an unusual type of hydrogen bond" in $PH^{\delta+...-\delta}HB$ manner.³⁵ This novel idea was not appreciated and unfairly forgotten until the 1990's. Then in 1968 Titov et al. explained the increased chemical reactivity of amineboranes toward the H₂ loss by "close spatial arrangement of oppositely charged hydrogen atoms".³⁶ In 1968–1974 Brown et al. investigated the IR spectra of L·BH₃ (L = Py, Me₂NH Me₃N, Et₃N, Et₃P) and Me₃NBH₂X (X = Cl, Br, I) in CCl₄ solutions and interactions of these compounds with weak acids (MeOH, ^tBuOH, PhOH, *p*-FC₆H₄OH).³⁷⁻³⁹ The low-frequency shift of v_{NH} band was observed for DMAB in CCl₄. It was found that the IR spectra of DMAB are "both concentration- and temperature-dependent in a manner characteristic of compounds undergoing intermolecular hydrogen bonding". The preliminary results of X-ray analysis of solid DMAB have shown the molecular association with short "B…HN" contacts.³⁷ The lowfrequency shift of OH stretching vibration was observed upon the interaction of amine- and phosphine-boranes with acids.³⁸⁻³⁹ On the basis of these data it was suggested that BH₃ and BH₂ groups can act as proton acceptors despite the lack of lone pairs or π electrons.³⁸ Even the

enthalpy of the interaction was estimated (1.7–3.5 kcal/mol), but no conclusion about the hydride ligand participation in hydrogen bonding was made.

Much later, in 1995–1999, the analysis of amine-borane dimers in Cambridge Structural Database⁴⁰ by Crabtree *et al.*²⁴⁻²⁵ revealed that in many cases the H···H distances (1.7–2.2 Å) are less than the sum of van der Waals radii of hydrogen atoms (2.4 Å) and the B–H···H(N) angles range from 95 to 175°. In the same time some of us investigated the ability of various main group hydrides (anionic ⁿBu₄NBH₄ and ⁿBu₄NGaH₄, neutral (EtO)₃PBH₃, Et₃NBH₃ and Me₃NAlH₃) to form BH····HX dihydrogen bond upon the interaction with proton donors in solution. It has been found these hydrides give the weak to medium strength DHBs adducts (1.1–6.5 kcal/mol).^{28, 41-42}

Recent publications^{14, 43-44} show still high interest to dihydrogen bonds in chemistry of BNH compounds. However there is no real conception of the role of DHB in the activation processes and the exact mechanisms of BH/NH activation (both off-metal and on-metal).

In this paper we present the results of the spectral and theoretical exploration of dimethylamine-borane (DMAB) reactivity aiming to establish its properties in intermolecular interactions and proton transfer reactions with organic acids and bases, to determine the structure of intermediates and the mechanism of the proton transfer processes.

Experimental section

General Considerations. All manipulations were performed under a dry argon atmosphere using standard Schlenk technique. Commercially available argon (99.9%) was additionally purified from traces of oxygen and moisture by sequential passage through Ni/Cr catalyst column and 4 Å molecular sieves.

The HPLC grade solvents (Acros Organics) were used for sample preparation after additional purification by standard procedures. Dichloromethane (DCM), fluorobenzene (FBz) and acetonitrile (MeCN) were dehydrated over CaH_2 , tetrahydrofuran (THF) – over Na/benzophenone, toluene – over Na. All solvents were freshly distilled under argon prior to use.

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Fluorinated alcohols provided by P&M (Moscow, Russia) and Fluka Analytical were used. Dimethylamine-borane (DMAB) was provided by Aviabor (Dzerzhinsk, Russia) as received. Other reagents were from Sigma Aldrich.

Variable-temperature IR measurements. IR spectra were recorded on FTIR Nicolet 6700 and FTIR Shimadzu IR Prestige-21 spectrometers using 0.04–0.22 cm CaF₂ cells. Low temperature IR studies were carried out in the 190–300 K temperature range using the home-modified cryostat (Carl Zeiss Jena). The cryostat modification allows transfer of the reagents (premixed at either low or room temperature) under an inert atmosphere directly into the cells. For measurements in the v_{OH} range, the acid concentrations were 10^{-2} – 10^{-3} M to avoid self-association, whereas DMAB was taken in 10-fold excess. For measurements in the v_{BH} range, the equimolar ratio or 10-fold excess acids were used.

NMR experiments. NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. ¹H chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) and were calibrated against the residual solvent resonance, while ¹¹B was referenced to $BF_3 \cdot Et_2O$.

A screwed-cap NMR tube was loaded with 1.8 mg of DMAB (0.06 mmol) under an inert atmosphere and then 500 μ L (final concentration ca. 0.06 M) of dry and degassed CD₂Cl₂ or acetone- d_6 was transferred into the tube *via* syringe, under inert atmosphere. From 1 to 5 eq. of proton donors (TFE, HFIP, TFA, PNP in solution) then was syringed into this solution at room temperature.

Products characterization. X-Ray diffraction studies.

Single crystals suitable for X-ray diffraction analysis were isolated directly from the reaction mixtures. X-ray diffraction measurements were carried out using Smart APEX II diffractometer. The frames were integrated and corrected for absorption by the APEX2 program package.⁴⁵ The details of crystallographic data and experimental conditions are given in Supplementary materials (Table S1).

 The structures were solved by the direct method and refined by full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the difference Fourier maps and refined in rigid body model. All calculations were performed using the APEX2 program package.⁴⁶

Crystallographic data for the structural analysis of $B(OH)_3 \cdot C_9 H_7 N \cdot C_9 H_7 N H^+ Cl^-$ and $Me_2 N H_2^+ [B(OCH_2 CF_3)_4]^-$ has been deposited with the Cambridge Crystallographic Data Centre⁴⁰, CCDC NOS. 1000135 – 1000136.

In IR spectra of isolated Me₂NH₂⁺[B(OCH₂CF₃)₄]⁻ product the following bands were observed (in nujol): $v_{\rm NH} = 3114 \text{ cm}^{-1}$, $v_{\rm BO}/v_{\rm CO} = 1290 \text{ cm}^{-1}$, 1165 cm⁻¹, 1107 cm⁻¹, 1040 cm⁻¹, $v_{\rm CF} = 975 \text{ cm}^{-1}$ and 963 cm⁻¹.

Computational details. Full geometry optimizations were carried out with the Gaussian09 (Revision C.01)⁴⁷ package at the density functional theory (DFT) level using the M06,⁴⁸ B3LYP,⁴⁹ BP86⁵⁰⁻⁵¹ and MP2⁵²⁻⁵⁶ levels of theory.

The $6-311^{++}G(d,p)^{57-58}$ basis set was used for all atoms. Frequency calculations were performed for all optimized complexes in the gas phase and are reported without the use of scaling factors. The nature of all the stationary points on the potential energy surfaces was confirmed by a vibrational analysis. Transition state (TS) structures showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.⁵⁹⁻⁶⁰

The complex formation energy was calculated in the gas phase taking into account the basis sets superposition error (by the Bernardi and Boys method, BSSE),⁶¹ ZPVE correction was determined from the unscaled harmonic frequencies.⁶²⁻⁶³

Inclusion of nonspecific solvent effects in the calculations was performed by using the SMD method.⁶⁴ The interaction energy was calculated in THF ($\epsilon = 7.4$), CH₂Cl₂ ($\epsilon = 8.9$), Me₂CO ($\epsilon = 20.5$), MeCN ($\epsilon = 35.6$) and H₂O ($\epsilon = 78.4$) for the gas phase optimized geometries.

Changes in Gibbs energies and enthalpies in the solvent were determined using corresponding corrections obtained for the gas phase⁶⁵:

$$\Delta H_{\rm DCM} = \Delta E_{\rm DCM} + \Delta H^{\rm corr}_{\rm gas}$$

 $\Delta G_{\rm DCM} = \Delta E_{\rm DCM} + \Delta G^{\rm corr}_{\rm gas}$

The magnetic shielding calculations were performed within the gauge-independent atomic orbitals (GIAO) framework.⁶⁶ The ¹¹B magnetic shielding were calculated on M06, B3LYP, BP86 and MP2 levels of theory with the IGLO-III basis set⁶⁷ using M06/6-311G⁺⁺(d,p) geometries. Chemical shifts were referenced to $BF_3 \cdot Et_2O$ as an external standard:

 $\Delta\delta(^{11}B) = \delta(BF_3 \cdot Et_2O) - \delta(^{11}B)$

Results and discussion

In this paper we present the results of combined variable temperature IR and NMR spectroscopic study of the DMAB interaction with organic acids and bases backed-up by theoretical calculations. The computational results are discussed in the end of the paper; some of the optimized structures are used as illustrations.

Self-association of DMAB

The coexistence of acidic and basic groups within the DMAB molecule allows the interaction between the two molecules, where the NH-group of one molecule acts as a proton donor and BH₃-group of another molecule plays the role of a proton acceptor. The existence of DMAB as a dimer (**Figure 1**) in the solid state is well recognized nowadays^{24-25, 68-69} but there are only old data on its self-association in solution limited to CCl_4 .³⁷



Figure 1. M06-optimized structures of DMAB and its self-associates. Formation SMD enthalpies calculated in DCM relative to DMAB monomer: $\Delta H_f^{\text{theor}}_{\text{DCM}}$ (dimer) = -6.5 kcal/mol; $\Delta H_f^{\text{theor}}_{\text{DCM}}$ (tetramer) = -11.6 kcal/mol.

Our IR measurements show DMAB self-association in non-polar solvents. Three BH stretching vibrations of DMAB were observed in CCl₄: v_{BH}^{as} at 2370 cm⁻¹, 2301 cm⁻¹ and v_{BH}^{s} at cm^{-1} (i.e., close to the literature values⁷⁰ in nujol at 2379, 2295 and 2264 cm^{-1}). However, this range is rather complicated for the analysis due to the overlap with the δ_{BH} bending vibration overtones⁷¹ and ¹⁰B–H stretching vibrations modes,⁷² that appear at higher frequency than ¹¹B–H and lead to bands broadening. Therefore, the quantitative data were obtained using the NH stretching vibrations. The DMAB monomer has the band of v_{NH}^{free} at 3299 cm⁻¹ (absorbance at band maximum A = 0.22; full width at half maximum FWHM = 10.8 cm⁻¹) in CCl₄ (ε = 2.2). The v_{NH}^{bond} appears at 3207 cm⁻¹ and its intensity is significantly greater than that of the v_{NH}^{free} band even at low DMAB concentration (c = 0.04 M) (Figure 2). Thus, in this solvent the major form is the associated one. The intensity of v_{NH}^{bond} band increases with the temperature lowering (295–265 K, Figure S1) and the concentration growth (0.04 M–0.11 M, Figure S3). The v_{NH}^{bond} position is close to that of DMAB in the solid state (3203 cm⁻¹ in nujol, 3211 cm⁻¹ in KBr).⁷⁰ The v_{NH}^{bond} band is non-symmetric and after the band deconvolution (Figures S2–S3) we obtained the three bands at 3233 cm⁻¹ ($\Delta v_{NH} = -66 \text{ cm}^{-1}$; A = 0.12; FWHM = 31.9 cm⁻¹), 3207 cm⁻¹ (the major form, $\Delta v_{\rm NH} = -92$ cm⁻¹; A = 0.85; FWHM = 28.8 cm⁻¹) and 3184 cm⁻¹ ($\Delta v_{\rm NH} =$ -115 cm^{-1} ; A = 0.04; FWHM = 21.4 cm⁻¹).



Figure 2. IR spectra of DMAB (0.04 M) in the v_{NH} region in CH₂Cl₂ (black solid line), CCl₄ (red dashed line) and in hexane (blue dash-dot line) at 290 K, l = 1.2 mm.

The quantity of the associated DMAB molecules in nonpolar hexane ($\varepsilon = 1.9$) is even higher than in CCl₄: the band deconvolution (Figure S4) gives v_{NH}^{free} at 3305 cm⁻¹ (A = 0.05; FWHM = 12.2 cm⁻¹) and four v_{NH}^{bond} bands at 3229 cm⁻¹ ($\Delta v_{NH} = -76 \text{ cm}^{-1}$; A = 0.25; FWHM = 47.8 cm⁻¹), 3213 cm⁻¹ ($\Delta v_{NH} = -92 \text{ cm}^{-1}$; A = 0.14; FWHM = 11.9 cm⁻¹), 3202 cm⁻¹ (the major form, $\Delta v_{NH} = -103 \text{ cm}^{-1}$; A = 0.91; FWHM = 13.2 cm⁻¹) and 3186 cm⁻¹ ($\Delta v_{NH} = -119 \text{ cm}^{-1}$; A = 0.22; FWHM = 38.3 cm⁻¹). The presence of several v_{NH}^{bond} bands allows suggesting the presence of other hydrogen-bonded forms of DMAB besides the dimer. These could be linear chains⁶⁹ linked by dihydrogen bond (Figure 1) or other forms of DMAB (e.g., trimers,⁶⁸ tetramers^{68, 73}).

In the solvent of medium polarity – CH_2Cl_2 ($\epsilon = 8.9$) DMAB is predominantly non-associated (v_{NH}^{free} at 3288 cm⁻¹; A = 1.26 ; FWHM = 14.8 cm⁻¹), (Figures S5–S6) and the growth of band intensity v_{NH}^{bond} at 3224 cm⁻¹ ($\Delta v_{NH} = -64 \text{ cm}^{-1}$; A = 0.05; FWHM = 63.8 cm⁻¹) with the increase of DMAB concentration or temperature is significantly smaller than in CCl₄ (Figure 2).

Blue-shifted H-bond. When DMAB is dissolved in fluorobenzene (FBz, $\varepsilon = 5.4$) a new blueshifted NH band v_{NH}^{b-s} (3312 cm⁻¹, $\Delta v_{NH} = +30$ cm⁻¹; A = 0.07; FWHM = 20.9 cm⁻¹, Figure S7– S9) appears in the range of NH group stretching vibrations besides the bands of DMAB monomer (3282 cm⁻¹; A = 0.17; FWHM = 19.2 cm⁻¹) and associated form (3215 cm⁻¹, $\Delta v_{NH} =$

-66 cm⁻¹; A = 0.01; FWHM = 24.5 cm⁻¹). The blue-shift of v_{NH} band can be explained by the formation of "improper" NH···F hydrogen bond that was predicted theoretically.⁷⁴⁻⁷⁶ Indeed, in perfluorobenzene (PFBz, $\varepsilon = 2.0$) DMAB exists only in two forms: dimeric (v_{NH} = 3216 cm⁻¹, $\Delta v_{NH} = v_{NH}^{\text{bond}}$ (in PFbz)– v_{NH}^{free} (in Fbz) = -66; A = 0.23; FWHM = 31.5 cm⁻¹) and NH···F hydrogen bonded one (v_{NH} = 3321 cm⁻¹, $\Delta v_{NH} = v_{NH}^{\text{bond}}$ (in PFbz)– v_{NH}^{free} (in Fbz) = +39 cm⁻¹; A = 0.06; FWHM = 19.2 cm⁻¹, Figure 3, Figure S10). In contrast only non-associated DMAB and its dimer are observed in toluene ($\varepsilon = 2.4$) exhibiting two bands $v_{NH}^{\text{free}} = 3269 \text{ cm}^{-1}$ (A = 0.36; FWHM = 16.3 cm⁻¹) and $v_{NH}^{\text{bond}} = 3213 \text{ cm}^{-1}$ ($\Delta v_{NH} = -56 \text{ cm}^{-1}$; A = 0.08; FWHM = 29.9 cm⁻¹, Figure 3 and Figure S11–S13). Absence of a high frequency v_{NH} band in this aromatic solvent argues that NH···π interaction does not lead to the high-frequency shift of v_{NH} band in fluorobenzenes. So, this is the first ever spectroscopic evidence of such "improper" NH···F



Figure 3. IR spectra of DMAB in the v_{NH} region in toluene (black solid line), FBz (red dashed line) and in PFBz (blue dash-dot line); 290 K, 1=0.4 mm.

The calculations reveal two types of "improper" hydrogen bonded complexes of DMAB with one and two molecules of FBz (Figure 4a, b) that give blue shifts of v_{NH} band by +4 cm⁻¹ and +8 cm⁻¹ at the MP2 level. "Improper" H-bonded complex was also obtained in the case of DMAB interacting with PFBz (Figure 4c; blue-shift of v_{NH} by +18 cm⁻¹ at the MP2 level). Note, the calculations at M06, B3LYP and BP86 theory level give red-shifted v_{NH} frequencies (Table 1).

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The MP2 method, which was typically used in theoretical calculations of blue shifted complexes^{74-75, 77}, is the only one that gives the v_{NH} blue-shift for HB complexes of DMAB with fluorobenzenes (Table 1). Note that the MP2-method provides better agreement between the experimental and calculated frequency shifts for all types of complexes investigated in this work (see part Theoretical investigation of DHB complexes *Frequency analysis*).



Figure 4. DFT MP2-optimized geometries of "improper" HB complexes DMAB–FBz (a), DMAB–2FBz (b) and DMAB–PFBz (c).

Table 1. The calculated frequencies of NH stretching vibrations of DMAB interacting with FBz

 or PFBz.

Method	DMA	B–FBz	DMAE	B–2FBz	DMAB-PFBz		
	$\Delta r_{\rm NH}$	$\Delta\nu_{\rm NH}$	$\Delta r_{\rm NH}$	$\Delta v_{\rm NH}$	$\Delta r_{\rm NH}$	$\Delta v_{\rm NH}$	
Experimental		+30		+30		+39	
MP2	0.001	+4	0.001	+8	0.000	+18	
M06	0.001	-4	0.003	+3	0.001	-7	
B3LYP	0.001	-10	0.002	-14	0.001	0	
BP86	0.003	-32	0.003	-32	0.001	-6	

The enthalpy of DMAB self-association $(\Delta H^{\circ}_{assoc})$ was determined using the Iogansen's empirical correlation (Eq. 1)⁷⁸⁻⁸⁰ which correlates the hydrogen bond formation enthalpy ($-\Delta H^{\circ}$, kcal/mol) with the experimental or theoretical values of the v_{XH} frequency shifts. Since the enthalpy depends on the solvent polarity, the ΔH°_{assoc} values decrease with the increase of the solvent dielectric permittivity ϵ (Table 2).

$$-\Delta H^{\circ} = \frac{18 \cdot \left| \Delta v_{\chi H} \right|}{720 + \left| \Delta v_{\chi H} \right|} \tag{1}$$

Table 2. The frequencies of NH stretching vibrations (in cm⁻¹) of DMAB measured in different solvents and DMAB association enthalpies (in kcal/mol).

Solvent	ϵ^{a}	$\nu_{NH}^{ free}$	$v_{ m NH}^{ m bond}$	$\Delta\nu_{\rm NH}$	ΔH^{o}_{assoc}
Hexane	1.9	3305	3202	-103	-2.3
PFBz	2.0	_	3215	-56 ^b	-1.5
CCl_4	2.2	3299	3207	-92	-2.0
FBz	5.4	3281	3215	-66	-1.5
CH_2Cl_2	9.1	3297	3218	-79	-1.8

^a dielectric permittivity values taken from ref.⁸¹; ^b $\Delta v_{\rm NH} = v_{\rm NH}^{\rm bond}$ (in PFbz)- $v_{\rm NH}^{\rm free}$ (in Fbz).

Interaction of DMAB with organic bases

In order to assess the proton-donating properties of NH-group we studied DMAB interactions with a number of organic bases (Y) of different strength – quinoline (Qu), pyridine (Py), $[CH_3(CH_2)_7]_3PO$ (TOPO), $[(CH_3)_2N]_3PO$ (HMPA), Et_3N (Figures S15–S16). The IR measurements were done in CCl₄ solution using excess of bases. This solvent allowed to avoid the overlap of bands in strong NH···Y complexes with C–H stretching vibrations of common organic solvents.

In the presence of bases the v_{NH} bands of DMAB monomer and dimer decrease or disappear simultaneously. The new broad v_{NH} bands corresponding to NH···Y bond (Y = N or O atom of base) appear at lower frequencies (Figure 5). Formation of H-bonded complexes with N-bases (Py, Qu, Et₃N) becomes evident at high base excess (20–50 equiv). The H-bonded complexes with HMPA and TOPO have much higher formation constants so in this case no DMAB monomer is visible.



Figure 5. IR spectra of DMAB (0.03 M) in the v_{NH} region in CCl₄ solution: in the presence of 10÷50 eq. NEt₃ at 270 K (left) and 10 eq. HMPA at 295–265K (right), 1=2.2 mm.

The value of Δv_{NH} increases with the increase of proton accepting ability of base (E_j, Table S4). The enthalpies of hydrogen bond formation determined by Eq. 1 ($-\Delta H^{\circ}$, Table 3) vary depending on the strength of the organic base from 1.2 to 4.1 kcal /mol in solvents ($\Delta H_{11}(CCl_4) = 5.3$) and from 1.5 to 6.0 kcal /mol for calculated HB complexes in gaseous phase ($\Delta H_{11}(gas) = 6.4$). The acidity factor P_i which characterizes the proton donating ability independent of proton acceptor and solvent, was determined for the NH-group of DMAB from the linear dependence $\Delta H^{\circ}_{(CCl_4)} vs E_j$ (Figure S20) (P_i = 0.45 ± 0.01). It is three times higher than P_i (Et₂NH) = 0.15 and slightly lower than P_i (Ph₂NH) = 0.50.⁷⁸ Thus, the coordination of the electron-deficient BH₃-group increases the proton donating ability of Me₂NH from 0.11 (calculated from the experimental data in ref. ⁸²⁻⁸³ by Eq. 1 and Eq. 3) to 0.45 in agreement with the increase of the gas-phase acidity from free Me₂NH to BH₃NHMe₂.⁸⁴

$$\Delta H^{\circ} = \Delta H_{11} \cdot P_i \cdot E_j \tag{3}$$

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Base	E_j^a	Solvent	$-\Delta H^{\circ}_{exp}{}^{d}$	$-\Delta H_{\text{theor}}(\Delta v)^e$
MeCN	0.75	MeCN	1.2	1.5
Me ₂ CO	0.93	Acetone	2.2	2.4
THF	1.04	THF	2.5	3.7
ТОРО	1.65	CH ₂ Cl ₂	2.8 ^c	_
HMPA	1.49	CCl ₄	3.6	4.8
Ру	1.53	CCl ₄	3.6	4.6
Qu	1.60 ^b	CCl ₄	3.8	4.7
ТОРО	1.65	CCl ₄	3.8	_
Et ₃ N	1.70	CCl ₄	4.1	6.0

 Table 3. Formation enthalpies (in kcal/mol) for H-bond of organic bases with DMAB.

^a The basicity factors E_j are taken from^{78, 85-86}; ^b calculated using the experimental data from ref. ⁸⁷; ^c calculated from the temperature dependence of formation constants. ^d $\Delta H^{\circ}_{exp}(\Delta v)$ calculated by Eq. 1 using experimental; ^e $\Delta H_{theor}(\Delta v)$ – and calculated by Eq. 1 using MP2 Δv_{XH} values.

IR spectra of DMAB in polar aprotic solvents (MeCN, Me₂CO, THF) feature only one band of NH stretching vibrations at frequencies lower than v_{NH}^{free} in the low polar non-coordinating solvents described above. We suggest that these bands belong to DMAB associates with the solvents through the NH····Y hydrogen bond where Y is the heteroatom of MeCN, Me₂CO or THF. The band shifts Δv_{NH} estimated relative to v_{NH}^{free} in CH₂Cl₂ change in the order -52 cm⁻¹ (MeCN) < -99 cm⁻¹ (Me₂CO) < -113 cm⁻¹ (THF) (Figure S34–S36). This sequence correlates with the order of the proton accepting properties (E_j)⁷⁸ of these solvent molecules $E_j^{\text{MeCN}}(0.75) < E_i^{\text{Me2CO}}(0.93) < E_i^{\text{THF}}(1.04)$.

DMAB interaction with acids

We have also studied the hydrogen bonding between the BH₃-group of DMAB and weak acids: CH₃OH, CH₃CH₂OH, FCH₂CH₂OH (MFE), CF₃CH₂OH (TFE), (CF₃)₂CHOH (HFIP), (CF₃)₃COH (PFTB), phenol (PhOH), *p*-NO₂C₆H₄OH (PNP) and indole. The IR measurements were performed in CH₂Cl₂ (under conditions that exclude self-association of DMAB); the changes in the regions of OH, NH and BH stretching vibrations were considered.

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The IR spectra of proton donors in the presence of DMAB show the intensity decrease of the proton donor band v_{XH}^{free} and appearance of new broad low-frequency band corresponding to v_{XH}^{bond} (Figure 6, Table 4). Such spectral picture evidences the involvement of XH-groups in H-bonding (XH···HB). The band shift, Δv_{XH} , depends on the proton donating ability of acids (Table 4). The low-frequency shifted v_{NH}^{bond} bands of DMAB are of low intensity and can correspond not only to the NH stretching vibrations in DMAB dimer. For DMAB dimer the v_{NH}^{bond} band was observed at 3218 cm⁻¹, $\Delta v_{NH} = 63$ cm⁻¹, with the intensity A= 0.05 (0.06 M DMAB in CH₂Cl₂ at 190 K) while this band drifts to lower frequencies and increases in intensity: e.g., it appears at 3216 cm⁻¹, $\Delta v_{NH} = 65$ cm⁻¹, A = 0.16 for 0.06 M DMAB in presence of 0.15 M PNP at 190K in CH₂Cl₂ (Figure 6, right). This can result from the superposition of the v_{NH}^{dimer} and $v_{NH \cdots 0}$ band of H-bonded complex where NH interacts with the oxygen atom of a proton donor (see below "Theoretical investigation of DHB complexes").



Figure 6. IR spectra in the v_{XH} region of DMAB-HOR mixture in CH₂Cl₂: 0.02 M HFIP in the presence of 0.06 M DMAB at 190–270 K (left) and 0.15 M PNP in the presence of 0.06 M DMAB at 210–270 K (right), l = 0.4 mm.

Table 4. Spectral characteristics (in cm^{-1}) and formation enthalpies (in kcal/mol) for hydrogen bonds of the proton donors with DMAB in CH₂Cl₂.

XH	P_i^a	XH : DMAB	$v_{\rm XH}^{\rm free}$	$v_{\rm XH}^{\rm bond}$	$\Delta\nu_{XH}$	$-\Delta H^{\circ}_{exp}(\Delta v)^{b}$	$-\Delta H_{\text{theor}}(\Delta v)^{c}$
Indole	0.50	1:10	3491	3426	-65	1.5	-
EtOH	0.63	1:10	3615	3531	-84	1.7	2.5 ^c

MFE	0.78	1:3.5	3606	3512	-94	2.1	3.0
TFE	0.89	1:5	3600	3479	-121	2.6	3.5
PhOH	1.00	1:3.5	3569	3414	-155	3.2	2.7
HFIP	1.05	1:5	3576	3412	-164	3.3	4.7
PNP	1.27	5:1	3547	3372	-175	3.5	3.2
PFTB	1.33	1:5	3525	3366	-179	3.6	4.9

 ^a The acidity factors for proton donors are taken from;^{86,96} $^{b}\Delta H^{\circ}_{exp}(\Delta v)$ calculated by Eq. 1 using experimental; $^{c}\Delta H_{theor}(\Delta v)$ – calculated by Eq. 1 using calculated MP2 Δv_{XH} values; ^c Calculated MP2 value for MeOH.

The intensity of v_{BH}^{as} and v_{BH}^{s} stretching vibration bands decreases upon DHB bond formation and new band v_{BH}^{bond} appears at lower frequency. The position of this band depends on the proton donor shifting to lower frequencies with the increase of the XH strength from 2338 cm⁻¹ for DMAB : PNP =1:1 in CH₂Cl₂ ($\Delta v_{BH} = 29 \text{ cm}^{-1}$, Figure 7, left) to 2319 cm⁻¹ for DMAB in MeOH ($\Delta v_{BH} = 48 \text{ cm}^{-1}$, Figure 7, right). Such changes indicate that BH₃ ligand is a proton accepting site in hydrogen bonding.⁸⁸ The v_{BH}^{bond} band is very narrow ($\Delta v_{1/2} = 5 \text{ cm}^{-1}$) in CH₂Cl₂ in comparison to $\Delta v_{1/2} = 36 \text{ cm}^{-1}$ in MeOH (Figure 7).



Figure 7. IR spectra in the v_{BH} region of DMAB: 0.06 M DMAB (black line), 0.06 M DMAB in the presence of 1 eq. PNP at 210–310 K in CH₂Cl₂ (left); 0.06 M DMAB in MeOH at 190–290 K (right), l = 0.4 mm.

The hydrogen bond formation enthalpy ($-\Delta H^{\circ}$; Table 4) determined by Eq. 1 shows linear dependence on the proton donor strength (acidity factors P_i, Figure S19). Its slope gives (Eq. 3)⁷⁸ the basicity factor $E_j = 0.62 \pm 0.02$ characterizing the proton accepting ability of boron hydride

independent of proton donor and solvent. This value is slightly higher than that of neutral borane complexes (EtO)₃PBH₃ ($E_j = 0.42$) and Et₃NBH₃ ($E_j = 0.53$),²⁸ but smaller than that of anionic BH₄⁻ ($E_j = 1.25$).

Theoretical investigation of DHB complexes

Structural analysis. Geometry optimizations were performed for H-bonded complexes of DMAB with MeOH, TFE and HFIP at DFT/M06, B3LYP, BP86 and MP2 theory levels, giving similar geometry of H-bonded complexes (Table S5–S7). All the minima were confirmed by all these approaches, except the complexes of II_{BH-NH} type, which do not possess local minima and converge into I_{BH-NH} complex during B3LYP and BP86 optimizations, indicating the instability of complexes of this type. The calculations revealed four possible types of complexes (Scheme 1): those with H-bond to one center of DMAB (I_{NH} and II_{BH}) and complexes where the alcohol acts simultaneously as a proton donor and a proton acceptor (I_{BH-NH} and II_{BH-NH}). The minimum corresponding to cyclic bifurcate DHB complex (II_{BH-NH}) was not found for MeOH. Three of the H-bonded complexes (I_{NH} , II_{BH} and I_{BH-NH}) are similar to complexes of DMAB interacting with phenol and aniline described previously⁸⁹⁻⁹⁰ by *ab initio* simulation. However, the influence of the alcohol strength on HB-complexes properties and proton transfer reaction pathway as well as the electron-density analysis were not studied at that time.



Scheme 1. Atom numbering scheme and possible types of DHB complexes of proton donors with DMAB.

Table 5. Structural parameters of M06-optimized H-bonded complexes of DMAB with alcohols.

	H	TFE			HFIP			
r	2	contact	r	۷	contact	r	Ζ	contact

I _{NH}	1.916	159	NH…O(H)	1.962	157	NH…O(H)	2.015	151	NH…O(H)
п	1.969	156	$OH \cdots H^{1}(B)$	1.933	156	$OH \cdots H^1(B)$	1.804	164	$OH \cdots H^1(B)$
пвн	2.118	133	$OH \cdots H^2(B)$	1.932	140	$OH \cdots H^2(B)$	2.014	130	$OH \cdots H^2(B)$
T	1.842	148	OH····H ³ (B)	1.683	160	$OH \cdots H^{3}(B)$	1.645	160	$OH \cdots H^2(B)$
IBH-NH	2.002	140	NH…O(H)	2.277	130	NH···O(H)	2.269	129	NH…O(H)
				1.813	148	$OH \cdots H^{3}(B)$	1.731	154	$OH \cdots H^{3}(B)$
II _{BH-NH}				2.283	121	$OH \cdots H^2(B)$	2.218	123	$OH \cdots H^2(B)$
				2.142	136	NH···O(H)	2.307	131	NH…O(H)
							1		

The structural parameters of these complexes are in the range typical for DHB involving boron hydrides.⁸⁸ The DHB distances are in the range 1.645–1.969 Å for primary (shorter) contact and 1.932–2.283 Å for secondary (longer) interaction, both are less than the sum of van der Waals radii of two hydrogen atoms (2.4 Å). The O–H····H angles for primary contact vary from 148 to 164°.

Formation of H-bonded complexes entails shortening of the B–N distance by 0.009–0.018 Å (Table S8) for all types of complexes, the largest changes being found for complexes of type I_{BH-NH} . In complexes with NH···O coordination (I_{NH} , I_{BH-NH} and II_{BH-NH}) the N–H bond interacting with the HOR oxygen atom elongates by 0.004–0.009 Å. The B–H bond primarily involved in DHB formation elongates by 0.002–0.011 Å. These changes are typical for H-bonded complexes formed by boron hydrides and amine-boranes.^{88, 91}

Interaction Energies. The formation energies of complexes differ by less than 4 kcal/mol in gas phase with the preference of I_{BH-NH} complex (Table 6). Taking into account basis set superposition error (BSSE) lowers the formation energies by ca. 10% only and does not change the relative order. Taking into account the nonspecific solvation by SMD method (CH₂Cl₂, acetone) leads to a significant lowering of formation energy and complex II_{BH} becomes slightly more stable than I_{BH-NH} and II_{BH-NH} . The enthalpies of H-bond complexes formation in dichloromethane (Table 6, $-\Delta H_{DCM} = 2.0 - 5.5$ kcal/mol) are comparable with the experimental

enthalpy values (Table 4, $-\Delta H^{\circ}_{exp} = 1.5 - 3.6$ kcal/mol). But by other criteria, including the QTAIM energy of HB formation ($E_{H\cdots X}$) derived from (3,-1) critical point characteristics, the most preferable are the cyclic complexes (I_{BH-NH} and II_{BH-NH}). That agrees with previous reports.⁸⁹

 Table 6. Formation energies (in kcal/mol) of M06-optimized H-bonded complexes of DMAB

 with HFIP.

Complex type	ΔΕ	ΔE _{ZPVE}	ΔE_{BSSE}	ΔH_{DCM}^{a}	ΔH _{Me2CO} ^a	$\Delta H_{theor} (\Delta v_{OH})^{b}$	$E_{H\cdots X}{}^{c}$
I _{NH}	-10.7	-9.0	-7.8	-3.2	-2.4	-	-6.6
II _{BH}	-11.7	-9.9	-8.8	-5.4	-5.2	-3.7	-6.5
I _{BH-NH}	-14.0	-12.2	-11.2	-5.5	-4.9	-4.7	$-8.5^{d}/-4.5^{e}$
II _{BH-NH}	-12.2	-10.3	-9.0	-4.3	-3.9	-4.8	-7.5 ^c /-3.9 ^d

^a ΔH_{DCM} and ΔH_{Me2CO} – energies with SMD solvent correction in CH₂Cl₂ and acetone, respectively; ^b $\Delta H_{theor}(\Delta v)$ – calculated by Eq. 1 using MP2-computed v_{NH} frequencies for I_{NH} and v_{OH} frequencies for complexes of other types; ^c E_{H···X} – energy of HB formation derived from QTAIM by equation E_{H···X} = 0.5 × V(r). ^d Energy of OH···HB bond; ^e Energy of NH···O(H)–R bond.

Frequency analysis. Frequency calculations were performed for the gas phase optimized geometries. The MP2-method provides better agreement between the experimental and calculated frequency shifts, which are presented on the example of complexes with TFE in Table 8. Formation of hydrogen bond where OH group acts as the proton donor (complexes I_{BH-NH} , II) leads to the expected large frequency shift Δv_{OH} ($\Delta v_{OH} = -132 \div -180 \text{ cm}^{-1}$). The exceptionally low frequency shift in complex I_{NH} ($\Delta v_{OH} = -17 \text{ cm}^{-1}$) is explained by the participation of OH group only as proton acceptor in NH···OH bonding.

Table 7. Frequency shifts (Δv , cm⁻¹) and intensity changes (ΔA , Km/mol) calculated for MP2optimized H-bonded complexes of DMAB with TFE.

Complex type	Δv _{oh}	ΔΑ	$\Delta v_{\rm NH}$	ΔΑ	Δv_{BH1}^{as}	ΔΑ	Δv_{BH2}^{as}	ΔΑ	$\Delta v_{BH}{}^{s}$	ΔA	Δv_{BN}	ΔA
I _{NH}	-13	5	-21	209	-11	30	-16	-22	-9	9	20	-2
II _{BH}	-134	378	24	3	18	-15	-4	-28	1	32	20	-3
I _{NH-BH}	-177	371	7	69	14	-12	-28	-75	-35	95	29	-3
II _{NH-BH}	-168	269	-21	90	13	-32	-19	-36	-27	88	23	-3

Cyclic complexes (I_{BH-NH} and II_{BH-NH}) exhibit the largest frequency shifts of v_{BH} bands, which are the most similar to the experimentally observed band shifts. In these complexes, the v_{BH2}^{as} and v_{BH}^{s} modes shift to lower frequencies by 20–33 cm⁻¹, while v_{BH1}^{as} mode undergoes a highfrequency shift. Such pattern is consistent with the experimental spectra, where the new band appears at lower frequency ($\Delta v_{BH} = -26 \div -48 \text{ cm}^{-1}$) (Figure 7). The decrease of the B–N distance upon H-bond formation results in the increase of v_{BN} stretching vibration frequency regardless of the complex type.

The computed frequencies can be used to estimate the hydrogen bond formation enthalpy $(\Delta H_{\text{theor}}(\Delta v))$, Table 6) and the basicity factor of BH-ligand. This value calculated by Eq. 1 and Eq. 3 and ΔH_{11} =6.4 kcal/mol in gas phase⁷⁹ is in perfect agreement with the experimental value of the proton donating ability (E_j = 0.62 ± 0.02). The E_j calculated for **I**_{NH-BH} complexes is 0.54 ± 0.05 what is significantly lower than the experimental value. The calculated value of P_i for NH in complexes **I**_{NH} (Table S10) is 0.48 ± 0.02, that is close to the experimental data (P_i = 0.45 ± 0.01).

So, the complexes of type I_{BH-NH} conform to the experimental observations by a number of criteria (energetic, spectral).

Electron-density analysis. Electron density redistribution, which occurs upon DHB formation, was analyzed using different approaches, namely, natural population analysis (NPA),⁹² Wiberg bond indexes (WBIs),⁹³ Bader's Quantum Theory of "Atoms in Molecules" (QTAIM)⁹⁴⁻⁹⁶ and

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analysis of non-covalent interaction indexes (NCIs).⁹⁷⁻⁹⁸ All these methods provide a powerful tool to recognizing hydrogen bond from other types of non-covalent interaction.⁹⁹⁻¹⁰¹

As expected, upon DHB formation the charge on the proton of HOR becomes more positive, whereas the charge on the interacting hydridic hydrogen(s) becomes more negative (Table S14). The charge of NH group proton becomes more positive upon bonding with O atom in complexes I_{NH}, I_{BH-NH} and II_{BH-NH}.

Within the framework of the QTAIM theory, a hydrogen bond is characterized by the presence of (3, -1) critical point that allows one to distinguish it from other types of interaction.¹⁰² The NH…O(H) interaction in complexes I_{NH} , I_{BH-NH} and II_{BH-NH} always possess a (3, -1) critical point ($\rho_c = 0.01-0.03$ au, $\varepsilon_{NH\cdots O} = 0.09-0.31$, Table S17). In bifurcate complexes (II_{BH} and II_{BH-} NH), the (3, -1) critical point was found only for the closest contact with the most linear O-H…H(B) arrangement (Figure 8a) despite the presence of secondary OH…HB contact. The values of the electron density at the (3, -1) bond critical point (ρ_c , Table S17) depend slightly on the proton donor strength being in the range 0.01–0.03 au. The presence of additional interactions causes deviation of the OH…H moiety from linearity and reflected in the values of the H…H bond ellipticity ($\varepsilon_{H\cdots H}= 0.19-0.26$ in I_{BH-NH} and II_{BH-NH}) (Figure 12a). Extremely high $\varepsilon_{H\cdots H}$ ellipticity values (0.92–3.54) are observed for bifurcate DHB complexes of type II_{BH} .

From the analysis of non-covalent interactions (NCI)⁹⁷⁻⁹⁸ we obtained NCI isosurfaces (Figure 8b, Figures S24, S26 and S28) which are similar to the QTAIM molecular graphs (Figures S24, S26 and S28) except for the **II**_{BH} complexes. The NCI analysis gives in this case two negative values of sign of $(\lambda_2)\rho(r)$ (-0.015 and -0.014, Table S18) indicating attractive (dihydrogen bonding) interaction between the proton and both BH ligands, which are spotted in blue color on gradient isosurfaces (Figure 8b). One positive value of sign $(\lambda_2)\rho(r)$ (+0.014) evidences the nonbonding overlap and is depicted in red color (Figure 12b). Thus NCI analysis allows assigning the **II**_{BH} complexes as bifurcate dihydrogen bond despite only one H-bond path in terms of QTAIM theory. In case of **II**_{NH-BH} complexes, which geometrical parameters are typical

for bifurcate H-bond, the analysis of electron density (NBO, QTAIM, NCI) shows only one XH…HB interaction.



Figure 8. Topological analysis of electron density for DMAB·MeOH complex of type II_{BH} : a) QTAIM molecular graph ($\varepsilon = 1.54$); b) NCI gradient isosurface for s = 0.3 au and blue-greenred color scale from $-0.01 < sign(\lambda_2)\rho(r) < +0.01$ au; c) plot of the reduced density gradient (RDG) versus $sign(\lambda_2)\rho(r)$.

DMAB protonation in non-aqueous media.

IR study. IR study ascertains that proton transfer proceeds via the H-bonded complex: the presence of excess proton donors leads to the appearance of new strong band of v_{BH}^{bond} stretching vibrations at low frequency in CH₂Cl₂ (Figure 9) as well as in coordinating solvents like MeCN, Me₂CO and THF (Figures S38–S40). Above 250 K the hydrogen evolution (Scheme 2) begins, taking several days at room temperature in low polar media (CH₂Cl₂, FBz). Thus, the reaction of DMAB with weak acid TFE (10 eqiv.) in low-polar FBz was completed in 14 days at room temperature. The monocrystals of [Me₂NH₂]⁺[B(OCH₂CF₃)₄]⁻ were isolated from the reaction mixture by slow solvent evaporation and characterized by X-ray (see below), IR and NMR spectroscopy. The use of coordinating solvent (MeCN, Me₂CO or THF) and stronger proton donors reduces the reaction time to several hours. The protonation of DMAB by 2 eqiv. HFIP in acetone has the reaction half-time of ca. 4 h at 290–310 K.

Scheme 2. Mechanism of the proton transfer to DMAB.

In the course of the reactions the gradual fall of all bands in the region of v_{BH} stretching vibrations is observed (Figure 9). Simultaneously two new bands v_{BH}^{prod} appear at higher frequencies (2402 and 2430 cm⁻¹), corresponding to the reaction products ([Me₂NH₂]⁺[X₂BH₂]⁻, where X could be OR or Solv).¹⁰³⁻¹⁰⁴ In the same time the decrease of the v_{NH}^{bond} band, which belongs to N–H group hydrogen bonded to acetone, is observed (Figure S30).



Figure 9. IR monitoring (v_{BH} region) of the reaction between DMAB (black line, 0.06 M) and 2 eqiv. HFIP (0.12 M) in acetone (310 K, l = 0.4 mm) over ca. 280 min.

The experimental kinetic data obtained for DMAB reaction with 2 eqiv. HFIP in acetone obey a second order reaction law (Eq. 4). The values of the rate constants determined vary from $(4.2 \pm 0.4) \times 10^{-5}$ to $(1.6 \pm 0.1) \times 10^{-3}$ mol⁻¹·s⁻¹ in the 190–310 K temperature range with $\Delta G^{\ddagger} = 14.8$ – 22.2 kcal/mol (Table S18).

$$-\frac{d[DMAB]}{dt} = k_{obs}[DMAB][HOR]$$
⁽⁴⁾

UV-Vis. The interaction of DMAB with *p*-NO₂C₆H₄N=NC₆H₄OH (PNAP) in CH₂Cl₂ could be conveniently investigated by UV-Vis spectroscopy. At low temperatures the spectra show strong blue shift of the PNAP band ($\lambda = 423$ nm, $\Delta \lambda = 45$ nm) indicative of DHB formation¹⁰⁵⁻¹⁰⁶

(Figure 10) and above 270 K the band of PNAP anion appears at 530 nm evidencing the beginning of the proton transfer reaction.



Figure 10. UV-Vis spectra of PNAP (black line, 0.003 M) and PNAP in the presence of 5 eq. DMAB in CH_2Cl_2 , l = 0.4 mm.

Characterization of the reaction products. The product of DMAB protonation by TFE in FBz - the compound $[Me_2NH_2]^+[B(OCH_2CF_3)_4]^-$ was isolated as individual monocrystals and ^{11}B characterized by X-ray diffraction (Figure 11). The singlet signals of $[Me_2NH_2]^+[B(OCH_2CF_3)_4]^-$ dissolved in CD₂Cl₂ appear at 2.7 and 2.4 ppm, these values are consistent with previously reported ¹¹B chemical shifts for $Na^+[B(OCH_2CF_3)_4]^-$ (2.9 ppm) and $Li^{+}[B(OCH_2CF_3)_4]^{-}(3.2 \text{ ppm})$.¹⁰⁷ Appearance of two ¹¹B singlets could be due to the formation of contact and solvent separated ion pairs in solution.¹⁰⁸ In the presence of even small amount of water this compound transforms into boric acid with a broad signal at 19.5–20.3 ppm.



Figure 11. General view of $[Me_2NH_2]^+[B(OCH_2CF_3)_4]^-$ structure according to XRD analysis (50% probability ellipsoids) (top) and M06 optimization (bottom).

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Similar $[B(OR)_4]^-$ products were obtained previously in NH₃BH₃ alcoholysis by MeOH¹⁰⁹ and TFE¹¹⁰ and in case of NaBH₄ methanolysis.¹¹¹ Another products were isolated by us as the result of DMAB interaction with quinoline and NEt₃ in CCl₄: $B(OH)_3 \cdot C_9 H_7 N \cdot C_9 H_7 N H^+ Cl^-$ (Figure 12) and $[Me_2NH_2]^+ Cl^-$. XRD study of dimethylammonium chloride revealed the same unit cell dimensions as published CSD-DMEACL05.¹¹²



Figure 12. General view of $B(OH)_3 \cdot C_9 H_7 N \cdot C_9 H_7 N H^+ Cl^-$ (50% probability ellipsoids).

NMR-monitoring of the reaction.

The ¹¹B NMR signal of initial DMAB in acetone- d_6 appears as a quartet at -13.6 ppm (q, J_{BH} = 97.0 Hz). Upon the DMAB reaction with 2 eqiv. HFIP (Figure S35) a new triplet signal appears at +3.1 ppm (t, J_{BH} = 113.6 Hz) in ca. 30 min after mixing, corresponding to [Me₂NH₂][BH₂(OR)₂].¹¹³ In low polar media (CH₂Cl₂) the reaction apparently yields Me₂NH–BH₂OR (+4.0 ppm, t, 111.2 Hz) and Me₂NH–BH(OR)₂ (+2.4 ppm, d, 78.1 Hz) species.^{104, 114} The hydrolysis products B(OH)₃ and BX₃ were observed at 20.3 ppm. When initial compound is almost consumed the new singlet signal is observed in ¹¹B{¹H} spectra at 2.2 ppm (Figure S32) assigned to [Me₂NH₂]⁺ [B(OR)₄]⁻

In the presence of 1 eqiv. *p*-nitrophenol (PNP) in acetone- d_6 solution of DMAB the new triplet of BH₂X₂ species is observed at -0.6 ppm (t, J_{BH} = 111.2 Hz) (Figure 13). The exact position of this signal is highly dependent on the OR⁻ nature (Table 8), supporting its asignment to [Me₂NH₂][BH₂(OR)₂] species. Similar spectral picture was observed in time for this and other proton donors (see Table 8 and Figures S33–S36).

It should be noted that ¹¹B signals in the $+3 \div -1$ ppm region could be assigned to the neutral, anionic or even cationic tetracoordinated boron in [BH₂(X)₂] species depending on the electron donating ability of X. In our case when RO⁻ residue (Me₂NHBH₂OR¹¹⁵ and [BH₂(OR)₂]⁻¹¹⁰) is formed as the result of proton transfer and H₂ evolution, the formation of cationic species like [BH₂X₂]⁺ (X = NHMe₂¹¹⁶ or Solv¹¹⁷⁻¹¹⁸) is quite unlikely.



Figure 13. The ¹¹B NMR spectra of DMAB (0.06 M) in the presence of PNP in acetone- d_6 at 297 K: a) DMAB:PNP (1:2) (black line) after 1.5 h of reaction, DMAB:PNP (1:3) (blue line) after 2 h of reaction, DMAB:PNP (1:4) (red line) after 2.5 h of reaction; b) DMAB:PNP (1:5) after 10.5 h of reaction; c) DMAB:PNP (1:5) after 3 days.

Table	8.	Experimental	values	of	'nВ	NMR	chemical	shifts	for	the	reaction	products	and
calcula	ited	by GIAO-MP2	?/IGLO	III 1	meth	od.							

ROH	[BH ₂ (OR) ₂] ⁻	[BH(OR) ₃] ⁻	[B(OH) ₄] ⁻	$[B(OR)_4]^-$	B(OH) ₃
Calculated	+4.0	+6.3	+1.3	+1.6	+18.0
for MeOH	$\left[\mathrm{Me_2NH_2}\right]^{+}\left[\mathrm{BH_2(OMe)_2}\right]^{-}$	$[\mathrm{Me}_{2}\mathrm{NH}_{2}]^{+}[\mathrm{B}(\mathrm{OMe})_{3}\mathrm{H}]^{-}$	1.5	1.0	10.0
TFF	_	_	_	+2.4 (s)	+19.5
ITL				+2.7 (s)	(broad s)
HEID	+3.1 (t)	_	_	+ 2 2(a)	+20.3
TIF IF	$J_{BH} = 113.6 \text{ Hz}$			+2.2(8)	(broad s)
PNP	-0.6 (t)	_	+1.1 (s)	+2.5 (s)	+19.3
1 1 1	$J_{BH} = 111.2 \text{ Hz}$		1.1 (5)	+2.6 (s)	(broad s)
TΕΛ	-1.1 (t)	+0.7(d)	_		+20.2
IIA	$J_{BH} = 118.3 \text{ Hz}$	$J_{BH} = 151.4 \text{ Hz}$			(broad s)

In ¹H NMR spectra of DMAB in acetone- d_6 the signal of NH-group is observed at 5.2 ppm (s), of CH₃-group - at 2.4 (d) and BH₃-group - at 1.5 (q). In the presence of 5 equiv. PNP the new signals appear at 5.7(s) and 2.6 (d) ppm that correspond to NH₂- and CH₃-groups of [Me₂NH₂]⁺, respectively. The BH-signals intensity decreases and a new broad line appears at 1.4 ppm (s) that can be assigned to X₂BH₂ species.

To predict the magnetic shielding of ¹¹B nuclei several approaches were used (GIAO-MP2/M06/B3LYP/BP86 with IGLO III basis set). The GIAO-MP2/IGLO III//M06/6-311++G (d,p) and GIAO-M06/IGLO III//M06/6-311++G(d,p) methods gave reliable results for ¹¹B NMR chemical shift calculations (Table S19) and therefore were used to calculate the ¹¹B magnetic shielding in $[Me_2NH_2]^+[BH_{(4-x)}(OR)_x]^-$ and B(OR)₃ alcoholysis products assisting the signals assignment in the experimental ¹¹B NMR spectra (Table 8,Table S19–S20).

Mechanism of proton transfer

 Several mechanisms for amine-boranes (AB) hydrolysis were proposed in the literature.¹¹⁹⁻¹²⁰ The first pathway implies the proton transfer to BH₃-group with hydrogen evolution and subsequent fast hydrolysis by the water present in the system.¹¹⁹ The second pathway involves electrophilic displacement of BH₃ through the proton attack to nitrogen, accompanied by the rupture of B–N bond and fast hydrolysis of solvated BH₃-group.¹¹⁹⁻¹²¹ Another pathway implies the dissociative activation of B–N bond.¹²⁰

However all these schemes were proposed for acid hydrolysis by strong inorganic acids (HCl, H_2SO_4) where the proton transfer reaction is fast making the intermediates observation impossible. We investigate the DMAB reaction with weak organic acids (fluorinated alcohols, substituted phenols) in the argon atmosphere in anhydrous solvents that allows observing the proton transfer reaction intermediates.

As it follows from the low-temperature IR and UV-study and DFT calculations in the presence of weak OH acids DMAB prefers to form cyclic HB complexes of type I_{BH-NH} rather than complexes of type II_{BH} with bifurcate BH····HX bonds. Having small difference in formation energy (less 4 kcal/mol) both these HB complexes can be envisaged as intermediates of the reaction leading to H₂ evolution. So, several pathways of proton transfer were considered in our quantum chemical calculations with or without direct participation of a solvent molecule. The calculations were performed taking into account the bulk solvent effect by means of SMD approach.

Proton transfer in non-coordinating low polar solvents. Three possible mechanisms for this reaction were considered (Scheme 3): the proton transfer to BH_3 -group (TS_{BH1}), the proton transfer from the alcohol to BH_3 -group assisted by proton transfer from NH group to the alcohol's oxygen (TS_{NH-BH}) and the insertion of proton donor into B–N bond (TS_{B-N}). Figure 14 presents the corresponding transition states obtained at the M06 theory level, the energy profiles are given on Figure 15.



Scheme 3. Possible pathways for DMAB protonation.

The direct protonation of BH-site (TS_{BH1}) proceeding via the DHB intermediate II_{BH} and yielding Me₂NH–BH₂OR has the highest activation barrier ($\Delta G^{\dagger}_{DCM} = G(TS) - G(H-bond) =$ 50.3 kcal/mol for HFIP, Figure 15). This pathway is similar to the first pathway suggested for AB hydrolysis but is not feasible without additional BH activation or B–N bond dissociation due to low BH basicity and hence high activation energy. The activation energy for subsequent proton transfer to second and third hydride ligands (TS_{BH2} and TS_{BH3} , Figure S48) is lower (37.2 and 38.4 kcal/mol, respectively). This trend is common for boronhydrides protonation.¹²²

The next possible mechanism is the double proton transfer (**TS**_{NH-BH}), which proceeds via cyclic HB complex of type **I**_{BH-NH} yielding Me₂N=BH₂ with lower activation barrier ($\Delta G^{\ddagger}_{DCM} = 28.4$ kcal/mol for HFIP and 24.4 kcal/mol for two HFIP molecules). The product of this process Me₂N=BH₂ is stable only at low temperatures¹²³⁻¹²⁴ and easily forms cyclic dimmer (Me₂N–BH₂)₂.¹²⁵⁻¹²⁷ However in the presence of alcohol excess it can react with HOR by Ad_E mechanism (**TS**_{Ad_E}, Scheme 3; $\Delta G^{\ddagger}_{DCM} = 28.2$ kcal/mol for HFIP and 21.2 kcal/mol for two HFIP molecules) yielding Me₂NH–BH₂OR species as in case of direct protonation of BH-site.

The third possible pathway is the dissociation of B–N bond (\mathbf{TS}_{B-N}) analogues to that proposed for the AB hydrolysis.¹¹⁹⁻¹²¹ It proceeds via the cyclic HB complex of type \mathbf{I}_{BH-NH} and implies the insertion of the OH-group of the proton donor into the B–N bond of DMAB ($\Delta G^{\dagger}_{DCM} = 32.2$ kcal/mol for HFIP) followed by proton transfer from BH₃(H)OR to the nitrogen atom of Me₂NH fragment. According to DFT calculations the activation barrier of proton transfer from BH₃(H)OCH(CF₃)₂ to NH₃ and Me₂NH (\mathbf{TS}_{PT2} , Scheme 3, Figure S47) is very low (less than 2 kcal/mol) that is less than the experimentally determined barrier for the proton transfer from 2,4dichlorophenol to triethylamine (activation free energy is 9.0 kcal/mol).¹²⁸ The resulting [Me₂NH₂]⁺[BH₃(OR)]⁻ species are 2–3 kcal/mol more stable. So, it can be assumed, that the equilibrium of proton transfer reaction is shifted toward [Me₂NH₂]⁺ and, ultimately, to [Me₂NH₂]⁺[B(OR)₄]⁻, the latter being characterized by X-ray diffraction as the reaction product.

According to the recent study¹²⁹ the spontaneous formation of $[(Me_2NH)BH_2]^+[BH_4]^-$ from DMAB at ambient conditions is quite unlikely. However the B–N dissociation is still possible within the DMAB dihydrogen bonded dimer, by the analogy with processes described for ammonia borane.¹³⁰ The activation energy for B–N dissociation in dihydrogen bonded dimer matches the BDE value for DMAB (36.9 kcal/mol; Figure S53 and Table S23). This value is greater than the activation energy of B–N dissociation mediated by ROH. Indeed our measurements of ¹¹B NMR spectra show that spontaneous B–N cleavage in DMAB is not observed.

Therefore relatively high but accessible barriers for the DMAB alcoholysis (TS_{NH-BH}) and the B–N bond dissociation (TS_{B-N}) pathways allow considering them as possible pathways in noncoordinating solvents of low polarity (CH_2Cl_2 , FBz, toluene). Taking into account the cooperative effects inside the alcohol clusters¹³¹ by addition of the second alcohol molecule on the example of NH–BH pathway, we computed lower activation barriers (by 1.7 kcal/mol for MeOH, 6.8 kcal/mol for TFE, 7.8 kcal/mol for PNP and 4.0 kcal/mol for HFIP, Table S22).



Figure 14. The M06-optimized geometries of transition states (TS) for different reaction pathways in Scheme 3.



Figure 15. Energy profile for the reaction of DMAB with HFIP. The energy values (ΔH_{DCM} in kcal/mol) are presented relative to the separated starting molecules (in CH₂Cl₂).

Increase of the proton donor strength reduces significantly the activation energy of the first (TS_{BH}) and third (TS_{NH-BH}) pathways, whereas the activation energy of the B–N dissociation changes weakly in dependence on the alcohol (Table S22).

So in low polar media two processes are feasible – alcohol assisted double hydrogen transfer (TS_{NH-BH}) followed by Ad_E reaction of alcohol with B=N double bond (TS_{Ad_E}) and dissociation of B–N bond (TS_{B-N}).

Proton transfer mediated by coordinating solvents. When protonation takes place in coordinating organic solvents, the solvent molecule can act as a Lewis base coordinating to the

boron atom and assisting B–N bond dissociation. This S_{N2} -substitution¹³² (Scheme 4) of Me₂NH in DMAB by the solvent molecule (Figure 16) has the activation enthalpies $\Delta G^{\ddagger}_{solv}$: 20.7 (THF) < 24.1 (MeCN) < 24.7 (Me₂CO) < 33.8 (H₂O) kcal/mol. This $\Delta G^{\ddagger}_{solv}$ order is in agreement with the basicity (E_j) of these solvents. This process is endothermic in agreement with the DMAB stability in these solvents. It should be noted that the classical S_{N2} transition state is found only for aprotic solvents (THF, Me₂CO, MeCN) whereas in the case of water or alcohol the transition state is a four-membered cycle (**TS**_{BN}, Figure **14** and Scheme 4 (left)) and the active intermediate for such process is cyclic H-bonded complex of the type **I**_{NH-BH}.



Figure 16. Energy profile for S_{N2} reaction of DMAB with H₂O, MeCN, THF and Me₂CO (top). Energy profile for S_{N2} reaction DMAB with these organic bases in presence of HFIP (bottom).

The energies (ΔG_{solv} , kcal/mol) are in the corresponding solvent (MeCN, THF, Me₂CO and H₂O).



Figure 17. M06-optimized geometries of transition state for S_{N2} substitution of Me₂NH by solvent molecule assisted by ROH (**TS**_{DHB-SN2}) on the example of acetone and HFIP.



Scheme 4. Possible pathways for B-N dissociation mechanisms assisted by coordinating solvent molecule (X, left) and non-assisted (right).

The proton donors stabilize DMAB·Solv complex as well as the products thus shifting the equilibrium toward the reaction products (Scheme 4, left). Note that energies of the hydrogen bonded intermediate DMAB·HFIP·Solv are highly affected by the type of HFIP coordination

(Figure S47) which is mostly OH···O(solv) in case of THF ($E_f(THF) = 1.04$) but is pure OH···H(B) ($E_f(DMAB) = 0.64$) in the case of acetone ($E_f(acetone) = 0.93$). Nevertheless, the TS energies for the S_{N2} process assisted by this alcohol (**TS**_{DHB-SN2}, Figure 17) are ca. 1.7–6.5 kcal/mol for PNP and 0.7–6.4 kcal/mol for HFIP lower than those for simple substitution, while the products are stabilized by 0.8–10.6 kcal/mol (Figure 16). The Me₂NH·HFIP complex easily undergoes proton transfer¹³³ yielding dimethylammonium-cation [Me₂NH₂]⁺ while BH₃ transforms gradually into [B(OR)₄]⁻ by the reaction with the excess alcohol. Protonation of neutral BH₃·Solv has higher barrier than the B-N bond dissociation (**TS**_{BH} of proton transfer from HFIP to BH₃·THF has activation energy $\Delta G^{\ddagger}_{THF} = 37.2$ kcal/mol). The comparison of the activation energy values suggests that this step is followed by the ligand exchange (BH₃·Solv transforms into BH₃·(OR)) and proton transfer to [BH₃·(OR)]⁻. Thus the data obtained show that the rate determining step of the DMAB reaction with alcohols in polar coordinating solvents should be the B–N bond dissociation. The theoretical value of the activation barrier for DMAB reaction with HFIP in presence of acetone $\Delta G^{\ddagger}_{theor}$ (acetone, 298 K) = 24.0 kcal/mol is agreement with the experimental value $\Delta G^{\ddagger}_{exp}$ (290 K) = 21.1 kcal/mol.

Conclusions

Analysis of the IR spectral and computational data showed the DMAB is self-associated in nonpolar (hexane, CCl₄) and low polar non-coordinating (CH₂Cl₂, FBz, toluene) media; the association enthalpy, $-\Delta H^{\circ}_{assoc}$, estimated experimentally varies from 1.5 to 2.3 kcal/mol. In FBz the existence of additional NH···F "improper" (blue-shifting) H-bonding is shown experimentally for the first time. The experimental data show that proton accepting ability of DMAB ($E_{j(BH)}^{DMAB}$ = 0.62) is lower than that of BH₄⁻ (E_j = 1.25) and proton donating ability ($P_{i(NH)}^{DMAB}$ = 0.45) is higher than that of Me₂NH (P_i = 0.11). Presence of both functionalities in the DMAB molecule determines its ability to form diverse hydrogen bonded adducts which are directing factors of DMAB reactivity. According to our computational analysis the active intermediate of proton

 transfer from OH acids to DMAB is cyclic HB complex of the type I_{BH-NH} which features both B-H···H(O) and NH···O(H) bonds.

In non-coordinating solvents the reaction of DMAB with proton donors (TFE, HFIP, PNP) is extremely slow (takes several days) and yields $[Me_2NH_2]^+[B(OR)_4]^-$ products characterized experimentally by X-ray, IR and NMR spectroscopy. In polar coordinating media, the solvent molecule assists the B–N dissociation process via S_{N2} mechanism, so the reaction goes significantly faster (with half-life ca. 4 hours).

Supporting Information Optimized geometries (Cartesian coordinates) for the calculated species; detailed computational results, AIM and NCI analysis; spectral and kinetics data. This material is available free of charge via the Internet at http://pubs.acs.org.

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