

STUDY OF PROTON–DEUTERIUM EXCHANGE IN TEN-VERTEX BORON HYDRIDES⁺

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The effect of electron-donating and electron-withdrawing substituents on the proton–deuterium exchange in derivatives of the *closo*-decaborate anion in methanol-*d*₄ was studied. Introduction of the electron-donating hydroxy (alkoxy) group into the apical position of the boron cage strongly promotes the H–D exchange at the antipodal apical vertex, whereas introduction of the electron-withdrawing diazonium group stops the H–D exchange completely. The general order of the proton–deuterium exchange in equatorially-substituted derivatives [2-B₁₀H₉R]ⁿ⁻ is 10 > 1 >> 7,8 > 4 > 3,5 ≈ 6,9. Formation of dihydrogen bonds between 1- and 2-hydroxy derivatives of the *closo*-decaborate anion and alcohols was investigated and their possible role in the H–D exchange was discussed.

Keywords: Boranes; Boron clusters; *closo*-Decaborate; Proton–deuterium exchange; Isotope effects; Hydrogen bonds; NMR spectroscopy; IR spectroscopy.

Study of proton–deuterium exchange in polyhedral boron hydrides is of great importance to gain an insight into reactivity of these systems. Polyhedral boron hydrides are generally accepted as three-dimensional aromatic systems² and electrophilic aromatic substitution is one of the main mechanisms of substitution in these moieties. The H–D exchange in polyhedral boron hydrides proceeding by attack of D⁺ could be considered a simplest example of electrophilic aromatic substitution and serve as a test for accessibility of various positions of boron hydride polyhedron to electrophilic attack. The proton–deuterium exchange in [CB₁₁H₁₂]⁻ (ref.³) and [1-CB₉H₁₀]⁻ (ref.⁴) in DCl/D₂O was found to proceed only at boron atoms that are the most distant from the carbon atom resulting in [7,8,9,10,11,12-D₆-CB₁₁H₆]⁻

+ Preliminary results, see ref.¹

and $[6,7,8,9,10\text{-D}_5\text{-1-CB}_9\text{H}_5]^-$, respectively. These results correlate well with data on electrophilic halogenation. On boron hydrides more active to electrophilic attack, such as $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$, the H–D exchange under the same conditions proceeds faster and results in the formation of the perdeuterated products $[\text{B}_{10}\text{D}_{10}]^{2-}$ and $[\text{B}_{12}\text{D}_{12}]^{2-}$, respectively⁵. In the case of less active boron hydrides, such as *ortho*- and *meta*-carboranes $\text{C}_2\text{B}_{10}\text{H}_{12}$, the proton–deuterium exchange in C_6D_6 requires the presence of AlCl_3 as a catalyst and proceeds first at boron atoms that are the most distant from the carbon atoms and the most accessible to electrophilic attack⁶. On the other hand, the boron atoms linked directly to both the carbon atoms which are least accessible to electrophilic attack can be deuterated using gaseous deuterium and transition metal hydride complexes as catalysts. Thus, the reactions of *ortho*- and *meta*-carboranes with D_2 in toluene in the presence of $[\text{RuHCl}(\text{PPh}_3)_3]$ as catalyst result in 3,6- D_2 -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ and 2,3- D_2 -1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$, respectively⁷. The above-mentioned results indicate that the H–D exchange can be considered important tool for estimation of reactivity of polyhedral boron hydrides.

In early work, Muetterties et al.⁵ found that the H–D exchange in the decahydro-*closo*-decaborate anion $[\text{B}_{10}\text{H}_{10}]^{2-}$ proceeds faster at the apical than at the equatorial vertices. The ratio of the H–D exchange rates is rather low ($k_{\text{H/D}}^{\text{ap}}/k_{\text{H/D}}^{\text{eq}} = 4.8$) and, that taking into account the ratio of both types of atoms in the boron hydride cluster ($\text{B}_{(\text{ap})}/\text{B}_{(\text{eq})} = 1:4$), synthesis of selectively deuterated compounds by the direct H–D exchange in acidic media is impossible. Recently we found that the selectively deuterated *closo*-decaborate anion $[\text{1,10-B}_{10}\text{H}_8\text{D}_2]^{2-}$ can be prepared by the reaction of the parent anion with methanol- d_4 at room temperature⁸.

In this contribution we report the effect of various substituents on the proton–deuterium exchange in derivatives of the *closo*-decaborate anion in methanol- d_4 .

EXPERIMENTAL

$(\text{Ph}_3\text{PCH}_2\text{Ph})_2[1\text{-(HO)B}_{10}\text{H}_9]$ ⁹, $(\text{Ph}_3\text{PCH}_2\text{Ph})_2[2\text{-(HO)B}_{10}\text{H}_9]$ ¹⁰, $(\text{Ph}_4\text{P})_2[1\text{-(EtO)B}_{10}\text{H}_9]$ ¹⁰, $(\text{Ph}_4\text{P})_2[2\text{-(EtO)B}_{10}\text{H}_9]$ ¹⁰, $(\text{Bu}_4\text{N})[2\text{-(NMP)B}_{10}\text{H}_9]$ ¹⁰, $(\text{Bu}_4\text{N})[1\text{-(NH}_3\text{)B}_{10}\text{H}_9]$ ¹¹, $(\text{Bu}_4\text{N})[2\text{-(NH}_3\text{)B}_{10}\text{H}_9]$ ¹², $(\text{Et}_3\text{NH})[1\text{-(N}_2\text{)B}_{10}\text{H}_9]$ ¹³ were prepared as described in the literature. The ^{11}B NMR spectra were collected in methanol- d_4 (Dr. Glaser AG (Basel, Switzerland), Deutero GmbH (Kastellaun, Germany), RSC Applied Chemistry (St. Petersburg, Russia)) using a Bruker Avance 400 and a Bruker AM 360 spectrometers and referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$. The IR spectra of dichloromethane solutions (CaF₂ cells, $d = 0.012\text{--}0.120$ cm) were measured on Infracum FT-81 (Lumex) and Specord M-82 (Carl Zeiss Jena) spectrometers. IR studies in the temperature range 200–300 K were carried out using a Carl Zeiss Jena cryostat with the accuracy of the temperature setting ± 0.5 K.

RESULTS AND DISCUSSION

closo-Decaborate derivatives with substituents of various nature at different positions of the boron cage were used to study the effect of substitution on the proton-deuterium exchange. Two criteria were taken into consideration for the substituent choice. The first one was a rather high range of their Hammett constant values reflecting electron-withdrawing and electron-donating effects of substituents, and the second one was synthetic availability of the *closo*-decaborate derivatives. In our laboratory we have prepared a number of *closo*-decaborate derivatives with B-N and B-O bonds^{9,10,12,14}. Some of these compounds as well as intermediate products of their synthesis were used in this study.

Hydroxy (alkoxy) and ammonium (alkylammonium) groups are known as strong electron-donating and electron-withdrawing substituents, respectively¹⁵ (Table I).

TABLE I
Hammett constant values for selected substituents

Substituent	Hammett constant, σ	
	<i>meta</i> -	<i>para</i> -
OH	0.13	-0.38
OMe	0.10	-0.28
NH ₂	-0.09	-0.57
NMe ₂	-0.15	-0.63
NH ₃ ⁺	0.86	0.60
NMe ₃ ⁺	0.88	0.82
N ₂ ⁺	1.65	1.93

It was logical to assume that introduction of an electron-donating substituent at one apical position of the *closo*-decaborate cage will facilitate the proton-deuterium exchange at the antipodal apical position. Indeed we found that introduction of the ethoxy group in the axial position (Fig. 1) results in a sharp increase in the H-D exchange rate at the antipodal vertex giving [1-(EtO)B₁₀H₈-10-D]²⁻ in a few minutes (we were unable to fix a signal of non-deuterated antipodal vertex in methanol-*d*₄), whereas the complete proton-deuterium exchange in the parent *closo*-decaborate⁸ takes

~3 days. It should be noted that no proton–deuterium exchange in the equatorial positions of the 1-ethoxy derivative was detected after six weeks. The H–D exchange in the corresponding 1-hydroxy derivative proceeds in a similar way in few minutes.

Introduction of electron-donating substituent in equatorial position of the *closo*-decaborate cage could be expected to produce different effects on reactivity of hydrogen atoms in the apical positions of the boron cage. This was really the case: the H–D exchange in the apical positions of $[2-(\text{HO})\text{B}_{10}\text{H}_9]^{2-}$ was found to proceed with different rates. To establish the order of the H–D exchange we used the corresponding ethoxy derivative $[2-(\text{EtO})\text{B}_{10}\text{H}_9]^{2-}$ that gives a more clear pattern due to better separation of signals of substituted (B(2)) and apical (B(1) and B(10)) boron atoms (Fig. 2). The H–D exchange proceeds faster with the boron atom more distant from the substituted one (position 10), than with the boron atom adjacent to the substituted one (position 1). It should be noted that both the processes proceed significantly slower than in the case of $[1-(\text{EtO})\text{B}_{10}\text{H}_9]^{2-}$, but faster than in the parent *closo*-decaborate.

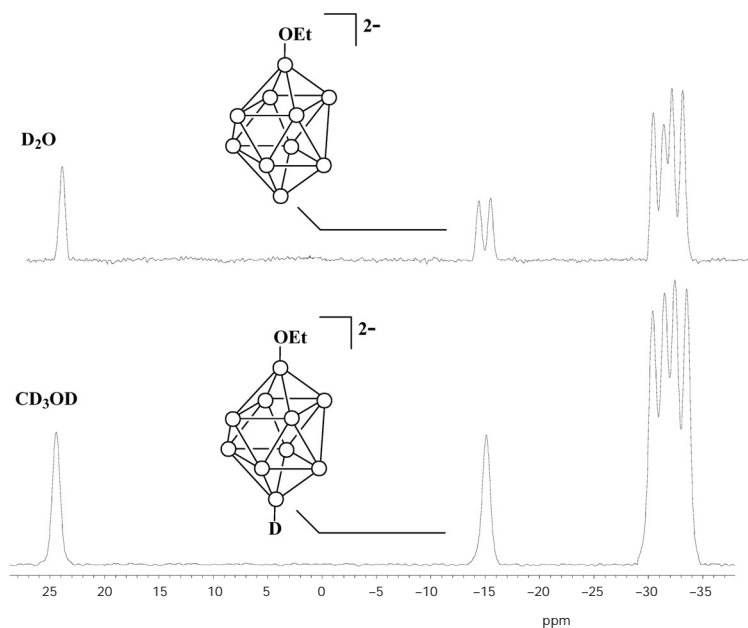


FIG. 1
 ^{11}B NMR spectra of $[1-(\text{EtO})\text{B}_{10}\text{H}_9]^{2-}$ in D_2O and CD_3OD

The most surprising was the formation of the perdeuterated product $[1-(\text{EtO})\text{B}_{10}\text{D}_9]^{2-}$ after standing for 1 week in methanol- d_4 . It should be noted that the proton-deuterium exchange rate depends strongly on the solvent purity. Thus, the H-D exchange in wet methanol- d_4 proceeded much slower than in dry solvent and stopped at the apical vertices stage resulting in $[2-(\text{EtO})\text{B}_{10}\text{H}_7-1,10-\text{D}_2]^{2-}$.

To establish the order of the H-D exchange in 2-substituted derivatives of the *closo*-decaborate anion we studied deuteration of $[2-(\text{NMP})\text{B}_{10}\text{H}_9]^-$ (NMP = *N*-methylpyrrolidone). The Hammett constant for this substituent is not known, but it is reasonable to assume that it should be higher than that of ethoxy group due to positive charge on the substituent, and, as a

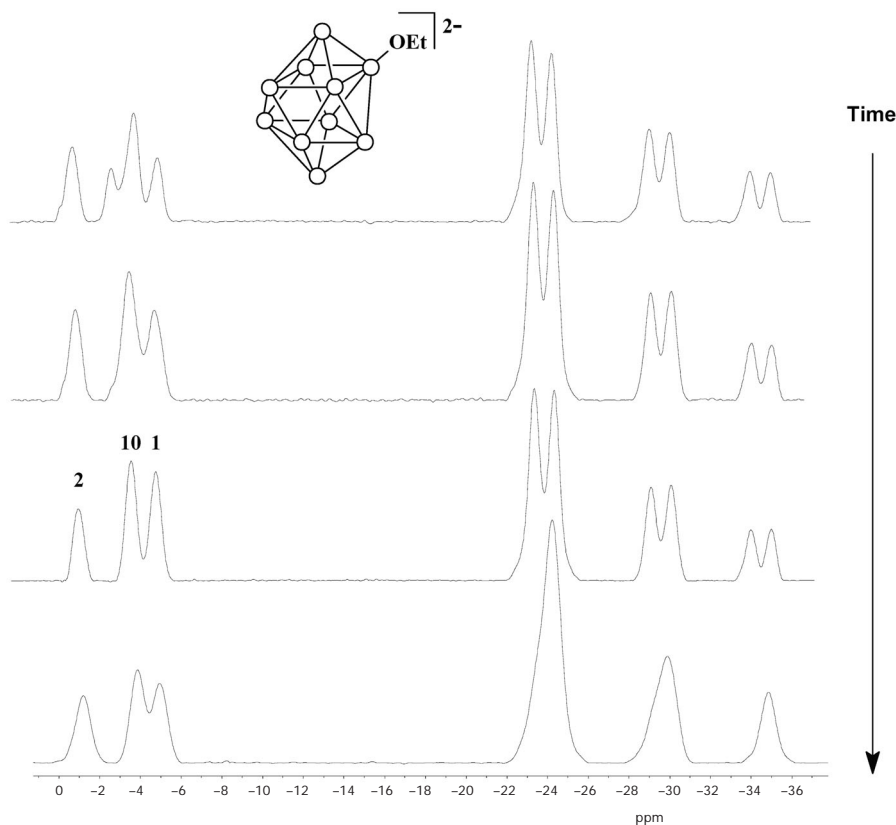


FIG. 2
The H-D exchange of $[2-(\text{EtO})\text{B}_{10}\text{H}_9]^{2-}$ in CD_3OD monitored by ^{11}B NMR spectroscopy

consequence, the H-D exchange in this derivative should proceed more slowly and/or at less extent than in the case of the 2-ethoxy derivative. The second, but even more important, reason for choice of this derivative was its ^{11}B NMR spectrum demonstrating separated signals of all non-equivalent types of boron atoms (Fig. 3). The $[2\text{-(NMP)B}_{10}\text{H}_9]^-$ derivative is well known^{16,17}; it was prepared as intermediate product in the synthesis of the 2-alkoxy derivatives¹⁰.

Indeed, we were able to determine a complete sequence of the proton-deuterium exchange in this compound. The first steps (the H-D exchange at the apical vertices) resemble those for the 2-ethoxy derivative. Further proton-deuterium exchange proceeds in the positions 7 and 8 and then in the position 4 resulting in $[2\text{-(NMP)B}_{10}\text{H}_4\text{-1,4,7,8,10-D}_5]^-$. No further proton-deuterium exchange was revealed after six weeks in methanol- d_4 .

As it was expected, introduction of electron withdrawing substituents results in a decrease in the proton-deuterium exchange rate. Thus, the H-D exchange at the antipodal apical vertex of $[1\text{-(R}_3\text{N)B}_{10}\text{H}_9]^-$ ($\text{R} = \text{H, Et}$) resulting in $[1\text{-(R}_3\text{N)B}_{10}\text{H}_8\text{-10-D}]^-$ proceeds much slower than in $[1\text{-(RO)B}_{10}\text{H}_9]^{2-}$ and somewhat slower than in the parent *closo*-decaborate. The *closo*-decaborate derivative with the diazonium group (the strongest electron-

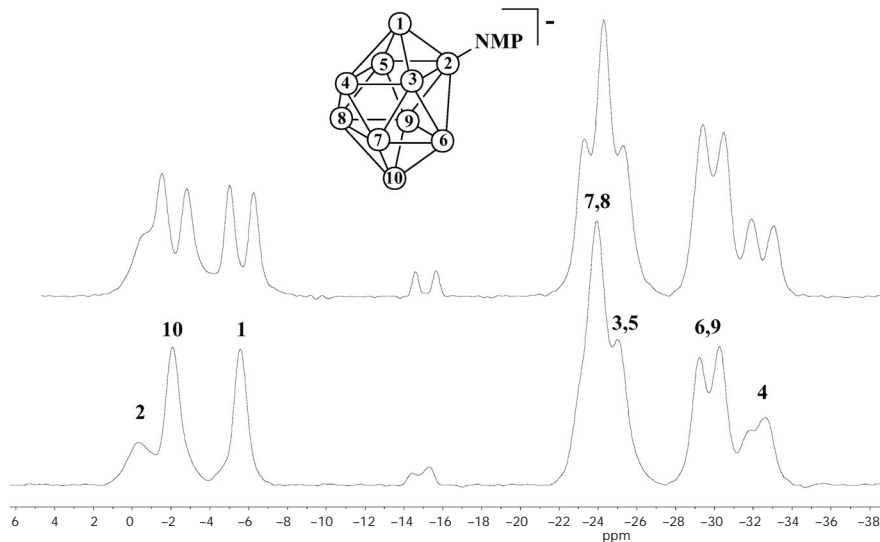


FIG. 3
 ^{11}B NMR spectra of $[2\text{-(NMP)B}_{10}\text{H}_9]^-$ and $[2\text{-(NMP)B}_{10}\text{H}_4\text{-1,4,7,8,10-D}_5]^-$ in CD_3OD

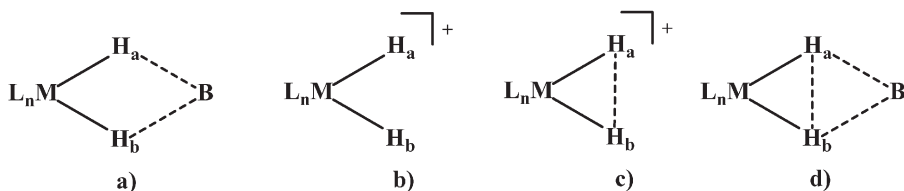
withdrawing substituent) $[1-(N_2)B_{10}H_9]^-$, demonstrated no proton-deuterium exchange in methanol- d_4 even after 2 months. A similar result was obtained for 1-carba-*closo*-decaborate anion $[1-CB_9H_{10}]^-$ where the B-N \equiv N grouping is substituted by the isolobal CH group.

The proton-deuterium exchange in $[2-(R_3N)B_{10}H_9]^-$ (R = H, Et) also proceeded slower than in the corresponding hydroxy/alkoxy derivatives and stopped at the first stage resulting in $[2-(R_3N)B_{10}H_8-10-D]^-$ as the final product. The *closo*-decaborate derivative with a diazonium group in equatorial position $[2-(N_2)B_{10}H_9]^-$ is unknown, but the corresponding 2-carba-*closo*-decaborate anion $[2-CB_9H_{10}]^-$ was found not to undergo proton-deuterium exchange in methanol- d_4 .

In that way, the activating effect of electron-donating substituents and the deactivating effect of electron-withdrawing substituents on the proton-deuterium exchange in the *closo*-decaborate anion were demonstrated and the order of the H-D exchange in equatorially-substituted derivatives $[2-RB_{10}H_9]^{n-}$ was found to be $10 > 1 \gg 7,8 > 4 > 3,5 \approx 6,9$. Does the established H-D exchange order reflect the *closo*-decaborate reactivity properly: that is the question? The answer is not simple. If we look at the chemistry of the $[B_{10}H_{10}]^{2-}$ anion, we will find that in most cases reactions proceeding through both aromatic electrophilic and electrophile-induced nucleophilic substitution mechanism result in equatorially-substituted products^{18,19}. Only a very limited number of reactions giving apically-substituted products are known^{20,21}. On the other hand, quantum chemical calculations² put more negative charge on the apical vertices of the *closo*-decaborate anion which, in principle, should result primarily in the attack of electrophilic agents at the apical vertex. Formation of equatorially-substituted products in this case could be explained by relative stability of arenium-like intermediates (transition states) formed by electrophile attack in apical and equatorial positions, respectively, taking into account different coordination numbers of boron atoms in these positions (more detailed consideration of this point is out the framework of this paper). However, if we consider reactions resulting in apically and equatorially substituted products separately, we will find that the revealed order of the H-D exchange correlates well with available literature data on substitution in $[2-RB_{10}H_9]^{n-}$. As a result, two different orders of reactivity of different boron vertices in $[2-RB_{10}H_9]^{n-}$ can be proposed: $10 > 1$ and $7,8 > 4 > 3,5 \approx 6,9$ for substitution at apical and equatorial vertices.

What is a possible mechanism of the H-D exchange in *closo*-decaborate derivatives in the presence of methanol- d_4 ? To answer this question we should address the H-D exchange in complex metal hydrides. A transition

state or intermediate of the type presented below (Scheme 1a) was proposed for the H-D exchange in $[\text{MH}(\text{CO})_4\text{L}]^-$ complexes ($\text{M} = \text{Cr}, \text{W}$)²². Similar structures are assumed to be involved in the H-D exchange with d_1 -alcohols or D_2O in a number of transition metal hydrides²³.



SCHEME 1

A general scenario for the protonation reactions of metal hydride complexes with alcohols involves dihydrogen-bonded complexes $[\text{MH}\cdots\text{HX}]$ and dihydride or $\eta^2\text{-H}_2$ complexes as intermediates (Scheme 1) on the reaction coordinate²⁴. It is reasonable to assume that the H-D exchange in boron hydrides should proceed in the same manner. We assume that the formation of dihydrogen bonds between the *closo*-decaborate derivatives and methanol- d_4 could be considered as a key factor determining selectivity of the proton-deuterium exchange. Selective formation of dihydrogen bonds between the axial hydride atoms in the parent *closo*-decaborate $[\text{B}_{10}\text{H}_{10}]^{2-}$ and alcohols was shown earlier²⁵.

The $[\text{1-(HO)B}_{10}\text{H}_9]^{2-}$ (**I**) and $[\text{2-(HO)B}_{10}\text{H}_9]^{2-}$ (**II**) anions were chosen as model system to study formation of dihydrogen bonds. These species possess several potential sites for formation of hydrogen bond: one of them is the hydroxy group which can act as a donor of proton as well as proton acceptor by the way of the oxygen lone pair. Besides, hydrogen atoms of BH groups may act as proton acceptors in dihydrogen-bonded complexes $[\text{BH}\cdots\text{HX}]$ ²⁶. To reveal all types of the hydrogen bonds formed, interactions of **I** and **II** with organic bases and alcohols were studied.

In the first step, we studied interactions of hydroxy groups in **I** and **II** with bases. The IR spectra of dilute solutions in dichloromethane ($C < 0.02 \text{ mol l}^{-1}$) of **I** and **II** contain intense narrow stretching bands of the OH groups ($\nu(\text{OH}_{\text{B}_{10}}^{\text{free}}) = 3653 \text{ cm}^{-1}$ for $[\text{1-(HO)B}_{10}\text{H}_9]^{2-}$ and $\nu(\text{OH}_{\text{B}_{10}}^{\text{free}}) = 3646 \text{ cm}^{-1}$ for $[\text{2-(HO)B}_{10}\text{H}_9]^{2-}$). Addition of a base leads to a decrease in the $\nu(\text{OH}_{\text{B}_{10}}^{\text{free}})$ intensity and appearance of a new broad band $\nu(\text{OH}_{\text{B}_{10}}^{\text{bonded}})$. The position of this new band depends on proton-accepting ability of a base and varies from 3417 to 3330 cm^{-1} (Table II).

TABLE II
Spectral and thermodynamic characteristics of hydrogen bonds of [1-(HO)B₁₀H₉]²⁻ (**I**) and [2-(HO)B₁₀H₉]²⁻ (**II**) with various proton acceptors

Hydride	Base	$\Delta\nu(\text{OH})^a$ cm ⁻¹	E_j	$-\Delta H^0$ kcal mol ⁻¹
I	pyridine	242	1.27	4.5
	dimethyl sulfoxide	279	1.35	5.0
	trioctylphosphine oxide	323	1.65	5.6
II	pyridine	229	1.27	4.3
	dimethyl sulfoxide	261	1.35	4.8
	trioctylphosphine oxide	296	1.65	5.2

^a $\Delta\nu(\text{OH}) = \nu(\text{OH}^{\text{free}}) - \nu(\text{OH}^{\text{bonded}})$.

The formation enthalpies ($-\Delta H^0$, kcal mol⁻¹) of hydrogen-bonded complexes were obtained from band displacement $\Delta\nu(\text{OH})$ using the Iogansen correlation proposed for organic systems²⁷. Its applicability to unconventional hydrogen bonds was proved by us earlier²⁸.

$$-\Delta H^0 = \frac{18\Delta\nu(\text{OH})}{\Delta\nu(\text{OH}) + 720}$$

The hydrogen bonds formed by the OH groups of **I** and **II** are of medium strength varying from 4.3 to 5.6 kcal mol⁻¹, the enthalpy values demonstrate medium strength of H bonds formed by these groups as donors of proton.

Linear relationships between $-\Delta H^0$ of the hydrogen-bonded complexes and the proton-accepting ability of organic bases were found. Analogous dependences were established earlier for transition metal hydrides and various classes of organic bases²⁸. Using these dependences we calculated the proton-donating ability of the OH groups (called as the acidity factor (P_j)).

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

Here $-\Delta H_{11}$ is the enthalpy of the hydrogen bond formation for a "standard" pair (phenol-diethyl ether, $P_i = E_j = 1.0$), $-\Delta H_{ij}$ is the experimentally obtained enthalpy, and P_i is the known acidity factor of proton donor^{26a}.

The E_j and P_i values are independent on partners and media and, therefore, are more convenient for comparison of the basicity and acidity of proton-accepting and proton-donating sites^{26b,26c,28}.

The proton-donating ability of the OH group in **I** and **II** was found to be 0.77 ± 0.06 and 0.74 ± 0.05 , respectively. These values can be compared with the acidity factor of 2-fluoroethanol ($P_i = 0.74$) and show rather high proton-donating ability of the hydroxydecaborates. It should be noted that the higher proton-donating ability of **I** correlates well with the stronger electron-withdrawing effect of the $[1-B_{10}H_9]^{2-}$ group as suggested on the basis of 1H NMR data for $[1-(RO)B_{10}H_9]^{2-}$ and $[2-(RO)B_{10}H_9]^{2-}$ (ref.¹⁰).

In the second step, the proton-accepting ability of **I** and **II** in reactions with alcohols of various acidity (2-fluoroethanol, 2,2,2-trifluoroethanol, hexafluoropropan-2-ol, 4-nitrophenol) was studied by IR spectroscopy in methylene chloride in the temperature range of 190–290 K. The **I** and **II** anions possess two potential proton-accepting sites: the oxygen lone pair of OH group and the hydride hydrogen of the BH groups (non-classical site). These two sites could compete for the hydrogen bonding with OH-acids leading to the formation of dihydrogen bonds (BH...HO) and/or classical hydrogen bonds (B(HO)...HX).

An addition of **II** to solution of 2-fluoroethanol in dichloromethane results in the decrease in the intensity of the free $\nu(OH_{ROH}^{free})$ bands which is accompanied by the appearance of two additional broad low-frequency bands of hydrogen-bonded OH groups ($\nu(OH_{ROH}^{bonded})$) (Fig. 4).

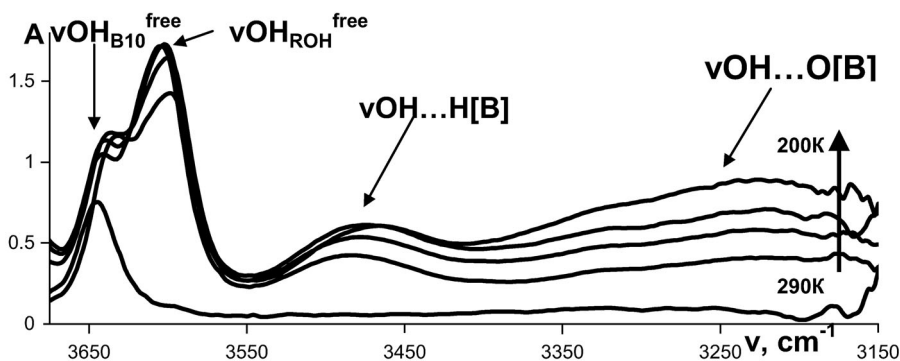
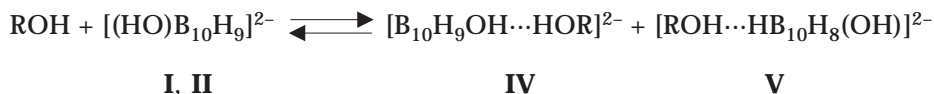


FIG. 4

IR spectra (OH region) of 0.016 M $[Ph_3PCH_2Ph]_2[2-(HO)B_{10}H_9]$ and 0.016 M 2-fluoroethanol in dichloromethane at different temperatures

These two bands could be assigned to hydrogen bonding of two possible proton-accepting sites (Scheme 2).



SCHEME 2

Comparison of the data in Table III with the spectral changes observed under interaction of the parent *closo*-decaborate $[\text{B}_{10}\text{H}_{10}]^{2-}$ with the same proton donors²⁵ allows to assign the band in 3500–3350 cm^{-1} range to the $[\text{OH}\cdots\text{HB}]$ dihydrogen-bonded complex. The differences between the $\Delta\nu(\text{OH})$ for dihydrogen-bonded complexes of the parent *closo*-decaborate and those of its hydroxy derivatives with the same proton donors are negligible and do not exceed 10 cm^{-1} .

TABLE III

Spectral characteristics of hydrogen bonds of anionic hydrides $[\text{1-(HO)B}_{10}\text{H}_9]^{2-}$ (**I**) and $[\text{2-(HO)B}_{10}\text{H}_9]^{2-}$ (**II**) with various proton donors

Hydride	ROH	OH...HB		OH...OB	
		$\nu(\text{OH}^{\text{bonded}})$ cm^{-1}	$\Delta\nu(\text{OH})^a$ cm^{-1}	$\nu(\text{OH}^{\text{bonded}})$ cm^{-1}	$\Delta\nu(\text{OH})^a$ cm^{-1}
I	2-fluoroethanol	3503	113	3287	328
	2,2,2-trifluoroethanol	3467	138	3187	417
	hexafluoropropan-2-ol	3363	220	<3100	>490
	4-nitrophenol	3340	226	<3100	>470
II	2-fluoroethanol	3491	124	3310	305
	2,2,2-trifluoroethanol	3453	152	3159	442
	hexafluoropropan-2-ol	3380	203	3060	520

$$^a \Delta\nu(\text{OH}) = \nu(\text{OH}^{\text{free}}) - \nu(\text{OH}^{\text{bonded}}).$$

The low-temperature experiment shows a shift of equilibrium (Scheme 2) to the right with the formation of both types of hydrogen-bonded complexes. Moreover, the classical hydrogen-bonded complex $[\text{B}(\text{HO})\cdots\text{HO}]$ formed primarily at low temperatures (<240 K) is more favorable (Fig. 4).

The IR spectra of **I** and **II** in the $\nu(\text{BH})$ stretching range contain an intense band of equatorial BH groups ($\nu(\text{BH}^{\text{eq}}) = 2452 \text{ cm}^{-1}$) accompanied by a shoulder of axial BH groups ($\nu(\text{BH}^{\text{ax}}) = 2496 \text{ cm}^{-1}$). In the presence of excess of proton donors, a high-frequency shift of the $\nu(\text{BH}^{\text{eq}})$ band is observed with $\Delta\nu(\text{BH}) = -(6-15) \text{ cm}^{-1}$. This band corresponds to the stretching of the equatorial BH groups which are not bonded to alcohol ($\nu(\text{BH}^{\text{free}})$). The $\nu(\text{BH}^{\text{bonded}})$ stretching of the $[\text{BH}\cdots\text{HO}]$ complex appears as a shoulder shifted to low frequencies (Fig. 5).

Formation of the $[\text{BH}\cdots\text{HO}]$ dihydrogen bonded complex should result in a high-frequency shift of the initial BH band ($\nu(\text{BH}^{\text{free}})$) and appearance of new low-frequency shifted band ($\nu(\text{BH}^{\text{bonded}})$) whereas the formation of the classical hydrogen-bonded complex $[\text{B}(\text{HO})\cdots\text{HO}]$ should lead to the pure high-frequency shift. Thus, the appearance of the $\nu(\text{BH}^{\text{bonded}})$ band confirms the formation of the dihydrogen-bonded complex; the high-frequency shifted $\nu(\text{BH}^{\text{free}})$ band is superposition of the BH stretching for both the $[\text{BH}\cdots\text{HO}]$ and $[\text{B}(\text{HO})\cdots\text{HO}]$ complexes.

Enthalpies of hydrogen bonds formed by **I** and **II** as proton acceptors vary from 2.4 to 4.3 kcal/mol for the $[\text{BH}\cdots\text{HO}]$ complexes and 5.4–7.5 kcal/mol for the $[\text{B}(\text{HO})\cdots\text{HO}]$ complexes (Table IV). Thus the classical hydrogen bonds in these anions are of medium strength and their energies are twice higher than for dihydrogen bonds with hydride ligands.

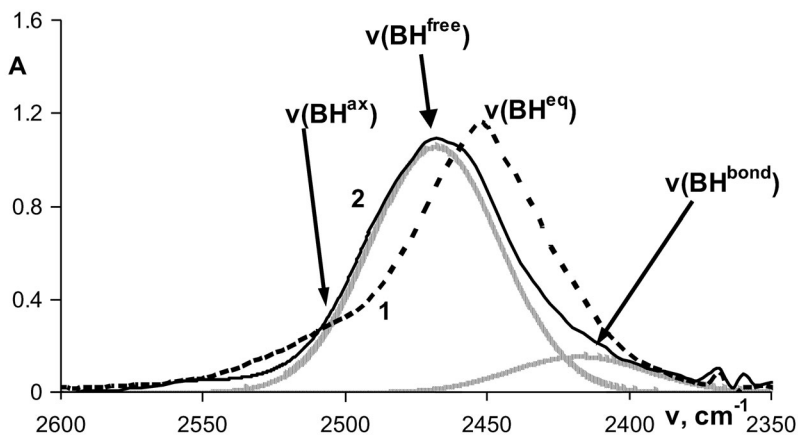


FIG. 5

IR spectra (BH region) of 0.013 M $[\text{Ph}_3\text{PCH}_2\text{Ph}]_2[1-(\text{HO})\text{B}_{10}\text{H}_9]$ in dichloromethane before (1) and after (2) addition of 0.013 M 4-nitrophenol and the band decomposition

TABLE IV
Formation enthalpy of hydrogen bonds of anionic hydrides $[1-(\text{HO})\text{B}_{10}\text{H}_9]^{2-}$ (**I**) and $[2-(\text{HO})\text{B}_{10}\text{H}_9]^{2-}$ (**II**) with various alcohols

Hydride	ROH	$-\Delta H_{\text{BH}\cdots\text{HO}}^{\text{H}}$ kcal mol ⁻¹	$-\Delta H_{\text{B}(\text{HO})\cdots\text{HO}}^{\text{H}}$ kcal mol ⁻¹
I	2-fluoroethanol	2.4	5.6
	2,2,2-trifluoroethanol	2.9	6.6
	hexafluoropropan-2-ol	4.2	>7
	4-nitrophenol	4.3	>7
II	2-fluoroethanol	2.6	5.4
	2,2,2-trifluoroethanol	3.1	6.8
	hexafluoropropan-2-ol	4.0	7.5

Thus, the basicity factors (E_j) of the investigated boron hydrides are $E_j^{\text{BH}} = 0.77 \pm 0.06$, $E_j^{\text{O}} = 1.62 \pm 0.12$ for $[1-(\text{HO})\text{B}_{10}\text{H}_9]^{2-}$ and $E_j^{\text{BH}} = 0.80 \pm 0.07$, $E_j^{\text{O}} = 1.60 \pm 0.10$ for $[2-(\text{HO})\text{B}_{10}\text{H}_9]^{2-}$. The E_j values for BH centers in **I** and **II** are close to those found for the parent *closo*-decaborate ($E_j = 0.78$)²⁵ demonstrating a negligible effect of the hydroxy substituent on basicity of BH groups in ten-vertex polyhedral boron hydrides.

A detailed study of mechanism and kinetics of the H–D exchange in *closo*-decaborate derivatives is in progress and its results will be published elsewhere.

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