

Infrared spectra and structures of hexamethyl- and hexaethylhydrodiborate ions, $\text{H}[\text{B}(\text{CH}_3)_3]_2^-$ and $\text{H}[\text{B}(\text{C}_2\text{H}_5)_3]_2^-$, in glycol ether solution

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(Received 1 April 1991; accepted 15 August 1991)

Abstract—Infrared spectra have been obtained of lithium hexamethyl- and hexaethylhydrodiborates and deuterodiborates in diglyme solution at temperatures near 0°C. Assignments are proposed and arguments are presented in support of the presence of linear hydrogen bridges in these compounds. The spectral data are compared with those of other hydrogen-bonded compounds having symmetrical H bonds.

INTRODUCTION

KHURI *et al.* [1, 2] reported some time ago that lithium hydride reacted with an excess of trialkylboranes in tetrahydrofuran or polyglyme solutions to form 1:2 adducts, $\text{LiH}(\text{BR}_3)_2$. They suggested that these compounds contained an anion in which two BR_3 groups were connected by a single hydrogen bridge, similar to the model predicted by DICKERSON and LIPSCOMB [3] for the B_2H_7^- ion. The existence of such a bridge in the B_2H_7^- case has recently been confirmed by X-ray and neutron diffraction investigations [4, 5] but similar structural evidence has not appeared for the alkyl compounds. A preliminary report of the infrared spectrum [6] indicates the non-methyl hydrogen is in a bridging position. In this study we report on more extensive infrared spectra of lithium hexamethyl- and hexaethylhydrodiborate ions, and include results for the species in which the bridging hydrogen has been replaced by deuterium.

EXPERIMENTAL

Diglyme (dimethylether of diethylene glycol) solutions of lithium hexa-alkylhydrodiborates, $\text{LiH}(\text{BR}_3)_2$, and their deuterated analogues, $\text{LiD}(\text{BR}_3)_2$, were prepared by the procedures described by KHURI [1, 2]. Typical concentrations of the ions were in the range of 0.10–0.15 M. Since the compounds were highly reactive and thermally sensitive, special techniques were necessary to handle the samples. For this purpose, a special infrared cell was constructed into which the samples could be transferred from the vacuum line without exposure to the atmosphere, and in which the solutions could be maintained at temperatures in the vicinity of 0°C [7]. Spectra were obtained with a Beckman IR-12 spectrometer using a cell with NaCl windows and path lengths in the range 0.1–0.2 nm.

RESULTS

Infrared spectra of $\text{LiH}[\text{B}(\text{CH}_3)_3]_2$ and $\text{LiD}[\text{B}(\text{CH}_3)_3]_2$ are shown in Fig. 1. Table 1 presents the observed band frequencies and proposed assignments for all species. Since the spectra were observed in solution, solvent interferences were present which obscured

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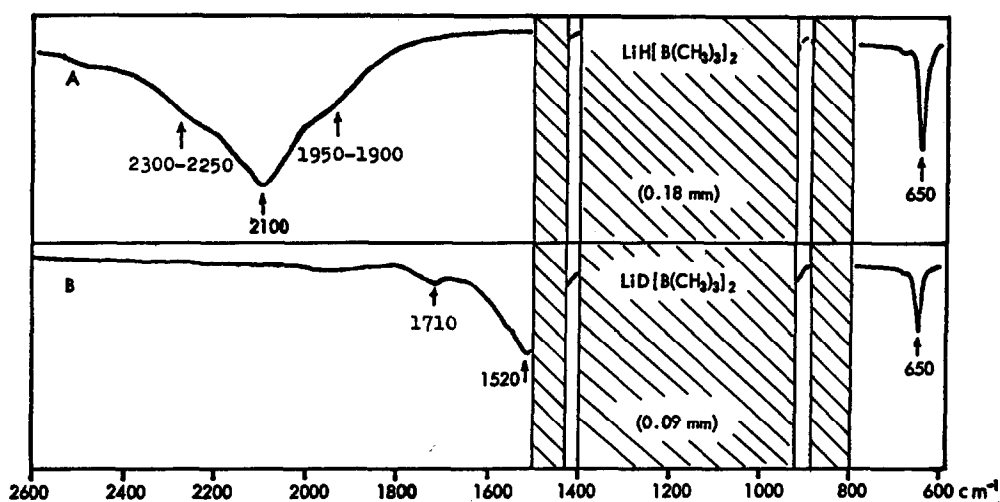


Fig. 1. Infrared spectra of $\text{LiH}[\text{B}(\text{CH}_3)_2]_2$ and $\text{LiD}[\text{B}(\text{CH}_3)_2]_2$ at about 4°C . (Parentheses show cell thickness.)

much of the spectra. Spectral windows for diglyme solvent with NaCl windows and a path length of about 0.18 mm were $600\text{--}800$, $890\text{--}910$, $1400\text{--}1420$ and $1500\text{--}2600\text{ cm}^{-1}$. Some limited information could be obtained from regions obscured by solvent.

The predominant feature of the spectra of the hydrogen species was a strong and broad band observed in the general region of $1800\text{--}2200\text{ cm}^{-1}$. In the hexamethyl compound, the maximum occurred at 2100 cm^{-1} and in the hexaethyl it was somewhat lower at 1915 cm^{-1} . When deuterium was substituted for the non-methyl hydrogen, this band shifted to 1520 cm^{-1} in the hexamethyl species; solvent interference prevented clear observation of the maximum in the hexaethyldeutero case but its position was estimated at around 1400 cm^{-1} . The isotope effect clearly associates these bands with the non-methyl hydrogens and their positions fall in the region which has been shown to be characteristic of hydrogen bridge motions in boron compounds known to have B–H–B bridges. It thus appears that the bridged hydrogen model proposed by KHURI *et al.* [1, 2] is correct.

Table 1. Infrared bands observed for $\text{LiH}(\text{BR}_3)_2$ and $\text{LiD}(\text{BR}_3)_2$ in diglyme solution at approximately 0°C (cm^{-1})

$\text{LiHB}_2(\text{CH}_3)_6$	$\text{LiDB}_2(\text{CH}_3)_6$	Designation
2250–2300 sh, br	1710 w, br	$\nu_{\text{as}}(\text{BHB}) + \nu_s(\text{BHB})$
2100 s, br	1520 m, br	Asym. B–H–B str.
1900–1950 sh, br		$\nu_{\text{as}}(\text{BHB}) - \nu_s(\text{BHB})$
650 m	650 m	Sym. BC_3 str.
$\text{LiHB}_2(\text{C}_2\text{H}_5)_6$	$\text{LiDB}_2(\text{C}_2\text{H}_5)_6$	
2050–2100 sh, br	1570 m, br	$\nu_{\text{as}}(\text{BHB}) + \nu_s(\text{BHB})$
1915 s, br	(1400) s, br	Asym. B–H–B str.
1700–1750 sh, br		$\nu_{\text{as}}(\text{BHB}) - \nu_s(\text{BHB})$
(1200–1250)	897 m	B–H–B deform.
754 s	756	B–C–C str.?
610 m	611 m	Sym. B–C str.

Figures in parentheses indicate estimated values.

Intensity: w, weak; m, medium; s, strong; sh, shoulder; br, broad.

Structural considerations

The X-ray and neutron diffraction studies carried out recently on the $B_2H_7^-$ ion [4, 5] have shown that the B–H–B bridge is bent with an angle of approximately 127° . In the alkyl compounds, steric interactions make it likely that the B–H–B bond is linear, or very nearly so. To explore the steric problem, geometrical calculations were carried out for several configurations.

Since the bridge frequency in the spectra of the hexamethyl ion occurs at approximately the same position as the bridge frequency in the $B_2H_7^-$ ion spectra [7], it is reasonable to expect that the B–H distances in the two ions are about the same. For the three slightly bent C_2 , C_s and C_{2v} structures with the B–H distance set at 1.325 \AA (the same as for the $B_2H_7^-$ ion) and the B–H–B angle set at a relatively flat angle of 170° , the distance of closest approach of at least two of the methyl groups on opposite ends of the molecule was calculated to be approximately 3.8 \AA , substantially less than 4.0 \AA , the sum of van der Waals' radii. Although a longer B–H distance (1.35 \AA) with the bridge angle at 170° reduced the steric interaction somewhat, the closest calculated methyl–methyl distance of 3.9 \AA was still significantly less than 4.0 \AA . Only for the linear D_{3d} model did all methyl–methyl distances equal or exceed the van der Waal's radius sum with the hydrogen bridge distances at 1.325 \AA .

A similar situation exists for the hexaethyl compounds since the van der Waal's radius of the methylene group is very nearly the same as that of the methyl group and the ethyl group as a whole is larger than the methyl. To the extent that one can rely on van der Waal's radii as an indication of steric interactions, these calculations thus favor linear, or very nearly linear, hydrogen bridges for these compounds.

VIBRATIONAL ASSIGNMENTS

The scarcity of observed frequencies for these compounds precludes any very extensive discussion of assignments. If the methyl groups are regarded as mass points, the vibrational structures for the skeleton of the D_{3d} model is $3A_{1g} + 3E_g + A_{1u} + 3A_{2u} + 4E_u$ with the gerade frequencies Raman-active and the ungerade infrared-active, except for the A_{1u} torsion which is inactive. The assignment of the A_{2u} asymmetric stretching motions of the bridge hydrogen in the H and D compounds has been mentioned previously and those assignments appear unequivocal.

The other infrared-active motion of the bridge hydrogen is the E_u deformation mode. Since this is expected to fall in regions obscured by solvent, the identification of this band in the two isotopomers was difficult. However, an unobscured band was observed at 897 cm^{-1} in the spectrum of the deuterated hexaethyl compound which shifted to give a maximum estimated at $1200\text{--}1250 \text{ cm}^{-1}$ in the hydrogen compound. This position is reasonable for the hydrogen deformation motion and the isotope shift confirms its association with the non-methyl hydrogen. The corresponding bands in the $B_2H_7^-$ ion have been assigned at 1120 cm^{-1} and approximately 1538 cm^{-1} [9] for the D and H species, respectively. The bridge hydrogen stretching motions for the methyl compound occur at slightly higher frequencies than for the ethyl, suggesting that the bridge deformation modes might also be higher. Although this prediction puts them in strongly obscured regions, there were indications that bands were present where expected.

The other bridge hydrogen motion is the A_{1g} stretching motion, which is more accurately described as a symmetric B–H–B stretch. This fundamental is not infrared-active but the transition may be observed in combination with infrared-active modes. In the $B_2H_7^-$ ion it has been identified at 290 cm^{-1} in the Raman spectrum [7]. The increased mass attached to the boron atom in the alkyl compounds may cause it to occur at a somewhat lower frequency. Weak shoulders are present on either side of the 2100 cm^{-1} band of the hexamethyl compound, which could be due to the presence of combination bands involving this mode. In the hexamethyl–deutero compound, a shoulder occurs at 1710 cm^{-1} which, if assigned as a combination with the B–H–B stretch, gives a frequency of 190 cm^{-1} for the fundamental. This value is consistent with the positions of shoulders

in the spectra of the hydrogen compound. Similar features were present in the spectra of the hexaethyl compounds, although somewhat less well defined.

Well-defined bands were observed at 650 cm^{-1} in the spectra of both methyl compounds which were not sensitive to deuterium substitution. Analogous bands were observed in the spectra of the hexaethyl compounds at 610 cm^{-1} . These bands are assigned to the A_{2u} symmetric BC_3 stretching motion by analogy to the $\text{B}(\text{CH}_3)_3$ spectrum, where the symmetric BC_3 stretch band has been observed in the Raman spectrum at 675 cm^{-1} [8].

The only remaining observed frequency is the well-defined band at 754 cm^{-1} in the spectra of the hexaethyl compound. This band also was insensitive to deuterium substitution, and we believe it corresponds to the band at 778 cm^{-1} in solutions of $\text{B}(\text{C}_2\text{H}_5)_3$ dissolved in diglyme [9], and also to the band at 779 cm^{-1} in the spectrum of gaseous triethylborane, both of which are yet unassigned [10]. It may be due to a B-C-C stretching motion.

In conclusion, it is of interest to compare the spectral characteristics of the present compounds with those of compounds known to have symmetrical hydrogen bonds, for example KHF_2 , $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$ and HCrO_2 . Although there is a formal similarity in the location of the bridging hydrogen, there is a basic difference in bonding which shows up in the spectra. The B-H-B group is bonded covalently with an electron pair spread over three centers. The individual B-H bond is similar to, although weaker than, a terminal B-H bond. In contrast, the X-H linkage in a symmetrical hydrogen bond, X-H-X^- , is largely ionic in character and only partially covalent. This difference in bond character shows up convincingly in the spectra in which the asymmetric bridge stretching motions in the hexa-alkylhydroboron compounds are observed at 2100 and 1915 cm^{-1} , not far from the range for terminal B-H bonds ($2350\text{--}2650\text{ cm}^{-1}$), whereas the same motions in the X-H-X^- ions are quite low and far removed from the covalent H-X frequencies in the free compounds [11].

For example, $\nu_{\text{as}}(\text{XHX})$ in the F-H-F^- ion occurs at 1450 cm^{-1} , compared to 3960 cm^{-1} in free HF. Other examples are cited in Ref. [11]. Differences in the symmetrical hydrogen stretching frequencies between the two groups also are appreciable, although they are not as dramatic as for the asymmetric bands. In the hexa-alkylhydroboron compounds, the symmetrical motions are estimated to occur in the vicinity of 190 cm^{-1} , while the same motion in the HF_2^- , HBr_2^- , hydrogen diacetate and hydrogen maleate ions occurs at frequencies of 600 , 168 , 320 and 370 cm^{-1} , respectively. The higher frequencies for the hydrogen-bonded compounds are interpreted as indicating greater coupling with the lattice because of the stronger Coulombic forces present.

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