

Vibrational spectra and structure of the heptahydrodiborate ion, [B₂H₇]⁻ in glycol ethers

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Abstract—The i.r. and Raman spectra of the heptahydroborate ion, [B₂H₇]⁻, and its deuterated derivative, [B₂D₇]⁻, have been obtained in solution and assignments have been made of the observed bands. The data are interpreted as indicating a bent C₂ structure in solution. Normal coordinate calculations based on this model are presented.

INTRODUCTION

There has been a continuing interest in the heptahydrodiborate ion, [B₂H₇]⁻, ever since its existence was first predicted by the topological theory of DICKERSON and LIPSCOMB [1]. Shortly after this prediction, sodium heptahydrodiborate, NaB₂H₇, was prepared and the empirical formula of the ion confirmed in diethylene glycol dimethyl ether (diglyme) solution by vapor pressure and electrolytic studies [2, 3]. Subsequently, the ¹¹B and ¹H NMR spectra of NaB₂H₇, reported by GAINES [4] and by DUKE *et al.* [5] were interpreted as evidence for the existence of a single hydrogen bridge in the species. Additional support for the presence of a hydrogen bridge was provided by a brief report of the i.r. and Raman spectra [6].

Although the existence of a single hydrogen atom bridging two boron moieties is now well accepted, evidence bearing on the actual conformation of the [B₂H₇]⁻ ion has been slow in coming. Theoretical calculations [7–11] have persisted in predicting a linear B–H–B bridge and it has only been quite recently that calculations including higher order terms have shown that a bent bridge structure is energetically slightly more stable than the linear [12]. The first experimental evidence that the bridge is bent came from an X-ray study of a salt with a complex cation [13]. Very recently, a neutron diffraction experiment [14] with the same salt has confirmed the X-ray results for the solid and provided reliable structural parameters for the ion in a crystal lattice.

Detailed spectroscopic studies involving the [B₂H₇]⁻ ion have not been found, and, aside from the short preliminary report mentioned above [6], vibrational data in the literature [15–17] are confined to i.r. frequencies obtained primarily for characterization. The present study reports the results of an i.r. and Raman investigation of solutions of NaB₂H₇ and NaB₂D₇ in diglyme and monoglyme (the methyl ether of ethylene glycol). The results are interpreted to

support a bent C₂ structure for the [B₂H₇]⁻ anion in solution.

EXPERIMENTAL

The reactivity and thermal instability of boron compounds containing a single bridging hydrogen made it necessary to employ special techniques for handling samples. To this end, a special solution i.r. cell was constructed to which it was possible to transfer solutions from the vacuum line at temperatures approaching those of dry ice without exposing the solution to the atmosphere. This cell contained an inner coolant reservoir separated by an evacuated space from an outer casing and was similar in design to cells previously described in the literature [18, 19]. Solutions were transferred to the sample compartment via a Teflon stopcock and small diameter stainless steel tubing which could be connected directly to the reaction vessel on the vacuum line. The limiting factor in the temperatures which could be maintained in the cell was set by the O-ring material confining the sample between the alkali halide plates. At about -40° Buna-N hardened to the point that the cell began to leak. With Silicone rubber, another twenty degrees could be attained. Fortunately, the solutions studied appeared quite stable in the range between -10° and -30°C.

Solutions were prepared in diglyme or monoglyme from NaBH₄ and diborane by the procedure described by BROWN [2]. Deuterated species were prepared using the appropriate deuterated compounds. In relatively dilute solutions with 0.1 mm cell thicknesses, solvent interference prevented observation of the solute spectra in the 3000–2700, 1500–1430, 1400–920 and 890–790 cm⁻¹ regions. Such interference could be reduced by using more concentrated solutions and smaller cell thicknesses, but with concentrations much richer than about a 4:1 molar ratio of solvent to solute, the mixtures became sufficiently viscous that they could not be stirred and transferred to the cell. Some additional information was obtained by coating CsI windows with a thin layer of a concentrated, gel-like, solution of NaBH₄ in diglyme and assembling them in a gas cell. After evacuating the cell, a small pressure of B₂H₆ was admitted which reacted quickly to give a concentrated solution of sodium heptahydrodiborate. Although decomposition occurred slowly, the presence of diborane reduced the rate at which the ion disappeared. It should be noted in passing that the [B₂H₇]⁻ ion is not stable in the absence of ether solvent and all attempts to obtain crystals of NaB₂H₇, free of ether have uniformly been unsuccessful. The diborane frequencies in the gas cell experiment were easily recognized and did not seriously obscure the bands of the ion. GAINES [4] has shown that solutions of sodium heptahydrodiborate decompose slowly to give sodium octahydrotriborate. Consequently the spectrum of

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Table 1. Observed i.r. and Raman frequencies for sodium diborohydride and diborodeuteride in solution

Sodium diborohydride		Sodium diborodeuteride		Assignments
Infrared	Raman	Infrared	Raman	
2405 s,br	2400 w,sh 2365 s,br,p	1810 s,br 1725 w,br	1800 m,br 1730 s,p	$\nu_1, \nu_2, \nu_{12}, \nu_{13}$ ν_3, ν_{14}
2300 w,sh	2285 ^w w,sh	1670 vw	1680 w	?
2050 m,br	2025 vw,br (1440) w,br	1510 m,br	1120 w,br,p	$2\nu_5$? ν_{15} ν_4
1030 s (825) vw	1165 w,dp (1030) vw (835) vw 645 w,p 290 m,br,p	850 vw,sh 803 s 630 vw	(850) vw (800) vw 630 w,dp 485 w,p 265 w,br,p	ν_5, ν_{16} ν_7, ν_{18} ν_8, ν_{19} ν_9, ν_{20} ? ν_{10}

s = strong, m = medium, w = weak, br = broad, sh = shoulder, p = polarized, dp = depolarized. Bands enclosed in parentheses were subject to solvent interference.

NaB_3H_8 in diglyme solution was obtained for comparison but no significant interferences were noted.

Infrared spectra were obtained using a Beckman IR-12 spectrometer while the Raman spectra were obtained photographically.

RESULTS AND DISCUSSION

The positions of the maxima of the observed bands are tabulated in Table 1 together with proposed assignments. Since the bands for the most part were rather broad and solvent interference was present for some, the precision at best was limited to about 2 cm^{-1} for the better defined bands, and from 5 to 10 cm^{-1} for weak or obscured bands. Reproductions of the observed spectra for the hydrogen and deuterium species are shown in Fig. 1 where the dashed portions indicate regions of strong solvent interference. Evidence for the existence of solute bands in such regions was provided by the spectra of the very concentrated solutions obtained in the gas cell.

The X-ray and neutron diffraction data from the complex solvated crystal mentioned previously [13,14] indicate that the $[\text{B}_2\text{H}_7]^-$ ion has C_s symmetry in that environment. In solution, two linear and three bent models may be considered. For the linear case, the symmetries are D_{3h} and D_{3d} . The latter can be eliminated immediately on the basis of the observation of the bridge mode at 1120 cm^{-1} in the Raman spectrum of the deuterated species since this would be inactive in the D_{3d} point group. Although obscured in the spectrum of the hydrogen compound, this band was clearly present in the $[\text{B}_2\text{D}_7]^-$ spectrum and polarized.

Although this transverse bridge mode would be active under D_{3h} symmetry, the BH_3 groups undoubtedly possess a low rotational barrier and rotate fairly freely. Consequently the ion would have an effective center of symmetry in which the B-H-B deformation again would be very weak or Raman inactive. Consequently, we feel the observation of this band, even though with low intensity, is strong evidence against a linear model.

For the bent model, the possible symmetries are C_{2v} , C_s and C_2 . These symmetries differ only in the orientation of the BH_3 groups with respect to the B-H-B plane. The most recent theoretical calculations [12] favor the C_2 model, although the authors state that the minimum is very flat. Since only 30° rotations of the BH_3 groups are necessary to convert one structure into the other, and in view of the fact that the energy difference among the rotamers is probably low, a mixture of forms undoubtedly exists in solution, although one form may predominate.

Spectroscopically, a bent C_s model has the vibrational structure ($13A' + 8A''$), the C_2 model has the structure ($11A + 10B$) and the C_{2v} model the structure ($7A_1 + 4A_2 + 4B_1 + 6B_2$). Although in principle these three symmetries might be distinguished on the basis of the number of polarized bands in the Raman effect, because of solvent interference and the incompleteness of the spectra, such differentiation was not possible. However, experimental evidence favoring the C_2 model can be obtained from consideration of the two bands at 645 and 485 cm^{-1} in the Raman spectra of the hydrogen and deuterium species, respectively. These two bands are assigned to the wagging motion of the BH_3 groups in which the local symmetry axes of the groups move out of the B-H-B plane (cf. symmetry coordinate S_9 in Table 2). The location of this type of motion of the BH_3 group has been established in other compounds [20]. Both of these bands in the present work were determined to be polarized. Although the spectra were obtained photographically, the mean of six determinations gave a value of 0.63 for the depolarization ratio of the hydrogen species while the value found for the deuterated species was 0.55. This mode falls in a totally symmetric class only in the C_2 model; in the C_s model it occurs in the A'' species and in the C_{2v} it is in the A_2 class. In neither of the latter two cases should it be polarized. The conclusion, therefore, is that the C_2 species predominates in solution.

To discuss assignments, the fundamental modes of the heptahydrodiborate ion can be divided into two

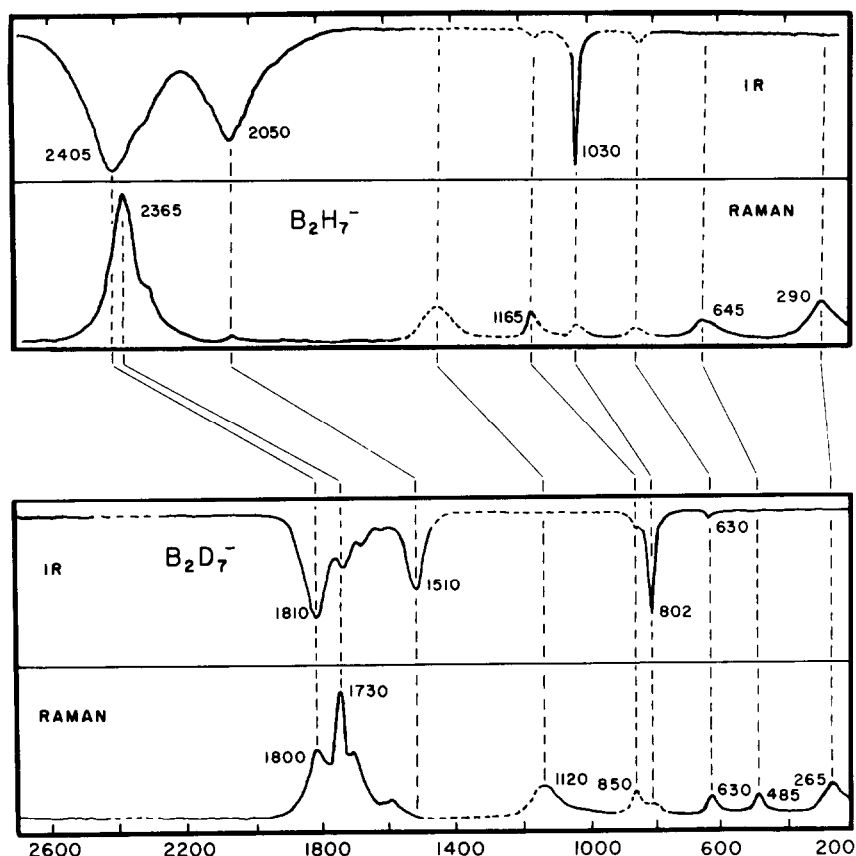
Fig. 1. Raman and i.r. spectra for the $[\text{B}_2\text{H}_7]^-$ and $[\text{B}_2\text{D}_7]^-$ ions.

Table 2. Symmetry coordinates for the diborohydride anion

A species	Description
$S_1 = \Delta r_1 - 2\Delta r_2 + \Delta r_3 + \Delta r_4 - 2\Delta r_5 + \Delta r_6$	Asym. terminal B-H stretch
$S_2 = \Delta r_1 - \Delta r_3 + \Delta r_4 - \Delta r_6$	Asym. terminal B-H stretch
$S_3 = \Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4 + \Delta r_5 + \Delta r_6$	Sym. terminal B-H stretch
$S_4 = \Delta R_1 + \Delta R_2$	Sym. hydrogen bridge stretch
$S_5 = \Delta\alpha_1 - 2\Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 - 2\Delta\alpha_5 + \Delta\alpha_6$	Asym. BH_3 deformation
$S_6 = \Delta\alpha_1 - \Delta\alpha_3 + \Delta\alpha_4 - \Delta\alpha_6$	Asym. BH_3 deformation
$S_7 = \Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + \Delta\alpha_4 + \Delta\alpha_5 + \Delta\alpha_6 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 - \Delta\beta_6$	Sym. BH_3 deformation
$S_8 = \Delta\beta_1 - 2\Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4 - \Delta\beta_5 + \Delta\beta_6$	BH_3 rock
$S_9 = \Delta\beta_1 - \Delta\beta_3 + \Delta\beta_4 - \Delta\beta_6$	BH_3 wag
$S_{10} = \Delta\phi$	B-H-B bridge deformation
$S_{11} = \Delta\tau_1 + \Delta\tau_2$	BH_3 torsion
B species	Description
$S_{12} = \Delta r_1 - 2\Delta r_2 + \Delta r_3 - \Delta r_4 + 2\Delta r_5 - \Delta r_6$	Asym. terminal B-H stretch
$S_{13} = \Delta r_1 - \Delta r_3 - \Delta r_4 + \Delta r_6$	Asym. terminal B-H stretch
$S_{14} = \Delta r_1 + \Delta r_2 + \Delta r_3 - \Delta r_4 - \Delta r_5 - \Delta r_6$	Sym. terminal B-H stretch
$S_{15} = \Delta R_1 - \Delta R_2$	B-H-B bridge stretch
$S_{16} = \Delta\alpha_1 - 2\Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 + 2\Delta\alpha_5 - \Delta\alpha_6$	Asym. BH_3 deformation
$S_{17} = \Delta\alpha_1\Delta\alpha_3 - \Delta\alpha_4 + \Delta\alpha_6$	Asym. BH_3 deformation
$S_{18} = \Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 - \Delta\alpha_4 - \Delta\alpha_5 - \Delta\alpha_6 - \Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4 + \Delta\beta_5 + \Delta\beta_6$	Sym. BH_3 deformation
$S_{19} = \Delta\beta_1 - 2\Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4 + 2\Delta\beta_5 - \Delta\beta_6$	BH_3 rock
$S_{20} = \Delta\beta_1 - \Delta\beta_3 - \Delta\beta_4 + \Delta\beta_6$	BH_3 wag
$S_{21} = \Delta\tau_2 - \Delta\tau_1$	BH_3 torsion

Note: The designations "Asym." and "Sym." refer to local BH_3 symmetry. Two redundant coordinates involving the BH_3 groups are not shown.

groups, those primarily associated with the internal motions of the BH_3 groups and the modes involving the B–H–B backbone. A qualitative description of the vibrational motions is given in Table 2. As can be seen from Table 1, considerably fewer than the expected 21 fundamentals were observed. This is not unexpected since the mechanical coupling between the two BH_3 groups across the hydrogen bridge undoubtedly is quite weak leading to the accidental degeneracy of most, if not all, of the fundamentals involving internal BH_3 modes. Assignments of these frequencies were quite straightforward and followed previous work on other related compounds (see, for example, Ref. [20]).

The motions of the B–H–B backbone of the ion, because the central atom is much lighter than the two end groups and the B–H bonds are relatively weak, are quite different than those found in, for example, the water molecule. The higher frequency symmetric mode can be envisaged as the motion primarily of the bridge hydrogen atom moving along the C_2 axis and perpendicularly to the B···B line. In this mode, the bridge bonds stretch in addition to the B–H–B angle deforming and the frequency should be strongly mass dependent. It has been assigned to the band observed at 1120 cm^{-1} for the deuterated species and the normal coordinate calculations place the corresponding hydrogen band at about 1500 cm^{-1} . Although a weak band is shown at about this position in the hydrogen spectrum in Fig. 1, solvent interference prevented its clear observation.

The other A species skeletal motion may be thought of as the motion of the two BH_3 groups away from each other along a line connecting them, essentially a breathing motion. Since the bridge force constants are relatively weak, the frequency associated with this mode may be expected to be quite low and is assigned to a band at 290 cm^{-1} in the spectrum of the hydrogen species, shifting to 265 cm^{-1} in the deuterium species. The frequency ratio of these two bands, 1.094, is almost exactly the value to be expected if the BH_3 and BD_3 groups are considered mass points.

In the asymmetric skeletal frequency, the bridging hydrogen atom probably is moving roughly parallel to the B···B axis and should show a marked mass dependence. This type of motion results in the characteristic bands in the range between 1500 and 2100 cm^{-1} [6] observed when bridging hydrogen atoms are present in boron compounds. Accordingly, the rather broad band centered around 2050 cm^{-1} in the i.r. spectrum shifting to 1510 cm^{-1} in the deuterated species is assigned to the asymmetric bridge motion. This band is quite weak in the Raman spectrum.

NORMAL COORDINATE CALCULATIONS

Normal coordinate calculations were carried out by fitting the observed frequencies using a standard least-squares program based on the Jacobian of the frequencies with respect to force constants [21]. Un-

observed or unidentified fundamentals were given estimated values and weighted to zero in the fitting process; uncertain frequencies were given very low weights. For purposes of the calculations, the B–H–B angle was assumed to be 136° which is the value reported in the X-ray studies of the related solid compound [14]; values for the B–H bonds were taken from the same work. Angles around the boron atoms were assumed to be tetrahedral. A sketch showing the molecular configuration and coordinate numbering is shown in Fig. 2 and the symmetry coordinates are defined in Table 2.

It was found possible to obtain a satisfactory fit in both the A and B classes with a nearly diagonal potential function, the only off-diagonal constants found useful being $F_{8,10}$ and $F_{19,20}$ connecting the BH_3 rock and the bridge deformation, and the BH_3 rock and BH_3 wag in the A and B classes, respectively. Observed and calculated frequency values are compared in Table 3. Considering the relatively high uncertainty associated with many of the experimental values, the agreement is quite satisfactory. The potential energy distributions associated with BH_3 modes were strongly diagonal indicating that these motions are well localized. The two A species skeletal modes, ν_4 and ν_{10} , however, were mixed to a substantial extent involving both the bridge angle and the B–H bridge bonds. For these two modes, the simplified descriptions implied by the symmetry coordinates in Table 2 do not apply.

The symmetry force constants derived from the frequencies are listed in Table 4 together with values for the valence stretching force constants. The difference between 3.10 and 3.11 mdyn/\AA in the valence constants for the terminal B–H bonds is not significant in terms of the precision of the calculations. The value of 3.1 mdyn/\AA agrees well with the values reported for the B–H bond in other complexes containing the BH_3 group, these generally falling in the range between 3.0 and 3.2 mdyn/\AA [20]. However, 3.1 mdyn/\AA is less than the values for the terminal B–H bonds in diborane which have values reported in the range 3.5 to 3.7 mdyn/\AA [22, 23] and, interestingly, it is significantly greater than the B–H constant in the borohydride ion, BH_4^- , which has a reported value of 2.77 mdyn/\AA [24]. It was difficult to find suitable comparison values for the stretching force constant for the bridge bonds, about the only data available being from analyses of diborane. Published values, none of them very recent, fall in the range of 1.7 to 1.8 mdyn/\AA

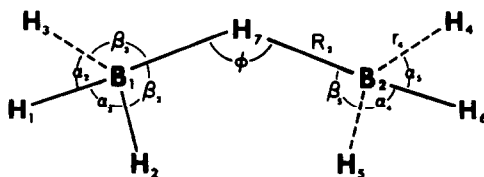


Fig. 2. Coordinate definitions for the $[\text{B}_2\text{H}_7]^-$ ion.

Table 3. Calculated frequencies for the diborohydride and diborodeuteride ions

	Diborohydride			Diborodeuteride		
	Obs.	Calc.	Δ	Obs.	Calc.	Δ
<i>A</i> ₁ species						
ν_1	2405	2410	-5	1810	1809	1
ν_2		2404	1		1810	1806
ν_3	2365	2373	-8	1715	1718	-3
ν_4		1503	—	1120	1117	3
ν_5	1164	1165	-1	849	838	11
ν_6		1162	—		848	—
ν_7	1030	1033	-3	803	797	6
ν_8	(825)	838	?	630	630	0
ν_9	645	642	3	485	490	-5
ν_{10}	290	301	-11	265	252	13
ν_{11}		99	—		71	—
<i>B</i> species						
ν_{12}	2405	2406	-1	1810	1806	4
ν_{13}		2400	5		1810	1800
ν_{14}	2365	2369	-4	1715	1721	-6
ν_{15}	2050	2065	-15	1510	1490	20
ν_{16}	1165	1165	0	850	848	2
ν_{17}		1112	—		805	—
ν_{18}	1030	1031	-1	803	785	18
ν_{19}	(825)	850	?	630	629	1
ν_{20}	645	645	0	485	485	0
ν_{21}		99	—		71	—

Numbers enclosed in parentheses represent uncertain values.

Table 4. Symmetry force constants and valence bond force constants for the diborohydride ion

Symmetry force constants for the <i>A</i> class:			
Index	Constant	Index	Constant
1, 1	3.058	7, 7	0.268
2, 2	3.044	8, 8	0.486
3, 3	3.233	9, 9	0.262
4, 4	2.007	10, 10	0.270
5, 5	0.296	11, 11	0.017
6, 6	0.305	8, 10	0.249
Symmetry force constants for the <i>B</i> class:			
12, 12	3.050	17, 17	0.313
13, 13	3.037	18, 18	0.274
14, 14	3.212	19, 19	0.281
15, 15	1.347	20, 20	0.112
16, 16	0.280	21, 21	0.0022
19, 20	-0.054		
Valence stretching force constants:			
B-H (terminal)	3.103	B-H' (terminal)	3.110
B-H (bridge)	1.677	B-H/B-H (bridge)	0.330
B-H/B-H (term)	0.063	B-H/B-H' (term)	0.056

(Units: mdyn/Å.)

with an *ab initio* value reported of 1.9 mdyn/Å [25]. These may be compared with the value 1.68 mdyn/Å in the present work. In summary, then, the valence force constants obtained appear quite reasonable and in satisfactory accord with data from other related compounds.

The effect of geometry was examined by calculating the vibrational frequencies for various values of the B-H-B bridge angle using the potential constants of Table 4. The other parameters were kept unchanged. As might have been expected, the BH₃ modes were quite insensitive to bridge angle through the range

from 100° to 160°. The two modes involving the bridge hydrogen atom, however, exhibited a marked change in magnitude over the same angle range, the *A* species mode moving from about 2300 cm⁻¹ at 100° to nearly 1300 cm⁻¹ at 160° while the *B* species mode increased from about 1500 cm⁻¹ to nearly 2200 cm⁻¹ over the same range. The results are not sufficiently sensitive, considering all the uncertainties involved, to be very useful in setting a value for the angle parameter. Clearly, however, very acute angles can be ruled out and a value in the vicinity of 130° is most concordant with the spectroscopic data.

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