Contribution from the Evans Laboratory of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Nuclear Magnetic Resonance Spectra of $B_2H_7^-$. Preparation and Properties of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$

R. K. HERTZ, H. D. JOHNSON, II, and S. G. SHORE*

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The salt $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ was isolated from the reaction of B_2H_6 with $[P(C_6H_5)_3CH_3^+][BH_4^-]$. Variable-temperature pmr spectra (−80 to +110°) of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ demonstrate intramolecular exchange of bridge and terminal hydrogens at temperatures above 50°. Spin coupling of bridge and terminal hydrogens was observed near −35°. The compound is stable in a closed system to nearly 100° but rapidly loses diborane at 100° under dynamic vacuum. The $B_2H_7^-$ ion is apparently unaffected by tetrahydrofuran. With $(CH_3)_2S$ the reaction

$$(CH_3)_2S + B_2H_7^- \xrightleftharpoons{CH_2Cl_2} (CH_3)_2SBH_3 + BH_4^-$$

is observed. The equilibrium constant as a function of temperature was determined from boron-11 nmr spectra. With $N(CH_3)_3$ the corresponding reaction is apparently complete.

Introduction

Evidence for the existence of lithium and sodium salts of the heptahydrodiborate(1−) ion, $B_2H_7^-$, was first obtained by Brown, Stehle, and Tierny[1] by means of tensimetric titrations of the respective alkali metal borohydrides with diborane in diglyme at 0°. To date, alkali metal salts have not been isolated.[2,3] More recently, however, tetraalkylammonium salts have been isolated as crystalline solids: $[N(C_2H_5)_4^+][B_2H_7^-]$[4,5] and $[N(C_4H_9)_4^+][B_2H_7^-]$.[5,6]

Proton nmr spectra of the $B_2H_7^-$ ion have not been previously reported. However, the boron-11 nmr spectrum of NaB_2H_7 in the presence of $NaBH_4$ reveals a broad quartet indicating the presence of BH_3 groups.[7] Bridge hydrogen coupling to boron was not observed.

The primary objective of the present study has been to obtain nmr spectra of the $B_2H_7^-$ ion from a pure salt in solution in the hope of observing details which were not present in the earlier reported spectra. While the salt $[N(C_4H_9)_4^+][B_2H_7^-]$ proved to be adequate for boron-11 nmr, interference from the proton resonances of the cation prevented the observation of useful pmr spectra. Therefore, the new salt $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ was prepared.

Results and Discussion

Nmr Spectra. Proton nmr spectra of $[P(C_6H_5)_3CH_3^+]$-$[B_2H_7^-]$ in CH_2Cl_2 and in $CHCl_2CHCl_2$ clearly confirm the structure of the anion as $H_3B\text{-}H\text{-}BH_3^-$. Figure 1 depicts variable-temperature pmr spectra. At 20° a quartet at lower field assigned to terminal BH and a broad singlet at higher field assigned to the bridging proton were observed. With decreasing temperature, both resonances become relatively sharp singlets. The loss of boron-hydrogen spin coupling is undoubtedly due to rapid nuclear quadrupolar relaxation at low temperatures.[8-10] From a boron-11 spin-decoupled pmr spectrum, the area ratio of the terminal proton resonance to the bridge proton resonance was determined and corrected for the presence of hydrogens attached to boron-10. A value of 5.9:1 was obtained.

Spin coupling of the terminal protons with the bridging proton is observed in the bridge resonance shown in Figure 2. This coupling was only evident while spin decoupling boron-11 nuclei at about −35°. Five lines of the expected septet are clearly visible. However, spin coupling of the bridging proton with terminal protons is not visible on the terminal resonance which is a singlet under the condition of boron-11 spin decoupling.

With increasing temperatures above 20° the B-H multiplet (Figure 1) collapses and shifts upfield (see Table I) while the B-H-B singlet becomes very broad (presumably moving downfield) and disappears into the base line. This suggests the possibility of exchange averaging of bridge and terminal hydrogen shifts as a result of rapid migration of hydrogen between bridge and terminal sites with increasing temperature. A solution of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ was examined over an extended temperature range to test this possibility. Below −22° the chemical shifts of the bridging and the terminal resonances appear to be independent of temperature with τ_{B-H} 8.9 ppm and τ_{B-H-B} 14.7 ppm (τ_{TMS} 10.00 ppm). Exchange averaging of the bridge and terminal resonances is expected to give a weighted-average chemical shift of τ 9.7 ppm. From +70 to +110° the observed value is 9.7 ppm. Above 110° rapid decomposition of the sample precluded further study. No coupling of hydrogen with boron was observed in the temperature range in which exchange averaging was complete.

The boron-11 nmr spectra of $[N(C_4H_9)_4^+][B_2H_7^-]$ and $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ in CH_2Cl_2 and $CHCl_2CHCl_2$ are in accord with the spectrum reported by Gaines[7] for NaB_2H_7 in the presence of $NaBH_4$ (see Table II). The quartet observed at ambient temperature (1:3:3:1) collapses to a broad singlet below −40°. It also collapses to a broad singlet above 50°. The loss of spin coupling below ambient temperature is attributed to quadrupolar relaxation while above ambient temperature rapid hydrogen exchange occurs between terminal and bridging sites as discussed above. The presence of BH_4^- in these systems added as $N(C_4H_9)_4BH_4$ or $P(C_6H_5)_3CH_3BH_4$ in a 1:1 ratio with respect to $B_2H_7^-$ did not significantly alter the appearance or chemical shift

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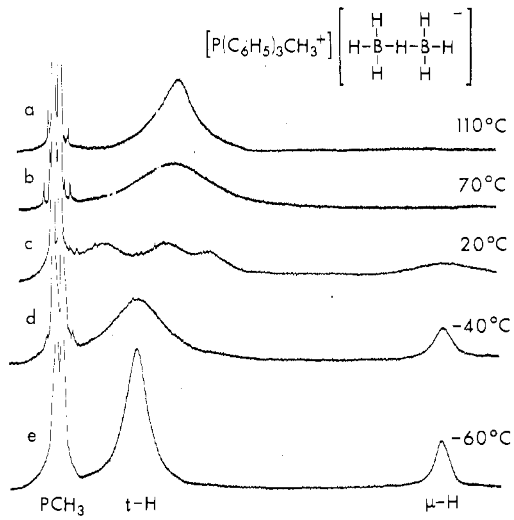

Figure 1. Variable-temperature 100-MHz pmr spectra of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$: a and b, $CHCl_2CHCl_2$ solution; c–e, CH_2Cl_2 solution.

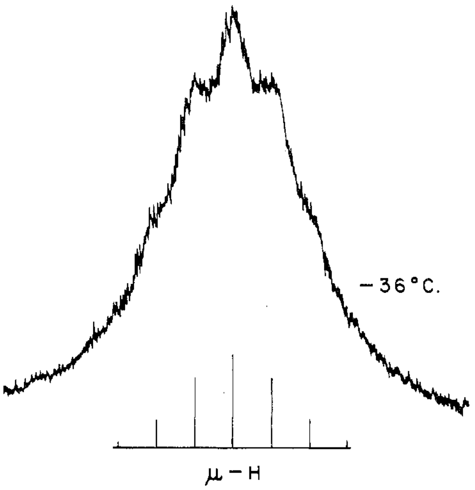

Figure 2. Detail of bridge hydrogen resonance. Boron-11 spin-decoupled 100-MHz pmr spectrum of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ in CH_2Cl_2 at −36°.

Table I. Pmr Data for $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$

	τ,[a] ppm		
Temp, °C	Terminal	Exchange averaged	Bridge
110		9.7	
90		9.7	
70		9.6	
50		9.2	
33[b]	9.1[c]		14.5
−3	8.9		14.7
−36[b]	8.8		14.7[d]
−64	8.8		14.7

[a] Chemical shifts are with respect to $(CH_3)_4Si$ (TMS), τ 10.0 ppm. $\tau \pm 0.1$ ppm. [b] Obtained in CH_2Cl_2 solution and adjusted to correct for the difference in diamagnetic susceptibility between CH_2Cl_2 and $CHCl_2CHCl_2$. All other spectra reported here were obtained from $CHCl_2CHCl_2$ solutions. [c] $J_{B-H_t} = 106 \pm 5$ Hz.[e] [d] $J_{H_t-H_\mu} = 5.6 \pm 0.3$ Hz.[e] [e] J signifies separation of measured peak maxima and not the true coupling constant.

Table II. Boron-11 Nmr Data

	δ[b]	J_{B-H}[c]
NaB_2H_7[7]	25.3	102
$N(C_4H_9)_4B_2H_7$[a]	24.6	89
$P(C_6H_5)_3CH_3B_2H_7$[a]	24.5	83

[a] Measurements were at room temperature in CH_2Cl_2 at 32.1 MHz. [b] Chemical shifts are in ppm relative to $BF_3 \cdot (C_2H_5)_2O$; $\delta \pm 0.3$ ppm. [c] Coupling constants are in hertz; $J_{B-H} \pm 5$ Hz (see footnote *e*, Table I).

of the $B_2H_7^-$ boron-11 resonance as a function of temperature from 30° (ambient temperature) to 110°. Although the borohydride spectrum (a quintet) broadens somewhat with increasing temperature, its chemical shift is essentially invariant. Thus there is no evidence for rapid hydrogen or borane, BH_3, exchange between $B_2H_7^-$ and BH_4^-. The absence of such exchange is consistent with the greater stability of the $B_2H_7^-$ ion in the systems studied herein compared to its stability in the presence of the Na^+ counterion in diglyme.[7]

Preparation and Properties of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$. Triphenylmethylphosphonium heptahydrodiborate(1−) was prepared in the reaction

$$[P(C_6H_5)_3CH_3^+][BH_4^-] + {}^1/_2B_2H_6 \xrightarrow[-78°]{CH_2Cl_2} [P(C_6H_5)_3CH_3^+][B_2H_7^-]$$

This salt is stable in CH_2Cl_2 at room temperature under vacuum. It is readily soluble in chlorinated hydrocarbons such as CH_2Cl_2, $CHCl_3$, and $CHCl_2CHCl_2$ but is insoluble or only slightly soluble in pentane, benzene, tetrahydrofuran, diethyl ether, dimethyl ether, and diglyme.

The salt is isolated as a crystalline solid which is stable for days at room temperature in a closed, evacuated container or in a continuously evacuated system. After 1 hr at 80° in a closed, evacuated system, a small amount of decomposition was detected. Decomposition was complete after 10 hr at 100°, yielding products according to the reaction

$$[P(C_6H_5)_3CH_3^+][B_2H_7^-] \xrightarrow{100°} [P(C_6H_5)_3CH_3^+][B_3H_8^-] + [P(C_6H_5)_3CH_3^+][BH_4^-] + H_2$$

By continuously pumping on the heated system, however, the salt is completely decomposed after 2 hr at 100° yielding products according to the reaction

$$[P(C_6H_5)_3CH_3^+][B_2H_7^-] \rightarrow [P(C_6H_5)_3CH_3^+][BH_4^-] + {}^1/_2B_2H_6$$

The infrared spectrum of the $B_2H_7^-$ ion in $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ is in good agreement with that reported for $[N(C_4H_9)^+][B_2H_7^-]$.[5,6] The spectrum consists of six bands which can be assigned as follows (cm^{-1}): B-H terminal stretch, 2395 (s), 2355 (m), 2295 (w), 2215 (m); B-H-B stretch, 2040 (s); B-H terminal deformation, 1030 (s) (s = strong, m = medium, w = weak). These bands were obtained by subtracting the infrared bands of $[P(C_6H_5)_3CH_3^+][I^-]$ from those of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$.

Stability of the Single Hydrogen Bridge to Lewis Base Attack. The bridge hydrogen of $B_2H_7^-$ is not displaced when a sample of $[N(C_4H_9)^+][B_2H_7^-]$ is dissolved in THF as shown by the boron-11 nmr spectrum. Furthermore, removal of the THF by distillation under vacuum at room temperature left solid $[N(C_4H_9)_4^+][B_2H_7^-]$, which was identified by its X-ray powder pattern.

Boron-11 nmr spectra show that in CH_2Cl_2 both $[N(C_4H_9)_4^+][B_2H_7^-]$ and $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ are cleaved to the corresponding borohydrides and $(CH_3)_3NBH_3$ by equimolar quantities of trimethylamine. The reactions appear to be complete.

With the weaker base dimethyl sulfide the equilibrium

$$[P(C_6H_5)_3CH_3^+][B_2H_7^-] + (CH_3)_2S \xrightleftharpoons{CH_2Cl_2} [P(C_6H_5)CH_3^+][BH_4^-] + (CH_3)_2SBH_3$$

is observed. From integrated areas of reactant and product resonances in the boron-11 nmr spectrum the equilibrium constant was determined as a function of temperature over the range −21 to +31°. A linear plot of log K *vs.* $1/T$ gave an average $\Delta H°$ of -5.3 ± 0.6 kcal/mol and an average $\Delta S°$ of -13.8 ± 2.6 eu over the temperature range. Values of K are noted in the Experimental Section.

The results cited above indicate that $B_2H_7^-$ is more resistant to hydrogen bridge displacement by nucleophiles than B_2H_6, which is readily cleaved into BH_3 adducts by THF[11-13] and $(CH_3)_2S$.[14]

Experimental Section

Materials. Sodium borohydride from Matheson Coleman and Bell and 25% methanolic $(C_4H_9)_4NOH$ from the same source were used as received. Triphenylphosphine and methyl iodide from J. T. Baker Chemical Co. were used as received. Diborane from Callery Chemical Co. was fractionated through a −140° trap before use. Solvents for vacuum line use were dried over $LiAlH_4$ and distilled under vacuum. Other solvents were used as received.

Apparatus. Nmr spectra were obtained using a Varian HA-100 high-resolution spectrometer. Spin decoupling was achieved with a General Radio Co. 1164-A Coherent Decade Frequency Synthesizer and an Electronic Navigation Industries Model 320L RF power amplifier.

Infrared spectra were obtained with a Perkin-Elmer Model 457 infrared spectrophotometer. Samples were run as Nujol mulls between sealed KBr plates.

X-Ray powder diffraction patterns were obtained with a Debye-Scherrer camera of 11.46-cm diameter using Cu Kα radiation.

Preparation of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$. Methyltriphenylphosphonium iodide was prepared from triphenylphosphine and methyl iodide,[15] dissolved in absolute ethanol, and converted to the chloride by passage through a Dowex 1-X8 anion-exchange column.

A solution of 2.4 g (64 mmol) of $NaBH_4$ in 100 ml of absolute ethanol was added with stirring to a solution of 7.8 g (25 mmol) of $P(C_6H_5)_3CH_3Cl$ in 200 ml of absolute ethanol. After 2 hr of stirring the solution was filtered to remove precipitated NaCl and evaporated to dryness. The residue was extracted with 50 ml of methylene chloride. The extract was concentrated to 15 ml. The $P(C_6H_5)_3CH_3BH_4$ was precipitated with 60 ml of diethyl ether, washed with diethyl ether, and dried under vacuum.

In a typical synthesis of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$, 3.00 mmol of $[P(C_6H_5)_3CH_3^+][BH_4^-]$ was placed in a 20-mm diameter reaction tube containing a Teflon-covered stirring bar. The tube was evacuated, and the $[P(C_6H_5)_3CH_3^+][BH_4^-]$ was dissolved in methylene chloride. The resultant solution was titrated tensimetrically with diborane at −78°. Excess diborane was recovered and measured. The methylene chloride was distilled off to yield $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ as a white solid. In an alternative preparation, $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ was precipitated with diethyl ether, filtered from the solution, and dried under vacuum.

The equivalence point for a typical tensimetric titration of $[P(C_6H_5)_3CH_3^+][BH_4^-]$ with B_2H_6 was 0.51. Recovery of excess B_2H_6 from the system showed the ratio of reactants $B_2H_6:BH_4^-$ to be 0.50.

X-Ray powder diffraction pattern data for $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$, *d*, Å (relative intensity): 8.21 (m), 7.34 (vs), 6.93 (w), 6.51 (vw), 6.00 (w), 5.80 (w), 5.49 (m), 5.06 (w), 4.85 (w), 4.62 (m), 4.46 (m), 4.29 (m), 4.19 (m), 4.08 (m), 3.99 (s), 3.86 (m), 3.80 (vw), 3.68 (vw), 3.57 (vw), 3.52 (vw), 3.38 (m), 3.21 (w), 3.16 (w), 3.04 (vw), 2.97 (w), 2.77 (vw), 2.69 (w), 2.63 (vw), 2.57 (w), 2.53 (vw), 2.41 (vw), 2.35 (vw), 2.31 (vw), 2.28 (vw), 2.22 (vw), 2.14 (vw), 2.12 (vw), 2.04 (vw), 2.00 (vw), 1.93 (vw), 1.85 (vw).

Infrared spectrum of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$, cm^{-1} (relative intensity): 2395 (s), 2355 (m), 2295 (w), 2215 (m), 2040 (s), 1580 (m), 1483 (w), 1438 (s), 1337 (w), 1317 (w), 1187 (vw), 1168 (w), 1115 (s), 1070 (vw), 1030 (s), 994 (w), 973 (vw), 924 (vw), 905 (s), 898 (s), 789 (m), 750 (m), 742 (s), 718 (s), 688 (s), 510 (sh), 503 (s), 488 (m), 445 (w), 430 (vw).

Preparation of $[N(C_4H_9)_4^+][B_2H_7^-]$. The preparation of $[N(C_4H_9)_4^+][B_2H_7^-]$ from $[N(C_4H_9)_4^+][BH_4^-]$ was completely analogous to that of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ from $[P(C_6H_5)_3CH_3^+][BH_4^-]$. The starting material $[N(C_4H_9)_4^+][BH_4^-]$ was prepared in the following way. To a solution of 2.73 g (72.2 mmol) of $NaBH_4$ in 10% methanolic NaOH was added 30 ml (30.6 mmol) of 31.4% methanolic $(C_4H_9)_4NOH$ with stirring. The solution was stirred for 2 hr and then evaporated to dryness. The residue was extracted with 60 ml of methylene chloride. The extract was concentrated to 25 ml, and $[N(C_4H_9)_4^+][BH_4^-]$ was precipitated with 50 ml of diethyl ether. The precipitate was filtered, washed with diethyl ether, and dried under vacuum.

The equivalence point for a typical tensimetric titration of $[N(C_4H_9)_4^+][BH_4^-]$ with B_2H_6 was 0.49. Recovery of excess B_2H_6 from the system showed the ratio of reactants $B_2H_6:BH_4^-$ to be 0.49.

X-Ray powder diffraction data for $[N(C_4H_9)_4^+][B_2H_7^-]$, *d*, Å (relative intensity): 10.5 (s), 6.67 (vs), 5.28 (m), 4.30 (m), 4.13 (w), 3.98 (w), 3.73 (w), 3.51 (vw).

Infrared spectrum of $[N(C_4H_9)_4^+][B_2H_7^-]$, cm^{-1} (relative intensity): 2400 (s), 2290 (w), 2195 (m), 2115 (w), 2035 (s), 1164 (m), 1106 (w), 1063 (m), 1027 (s), 922 (w), 882 (m), 799 (w), 736 (m).

Equilibrium Study of the $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ System. In a typical experiment 0.0519 g (0.170 mmol) of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ and 0.0162 g (0.260 mmol) of $(CH_3)_2S$ were dissolved in 0.1553 g of methylene chloride. The boron-11 nmr spectrum of the solution revealed three resonances due to $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$, $(CH_3)_2SBH_3$, and $[P(C_6H_5)_3CH_3^+][BH_4^-]$. Broad-band spin decoupling of the hydrogen nuclei made the determination of peak areas possible. The ratio of the area of the $(CH_3)_2SBH_3$ resonance to that of $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$ allowed the determination of the equilibrium constant for the reaction

$$[P(C_6H_5)CH_3^+][B_2H_7^-] + (CH_3)_2S \rightleftarrows [P(C_6H_5)_3CH_3^+][BH_4^-] + (CH_3)_2SBH_3$$

at temperatures in the range −21 to +31°. Plotting log K against $1/T$ gave a series of points which clearly corresponded to a straight line. A linear least-squares curve corresponding to the equation log $K = -\Delta H°/2.3RT + \Delta S°/2.3R$, $\Delta H°$, and $\Delta S°$ were calculated for the reaction in the temperature range studied.

Equilibrium constant (temperature, °C): 41.1 (−21°), 28.3 (−15°), 19.6 (−4°), 14.8 (3°), 11.4 (11°), 7.84 (21°), 7.02 (30°), 6.16 (31°). $\Delta H° = -5.3 \pm 0.6$ kcal/mol. $\Delta S° = -13.8 \pm 2.6$ eu.

Registry No. $[P(C_6H_5)_3CH_3^+][B_2H_7^-]$, 40001-24-9; $[N(C_4H_9)_4^+][B_2H_7^-]$, 40001-25-0; $[P(C_6H_5)_3CH_3^+][BH_4^-]$, 40001-26-1; $[N(C_4H_9)_4^+][BH_4^-]$, 33725-74-5; $(CH_3)_2S$, 75-18-3; $(CH_3)_2SBH_3$, 13292-87-0; boron-11, 14798-13-1; diborane, 19287-45-7.

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