J. inorg. nucl. Chem., 1971, Vol. 33, pp. 3671-3676. Pergamon Press. Printed in Great Britain

STUDIES IN BORON HYDRIDES–V*

ASSIGNMENT OF THE ^{11}B NMR SPECTRUM OF THE TRIDECAHYDRO DECABORATE(1–) ION

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(*Received* 22 *December* 1970)

Abstract—The 70·6 MHz ^{11}B NMR spectrum of $B_{10}H_{13}^-$ consists of four doublets of relative intensities 2:1:5:2 which are assigned to B(6, 9); B(1 or 3): B(5, 7, 8, 10 and 1 or 3); and B(2, 4) respectively. This data is consistent with a *3630* model for the solution structure.

INTRODUCTION

In a variety of donor solvents, decaborane behaves as a monoprotic acid and, upon treatment with suitable bases such as amines or ylides, affords the tridecahydrodecaborate(1–) ion, $B_{10}H_{13}^-$[1]. Previous ^{11}B NMR studies[2], done at lower field strengths, did not allow an interpretation of these spectra. In this communication, spectra of $B_{10}H_{13}^-$ and some of its derivatives, recorded at 70·6 MHz, are reported. They are sufficient to allow an assignment of the ^{11}B NMR spectrum.

The 70·6 MHz ^{11}B spectrum of $(C_2H_5)_3NH^+B_{10}H_{13}^-$ in acetonitrile, Fig. 1a, is substantially more complex than the 32 MHz ^{11}B spectrum reported by Norman *et al.*[3]. It consists of four doublets of relative intensity 2:1:5:2 in order of increasing field. The spectrum of this salt is relatively insensitive to solvent: in acetonitrile-diethyl sulfide, the two doublets at lowest field begin to merge, while in benzene–dichloromethane, there is in addition a loss of apparent splitting in the doublet of relative intensity 5. Similar effects, although smaller in degree, are seen in dichloromethane solvent. The similarity of the spectra in both non-coordinating and donor solvents strongly indicates that one is not observing a species of the type $B_{10}H_{13}\cdot L^-$, where L is a coordinated solvent.

The spectrum of $(C_2H_5)_3NH^+$ 1,2,3,4-$B_{10}D_4H_9^-$ is shown in Fig. 1b. Deuteration in these positions causes collapse of the doublets at −2·0 and 35·4 ppm. The collapse is complete, and there is no alteration of the doublets at −6·8 and 5·0

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2. G. R. Eaton and W. N. Lipscomb, *N.M.R. Studies of Boron Hydrides and Related Compounds* p. 186. Benjamin, New York, (1969).
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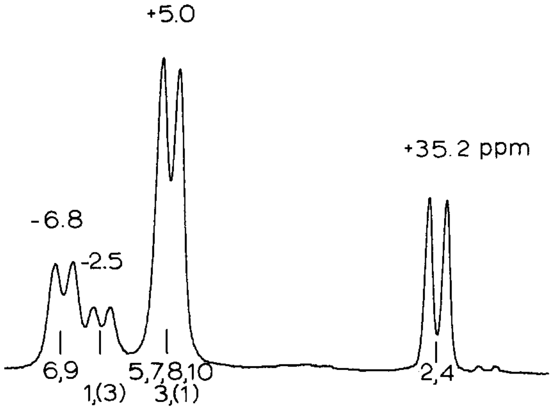

Fig. 1(a).

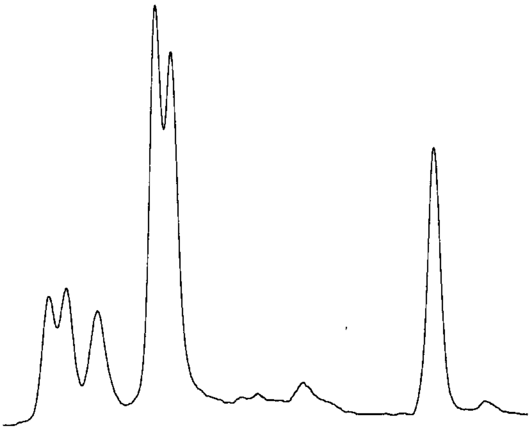

Fig. 1(b).

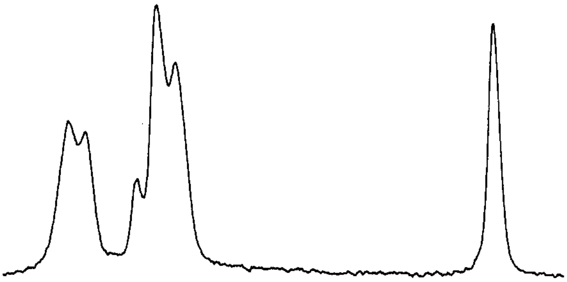

Fig. 1(c).

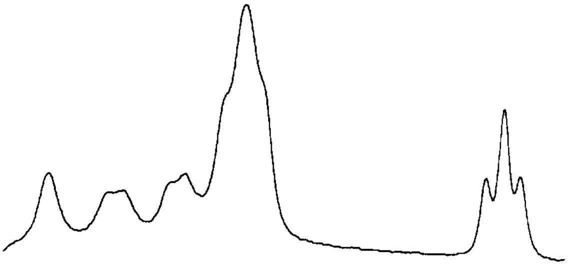

Fig. 1(d).

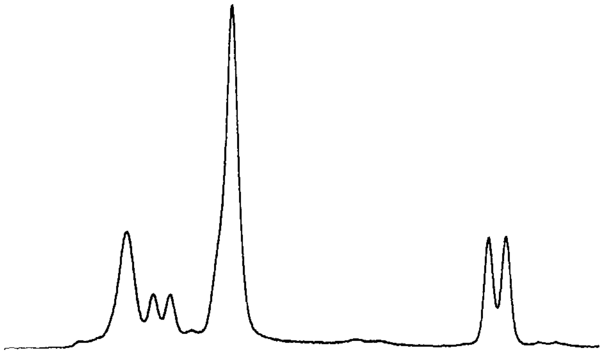

Fig. 1(e).

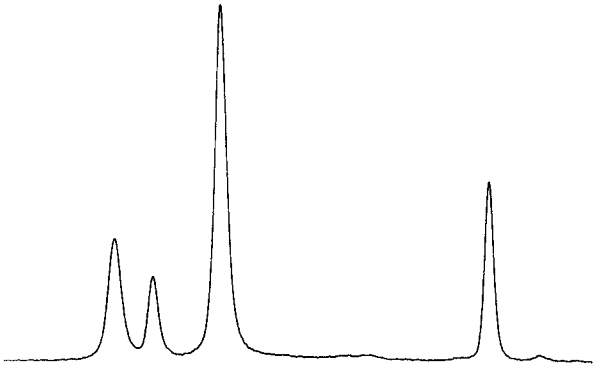

Fig. 1(f).

Fig. 1. The 70·6 MHz ^{11}B NMR spectra in acetonitrile of: (a) $(C_2H_5)_3NH^+$ $B_{10}H_{13}^-$; (b) $(C_2H_5)_3NH^+$ 1,2,3,4-$B_{10}D_4H_9^-$; (c) $(C_2H_5)_3NH^+$ 2,4-$B_{10}I_2H_{11}^-$; (d) $(C_2H_5)_3NH^+$ 6-$PhCH_2B_{10}H_{12}^-$; (e) $(C_2H_5)_3NH^+$ μ_3-5,6,7,8,9,10-$B_{10}D_9H_4^-$; (f) $(C_2H_5)_3NH^+$ $B_{10}H_{13}^-$, ^{1}H decoupled.

ppm, which implies that the deuterium label has not been scrambled. The assignment of the high field doublet to B(2, 4) can then be made on the basis of the spectrum of $(C_2H_5)_3NH^+$ 2,4-$B_{10}I_2H_{11}^-$, shown in Fig. 1c, since the positions of iodination in the parent decaborane have been elucidated by a X-ray crystal structure determination[4]. The doublet of relative intensity one at −2·5 ppm in the structure of $B_{10}H_{13}^-$ apparently has shifted to −6·5 ppm in the spectrum of the diiodo derivative. A second doublet of relative intensity one appears at +1·3 ppm in the spectrum of 2,4-$B_{10}I_2H_{11}^-$. These two doublets of unit area are assigned to B(1) and B(3) but which is which is not known.

The spectrum of $(C_2H_5)_3NH^+$ 6-$PhCH_2B_{10}H_{12}^-$ is shown in Fig. 1d. In this spectrum, the low field doublet has been halved in intensity and in addition a singlet due to B(6) appears at −16·5 ppm. This indicates that the doublet at lowest field, of area 2, is due to B(6, 9). Since B(2, 4) no longer lie on a mirror plane they now appear as two overlapping doublets, which gives added credence to the assignment of these two positions. This effect has also been observed in the ^{11}B NMR spectrum of 6-$PhCH_2B_{10}H_{13}$.

Further confirmation of this assignment was provided by the spectrum of $(C_2H_5)_3NH^+$ μ_3,5,6,7,8,9,10-$B_{10}D_9H_4^-$, Fig. 1e, in which the expected collapse of the doublets at −6·8 ppm and 5·0 ppm, with relative intensities 2:5, occurs. The distorted line shape of the low field portion of the resonance at 5·0 ppm is suggestive of a doublet of area one due to either B(1) or B(3) superimposed on the B(5, 7, 8, 10) resonance.

In Fig. 1f is shown the spectrum of $(C_2H_5)_3NH^+$ $B_{10}H_{13}^-$, in which a wide band, white noise ^1H decoupling experiment was performed. Unfortunately, it was not possible to conclusively demonstrate the existence of two distinct boron environments beneath this resonance at 5·0 ppm.

A disturbing feature of the ^{11}B NMR spectrum of $B_{10}H_{13}^-$ is the gross nonequivalence of B(1) and B(3), while B(2, 4), and B(5, 7, 8, 10) are apparently magnetically equivalent. In the ^{11}B spectrum of $NaB_{10}H_{13}$ in diethyl ether, the +5 ppm region consists of two overlapping doublets of relative areas 2:3. The resonances due to B(5, 10) and B(7, 8) may be resolved in this case. These results are inconsistent with the various structures suggested by Lipscomb[5].

A study of the PMR of $(C_2H_5)_3NH^+$ $B_{10}H_{13}^-$ at 220 MHz in various solvents has demonstrated the existence of two distinct bridge resonances, which were markedly solvent dependent[6]. In acetonitrile, these resonances occurred at 3·2 and 3·61 ppm upfield from TMS, with relative intensities that appeared to be 1:2. In a diethyl ether solution of Na^+ $B_{10}H_{13}^-$, the bridge resonances became sufficiently well resolved to allow confirmation of their relative intensities as 1:2. There was no evidence of collapse in these two resonances, upon cooling to −30°C. These observations along with the ^{11}B NMR data, leads us to postulate a static 3630 structure, on an NMR time scale. This structure, shown in Fig. 2, appears to fit all the presently available data. The numbering of this structure has been made identical to that of $B_{10}H_{14}$ for convenience. Alternatively, a nonstatic

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6. Similar results were obtained for the bridge resonance in $B_{10}H_{14}$; G. M. Bodner and L. G. Sneddon, *Inorg. Chem.* 9, 1421 (1970).

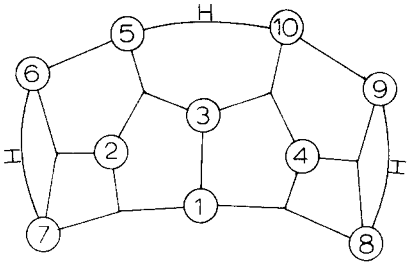

Fig. 2. The proposed structure for the $B_{10}H_{13}^-$ ion in solution.

Table 1. 70·6 MHz ^{11}B chemical shifts[a]

Compound	B(6,9)	B(1)[b]	B(5,7,8,10) B(3)[c]	B(2,4)
$(C_2H_5)_3NH\,[B_{10}H_{13}]$	−6·8 (140)	−2·5 (135)	+5·0 (135)	+35·2 (150)
$(C_2H_5)_3NH\,[1,2,3,4\text{-}B_{10}D_4H_9]$	−6·8	−2·2	+5·0	+35·4
$(C_2H_5)_3NH\,[2,4\text{-}B_{10}I_2H_{11}]$	−6·5	−6·5	(+1·3, +3·6)	+40·4
$(C_2H_5)_3NH\,[\mu_3,5,6,7,8,9,10\text{-}B_{10}D_9H_4]$	−6·5	−2·6	+5·0	+35·2
$(C_2H_5)_3NH\,[6\text{-}PhCH_2B_{10}H_{12}]$	(−16·5[d], −8·8)	−1·9	(+4·4, +6·5)	(+33·8, +35·8)

[a] In acetonitrile; relative to $BF_3 . O(C_2H_5)_2 = 0$ ppm.
[b] or B(3).
[c] or B(1).
[d] B(6).

structure may be envisioned in which rapid hydrogen exchange occurs on only one side of the ion such that B(1) and B(3) remain non equivalent. A single crystal X-ray study of $B_{10}H_{13}^-$ is now underway in this department in an attempt to elucidate the solid state structure of this ion.

EXPERIMENTAL

^{11}B NMR spectra were recorded on a Varian HR-220 spectrometer with digitized frequency sweep. Chemical shifts were calibrated with an external capillary and are reported in ppm from $BF_3 \cdot O(C_2H_5)_2$, ±0·15 ppm.

6-Benzyldecaborane[7], $1,2,3,4\text{-}B_{10}D_4H_{10}$[8], $\mu_4\text{-}5,6,7,8,9,10\text{-}B_{10}D_{10}H_4$[8] and $2,4\text{-}B_{10}I_2H_{12}$[9] were prepared by literature methods and converted to the corresponding $B_{10}H_{13}^-$ salts with triethylamine[1].

$(C_2H_5)_3NH^+\ 6\text{-}C_6H_5CH_2B_{10}H_{12}^-$

To 1·05 m-mole 6-benzyldecaborane in 8 ml dry benzene was added under nitrogen with stirring 1·0 m-mole triethylamine in 2 ml benzene, whereupon a yellow oil separated. Cooling and trituration with benzene–heptane induced the formation of nearly white, air sensitive crystals which were collected on a filter and dried *in vacuo*, wt. 0·27 gm, m.p. 97° (dec.), λ_{max} (CH_3CN) 326 nm (7700). *Anal.* Calcd. for $C_{13}H_{35}NB_{10}$: C, 49·84; H, 11·18. Found: C, 49·15; H, 1158.

A sample of this salt was dissolved in dichloromethane and treated with anhydrous hydrogen

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8. J. A. Dupont and M. F. Hawthorne, *J. Am. chem. Soc.* **84**, 1804 (1962).
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chloride. A white precipitate formed and was removed by filtration. Evaporation of the filtrate under nitrogen afforded a white solid which was sublimed *in vacuo* (50°/0·001 mm). The melting point and infrared spectrum of this recovered benzyldecaborane were identical with that of the starting material.

$(C_2H_5)_3NH^+$ 2,4-$B_{10}H_{11}I_2^-$

To 0·187 g (0·5 m-mole) 2,4-$B_{10}H_{12}I_2$ suspended in 2·5 ml acetonitrile was added with stirring 0·05 g (0·5 m-mole) triethylamine in 0·5 ml acetonitrile. The iododecaborane dissolved and the solution became yellow. Concentration of this solution and addition of cyclohexane produced 0·22 g of yellow oil which was separated and dried *in vacuo* for 24 hr. The product was very sensitive to moisture. All attempts to induce crystallization failed. *Anal*: Calcd. for $C_6H_{27}NI_2B_{10}$: C, 15·16; H, 5·68; B 22·73. Found: C, 15·33; H, 5·95; B, 23·29.

Acknowledgements—We are grateful to W. C. Jankowski for preliminary 32 MHz ^{11}B spectra, to Professor A. D. Norman for communicating some of his results prior to publication, and to A. O. Clouse for help in obtaining the spectra. The ^{11}B NMR probe for the HR-220 spectrometer was made available through Grant GP-10483 from the National Science Foundation. This work was supported in part by the Office of Naval Research.