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High Field (360 MHz) Proton Nuclear Magnetic Resonance Spectra of the Octahydrotriborate (1–) Ion, $[B_3H_8]^-$, and its Monosubstituted ($[B_3H_7X]^-$) and Disubstituted ($[B_3H_6X_2]^-$) Derivatives

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Abstract

Examination of the high field (360 MHz) proton NMR spectra of the octahydrotriborate (1–) ion, $[B_3H_8]^-$, and its mono and disubstituted derivatives using the line-narrowing technique has shown that the spectral line shapes are best interpreted on the basis of partial quadrupolar relaxation. The extent of quadrupolar decoupling increased with increasing substitution, and with substituents in the order $H < Cl < NCBH_3 \leqslant NCS$. Quadrupolar decoupling was more extensive in the weakly polar $CDCl_3$ than in the more polar CD_3CN.

Introduction

Although the ^{11}B NMR spectrum and parameters of the octahydrotriborate (1–) ion, $[B_3H_8]^-$, have been described previously in some detail [1–3], the corresponding ^1H spectrum has been reported only as a broad resonance having some unresolved fine structure resulting from $^1H-^{11}B$ coupling [3, 4]. The ^{11}B spectra of the substituted ions $[B_3H_7X]^-$ and $[B_3H_6X_2]^-$ have been interpreted on the basis of fluxional species in which partial quadrupolar relaxation was important in determining the observed line shapes of the multiplets [5, 6]. Their proton spectra have not been reported previously.

It was of interest, therefore, to examine the ^1H spectra of $[B_3H_8]^-$ and its derivatives $[B_3H_7X]^-$ and $[B_3H_6X_2]^-$ under high field conditions with the additional resolution obtainable from the line-narrowing technique to see if the factors which were proposed to influence the ^{11}B spectra also applied to the ^1H spectra, and to compare the spectral parameters from each nucleus.

Experimental

Reagents and Compounds

$[NMe_4][B_3H_8]$ was purchased from Callery Chemical Co., and recrystallized before use. $[N(PPh_3)_2]^+$ salts of $[B_3H_7Cl]^-$, $[B_3H_7(NCBH_3)]^-$ and $[B_3H_7(NCS)]^-$ were prepared as previously described [7], as were those of $[B_3H_7(NCO)]$, $[B_3H_6Cl_2]^-$, $[B_3H_6Cl(NCS)]^-$ and $[\{B_3H_6Cl(NC)\}_2\text{-}Ag]^-$ [6].

NMR Spectra

^1H NMR spectra (360 MHz) were recorded as solutions in $CDCl_3$ or CD_3CN on a Brüker WH 360 spectrometer. Lock was achieved with the deuterated solvent. Spectra were obtained at ambient temperature unless stated otherwise. Chemical shifts are quoted as being positive to low field of the reference standard, tetramethylsilane. Spectra of the substituted derivatives were, in general, recorded in the modes ^1H, $^1H\{^{11}B$, off resonance$\}$, $^1H\{^{11}B$, broad band$\}$, and $^1H\{^{11}B$, continuous wave$\}$ at specific boron resonances. Resolution was enhanced by selecting appropriate values for the GB and LB parameters for data manipulation prior to transforming the F.I.D.

Results

The Octahydrotriborate (1–) Ion, $[B_3H_8]^-$

The ^1H NMR spectrum in CD_3CN of $[B_3H_8]^-$ with line-narrowing is presented in Fig. 1. It can be seen that the spectrum consists of a complex multiplet at $\delta = 0.175$ ppm which may be interpreted as arising from $^1H-^{11}B$ and $^1H-^{10}B$ couplings from various isotopic species. By considering the relative abundances of ^{11}B and ^{10}B and the probabilities of each occurring in a B_3 unit, the relative abundances of the isotopic species $^{11}B_3$, $^{11}B_2{}^{10}B$, $^{11}B^{10}B_2$ and $^{10}B_3$ are 64, 48, 12 and 1, respectively. In view of the small contributions from the species $^{11}B^{10}B_2$ and

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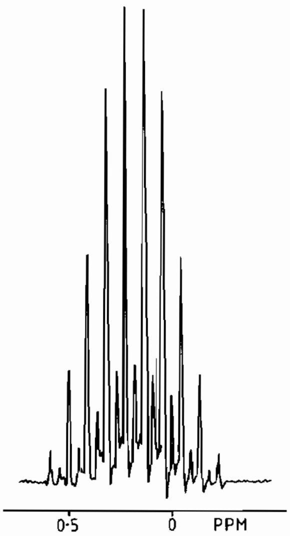


Fig. 1. 360 MHz ^1H NMR spectrum of $[B_3H_8]^-$ (line-narrowed).

$^{10}B_3$, only the isotopic species $^{11}B_3$ and $^{11}B_2{}^{10}B$ need to be considered for the analysis of the line shape of the multiplet.

The eight equivalent hydrogens coupling to three equivalent boron nuclei of spin quantum number 3/2 clearly shows a multiplet of ten lines with relative intensities close to 1:3:6:10:12:12:10:6:3:1. The measured value of $J_{^1H-^{11}B}$ is 32.7 Hz. Further structure, observed between these lines, correlates with eight equivalent hydrogens coupling to two equivalent boron-11 nuclei of spin quantum number 3/2 and further coupling with a boron-10 nucleus of spin quantum number 3 giving rise to a multiplet of twenty five lines of relative intensities 1:1:1:3:3:3:6:5:5:9:7:7:10:7:7:9:5:5:6:3:3:3:1:1:1. These lines are not all observed as some lines are obscured by the more intense lines resulting from ^1H and $^{11}B_3$ coupling. The observed ratio of the coupling constants $J_{(^{10}BH)}/J_{(^{11}BH)}$, is in agreement with the ratio of gyromagnetic ratios, γ, of the boron isotopes:

$$\frac{J_{(^{10}BH)}}{J_{(^{11}BH)}} = \frac{\gamma_{(^{10}B)}}{\gamma_{(^{11}B)}} = \frac{4.575}{13.660} = 0.335$$

Monosubstituted Octahydrotriborate (1–) Ions, $[B_3H_7X]^-$

The $^1H\{^{11}B\}$ NMR spectra of $[B_3H_7(Cl)]^-$ in CD_3CN and $CDCl_3$, obtained with broad band irradiation or continuous wave specific frequency irradiation of the ^{11}B resonances, are presented in Figs. 2 and 3.

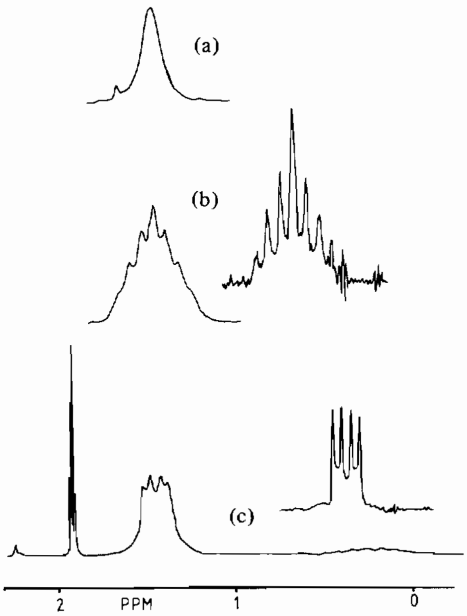


Fig. 2. 360 MHz $^1H\{^{11}B\}$ NMR spectra of $[B_3H_7(Cl)]^-$ in CD_3CN; (a) Broad band irradiated; (b) Irradiation of the substituted boron, B(3); (c) Irradiation of the unsubstituted borons, B(1,2).

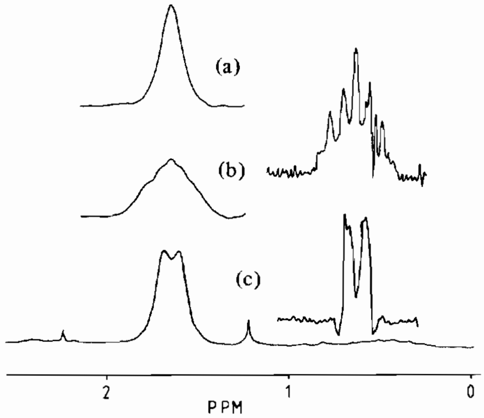
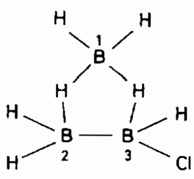


Fig. 3. 360 MHz $^1H\{^{11}B\}$ NMR spectra of $[B_3H_7(Cl)]^-$ in $CDCl_3$; (a) Broad band irradiated; (b) Irradiation of the substituted boron, B(3); (c) Irradiation of the unsubstituted borons, B(1,2).

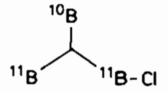
In CD_3CN, the $^1H\{^{11}B$, broad band$\}$ spectrum showed a proton resonance of seven hydrogens at δ = 1.46 ppm. The spectrum resulting from irradiation of the unsubstituted borons B(1) and B(2) [Fig. 2(c)] showed a coupling pattern comprising a partly relaxed 1:1:1:1 quartet which resulted from the remaining coupling of the seven equivalent hydrogens to boron atom, B(3) with an apparent coupling constant $J_{^1H-^{11}B(3)}$ of 18.0 Hz. The coupling pattern



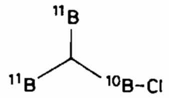
observed on irradiating substituted boron atom B(3) comprises an apparent seven line multiplet of the expected relative intensities 1:2:3:4:3:2:1 with additional fine structure probably resulting from other isotopic species of the B_3 system, together with a trace of impurity. The $J_{^1\text{H}-^{11}\text{B}(1,2)}$ measured was 25 Hz.

There are apparent discrepancies: first, the observed couplings $J_{^1\text{H}-^{11}\text{B}(3)}$ of 18.0 Hz and $J_{^1\text{H}-^{11}\text{B}(1,2)}$ of 25 Hz and second, the couplings observed in the ^{1}H spectra and those derived earlier from the ^{11}B spectra where $J_{^{11}\text{B}-^1\text{H}}$ was found to be 39.0 Hz [5]. These are discussed later.

It should be noted that coupling ^{1}H—^{10}B is less well resolved in $[B_3H_7(Cl)]^-$ than that in $[B_3H_8]^-$, and this is probably due to a decrease in relative abundance of $^{11}B_2{}^{10}B$ unit. The relative abundance of $^{11}B_2{}^{10}B$ reduced from 48 in $[B_3H_8]^-$ to 32 and 16 in $[B_3H_7(Cl)]^-$ due to the substituent as shown below.



relative abundance 32



relative abundance 16

In $CDCl_3$, the ^{1}H {^{11}B} NMR spectra showed more extensive quadrupolar relaxation. This observation is consistent with earlier work [5].

The ^{1}H {^{11}B} NMR spectra of $[B_3H_7(NCS)]^-$ and $[B_3H_7(NCO)]^-$ each showed resonance of seven hydrogens (with respect to the 30 proton resonances of the $[N(PPh_3)_2]^+$ counter ion at $\delta = 7.5$ ppm) at chemical shifts of $\delta = 1.4$ ppm and $\delta = 1.2$ ppm respectively. The ^{1}H {^{11}B} NMR spectra with specific frequency irradiations of the boron resonances did not show any resolvable fine structure due to ^{1}H—^{11}B coupling.

The ^{1}H {^{11}B, noise} NMR spectrum of $[B_3H_7(NCBH_3)]^-$ in CD_3CN showed two resonances, of which that at $\delta = +1.5$ ppm corresponded to seven hydrogens and that of $\delta = 0.4$ ppm corresponded to three hydrogens with respect to the proton resonances at $\delta = 7.5$ ppm of $[N(PPh_3)_2]^+$ containing thirty hydrogens. The ^{1}H {^{11}B}NMR spectra with continuous wave specific frequency irradiation of the ^{11}B resonances presented in Fig. 4 are similar to those of $[B_3H_7(Cl)]^-$ but show a greater degree of quadrupolar relaxation. On irradiating the two unsubstituted boron atoms B(1) and B(2), the spectrum contained a resonance at 0.4 ppm which comprised a 1:1:1:1 quartet of area three, and which arose as a result of the three hydrogens in the H_3BCN moiety coupling with B(4). The coupling constant, $J_{^1\text{H}-^{11}\text{B}(4)}$, is 90 Hz. The resonance at 1.5 ppm of relative intensity seven which had the appearance of a partly relaxed 1:1:1:1 quartet, was assigned to seven fluxional hydrogens coupling to B(3) with $J_{^1\text{H}-^{11}\text{B}(3)}$ of 25.2 Hz. The spectrum resulting from irradiation of the substituted boron, B(3), showed a multiplet of the intensity ratio 1:2:3:4:3:2:1 expected for seven equivalent hydrogens coupling with boron atom B(1) and B(2) and with $J_{^1\text{H}-^{11}\text{B}(1,2)}$ of 36 Hz together with fine structure as discussed in $[B_3H_7(Cl)]^-$. A spike between the apparent seven lines of the multiplet was likely to have resulted from impurities because it also appeared in spectrum shown in Fig. 4(c). On irradiating the boron in the BH_3CN moiety, the spectrum showed a sharp peak corresponding to three hydrogens in H_3BCN moiety and a broad peak of intensity corresponding to seven hydrogens without any structure due to ^{1}H—^{11}B coupling within the B_3 moiety. A spike of impurities was also observed in the broad peak.

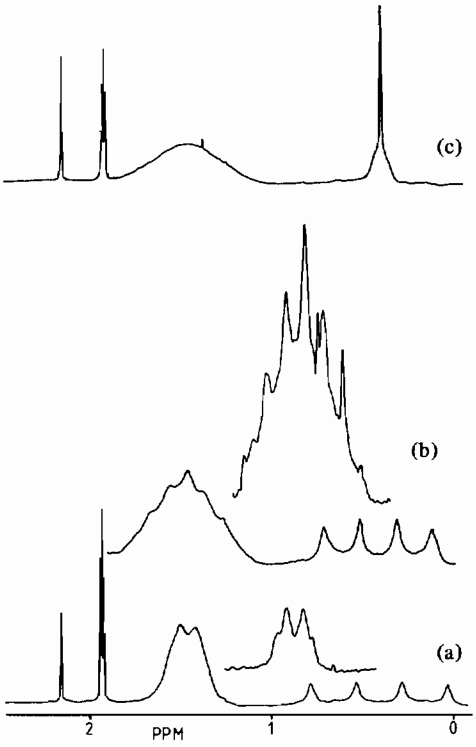
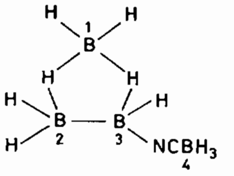


Fig. 4. 360 MHz ^{1}H {^{11}B} NMR spectra of $[B_3H_7(NCBH_3)]^-$ in CD_3CN; (a) Irradiation of the unsubstituted borons, B(1,2); (b) Irradiation of the substituted boron, B(3); (c) Irradiation of substituent boron, B(4).



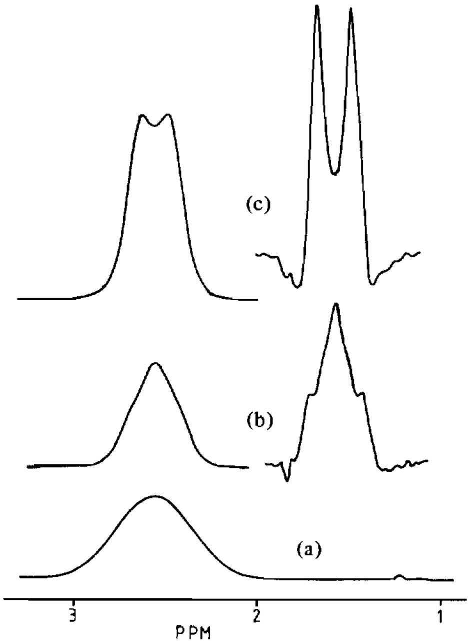
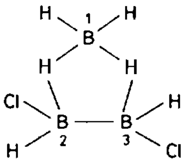


Fig. 5. 360 MHz $^1H\{^{11}B\}$ NMR spectra of $[B_3H_6(Cl)_2]^-$ in $CDCl_3$; (a) Irradiation off-resonance; (b) Irradiation of the unsubstituted boron, B(1); (c) Irradiation of the substituted borons, B(2,3).

Disubstituted Octahydrotriborate (1–) Ions, $[B_3H_6X_2]^-$

The $^1H\{^{11}B\}$ NMR spectra of $[B_3H_6(Cl)_2]^-$ in $CDCl_3$ obtained with off-resonance or continuous wave specific frequency irradiation of the ^{11}B resonances are given in Fig. 5. The $^1H\{^{11}B$, off resonance$\}$ spectrum showed a broad band (δ = 2.57 ppm) corresponding to six hydrogens with respect to the thirty hydrogens in the $[N(PPh_3)_2]^+$ counter-ion (δ = 7.5 ppm). The proton spectrum resulting from irradiation of the unique unsubstituted boron atom, B(1) [Fig. 5(b)] shows a resonance of relative intensity of six equivalent hydrogens with fine structure corresponding to coupling to the remaining two boron atoms, B(2) and B(3). The coupling pattern was distorted from the theoretical 1:2:3:4:3:2:1, probably as a result of a quadrupolar relaxation effect. On irradiating the substituted boron atoms, B(2) and B(3), the remaining coupling of the six equivalent hydrogens with boron atom B(1) would be expected to be a 1:1:1:1 quartet. However, it is shown in Fig. 5(c) that the quartet has collapsed to a broad doublet with an apparent coupling constant of 65 Hz.



The $^1H\{^{11}B$, broad band$\}$ NMR spectrum of $[N(PPh_3)_2][\{B_3H_6(Cl)(NC)\}_2Ag]$ in $CDCl_3$ showed proton resonances at δ = 7.5 ppm with relative area thirty and at δ = 2.24 ppm with relative area twelve which corresponded to the hydrogens in $[N(PPh_3)_2]^+$ and those in the $[\{B_3H_6(Cl)(NC)\}_2Ag]^-$ anion. The specific frequency irradiation at each unique boron did not show any fine structure attributable to coupling between hydrogen and boron.

The relevant ^1H NMR parameters for the octahydrotriborate derivatives are presented in Table I.

Discussion

Quadrupolar Relaxation

The ^1H NMR spectra of the octahydrotriborate (1–) ion, and its mono- and disubstituted derivatives

TABLE I. ^1H NMR Data for Octahydrotriborate (1–) Derivatives at 360 MHz.

Compound	(^1H)/ppm	$J_{^1H-^{11}B}$/Hz	Solvent
$[B_3H_8]^-$	+0.175	$^1H-^{11}B$ = 32.7 $^1H-^{10}B$ = 10.96	CD_3CN
$[B_3H_7(Cl)]^-$	+1.46	H–B(3) = 18.0 H–B(1,2) = 25.0	CD_3CN
$[B_3H_7(Cl)]^-$	+1.63		$CDCl_3$
$[B_3H_7(NCS)]^{-a}$	+1.4		CD_3CN
$[B_3H_7(NCO)]^-$	+1.22		$CDCl_3$
$[B_3H_7(NCBH_3)]^-$	+1.5	H–B(3) = 25.2 H–B(1,2) = 36 H–B(4) = 90	CD_3CN
$[B_3H_6(Cl)_2]^-$	+2.57	H–B(1) = 65	$CDCl_3$
$[B_3H_6(Cl)(NCS)]^-$	+2.30		$CDCl_3$
$[\{B_3H_6(Cl)(NC)\}_2Ag]^-$	+2.24		$CDCl_3$

[a] At 303 and 220 K.

reveal that previously reported [5, 6] effects of substituents and solvent polarity on quadrupolar relaxation in the ^{11}B studies also apply to these studies. The effect of substituents, shown in the ^{1}H NMR spectra of $[B_3H_7(Cl)]^-$ and $[B_3H_7(NCBH_3)]^-$, is that more extensive quadrupolar decoupling was observed in $[B_3H_7(NCBH_3)]^-$ than in $[B_3H_7(Cl)]^-$. This is in agreement with previous studies of the ^{11}B NMR spectra of these compounds. The effects of solvent polarity, demonstrated in the ^{11}B NMR spectra of $[B_3H_7Cl]^-$ and $[B_3H_6(Cl)_2]^-$, are also exhibited in the ^{1}H NMR spectra of $[B_3H_7(Cl)]^-$ in different solvents such as CD_3CN or $CDCl_3$. The results support previous observations [5] that greater quadrupolar relaxation was found in the less polar solvent, $CDCl_3$.

In general a comparison of the ^{11}B or ^{1}H NMR spectra of $[B_3H_7(Cl)]^-$ with those of $[B_3H_6(Cl)_2]^-$ and the spectra of $[B_3H_7(NCS)]^-$ with those of $[B_3H_6(Cl)(NCS)]^-$ showed that the quadrupolar decoupling effect is greater in disubstituted derivatives than in monosubstituted derivatives. Presumably this was due to the presence of an additional substituent, Cl^-, in which the chlorine ($I = 3/2$) possesses an electric quadrupole moment, capable of causing fluctuating electric-field gradients and therefore possibly increases the rate of relaxation of coupled boron or proton nuclei. Furthermore, addition of a chlorine atom to the molecule increases the size of the molecule such that the tumbling motion is slowed and hence the correlation time of the molecule in solution is increased and the electric-field gradients around boron or proton nuclei become more effective in the quadrupolar relaxation mechanism.

Coupling Constants

The ^{11}B–^{1}H coupling constants observed in the ^{11}B NMR spectra of $[B_3H_7(X)]^-$ ($X = Cl^-, NCS^-, NCBH_3, NC^-$)[≠] were reported [5] to be in the range of 38.0–40.0 Hz. However, in this work, the coupling constants measured from the ^{1}H NMR spectra appeared to be different from one anion to another, and even in an individual anion the coupling constants resulting from protons coupling with different borons were different (Table I). It can be seen that in ^{1}H NMR spectra of $[B_3H_7(Cl)]^-$ and $[B_3H_7(NCBH_3)]^-$, the ^{1}H–^{11}B coupling constants observed are smaller than those observed in ^{11}B NMR spectra whereas in the ^{1}H NMR spectra of $[B_3H_6(Cl)_2]^-$, the ^{1}H–^{11}B coupling constant observed is larger than that observed in ^{11}B NMR spectrum. The discrepancies possibly could arise as a result of several factors. (a) The data were obtained from ^{1}H{^{11}B, C.W.} spectra, in which one of the two boron resonances was irradiated with sufficient power to cause decoupling of the protons attached to that specific boron atom. It may not be possible experimentally to decouple one boron resonance without simultaneously affecting the other, and as a result, any ^{1}H–^{11}B coupling constants may be unreliable. It can be seen that the chemical shift difference between the boron resonances in $[B_3H_7(NCBH_3)]^-$ is greater than those in either $[B_3H_7Cl)]^-$ or $[B_3H_6(Cl)_2]^-$; as a result, the discrepancies in coupling constants obtained from the ^{11}B and ^{1}H{^{11}B} NMR spectra are found to be greater in $[B_3H_7(Cl)]^-$ and $[B_3H_6(Cl)_2]^-$ than in $[B_3H_7(NCBH_3)]^-$. Furthermore, the discrepancies are also found to be greater when resonance containing two equivalent boron atoms was irradiated than on irradiating that of the unique boron atom. (b) A further factor may involve the fluxional nature of the compounds. All the hydrogens are fluxional, and hence spin couple equally to all three boron atoms. The observed coupling constant must result from contributions to coupling involving all three atoms. If one or two of these are subsequently decoupled by double irradiation, then it is likely that the observed coupling constant to the remaining (unirradiated) boron atoms will be affected.

Acknowledgements

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[≠] In $[\{B_3H_7(NC)\}_2Ag]^-$ complex.