Student Corner

^{11}B NMR Spectroscopy

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Boron hydrides are known as electron deficient compounds. There are two NMR active isotopes (*e.g.*, ^{10}B and ^{11}B). Boron-11 NMR spectroscopy is widely used to find out molecular structures and exchange processes of boron hydrides. ^{11}B is 750 times more receptive than ^{13}C. Some properties of the two isotopes of boron are given in Table 1.

Table 1. Properties of boron isotopes

Property	^{10}B	^{11}B
Natural abundance (%)	19.4	80.6
Nuclear spin, I	3	$\frac{3}{2}$
Magnetic moment, μ	1.8005	2.688
Operating frequency in MHz at 2.35 Tesla	10.7	32.1
Relative receptivity (*c.f.* H = 1.00)	0.0199	0.165
Electrical quadrupole moment x 10^{26} (cm^2)	7.4	3.55
Gyromagnetic ratio x 10^{-7} rad T^{-1} s^{-1}	2.87	8.58

NMR spectra give rise to **broad signals** due to the presence of quadrupole moments in boron nuclei. When compared to properties of ^{10}B, ^{11}B generates much better NMR spectra. For example, a proton attached to ^{10}B nucleus gives rise to seven lines of equal intensity (**2nI+1** = $2 \times 1 \times 3 + 1 = 7$); thus, the proton resonances of ^{10}B compounds are rarely observed.

Chemical shifts

Boron hydrides can be grouped into three main classes; (i) $B_nH_n^{2-}$ - *closo*, (ii) B_nH_{n+4} - *nido*, and (iii) B_nH_{n+6} - *arachno*. *Arachno* compounds are more open and more reactive than *nido* and *closo* compounds. Boron compounds contain specific bonds such as (i) (2-centre-2-electron) bonds such as B-B and B-H$_t$ bonds (t = terminal), and (ii) (3-centre-2-electron) bonds such as B-H$_\mu$-B and BBB (linear and triangular) bonds.

Structures of *nido*-B_2H_6 (**1**), *arachno*-$B_3H_8^-$ (**2**), *nido*-B_5H_9 (**3**), *closo*-$B_6H_6^{2-}$ (**4**) and *closo*-$B_{12}H_{12}^{2-}$ (**5**) are given in Fig.1.
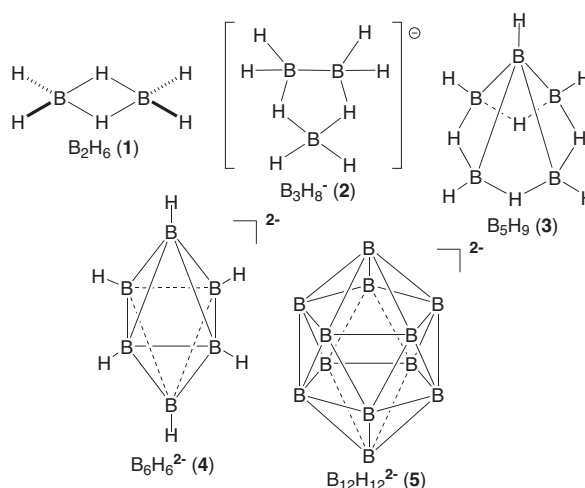
Figure 1. Structures of some boron hydrides; H atoms in (**5**) are omitted for clarity

Boron-11 and proton chemical shifts and coupling constants very much depend on the connectivity and the types of bonds around each atom. Some of the chemical shifts and ^{1}J(BH) values are given in Table 2.

Table 2 : Chemical shifts (δ_B) and coupling constants, ^{1}J(BH).

Compound/ion	δ_B/ppm	^{1}J(BH)/Hz
$Et_2O \cdot BF_3$	0	0
BH_4^-	-39	82
nido-B_2H_6 (**1**)	17	135,45
arachno-$B_3H_8^-$ (**2**)	29	35
nido-B_5H_9 (**3**)	-51.8(apical)	176
	12.7 (basal)	166
closo-$B_6H_6^{2-}$ (**4**)	13	122
closo-$B_{10}H_{10}^{2-}$ (**5**)	0.7 (apical)	138
	28.9 (basal)	125
closo-$B_{12}H_{12}^{2-}$ (**6**)	14	115
$Et_3N \cdot BH_3$	-12	98
$PhMe_2P \cdot BH_3$	-37	100

The chemical shift range of ^{11}B compounds varies from 200 to -200 ppm. $Et_2O \cdot BF_3$ is used as the reference compound.

The proton chemical shifts (δ_H) of boron compounds are given in Table 3.

Table 3 : δ_H Values of boron compounds

Type	δ_H-range/ppm
B-H (terminal)	5 to 0
B-H_μ-B (bridging)	0 to -5
B-H_μ-M (bridging)	-5 to -20

Coupling constants

The one-bond coupling constants $^1J(BH_t)$ values are in the range of 100 to 190 Hz whereas $^1J(BH_\mu)$ are less than 50 Hz, *i.e.*, $^1J(BH_t) > ^1J(BH_\mu)$. Quadrupole effect causes broadening the signals and $^1J(BB)$, $^1J(BH_\mu)$ and $^2J(H_tH_\mu)$ values are not usually resolved.

NMR spectra of boron compounds

Let us look at the simplest and stable borate ion, BH_4^-.

Tetrahydroborate (-1) BH_4^-

Tetrahydroborate anion is isoelectronic and isostructural with CH_4. It has the tetrahedral geometry, and four protons are equally coupled to B. The ^{11}B NMR spectrum gives a 1:4:6:4:1 **quintet** with $^1J(BH) = 82$ Hz.

A normal boron sample contains 80% of $^{11}BH_4^-$ and 20% of $^{10}BH_4^-$. In the ^1H NMR spectrum, proton signal due to $^{11}BH_4^-$ is a 1:1:1:1 **quartet** ($2nI+1 = 2 \times 1 \times \frac{3}{2} + 1 = 4$), while that of $^{10}BH_4^-$ is 1:1:1:1:1:1:1 septet ($2nI+1 = 2 \times 1 \times 3 + 1 = 7$). A proton spectrum with both components is shown in Fig. 2.
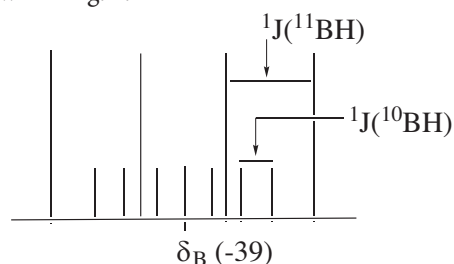

Figure 2. ^1H NMR spectrum of BH_4^-. Larger four lines are for $^{11}BH_4^-$ and smaller seven lines are for $^{10}BH_4^-$

nido-**Diborane (6) B_2H_6**

B_2H_6 (**1**) (Fig. 1) is a symmetrical molecule having C_2-axes and an inversion centre. In the ^{11}B NMR spectrum, the two boron nuclei are equivalent and each one is coupled to two equivalent terminal hydrogen atoms (H_t) and two equivalent bridging hydrogen atoms (H_μ), {Note that $^1J(BH_t) > ^1J(BH_\mu)$}.

Coupling of two terminal hydrogen generates a larger (1:2:1) triplet ($2nI+1 = 2 \times 2 \times \frac{1}{2} + 1 = 3$); each line is again split by two bridging hydrogens into a smaller 1:2:1 triplet. Thus, the ^{11}B NMR spectrum of (**1**) is a triplet of triplets as shown in Fig. 3.
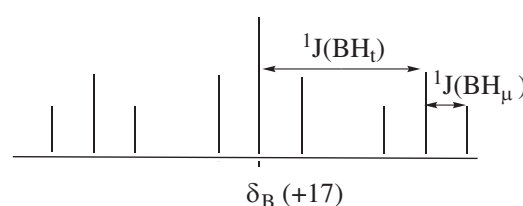

Figure 3. ^{11}B NMR spectrum of B_2H_6

The ^1H NMR spectrum of B_2H_6 consists of two signals where one is due to four equivalent terminal protons. Each H_t is coupled to one boron atom giving a 1:1:1:1 quartet ($2nI+1 = 2 \times 1 \times \frac{3}{2} + 1 = 4$) and the second signal is due to two equivalent bridging hydrogens, each one is coupled to two boron atoms giving a 1:2:3:4:3:2:1 seven-line multiplet ($2nI+1 = 2 \times 2 \times \frac{3}{2} + 1 = 7$).
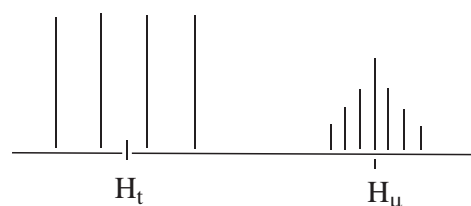

Figure 4. ^1H NMR spectrum of B_2H_6

arachno-**Octahydrotriborate (-1) $B_3H_8^-$**

$B_3H_8^-$ (**2**) (Fig. 1) possesses a plane of symmetry and it contains two different types of boron nuclei (2:1 ratio) and three proton environments in the ratio of 2:4:2. If $B_3H_8^-$ was not fluxional, the ^{11}B NMR spectrum might show a doublet of triplets for the two equivalent boron atoms and a triplet of triplets for the other boron atom. In this case, the ^1H NMR spectrum (**2**) might show two (1:1:1:1) quartets for the two types of terminal hydrogen

atoms, and a complex multiplet for the two equivalent bridging hydrogen atoms.

However, the observed ^{11}B and ^{1}H NMR spectra are simplified, as $B_3H_8^-$ is found to be **highly fluxional** in solution at room temperature. Those NMR spectra are in agreement with an anion containing *one type of boron nuclei and one type of protons* because protons exchange their positions (terminal ↔ bridging) rapidly. As a result, all three boron nuclei have also become equivalent due to rapid movement of the **B-B** bond among the three boron atoms as shown in Fig. 5.

Proton exchange is extremely fast and at a given time each proton is coupled to all three boron atoms and each boron atom is coupled to all protons. In other words, all hydrogen atoms appear to be equivalent and all the boron atoms appear to be equivalent.
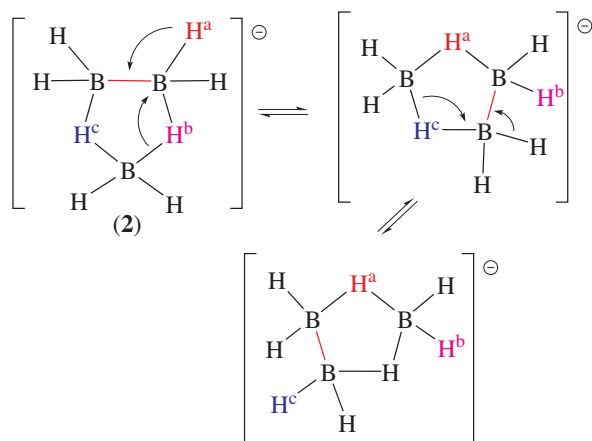
Figure 5. Rotation of the B-B bond *via* exchange of H_t and H_μ

Thus, ^{11}B NMR spectrum shows a binomial nonet as predicted by the (n+1) rule, with an average ^{1}J(BH) value of 35 Hz, and the proton resonance consists of a broad 10-line multiplet (2nI+1 = 2 × 3 × ³⁄₂ + 1 = 10).

nido-Pentaborane (9) B_5H_9

B_5H_9 (**3**) has a four-fold rotational axis passing through the apical boron atom. There are two types of boron atoms (1:4 ratio) and three types of protons - apical H_t, four basal H_t and four bridging hydrogen atoms (H_μ). Bridging hydrogens exchange rapidly along the open basal frame.
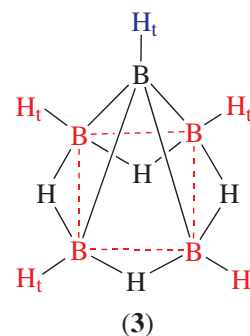
Figure 6. Square pyramidal shape of (**3**)

The ^{11}B NMR spectrum of (**3**) shows a broad doublet at 51.8 ppm with ^{1}J(BH$_t$) = 176 Hz for the apical boron atom. The high-field boron chemical shift of –51.8 ppm is characteristic of a shielded apical boron atom. In the ^{11}B NMR spectrum, the basal boron atoms give rise to a broad doublet at 12.7 with ^{1}J(BH$_t$) = 166 Hz. The proton-decoupled ^{11}B NMR (*i.e.*, **^{11}B{^{1}H}** NMR) spectrum shows a 1:1:1:1 quartet with ^{1}J(BB) = 19.5 Hz for basal boron atoms.

Let us consider the NMR spectra of the carborane, 1,6-Me$_2$-*closo*-1,6-C$_2$B$_4$H$_4$ (**6**).
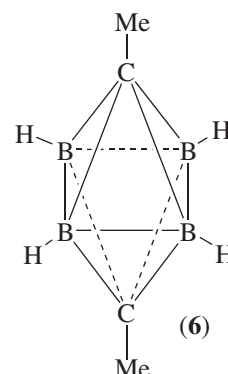
It is a symmetrical molecule and it has only one type of boron atoms and two types of hydrogens. The ^{11}B NMR spectrum of (**6**) shows a doublet as ^{3}J(BH) = 0 Hz. The ^{1}H NMR spectrum shows a singlet and a 1:1:1:1 quartet in the ratio of 6:4 for the methyl and BH groups, respectively.

Q: Thiaborane, SB$_4$H$_{10}$ (**7**) is one of the products of the reaction between B$_2$H$_6$ with H$_2$S. The ^{11}B NMR spectrum of (**7**) shows a triplet of doublets with ^{1}J(BH) = 140 Hz and 40 Hz, where the large coupling corresponds to the triplet. Determine the structure of (**7**) and comment on the NMR spectrum.

A: The ^{11}B NMR spectrum of (**7**) suggests all B atoms to be chemically equivalent. Each B atom has two terminal hydrides as the larger coupling with $^1J(BH) = 140$ Hz corresponds to a triplet (see Table 1). Each B atom is also connected to another bridging hydride as the smaller coupling corresponds to a doublet with $^1J(BH) = 40$ Hz. The structure of (**7**) is as shown in Fig. 7.

(7)
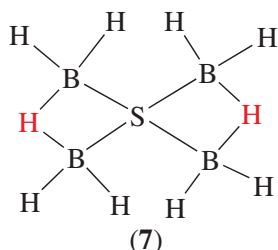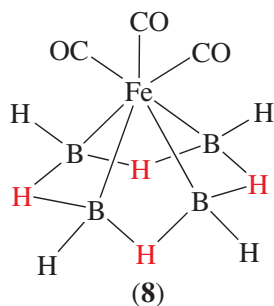
Figure 7. The structure of (**7**)

Let us consider the ^{11}B NMR spectrum of metallaborane $1,1',1''-(OC)_3-1-FeB_4H_8$ (**8**)

(8)

It is a symmetrical molecule and it has only one type of boron atoms. If it is not fluxional, the ^{11}B NMR spectrum might show a doublet of triplets where the large coupling corresponds to the doublet.

Problems

1. Predict the ^{11}B and ^{1}H NMR spectra of $(\mu\text{-}X)B_2H_5$, where I = 0 for X.

2. Predict the ^{11}B NMR spectrum of $2\text{-}ClB_5H_8$. Indicate the assumption that you have made.

3. Predict the ^{11}B and ^{1}H NMR spectra of $closo\text{-}1,2\text{-}C_2B_4H_6$.

4. Predict the ^{11}B and ^{1}H NMR spectra of closo $B_6H_6{}^{2-}$.

5. Predict the ^{11}B and ^{1}H NMR spectra of $ortho$-carborane, $closo\text{-}1,2\text{-}C_2B_{10}H_{12}$.

6. Predict the ^{11}B NMR spectrum of $nido\text{-}B_{10}H_{14}$. state the assumption that you have made.

7. Predict the ^{11}B NMR and ^{19}F NMR spectra of $^{11}BF_3$ (isotopically enriched).