

A ^{13}C NMR STUDY ON SOME PHENYLBORANE DERIVATIVES

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Summary

The intensity of ^{13}C NMR signals of carbon atoms bonded to boron can frequently be increased by recording the spectra at low temperatures. Though this procedure results in a loss of fine structure, it enables the determination of chemical shift data for NMR signals that are either broad or unobservable at ambient temperature. On the other hand, high temperature recording of spectra seems to be a useful technique for resolving multiplet resonance signals that are collapsed in ambient temperature spectra. ^{13}C NMR data are reported for a variety of phenylborane derivatives; no simple correlation seems to exist between $\delta^{13}\text{C}$ of the phenyl carbon atom bonded to boron and $\delta^{11}\text{B}$ of the phenylborane species.

Introduction

Very few ^{13}C NMR data on organoboranes are known though it appears that Fermi contact shift is a major factor in governing ^{11}B — ^{13}C coupling constants [1] and that a linear correlation exists between the chemical shifts $\delta^{13}\text{C}$ and $\delta^{11}\text{B}$ of methylborane derivatives [2]. This latter observation suggests that, in the absence of ^{11}B NMR data, $\delta^{13}\text{C}$ of boron-bonded carbon may provide an indication of the shielding of the adjacent boron atom in organoborane species. There is even some limited evidence available that a linear correlation exists between $\delta^{13}\text{C}$ and $\delta^{11}\text{B}$ of several trimethylamine-boranes, $(\text{CH}_3)_3\text{NBXX}'\text{X}''$ [3].

The majority of the spectra of organoboranes obtained by direct ^{13}C NMR techniques exhibit the boron-attached carbon atoms as a broad singlet or as a partially collapsed quartet [4–6]; in some cases, boron-bonded carbon could not be observed at all [5]. The available data also suggest that the more symmetrical the environment of a boron atom bonded to carbon, the more likely it is that a well-defined quartet will be observed for these carbon atoms.

The present work is concerned primarily with a study of ^{13}C NMR spectra of several phenylborane derivatives. The tetraphenylborate ion, $[\text{B}(\text{C}_6\text{H}_5)_4]^-$, is the only representative of this class of compounds where the ^{13}C NMR spectrum has heretofore been recorded [7–9].

Results and discussion

Initial attempts to obtain a complete ^{13}C NMR spectrum of triphenylborane, $\text{B}(\text{C}_6\text{H}_5)_3$, gave only the resonance signals of the *ortho*, *meta*, and *para* carbon atoms of the phenyl groups. Utilizing a pulse delay of 60 seconds it was, however, possible to locate the boron-bonded carbon atoms of triphenylborane as a broad and low-intensity singlet; longer pulse delays showed no enhancement of this latter signal. The addition of chromium(III) acetylacetonate as relaxation agent [10,11] to the triphenylborane sample approximately doubled the intensity of the signal of the *para* carbon atoms but did not affect the intensity of the signal due to the boron-bonded carbon atoms.

The wide range of line shapes of the ^{13}C resonance signals of organoboranes observed in the present work as well as in earlier reports is reminiscent of the variable temperature behavior predicted from theoretical considerations for a proton bonded to a nucleus with a spin of $3/2$ [20–23] and observed experimentally for $(-\text{BH}-\text{NCD}_3-)_3$ [24] and in the long-range coupling between boron and hydrogen of some amine-haloboranes and dihaloboronium salts [12]. Therefore a variable-temperature study of the ^{13}C NMR spectrum of a suitable organoborane was undertaken. Triethylborane, $\text{B}(\text{C}_2\text{H}_5)_3$, was selected as sample compound since it is a liquid over a wide temperature range and the ambient temperature ^{13}C NMR spectrum of the compound is an almost completely collapsed quartet with an estimated coupling constant $J(\text{BC})$ of approximately 52 Hz [6]. The line shapes observed for the boron-bonded carbon atoms in the ^{13}C NMR spectrum of triethylborane at six temperatures ranging from -50°C to $+132^\circ\text{C}$ are illustrated in Fig. 1. It is apparent that high temperatures promote the recognition of fine structure and, at $+132^\circ\text{C}$, the expected quartet is clearly evident; the two central peaks exhibit a separation of about 60 Hz and from their corresponding outside peaks the separation is about 40 Hz. On the other hand, low temperature causes a collapse of fine structure which is, however, accompanied by an increase in the line intensity; at -50°C only a reasonably sharp singlet of enhanced intensity can be seen for the boron-bonded carbon atoms of triethylborane. Line contour calculations for the collapse of a multiplet produced from the coupling of a ^1H nucleus with nuclei of spin $I = 1, 3/2, 2, 5/2$ or 3 illustrate that with increasing correlation time for the molecule the collapse proceeds with an initial broadening of the resonance signals and a shift in the maxima, followed by overlapping of peaks as they merge into fewer diffuse peaks and ultimately into a singlet; for a quartet ($I = 3/2$, i.e., ^{11}B) the outer peaks collapse faster than the inner peaks [21]. The present variable temperature study of triethylborane is an experimental demonstration of the theoretically predicted collapse of a quartet though, in this case, it is produced from the coupling of a ^{11}B nucleus to ^{13}C instead of ^1H .

In the present work on phenylboranes, all of the studied derivatives gave either signals of low intensity or no signal whatsoever for the boron-attached carbon atom of the phenyl groups at ambient temperature. In all cases the observed signals could be enhanced, and in most cases where no signal whatsoever was observed at room temperature a broad and low-intensity signal was found, by increasing the correlation times of the molecules as a result of recording the spectra at low temperature.

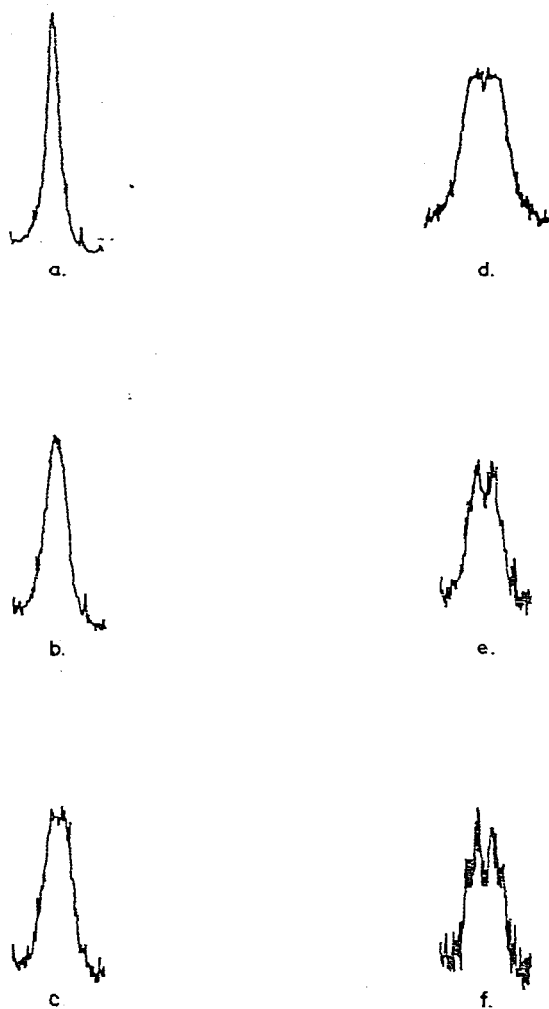


Fig. 1. Line shape of the ^{13}C NMR signal of boron-bonded carbon of triethylborane at various temperatures (in $^{\circ}\text{C}$): (a) = -50 ; (b) = -26 ; (c) = 0 ; (d) = $+36$; (e) = $+71$; (f) = $+132$.

The increase in the signal intensity of the ^{13}C NMR signal of boron-bonded carbon atoms at low temperature is exemplified by the ^{13}C NMR spectrum of (bromo)diphenylborane as shown in Fig. 2. At ambient temperature the cited signal is barely recognizable whereas at -53°C it becomes even more intense than that due to the *para* carbon atoms of the phenyl rings.

The technique of increasing the intensity of a ^{13}C NMR signal by lowering the recording temperature permits the observation of the boron-bonded carbon atoms of a variety of phenylborane derivatives such as $(2\text{-H}_2\text{N-C}_5\text{H}_4\text{N})\text{B}(\text{C}_6\text{H}_5)_3$, $\text{C}_6\text{H}_5\text{B}[\text{N}(\text{CH}_3)_2]_2$, $\text{C}_6\text{H}_5\text{B}(\text{-NCH}_3\text{-CH}_2\text{-})_2$, and $\text{C}_6\text{H}_5\text{B}(\text{-NCH}_3\text{-CH}_2\text{-})_2\text{CH}_2$. At ambient temperature, no resonance signal can be observed for the boron-attached carbon atoms of these compounds; however, at low temperature, an additional broad singlet appears in each spectrum and can be assigned to the resonance signal of the cited carbon atoms. The procedure used to evaluate the low tempera-

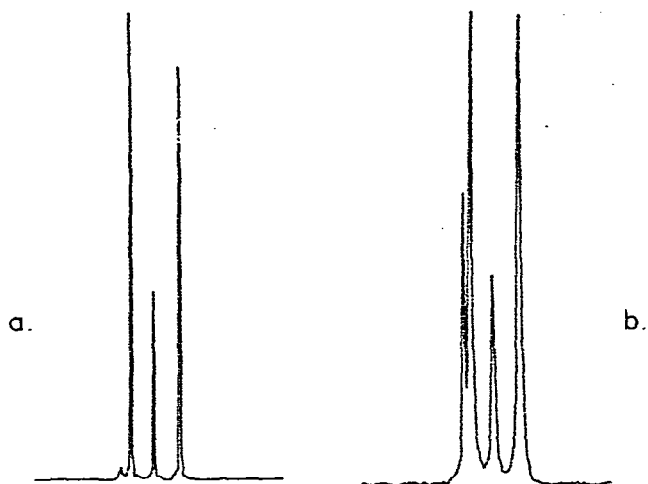


Fig. 2. The ^{13}C NMR spectrum of (bromo)diphenylborane at ambient temperature (a) and -53°C (b).

ture ^{13}C NMR spectra is illustrated in Fig. 3 for $\text{C}_6\text{H}_5\text{B}(\text{—NCH}_3\text{—CH}_2\text{—})_2$. The proton-noise decoupled spectrum is obtained first (a) and is searched for peaks that are not observed at room temperature. In the present case, a new signal is observed in the region of aromatic C atoms at $\delta = 134.3$ ppm. If there is any doubt as to the assignment of the new peak, then a proton-noise coupled spec-

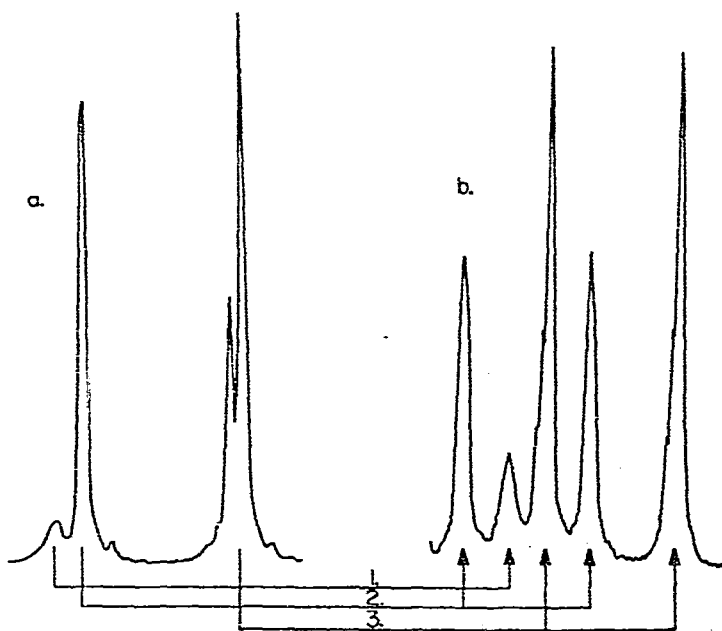


Fig. 3. ^{13}C NMR signals of the phenyl carbon atoms of $\text{C}_6\text{H}_5\text{B}(\text{—NCH}_3\text{—CH}_2\text{—})_2$ at -37°C : (a) = proton-noise decoupled spectrum; (b) = proton-noise coupled spectrum; (1) = boron-bonded carbon; (2) = *meta* carbon; (3) = *ortho* and *para* carbon.

trum (b) is also recorded at low temperature in order to verify the assignment.

All attempts to determine the coupling constants $J(BC)$ of those phenylboranes that exhibited a ^{13}C resonance signal for the boron-bonded carbon atom of the phenyl group at ambient temperature were in vain. On increasing the recording temperature of the spectra (in analogy to the experiment with triethylborane) an initial broadening of the resonance line was observed accompanied by a decrease in signal intensity and finally complete loss of the signal.

The preceding observations indicate that the line shape and the intensity of ^{13}C NMR signals of boron-bonded carbon atoms of organoboranes are relatively unpredictable but are definitely temperature dependent. The present data also suggest that if an organoborane gives a partially collapsed quartet for the ^{13}C resonance signal of boron-bonded carbon at ambient temperature and if the B—C coupling constant is of interest, then a high temperature study is in order. On the other hand, if this resonance signal is not observed at all or is either too broad or too weak for determining the individual chemical shift at ambient temperature, then a low temperature study may provide signal enhancement and thus permit the recording of ^{13}C chemical shift data.

However, additional studies are needed in order to obtain reasonable guidelines for the direct observation of ^{13}C NMR signals of the boron-bonded carbon atoms in organoboranes. For example, as of now it was not possible to detect the cited type of carbon atoms in the spectrum of (chloro)diphenylborane, $(\text{C}_6\text{H}_5)_2\text{BCl}$, or pyridine-triphenylborane, $(\text{C}_5\text{H}_5\text{N})\text{B}(\text{C}_6\text{H}_5)_3$.

In order to study the possible correlation of $\delta^{13}\text{C}$ of boron-bonded carbon atoms with $\delta^{11}\text{B}$ of an organoborane, the ^{13}C NMR spectra of various phenylborane derivatives were recorded. These data are summarized in Table 1.

TABLE 1

THE CHEMICAL SHIFTS $\delta^{13}\text{C}$ OF BORON-BONDED CARBON ATOMS AND $\delta^{11}\text{B}$ OF PHENYLBORANE DERIVATIVES^a

Compound	$\delta^{13}\text{C}$ (ppm)	$\delta^{11}\text{B}$ (ppm)
$[\text{B}(\text{C}_6\text{H}_5)_4]^-$	164.8 ^b	6.3 ^c
$(2\text{-H}_2\text{N}-\text{C}_5\text{H}_4\text{N})\text{B}(\text{C}_6\text{H}_5)_3$	151.6 ^d	2.1 ^e
$\text{B}(\text{C}_6\text{H}_5)_3$	144.9 ^f	-68 ^g
$(\text{C}_6\text{H}_5)_2\text{B}-\text{N}(\text{CH}_3)_2$	143.1 ^h	-41.8 ^u
$\text{C}_6\text{H}_5\text{B}[\text{N}(\text{CH}_3)_2]_2$	141.2 ^v	-32.5 ^u
$\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2)_2\text{CH}_2$	140.0 ^v	-29.0
$(\text{C}_6\text{H}_5)_2\text{BBr}$	139.2 ⁱ	
$(-\text{BC}_6\text{H}_5-\text{NH}-)_3$	135.4 ^j	-33.8 ^k
$(\text{C}_6\text{H}_5)_2\text{B}-\text{O}-\text{B}(\text{C}_6\text{H}_5)_2$	134.7 ^l	-28.5 ^m
$(-\text{BC}_6\text{H}_5-\text{O}-)_3$	134.3 ^r	-29.0 ^o
$\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2)_2$	134.3 ^l	-32.2 ^p
$\text{C}_6\text{H}_5\text{B}(\text{OH})_2$	132.2 ^q	-32.4 ^r
$(\text{C}_6\text{H}_5)_2\text{B}-\text{N}-\text{C}(\text{CF}_3)_2$	132.2 ^s	-46.3 ^t

^a $\delta^{13}\text{C}$ vs. TMS as standard, $\delta^{11}\text{B}$ vs. $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$. ^b In THF/D₂O. ^c For $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ [25]. ^d In THF at -47°C using 1 second pulse delay. ^e In THF [13]. ^f In THF; $\delta^{13}\text{C}$ (in CH_2Cl_2) = 143.3 ppm. ^g Ref. 26. ^h In CD_2Cl_2 at -37°C. ⁱ In CH_2Cl_2 ; ¹¹B NMR signal too broad for assignment of chemical shift. ^j In THF/ CDCl_3 at -43°C. ^k Value in benzene; H. Nöth, W. Tinhof and T. Taeger, Chem. Ber. 107 (1974) 3113; $\delta^{11}\text{B}$ in DMF = -31.7 ppm, in CH_3CN = -34.7 ppm; B. Figgis (in: H. Steinberg, R.J. Brotherton, "Organoboron Chemistry", Vol. 2, New York (1966), p. 365). ^l In CDCl_3 at -37°C. ^m In benzene [25]. ⁿ In THF/ CD_2Cl_2 at -34°C. ^o Ref. 27. ^p Ref. 28. ^q In $\text{CH}_3\text{OH}/\text{D}_2\text{O}$ at -41°C. ^r Ref. 29. ^s In CCl_4 using 60 seconds pulse delay. ^t Ref. 16. ^u Ref. 30. ^v At -50°C in CDCl_3 .

TABLE 2

^{13}C CHEMICAL SHIFTS δ (in ppm downfield from TMS) OF THE *ortho*, *meta* AND *para* CARBON ATOMS OF THE PHENYL GROUPS OF PHENYLBORANE DERIVATIVES AND COUPLING CONSTANTS $J(\text{CH})$ (in Hz)

Compound	<i>ortho</i>		<i>meta</i>		<i>para</i>		Remarks
	δ	J	δ	J	δ	J	
(2- $\text{H}_2\text{N}-\text{C}_5\text{H}_4\text{N}$) $\text{B}(\text{C}_6\text{H}_5)_3$	127.5		135.5		125.5		in THF
($\text{C}_5\text{H}_5\text{N}$) $\text{B}(\text{C}_6\text{H}_5)_3$	127.2	156	134.8	150	125.3	163	in CD_2Cl_2
$\text{B}(\text{C}_6\text{H}_5)_3$	127.6	159	138.8	166	131.5	160	in CH_2Cl_2 , 60 sec, pulse delay, 100 transients
	127.9	159	138.3	166	130.8	160	in THF
(C_6H_5) $_2\text{BCl}$	127.9	160	137	160	133	160	in CH_2Cl_2
(C_6H_5) $_2\text{BBr}$	128.1	160	137.9	161	133.4	160	in CD_2Cl_2 at -53°C
(C_6H_5) $_2\text{B}-\text{N}(\text{CH}_3)_2$	127.4	156	133.7	156	127.9	156	neat
(C_6H_5) $_2\text{B}-\text{N}=\text{C}(\text{CF}_3)_2$	128.3		135.3		131.4		
(C_6H_5) $_2\text{B}-\text{O}-\text{B}(\text{C}_6\text{H}_5)_2$	127.8	160	135.7	154	131.1	159	in CDCl_3
$\text{C}_6\text{H}_5\text{B}(\text{OH})_2$	127.6		133.7		130.5		in $\text{CH}_3\text{OH}/\text{D}_2\text{O}$
($-\text{BC}_6\text{H}_5-\text{O}-$) $_3$	127.4	161	133.6	158	130.3	159	in $\text{THF}/\text{CD}_2\text{Cl}_2$ at -34°C
($-\text{BC}_6\text{H}_5-\text{NH}-$) $_3$	127.9	158	132.3	157	129.7	160	in THF
$\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2-)_2$	127.7	158	133.2	158	128.1	158	in CDCl_3
$\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2-)_2-\text{CH}_2$	127.5	158	132.3	159	126.8	158	in CDCl_3
$\text{C}_6\text{H}_5\text{B}[\text{N}(\text{CH}_3)_2]_2$	127.4		134.0		127.4		in CDCl_3 at -50°C .

The chemical shift data compiled in Table 1 dispute any linear relationship between $\delta^{13}\text{C}$ of boron-bonded carbon and $\delta^{11}\text{B}$ of the various phenylborane derivatives. This is in contrast to the earlier [2] ^{13}C NMR study on methylborane species. Though the present data do not yet permit an explanation of this discrepancy, it seems reasonable to assume that steric factors influence the π -back-bonding in phenylboranes and thus prevent a simple linear correlation of $\delta^{13}\text{C}$ and $\delta^{11}\text{B}$ in these species.

The ^{13}C chemical shifts of the carbon atoms in *ortho*, *meta* and *para* position to the one that is bonded to the boron in the phenylborane derivatives studied in the present works are fairly constant; relevant numerical values are summarized in Table 2. Only the chemical shifts of the *para* carbon atoms exhibit a relatively wide range but no apparent correlation seems to exist between the chemical shift data and the nature of the additional boron substituents.

Experimental

All ^{13}C NMR spectra were obtained on a Varian CFT-20 NMR spectrometer. Lock signals were provided from a deuterated solvent or a sealed capillary tube filled with acetone- d_6 (low temperature spectra), dimethylsulfoxide- d_6 or D_2O . Chemical shifts are reported in ppm downfield from TMS; chemical shift values vs. TMS for the solvents used as secondary references are as follows: CH_2Cl_2 , -54.0 ; CH_3OH , -49.0 ; CDCl_3 , -76.9 ; CD_2Cl_2 , -53.6 ; THF, -67.7 ; C_6D_6 ,

—128.0; CCl_4 , —96.0 ppm. The ^{13}C NMR data compiled in Table 2 were obtained from the combined results of a proton noise decoupled spectrum and a proton noise coupled spectrum. For variable-temperature studies the conditions of data acquisition were the same as those used at ambient temperature.

Sodium tetraphenylborate, triphenylborane and triethylborane were commercial products; the following previously described materials were prepared by the indicated literature procedures:

(2- $\text{H}_2\text{N}-\text{C}_5\text{H}_4\text{N}$) $\text{B}(\text{C}_6\text{H}_5)_3$ [13], $(\text{C}_6\text{H}_5)_2\text{BX}$ (X = Cl, Br) [14], $(\text{C}_6\text{H}_5)_2\text{B}-\text{N}(\text{CH}_3)_2$ [14], $(\text{C}_6\text{H}_5)_2\text{B}-\text{O}-\text{B}(\text{C}_6\text{H}_5)_2$ [15], $(\text{C}_6\text{H}_5)_2\text{B}-\text{N}=\text{C}(\text{CF}_3)_2$ [16], $\text{C}_6\text{H}_5\text{BCl}_2$ [17], $\text{C}_6\text{H}_5\text{B}[\text{N}(\text{CH}_3)_2]_2$ [14], $\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2-)_2$ [14], $\text{C}_6\text{H}_5\text{B}(-\text{NCH}_3-\text{CH}_2-)_2\text{CH}_2$ [18], $(\text{CH}_3)_2\text{BBr}$ [19]. $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$ was obtained by hydrolysis of $\text{C}_6\text{H}_5\text{BCl}_2$, $(-\text{BC}_6\text{H}_5-\text{NH}-)_3$ was prepared by reaction of the latter compound with anhydrous ammonia in benzene solution.

Pyridine—triphenylborane, $(\text{C}_5\text{H}_5\text{N})\text{B}(\text{C}_6\text{H}_5)_3$, was prepared by dropwise addition of pyridine to a solution of $\text{B}(\text{C}_6\text{H}_5)_3$ in CH_2Cl_2 . A colorless precipitate formed which was filtered off and dried, melting point 241—245°C. The IR spectrum of the material (mineral oil mull, recorded on a Perkin—Elmer Model 621 spectrometer under standard operating conditions) exhibits absorptions at 3170—3140, 1617, 1586, 1260, 1216, 1185, 1164, 1150, 1075, 868, 800, 770, 743, 728, 704, 693, and 615 cm^{-1} . The mass spectrum of the material shows only the free acid-base pair.

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