Proton Magnetic Resonance of Ammonia-Borane Derivatives

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The present authors have already studied the proton magnetic resonance of borazole and some of its derivatives[1,2]. There is another group of compounds having a bond between boron and nitrogen known as ammonia-boranes (or borazanes), i.e., the derivatives of ammonia-borane H_3NBH_3[3]. For instance, both boron trichloride (or trichloroborane) BCl_3 and triethylborane $B(C_2H_5)_3$ are known to form addition compounds with amines through a donor-acceptor bond. Whereas borazole is isoelectronic with benzene, ammonia-borane is isoelectronic with ethane. Accordingly, one has in ammonia-boranes a typical example of donor-acceptor bonds as contrasted with the case of borazoles, in which covalent σ bonds are involved in addition to donor-acceptor bonds between boron and nitrogen. This paper presents the results of investigation on the proton magnetic resonance of ammonia-boranes.

Experimental

Triethylborane was prepared by adding the calculated amount of the addition compound between boron trifluoride and *n*-butyl ether, $BF_3 \cdot O(C_4H_9)_2$, drop by drop to the solution of ethylmagnesium bromide in *n*-butyl ether at room temperature. The resulting triethylborane was purified by distillation in the stream of nitrogen at ordinary pressure, b.p. 95~96°C (lit.[4] 94~97°C).

Trimethylamine-triethylborane $(CH_3)_3NB(C_2H_5)_3$ was synthesized by a method due to Brown[4]. Triethylborane was treated with an excess of trimethylamine. After the excess was removed by distillation from the reaction mixture, the liquid was subjected to distillation at low temperature under reduced pressure, m.p. −47 to −46°C (lit.[4] −46 to −45°C).

Triethylamine-triethylborane $(C_2H_5)_3NB(C_2H_5)_3$ was synthesized from triethylborane and excess triethylamine and purified in the same manner as above. This compound decomposes in the gas phase at room temperature, decomposition products being presumed to exist in the liquid state also. No data are available in the literature for comparison.

Trimethylamine-trichloroborane $(CH_3)_3NBCl_3$ was prepared by allowing boron trichloride to react with the equivalent amount of trimethylamine in carbon tetrachloride at −70°C. The addition compound was soluble with difficulty in this solvent. After filtration, the precipitates were recrystallized from ethanol, m. p. 243~244°C (lit.[5] 243~244°C). Anal. Calcd. for $(CH_3)_3NBCl_3$: N, 7.96%. Found: N, 7.89%.

Triethylamine-trichloroborane $(C_2H_5)_3NBCl_3$ was synthesized from boron trichloride and triethylamine in a similar manner to above and was recrystallized from methanol. It decomposed on melting at 81~83°C (lit.[6] 75°C). Anal. Calcd. for $(C_2H_5)_3NBCl_3$: N, 6.42%. Found: N, 6.16%.

The proton magnetic resonance spectra were recorded at room temperature by means of a JNM-3 high-resolution NMR spectrometer of Japan Electron Optics Laboratory Company operating at 40 Mc. Chemical shifts were evaluated using appropriate internal standards so as to avoid the overlap of signals of samples under investigation with that of the standard used. In case when samples were unstable, they were sealed in a cell with an external standard. No correction was made for the bulk magnetic susceptibility of the samples.

Assignments

The NMR spectra of triethylborane were recorded in pure liquid state as well as in carbon tetrachloride solution with cyclohexane as an internal standard. These spectra were essentially identical with each other. The spectra showed a fairly sharp composite signal attributable to ethyl groups bonded to boron as illustrated in Fig. 1a.

Trimethylamine-triethylborane was examined in pure liquid state with water as an external standard. A very sharp intense line appearing at −0.77 p.p.m. as calculated with cyclohexane as the standard* was ascribed to protons in methyl groups bonded to nitrogen. In addition,

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1) K. Ito, H. Watanabe and M. Kubo, *J. Chem. Phys.*, **32**, 947 (1960); This Bulletin, **33**, 1588 (1960).

2) K. Ito, H. Watanabe and M. Kubo, *J. Chem. Phys.*, **34**, 1043 (1961).

3) S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 6084 (1955); **80**, 8 (1958).

4) H. C. Brown, ibid., **67**, 374 (1945).

5) E. Wiberg and W. Sütterlin, *Z. anorg. u. allgem. Chem.*, **202**, 31 (1931); J. Goubeau, M. Rahtz and H. J. Becher, ibid., **275**, 161 (1954).

6) F. Gallais and J. P. Laurend, *Compt. rend.*, **244**, 1636 (1957); H. C. Brown, P. F. Stehle and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

* Numerical values for chemical shifts given below refer to cyclohexane as the standard. Conversion was made with the proton chemical shifts −3.4 and +1.6 p.p.m. of water and tetramethylsilane referred to cyclohexane. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959), pp. 89, 236.

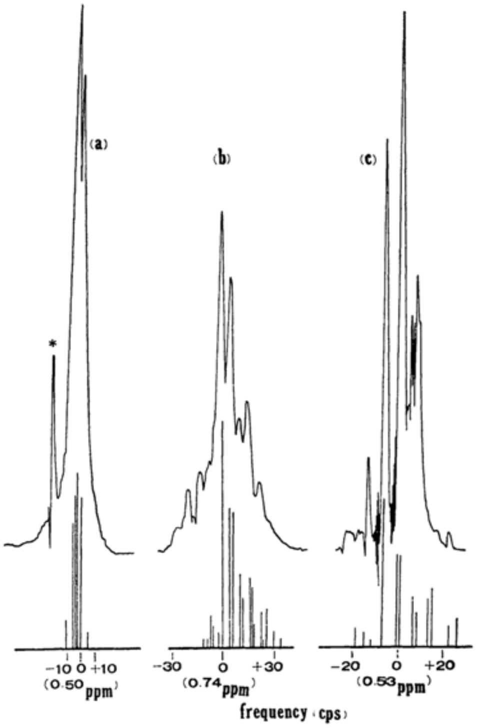

Fig. 1. B-C_2H_5 proton signals of (a) triethylborane, (b) trimethylamine-triethylborane and (c) triethylamine-triethylborane. The theoretical patterns are shown below. For the sake of clarity, some sets of closely spaced theoretical lines are shown by single bars. The peak marked with an asterisk is the reference line of cyclohexane. In order to increase resolution, a different sweep rate was employed for (c).

a group of weak peaks appeared on the lower field side of this peak. Presumably, some decomposition products were responsible for it. Ethyl groups in this compound yielded a complicated group of lines shown in Fig. 1b, suggesting that intermediate coupling exists rather than weak coupling, in which case one would have a simple three-four pattern for the signal of ethyl groups[7].

Triethylamine-triethylborane was studied in pure liquid state with water as an external reference. The spectrum showed a quartet at -2.13 p.p.m. attributable to methylene protons in ethyl groups bonded to nitrogen. The separation between multiplet components yielded the spin coupling constant J_{HH} equal to 6.7 c.p.s. The corresponding signal of methyl protons appeared at about 0.16 p.p.m., although the triplet structure was not very clear because of masking by BC_2H_5 signals described below. As in the spectra of the foregoing two compounds, ethyl groups bonded directly to boron gave rise to a complicated signal shown in Fig. 1c. This compound readily decomposes in the gaseous state. In fact, signals presumed to be due to some decomposition products from intensity considerations appeared between the triplet and the quartet of ethyl groups bonded to nitrogen, rendering unequivocal assignment very difficult.

Trimethylamine-trichloroborane was dissolved in chloroform and the NMR spectrum was recorded with tetramethylsilane as an internal reference. The spectrum showed a group of closely spaced lines centered at -1.57 p.p.m. in addition to a very strong peak attributable to chloroform, which was accompanied by spinning side bands and weak satellites due to $^{13}CHCl_3$. Unlike the signals of NCH_3 protons in *N*-trimethylborazoles, which were found to be rather sharp, that of this compound consisted of four almost equally spaced quartet lines separated by 2.6 c.p.s., a line at the highest field being weaker than three others. The small separation of this magnitude[2] suggests spin coupling between protons and a nitrogen nucleus separated by two chemical bonds, although the reason for the appearance of a quartet rather than a triplet is not clear.

Triethylamine-trichloroborane was dissolved in chloroform and the spectrum was taken with tetramethylsilane as an internal standard. The spectrum was comprised of a typical 1 : 2 : 1 triplet centered at 0.04 p.p.m. attributable to methyl protons in ethyl groups and a quartet centered at -2.37 p.p.m. originating from methylene protons. The spin coupling constant J_{HH} was evaluated at 7.6 c.p.s. In addition, a very strong peak due to $^{12}CHCl_3$, weak satellites arising from $^{13}CHCl_3$ and spinning side bands were recorded.

Discussion

The numerical values of chemical shifts and spin coupling constants are summarized in Table I. Those of trimethylamine[8], triethylamine[8] and borazoles[1,2] also are listed for comparison. The observed chemical shifts and spin coupling constants are of the correct order of magnitude compared with those of borazole[1,2] already studied, indicating the adequacy of the present assignments.

The observed NCH_2 and $NCCH_3$ proton chemical shifts of triethylamine, triethylamine-triethylborane and triethylamine-trichloroborane decreases in this order in agreement with increasing extent of charge transfer from nitrogen to boron due to the formation of an

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[7] P. L. Corio, *Chem. Revs.*, **60**, 363 (1960).

[8] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

TABLE I. PROTON CHEMICAL SHIFTS (p.p.m.) AND SPIN COUPLING CONSTANTS J (c.p.s.) OF TRIETHYLBORANE AND SOME AMMONIA-BORANES. REFERENCE: CYCLOHEXANE.

Compounds	NCH_2	NCH_3	$NCCH_3$	BC_2H_5	J
$B(C_2H_5)_3$				0.00−0.74	
$(CH_3)_3NB(C_2H_5)_3$		−0.77		0.14−1.54	
$(C_2H_5)_3NB(C_2H_5)_3$	−2.13		0.16	0.16−0.84	$J_{HH}=6.7$*
$(CH_3)_3NBCl_3$		−1.57			$J_{NCH}=2.6$
$(C_2H_5)_3NBCl_3$	−2.37		0.04		$J_{HH}=7.6$
$N(CH_3)_3$		−0.77			
$N(C_2H_5)_3$	−1.33		0.50		
Borazoles**	−2.20 −1.98 −2.17	−1.75 −1.60 −1.58 −1.50	0.38 0.40 0.40	0.45 0.52 1.05	$J_{HH}=8.0$, 7.2, 8.1 $J_{NCH}=3.0$

* In ethyl groups attached to nitrogen. ** For detailed description of borazole derivatives, see Ref. 2.

N→B bond and the effect of electronegative chlorine atoms. The same trend is observed for the NCH_3 proton chemical shifts of trimethylamine, trimethylamine-triethylborane and trimethylamine-trichloroborane.

A striking difference between ammonia-boranes and borazoles is that whereas ethyl groups attached to boron in the latter compounds give rise to a single sharp signal of proton resonance, those in the former yield a group of lines showing a complicated pattern of line spacings and relative intensities. The observed ethyl signals of triethylborane, trimethylamine-triethylborane and triethylamine-triethylborane were compared with theoretical calculations by Corio[7] for an A_3B_2 spin system. In other words, further splitting of ethyl proton signals due to magnetic boron nuclei was disregarded for the following reasons. In the first place, the spin coupling constants between a boron nucleus having a small atomic number and ethyl protons across two or more chemical bonds are presumed to be small[9]. Secondly, because boron nuclei have an electric quadrupole moment, spin decoupling is presumed to take place between boron nuclei and protons. In fact, Onak et al.[10] have observed the ^{11}B nuclear magnetic resonance spectra of a number of boron compounds including triethylborane and evaluated spin coupling constants between directly bonded boron and hydrogen but not those between boron nuclei and protons separated by two or more chemical bonds. Considering possible overlap of closely spaced theoretical lines, the relative internal shifts δ (unmodified by spin interactions) between methyl and methylene proton signals and spin-spin coupling constants were evaluated as shown in Table II. Theoretical spectra calculated with these values yield a fairly good fit with experiments as shown in Fig. 1.

TABLE II. THE INTERNAL CHEMICAL SHIFTS (p.p.m.) AND THE SPIN-SPIN COUPLING CONSTANTS (c.p.s.) OF BC_2H_5 PROTONS IN TRIETHYLBORANE AND RELATED COMPOUNDS.

Compound	$\Delta CH_3 - \Delta CH_2$	J	Electro-negativity of boron
$B(C_2H_5)_3$	+0.19	7.2	1.8, 2.2*
$(CH_3)_3NB(C_2H_5)_3$	−0.47	7.1	1.4, 1.8*
$(C_2H_5)_3NB(C_2H_5)_3$	−0.43	7.3	1.4, 1.8*

* The modified Dailey-Shoolery equation was employed in the calculation.

Dailey and Shoolery[8] have shown that the methyl signal and the methylene signal of an ethyl group showing the characteristic three-four pattern ($J \ll \delta$)* draw together as the electronegativity of an atom bonded to the ethyl group decreases: a linear relation holds between the electronegativity and the difference, $\delta = \Delta CH_3 - \Delta CH_2$, between the chemical shifts of methyl protons and methylene protons in an ethyl group.

$$\text{E.N.} = 0.695(\Delta CH_3 - \Delta CH_2) + 1.71$$

When the difference between the chemical shifts (in frequency units) of these two groups becomes small and comparable with the spin-spin coupling constant, one has the case of intermediate coupling ($J \approx \delta$) as in triethylborane. In the extreme case in which the spin-spin coupling predominates over the effect of chemical shifts ($J \gg \delta$), a single sharp line results as in *B*-triethylborazoles[11]. When δ

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9) P. T. Narasimhan and M. T. Rogers, *J. Chem., Phys.*, 34, 1049 (1961).

10) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, 63, 1533 (1959).

* The sign of J is trivial in interpreting the present spectra. J refers to absolute values and hence is positive.

11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959), p. 116.

decreases further to assume a negative value with its absolute value comparable with the spin-spin coupling constant, we have again the case of intermediate coupling as in trimethylamine-triethylborane and triethylamine-triethylborane. The negative internal chemical shifts between methyl and methylene protons have already been reported for aluminum triethyl, diethylaluminum chloride[12], some mercury dialkyls[13], mercury diethyl[14] and tin tetraethyl[9].

The aforementioned empirical equation first proposed by Dailey and Shoolery for electronegativity values ranging over 2.6∼3.9 was found by Baker[12] to be valid approximately even for electronegativity values less than 1.71, i.e., for negative internal shifts of ethyl groups. The electronegativity of boron calculated for triethylborane and related compounds are shown in Table II along with values calculated by the modified Dailey-Shoolery equation[15], in which the constant in the original equation is changed from 1.71 to 2.10 for atoms of low electronegativity.

The present results lead to the conclusions that the formation of an N→B bond interchanges the positions of the methyl and methylene signals of triethylborane and that boron in ammonia-boranes is less electronegative than that in borazoles. This supports the view that the extent of electron transfer from nitrogen to boron in ammonia-boranes is almost the same as but slightly greater than that in borazoles.

Mention should be made in this connection that Becher[16] has determined the dipole moments of some ammonia-boranes (ammonia-trimethylborane $H_3NB(CH_3)_3$ and trimethylamine-trimethylborane $(CH_3)_3NB(CH_3)_3$) and aminoboranes (aminodimethylborane $H_2NB(CH_3)_2$ and dimethylaminodimethylborane $(CH_3)_2NB(CH_3)_2$) in benzene solutions and evaluated from them the NB bond moment in ammonia-boranes and aminoboranes (or borazenes). The former was found to amount to about 30% of the value calculated for the N→B bond. This implies that ammonia-boranes resonate between the no-bond structure $R_3N.BR_3$ and the donor-acceptor bond structure $R_3N \rightarrow BR_3$ (R=alkyl group), the contribution of the latter being about 30%. On the other hand, from the measurement of the diamagnetic susceptibilities of borazole and some of its derivatives, the present authors[17] have estimated the diamagnetic anisotropy of a borazole ring and concluded that the contribution of the donor-acceptor double bond structure to the normal state of borazole is 24%.

From the greater extent of the donor-acceptor bond character in ammonia-boranes than that in borazoles, one might expect that nitrogen in the former compounds is more electronegative and hence the chemical shift difference $\Delta CH_3 - \Delta CH_2$ of ethyl groups attached to nitrogen is greater than the corresponding values of the latter compounds. However, as shown in Table III, the chemical shift differences of triethylamine-triethylborane and triethylamine-trichloroborane are smaller than those of hexaethylborazole and *B*-trichoro-*N*-triethylborazole, respectively. The reason for this is presumed to be twofold. In the first place, the diamagnetic ring current induced by the external magnetic field in a borazole ring makes a negative contribution[18] to the chemical shifts of protons in the same molecule. Owing to the greater distance from the ring, the effect is smaller for methyl protons than for methylene protons. As a result, the diamagnetic ring current increases the internal chemical shift of ethyl groups in borazoles, regardless of whether the ethyl groups are attached to nitrogen or boron. Secondly, although charge migration from nitrogen to boron is slightly greater in ammonia-boranes than in borazoles, electron withdrawal by nitrogen from three ethyl groups in ammonia-boranes rather than one as in borazoles, more than compensates the decrease in the electronic population of the nitrogen atom due to the formation of an N→B bond. Accordingly, the nitrogen in ammonia-boranes becomes less electronegative than that in borazole derivatives

TABLE III. THE INTERNAL CHEMICAL SHIFTS (p.p.m.) OF NC_2H_5 PROTONS IN TRIETYLAMINE, TRIETHYLAMINE-BORANES AND *N*-TRIETHYLBORAZOLES.

Compound	$\Delta CH - \Delta CH_2$	Electronegativity of nitrogen
$N(C_2H_5)_3$	1.83*	2.98
$(C_2H_5)_3NB(C_2H_5)_3$	2.29	3.30
$(C_2H_5)_3NBCl_3$	2.41	3.38
$[(C_2H_5)NB(CH_3)]_3$	2.38	3.36
$[(C_2H_5)NB(C_2H_5)]_3$	2.57	3.50
$[(C_2H_5)NBCl]_3$	2.58	3.50

* Coyle and Stone give 1.50 p.p.m. See Ref. 19.

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[12] E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

[13] R. E. Dessy, T. J. Flautt, H. H. Jaffé and G. F. Reynolds, ibid., **30**, 1422 (1959).

[14] P. T. Narasimhan and M. T. Rogers, ibid., **31**, 1430 (1959); *J. Am. Chem. Soc.*, **82**, 34 (1960).

[15] J. N. Shoolery, Lecture Notes, Varian Associates Conference (Nov. 1957). See also Ref. 14.

[16] H. J. Becher, *Z. anorg. u. allgem. Chem.*, **270**, 273 (1952).

[17] H. Watanabe, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, **82**, 3294 (1960).

[18] H. J. Bernstein, W. G. Schneider and J. A. Pople, *Proc. Roy. Soc.*, **A236**, 515 (1956).

as was actually found by the present investigation. This complication does not arise in discussing the BC_2H_5 proton resonance, because electron transfer between boron and ethyl groups is inappreciable as suggested by the electronegativity of boron in triethylborane, which is close to that of a free boron atom equal to 2.0. For this reason, BC_2H_5 proton signals are more suitable than NC_2H_5 signals in discussing the nature of NB bonds in ammonia-boranes and borazoles.

Coyle and Stone[19] have reported the results of measurements on the proton chemical shifts in some boron-containing addition compounds of Lewis bases and showed that the chemical shift criterion is not uniformly successful in predicting the stabilities of addition compounds. However, direct comparison between their results and the present conclusion is not feasible, because no compounds were examined both by them and by the present authors.

Summary

The proton magnetic resonance spectra of triethylborane, trimethylamine-triethylborane, triethylamine-triethylborane, trimethylamine-trichloroborane and triethylamine-trichloroborane were recorded at room temperature using an NMR spectrometer operating at 40 Mc. The assignments of observed signals were made and the chemical shifts and spin coupling constants were evaluated. The extent of electron transfer from nitrogen to boron in ammonia-boranes is slightly greater than that in borazoles.

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[19] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 4138 (1961).