Proton Magnetic Resonance of Borazole[1]

By Kazuo ITO, Haruyuki WATANABE and Masaji KUBO

(Received June 8, 1960)

The work described in this paper is part of a physicochemical investigation which has as its object the elucidation of the molecular structures and electronic states of borazole and its derivatives. Previous papers of this series have been concerned with the infrared absorptions of some borazole derivatives[2], the dipole moments of borazole and its derivatives[3] and the diamagnetic anisotropy of a borazole ring[4]. The present paper presents the results of investigation on the proton magnetic resonance of borazole. The problem is of particular interest from the standpoint of both chemical shifts and splittings for the following reasons. In the first place, all the NMR spectra which have ever been recorded on compounds having hydrogen atoms attached to boron are outnumbered by the profusion of those on other types of compounds. Secondly, the nuclei of nitrogen ^{14}N as well as those of boron isotopes, ^{11}B and ^{10}B, have an electric quadrupole moment capable of affecting through its spin-lattice relaxation the relative broadening of multiplet components. The ^{11}B magnetic resonance was also studied in order to facilitate assignments.

Experimental

Sample. — B-Trichloroborazole was prepared by the same method as that described by Brown and Laubengayer[5]. After being sublimed several times under reduced pressure, it was identified by its melting point 83.5∼84.5°C, the value reported in the literature being 83.9∼84.5°C [5]. The infrared spectra[2] showed absorption bands characteristic of a borazole ring. This compound was reduced to borazole by essentially the same method as that proposed by Schaeffer et al[6]. differing in that $NaBH_4$ was used as a reducing agent in place of $LiBH_4$ and that triethylene glycol dimethyl ether rather than dibutyl ether was employed as a solvent[7]. Triethylene glycol dimethyl ether having a boiling point quite different from that of borazole was more suitable than diethylene glycol dimethyl ether suggested by Schaeffer[8]. Hence, 23.5 g. of sodium borohydride was dissolved in 120 cc. of triethylene glycol dimethyl ether in an atmosphere of dry nitrogen. To this solution, the suspension of 30 g. of B-trichloroborazole in 75 cc. of the same solvent was gradually added at room temperature. Stirring was continued for about 2 hr. After the reaction was over, the product was distilled under reduced pressure and was collected in a trap cooled with dry ice. The yield of crude borazole was about 10 g. Vacuum distillation was repeated several times before use.

Apparatus and Experimental Procedure. — The proton magnetic resonance spectrum was recorded at room temperature by means of a JNM-3 high-resolution NMR spectrometer of Japan Electron Optics Laboratory Company operating at 40 Mc./sec. Cyclohexane was used as an internal standard. Accordingly, corrections for the bulk magnetic susceptibility of the sample were not required. It was further confirmed that dilution with carbon tetrachloride did not affect the spectrum in an appreciable manner. The NMR absorption derivative spectrum of ^{11}B was also recorded with the same spectrometer operated at 12.6 Mc./sec.

Results and Discussion

The proton magnetic resonance spectrum obtained is shown in Fig. 1, in which the absorption intensity is plotted against decreasing magnetic field strength. Chemical shifts defined by

$$\delta = 10^6 (H_s - H_r)/H_r$$

are also protted along the abscissa. Here, H_s denotes the applied magnetic field for the proton signal of the sample and H_s is that of cyclohexane used as a standard. The signal of cyclohexane was identified by the increase in its intensity on further addition of the standard. Two peaks at 1.4_7 and -1.4_9 were ascribed to spinning side bands, because they shifted depending on the spinning rate.

The spectrum is comprised of a triplet centered at -4.0_5 and less intense broad peaks at 2.1_2, -1.3_4 and -8.2_6. The triplet was unequivocally assigned to the proton signal of

---

[1] A part of the results presented here has been reported at the 13th Annual Meeting of the Chemical Society of Japan Tokyo, April 5, 1960. A preliminary report has been published in a short communication: K. Ito, H. Watanabe and M. Kubo, *J. Chem. Phys.*, **32**, 947 (1960).

[2] H. Watanabe, M. Narisada, T. Nakagawa and M. Kubo, *Spectrochim. Acta*, **16**, 78 (1960). H. Watanabe, T. Totani, T. Nakagawa and M. Kubo, ibid., **16** (1960).

[3] H. Watanabe and M. Kubo, *J. Am. Chem. Soc.*, **82**, 2428 (1960).

[4] H. Watanabe, K. Ito and M. Kubo, ibid., **82**, 3294 (1960).

[5] C. A. Brown and A. W. Laubengayer, ibid., **77**, 3699 (1955).

[6] R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, ibid., **76**, 3303 (1954).

[7] L. Hohnstedt and D. T. Haworth, ibid., **82**, 89 (1960).

[8] G. W. Schaeffer, private communication.

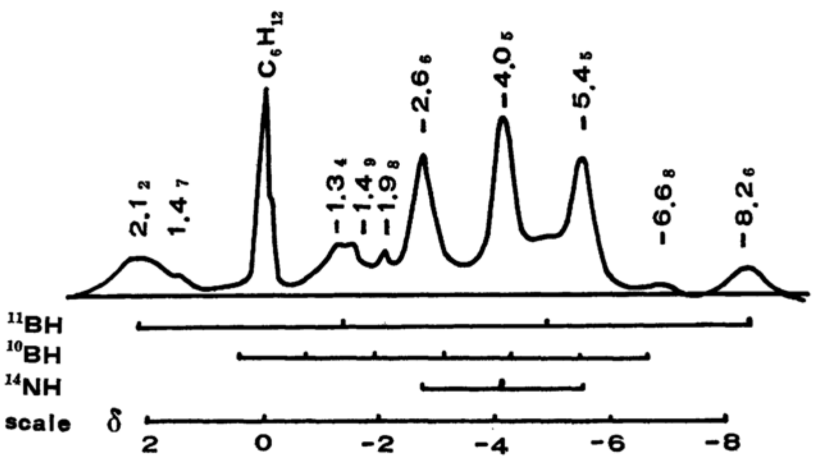

Fig. 1. Proton magnetic resonance spectrum of borazole. The numerical values of shifts are given for major absorption peaks.

^{14}NH with a spin coupling constant $J(^{14}NH)=$ 56 cps, because the signal is expected to split into three equally spaced peaks owing to the $2I+1$ orientations of a ^{14}N spin with $I=1$. The spin coupling constant is of the right order of magnitude, since the value for $^{14}NH_3$ is 46 cps$^{9)}$. In this triplet pattern, not all of the peaks have the same height, the central line being stronger than the two outer ones, which have the same intensity. Deviation from a simple 1 : 1 : 1 triplet, i. e., the partial collapse of spin multiplets can be ascribed to the presence of ^{14}N nuclei having an electric quadrupole moment, which gives rise to spin-lattice relaxation in fluctuating electric field gradients. A similar pattern has been shown clearly by Ogg and Ray$^{9)}$, who compared the proton spectra of anhydrous $^{14}NH_3$ and $^{15}NH_3$. An approximate quantitative theory of this collapse mechanism has been developed by Pople$^{10)}$, who showed that the broadening of the outer components of the proton triplet spectrum should be three halves as great as that of the central component. Strictly speaking, the outer peaks of the triplet draw together as they broaden. Consequently, the separation between adjacent peaks does not correspond exactly to the spin coupling constant. However, the effect is presumed to be very small in the present case, in which the signals are fairly sharp.

Although the number of hydrogen atoms attached to boron in a borazole molecule is exactly the same as that of hydrogen atoms bonded to nitrogen, the proton signal of BH must be weak, because the abundance ratio of boron isotopes is $^{11}B : ^{10}B = 81.17\% : 18.83\%$ and also because these isotopes have a greater nuclear spin than that of ^{14}N, the abundance of which amounts to as much as 99.635%. Therefore, the proton signal of ^{11}BH must split into four equally spaced peaks in accordance with the spin $I=3/2$ of ^{11}B. The separation, 3.4_6, between the two peaks at 2.1_2 and -1.3_4 is equal to half the difference, 6.9_2, between those at -1.3_4 and -8.2_6, suggesting the presence of another peak at -4.8_0, which, although masked by the ^{14}NH triplet, appears as a hump between two peaks at -4.0_5 and -5.4_5 of the triplet. These four peaks complete the proton quartet of ^{11}BH with $J(^{11}BH)=138$ cps. This assignment is also consistent with the ^{11}B NMR spectrum of the same sample. Fig. 2 reproduces the NMR absorption derivative spectrum of ^{11}B in a borazole molecule. The curve is symmetric across a point, indicating

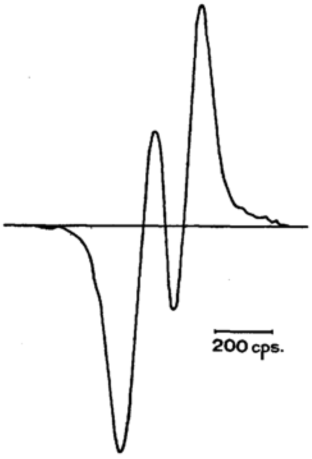

Fig. 2. The NMR absorption derivative spectrum of ^{11}B of borazole.

---

9) R. A. Ogg, Jr., and J. D. Ray, *J. Chem. Phys.*, **26**, 1515 (1957).

10) J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

the presence of two lines of equal intensity separated by 140 cps in good agreement with 138 cps evaluated from the aforementioned proton magnetic resonance spectrum. Philips et al.[11] has carried out the ^{11}B magnetic resonance study of boron compounds and reported that $J(^{11}\mathrm{BH})$ was equal to 136 cps for borazole.

The three components of the proton quartet of ^{11}BH have practically the same peak height. Although the intensity of the fourth line, which overlaps with the ^{14}NH proton triplet, is difficult to estimate exactly, it is very likely that the peak height is the same as those of other members of the quartet. The theory of quadrupole relaxation has already been extended to cover the broadening of multiplet components for protons bonded to nuclei with spin greater than unity[10]. It is predicted that, for spin 3/2, all components of the proton 1 : 1 : 1 : 1 quartet should be broadened equally, instead of showing different peak heights as in the ^{14}NH proton triplet. The present results are in agreement with Pople's[10] prediction. A similar quartet pattern having equal spacings and equal peak heights has been shown most clearly for sodium borohydride, $\mathrm{NaBH_4}$[12,13]. The partly resolved spectrum of the terminal protons of diborane[13] also appears to be consistent with the prediction.

There are still two weak peaks at -1.9_8 and -6.6_8 remaining unassigned. A possible interpretation is afforded by the proton signal of ^{10}BH. If the peak at -6.6_8 is assumed to be the outermost low-field member of seven peaks predicted for the signal of protons bonded to ^{10}B with its nuclear spin equal to 3, the peak at -1.9_8 can be considered to be the third high-field member of the septet, because the center of the ^{11}BH quartet must coincide with the central line of the ^{10}BH septet. The adequacy of this interpretation is strongly supported by an agreement between the observed spin coupling constant $J(^{10}\mathrm{BH})=48$ cps and the calculated one, 46 cps, based on the observed $J(^{11}\mathrm{BH})=138$ cps and the gyromagnetic ratios γ of boron isotopes.

$$\frac{J(^{10}\mathrm{BH})}{J(^{11}\mathrm{BH})}=\frac{\gamma(^{10}\mathrm{B})}{\gamma(^{11}\mathrm{B})}=\frac{4.575}{13.660}$$

where the numerical denominator and numerator are, respectively, the NMR frequencies of ^{11}B and ^{10}B in Mc. for a 10 kilogauss field. Three peaks between these two observed ones will escape detection owing to overlap with the strong ^{14}NH triplet. Two other peaks expected to appear at about -0.7 and $+0.5$ have not been observed.

The nuclei of ^{10}B have also an electric quadrupole moment. The broadening of multiplet components for protons bonded to nuclei with spin equal to 3 presents an interesting problem from the theoretical point of view. However, it is not feasible to discuss the broadening of the multiplet structure of the septet on the basis of the present investigation.

The proton chemical shifts, -4.0_5 and -3.0_7, of NH and BH in borazole, as referred to cyclohexane, lead to about -0.7 and $+0.3$, respectively, referred to water as a standard[14]. The former differs definitely from the δ values $4.3\sim4.5$ for secondary alkyl amines[15], and is intermediate between about 2.0 for secondary aryl amines[15] and about -2.1 for pyrrole[14]. This is quite reasonable since nitrogen atoms in borazole assume sp^2 hybridization and π-electrons are presumed to migrate to some extent from nitrogen to boron[4,16]. The chemical shift and the spin coupling constant $J(^{11}\mathrm{BH})$ of a BH proton, $+0.3$ and 138 cps, in borazole are closer to those of a terminal proton, $+2.0$ and 125 cps, in diborane, respectively, than to those of a bridge proton, $+6.3$ and 43 cps, in the same molecule[15].

Summary

The proton and ^{11}B magnetic resonances of borazole were recorded at room temperature. The proton magnetic resonance spectrum showed a ^{14}NH triplet, a ^{11}BH quartet and a part of ^{10}BH septet. The broadening of multiplet structure was discussed and the peak heights of the multiplet components were explained in terms of the quadrupole relaxation of nuclei bonded to hydrogen. The chemical shifts and the spin coupling constants were compared with those of related compounds.

The authors wish to thank Dr. T. Seki of Japan Electron Optics Laboratory Company for recording the high-resolution NMR spectra.

Chemistry Department
Faculty of Science
Nagoya University
Chikusa, Nagoya

---

[11] W. D. Philips, H. C. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

[12] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954).

[13] J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

[14] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill Book Company, Inc., New York (1959).

[15] L. H. Meyer, A. Saika and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

[16] B. L. Crawford, Jr., and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939). C. C. J. Roothaan and R. S. Mulliken, ibid., **16**, 118 (1948). C. W. Rector, G. W. Schaeffer and J. R. Platt, ibid., **17**, 460 (1949).