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Proton Magnetic Resonances of Some Borazole Derivatives

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The proton magnetic resonance spectra of ten borazole derivatives were recorded and assignments were carried out. The chemical shifts of BH and NH protons are close to each other, the values being nearly equal to the sum of the contribution of a diamagnetic ring current and the chemical shift of C = CH - Cprotons. The signals of NH and BH protons showed the partial collapse of multiplet structures due to quadrupole relaxation. BC₂H₅ protons gave a single sharp line instead of showing both methyl and methylene signals each split by I-I coupling. An explanation is given in terms of electronegativity considerations.

BORAZOLE and its derivatives present an interest-ing group of compounds, because they are unique in having a borazole ring, which simulates a benzene ring in many ways, although the analogy is by no means complete. In a series of physical investigations, the present authors have obtained information on the molecular structure^{1,2} and electronic state¹ of these compounds. The present investigation has been undertaken in order to obtain further knowledge on the electronic state of a borazole ring from the observation of chemical shifts and splittings. The proton and B¹¹ magnetic resonances of borazole have already been reported.^{3,4} Borazole is distinct from benzene in that each proton is bonded to boron or nitrogen having a nuclear spin and also an electric quadrupole moment capable of affecting through its spin-lattice relaxation the relative broadening of multiplet components. Therefore, a systematic study was carried out on the proton magnetic resonances of a number of borazole derivatives.

EXPERIMENTAL

The method of synthesis and purification has already been described elsewhere^{1,2,4} for seven borazole derivatives used in the present investigation. The identification was made by means of their melting points, boiling points, infrared absorption spectra, freezing point depressions, etc. N-Trimethylborazole was prepared by Hohnstedt and Haworth's method,⁵ i.e., by the reduction of B-trichloro-N-trimethylborazole with sodium borohydride NaBH4 in triethylene glycol dimethyl ether solution. It was purified by distillation under reduced pressure, bp 133° C, mp -7.5° C as compared with 133° C and -7.8° C reported in the litera-

ture. B-trichloro-N-triethylborazole was synthesized from boron trichloride and ethylamine in accordance to Turner and Warne's method,6 dehydrochlorination being promoted by means of triethylamine. The identification was made by the determination of its mp (57°C) and the infrared spectra and also by the derivation from it of hexaethylborazole, which was already identified.1 B-Trimethyl-N-triethylborazole was prepared by the reaction of *B*-trichloro-*N*-triethylborazole with a suitable Grignard reagent and purified by fractionation. The resulting liquid was a new compound. Therefore, there are no physical data available in the literature for comparison.

The proton magnetic resonance spectra were recorded at room temperature by means of a INM-3 high-resolution NMR spectrometer of Japan Electron Optics Laboratory Company operating at 40 Mc. Chemical shifts defined by

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

were evaluated using cyclohexane as an internal standard. Here, H_s denotes the applied magnetic field for the proton signal of the sample and H_r is that for the reference signal.

ASSIGNMENTS

B-Trichloroborazole (Fig. 1) shows a single unresolved broad peak at -3.9_3 ppm due to protons bonded to nitrogen. The spectrum of B-trichloro-Ntrimethylborazole (Fig. 2) has a single sharp absorption at -1.7_5 ppm attributable to methyl groups. B-Trichloro-N-triethylborazole (Fig. 3) gives rise to a triplet centered at $+0.3_8$ ppm originating from methyl groups in ethyl groups and a quartet centered at -2.2_0 ppm attributable to methylene groups. The quartet has a slightly complicated structure due to the presence of nitrogen directly bonded to methylene groups.

N-Trimethylborazole (Fig. 4) shows a sharp intense absorption peak at -1.6_0 ppm attributable to methyl protons, in addition to fairly broad quartet lines

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¹H. Watanabe and M. Kubo, J. Am. Chem. Soc. 82, 2428 (1960); H. Watanabe, K. Ito, and M. Kubo, *ibid*. 82, 3294 (1960). ²H. Watanabe, M. Narisada, T. Nakagawa, and M. Kubo, Spectrochim. Acta 16, 78 (1960); H. Watanabe, T. Totani, T. Nakagawa, and M. Kubo, *ibid*. (to be published). ³K. Lio, H. Watanabe, and M. Kubo, *ibid*. (to be published).

⁸ K. Ito, H. Watanabe, and M. Kubo, J. Chem. Phys. 32, 947

⁴ K. Ito, H. Watanabe, and M. Kubo, Bull. Chem. Soc. Japan 33, 1588 (1960).

⁵L. Hohnstedt and D. T. Haworth, J. Am. Chem. Soc. 82, 89 (1960).

⁶ H. S. Turner and R. J. Warne, Chem. & Ind. (London) 18, 526 (1958).



FIG. 1. NMR spectrum of B-trichloroborazole in 10% carbon tetrachloride solution.

centered at -3.0_5 ppm due to protons bonded to B¹¹ having a nuclear spin equal to $\frac{3}{2}$. The effect of the less abundant isotope B¹⁰ was hardly discernible. A component line of the quartet could not be located exactly, because it was masked by the intense line of



FIG. 2. B-Trichloro-N-trimethylborazole in 10% carbon tetra-chloride solution.

methyl protons. Hexamethylborazole (Fig. 5) shows two sharp lines of equal intensity at -1.5_8 and 1.0_0 ppm. Considering the spectrum of *B*-trichloro-*N*trimethylborazole, the former was assigned unequivocally to protons in methyl groups bonded to nitrogen, while the latter to those bonded to boron. *B*-Trimethyl-*N*-triethylborazole (Fig. 6) shows a sharp line at $+0.9_3$ ppm due to BCH₃ protons and also a characteristic three-four pattern of ethyl groups centered at $+0.4_0$ and -1.9_8 ppm.



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B-Triethyl-N-trimethylborazole (Fig. 7) shows a sharp absorption at $+0.4_5$ ppm and a composite one at -1.5_0 ppm. The former was interpreted as an unresolved peak arising from protons in ethyl groups bonded to boron, while the latter was presumed to be a triplet attributable to NCH₃ protons, although the triplet structure was not very convincing. Mention should be made here that this compound underwent gradual decomposition, as has already been reported.¹ The spectrum of hexaethylborazole (Fig. 8) is comprised of a typical guartet centered at -2.1_7 ppm and three other prominent peaks. The former was assigned unequivocally to methylene protons in ethyl groups bonded to nitrogen. The highest peak at $+0.5_2$ ppm was presumed to be the unresolved signal of protons in ethyl groups attached to boron. A hump on its higher magnetic field side and the remaining two peaks constitute a triplet centered at $+0.4_0$ ppm. This triplet was attributed to methyl protons in ethyl groups bonded to nitrogen.



FIG. 5. Hexamethylborazole in 5% carbontetrachloride solution.

B-Trimethyl-*N*-triphenylborazole (Fig. 9) shows a peak at $+1.6_0$ ppm attributable to BCH₃ protons and another peak at -5.7_5 ppm having a structure to some extent. Although the resolution of the latter peak is open to suspicion, this peak was interpreted as the proton signal of phenyl groups. *B*-Triethyl-*N*-triphenylborazole (Fig. 10) yields two lines at $+1.0_5$ and -5.7_5 ppm. The former was assigned to the unresolved signal of BC₂H₅ protons while the latter to that of phenyl protons.

The numerical values of chemical shifts δ and spin coupling constants J are shown in Table I.

DISCUSSION

BH and NH Proton Chemical Shifts

The BH proton signals of *N*-trimethylborazole and the NH proton signal of *B*-trichloroborazole are very broad owing to the quadrupole relaxation arising from the presence of B^{11} and N^{14} nuclei, respectively. It has already been reported that, in the proton magnetic resonance spectrum of borazole, the multiplet structure



FIG. 6. B-Trimethyl-N-triethylborazole in 22% carbon tetra-chloride solution.

of an NH triplet is well resolved^{3,4} with its central line slightly stronger than the two outer ones. The corresponding triplet of *B*-trichloroborazole is collapsed to such an extent that the multiplet structure is hardly discernible. It is interesting to note that chlorine atoms bonded to boron affect the electric field gradient at N¹⁴ nuclei.

The chemical shifts, -3.0_5 and -3.9_3 of BH and NH protons (chemical shifts are expressed in ppm units) in these two compounds are close to those in borazole, -3.0_7 and -4.0_5 , respectively. According to studies on the ultraviolet spectra of borazole and its derivatives,⁷ a methyl group bonded to nitrogen and also a chlorine atom bonded to boron are known to



FIG. 7. B-Triethyl-N-trimethylborazole in 22% carbon tetra-chloride solution.

 7 C. W. Rector, G. W. Schaeffer, and J. R. Platt, J. Chem. Phys. 17, 460 (1949).



FIG. 8. Hexaethylborazole in 10% carbon tetrachloride solution.

affect the electronic state of the borazole ring: the former increases while the latter decreases the donoracceptor double bond character of BN bonds in the ring. However, the chemical shifts seem to be insensitive to this effect.

The chemical shifts of BH and NH protons in borazole and its derivatives are fairly close to each other, despite a considerable difference between the electronegativities of boron and nitrogen. As in a benzene ring,⁸ the diamagnetic ring current induced by the external magnetic field in a borazole ring is presumed to contribute to the chemical shifts of BH and NH protons. This contribution is estimated from the diamagnetic anisotropies of a borazole ring and a benzene ring,1 the molceular dimensions of these rings,9 and the contribution, -1.50, of the diamagnetic ring current to the chemical shift of protons in benzene¹⁰ as -0.9 and -1.1 for BH and NH protons, respec-



FIG. 9. B-Trimethyl-N-triphenyl borazole in 5% carbon tetrachloride solution.

tively. Subtracting this value from the observed BH and NH proton chemical shifts, one has -2.2 and -2.9respectively, as referred to cyclohexane, or +1.2 and +0.5 as referred to water as a standard. The latter values are close to the chemical shift of protons in a C=CH-C group ranging from -0.9 to $+1.0^{11}$ as observed for various compounds, rather than, for instance, to the NH proton chemical shift ranging over 1.9-2.0 in secondary amines. The result is plausible, since BN bonds in a borazole ring, which are isoelectronic with CC bonds in a benzene ring, are known to have a partial double-bond character.^{1,2,7,12}

BCH₃ and NCH₃ Proton Chemical Shifts

The proton chemical shift, 1.60, of BCH3 in B-trimethyl-N-triphenylborazole is greater by about 0.6 ppm than those in hexamethylborazole and B-trimethyl-N-triethylborazole, 1.0_0 and 0.9_3 . As has already been pointed out by the present authors,1 phenyl groups are bonded to a borazole ring with their planes perpendicular to the borazole ring. Accordingly, the diamagnetic ring current induced by the external field in the phenyl rings will shift the BCH₃ proton signal to a higher magnetic field. A calculation similar to that employed for the proton signal of benzene⁸ has led to a shift of about 0.5 ppm in good agreement with 0.6 ppm mentioned above. A similar relation holds for the proton signals of the corresponding Btriethyl-N-triY-compounds. Accordingly, the chemical

¹¹ J. A. Pople, W. G. Schneider, and H. J. Bernstein, *Highresolution Nuclear Magnetic Resonance* (McGraw-Hill Book Company, Inc., New York, 1959), pp. 242, 245. ¹² Electron diffraction: A. Stock and R. Wierl, Z. anorg. u. allgem. Chem. 203, 228 (1931); S. H. Bauer, J. Am. Chem. Soc. 60, 524 (1938); K. P. Coffin and S. H. Bauer, J. Phys. Chem. 59, 193 (1955). X-ray: D. L. Coursen and J. L. Hoard, J. Am. Chem. Soc. 74, 1742 (1952). uv spectra: C. C. J. Roothaan and R. S. Mulliken, J. Chem. Phys. 16, 118 (1948). IR and Raman spectra: B. L. Crawford, Jr., and J. T. Edsall, J. Chem. Phys. 7, 223 (1939); W. G. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, Discussions Faraday Soc. 9, 131 (1950). Dipole moments: K. L. Ramaswamy, Proc. Indian Acad. Sci. Dipole moments: K. L. Ramaswamy, Proc. Indian Acad. Sci. A2, 364 (1935).

⁸ H. J. Bernstein, W. G. Schneider, and J. A. Pople, Proc. Roy. Soc. (London) A236, 515 (1956).
⁹ S. H. Bauer, J. Am. Chem. Soc. 60, 524 (1938); B. P. Stoicheff, Can. J. Phys. 32, 339 (1954); K. Kimura and M. Kubo, J. Chem. Phys. 32, 1776 (1960).
¹⁰ J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc. 79, 846 (1957).

FIG. 10. B-Triethyl-N-triphenylborazole in 25% carbon tetrachloride solution.

shift of BCH₃ protons devoid of the effect of ring currents in phenyl groups is about 0.9-1.1 as referred to cyclohexane, or 4.3-4.5 as referred to water. The latter value is higher than the chemical shift, 3.6-4.4, of CCH₃ protons as expected from the electronegativity of boron.

The dependence of the chemical shift of NCH₃ in B-triX-N-trimethylborazoles on the B-substituents is related to the inductive effect rather than to the electromeric effect of the substituents. In other words, both the chemical shift of NCH₃ and the -I effect¹³ of the B-substituents increase progressively in the order of B-trichloro-N-trimethylborazole, N-trimethylborazole, hexamethylborazole, and B-triethyl-N-trimethylborazole, in agreement with a prediction from electronegativity considerations. The observed chemical shifts of NCH₃ protons ranging over 1.7-1.9 as referred to water are close to those of OCH₃ protons, 1.3-1.7, rather than to those of typical NCH₃ protons, 2.1-2.9.14 The result can be explained, because the electronegativity of nitrogen in a borazole ring is closer to that of oxygen than to that of nitrogen in ordinary nitrogen compounds, as described below.

BC₂H₅ and NC₂H₅ Proton Chemical Shifts

The proton signal of NC₂H₅ shows a normal threefour pattern, whereas that of BC₂H₅ is a single peak having no I-I splittings. Dailey and Shoolery¹⁵ have studied the proton magnetic resonance spectra of an ethyl group in C_2H_5X type compounds and found that the difference between the chemical shift of methyl protons and that of methylene protons is in linear rela-

TABLE I. Chemical shifts δ (in ppm) and spin coupling constants J (in cps) of B-triX-N-triY-borazoles. For borazole, J_{NH} denotes the spin coupling constant between nitrogen and hydrogen atoms directly bonded to each other. In B-triethyl-N-trimethylborazole, the same notation is used for the same pair of atoms separated by two chemical bonds.

					NCH ₃		BCH ₃	
х	Y	C_6H_5	NH	BH	NCH ₂	CCH₃	BC ₂ H ₅	J
Cl	Н		-3.98					
Cl	CH_3				-1.75			
Cl	C_2H_5				-2.2_{0}	+0.38		$J_{\rm HH} = 8.0$
н	\mathbf{H}		-4.0_{5}	-3.07				$J_{\rm NH} = 56, J_{\rm BH} = 138$
н	CH_3			-3.0_{5}	-1.60			$J_{\rm BH} = 125$
\mathbf{CH}_{3}	CH_3				-1.58		+1.00	
${ m CH}_{3}$	C_2H_5				-1.98	$+0.4_{0}$	$+0.9_{3}$	$J_{\rm HH} = 7.2$
C_2H_5	CH_3				-1.5_{0}		$+0.4_{5}$	$J_{\rm NH} = 3.0$
C_2H_5	C_2H_5				-2.17	$+0.4_{0}$	$+0.5_{2}$	J _{HH} =8.1
CH_3	C_6H_5	-5.75					+1.60	
C_2H_5	C_6H_5	-5.75					$+1.0_{5}$	

¹³ M. J. S. Dewar, The Electronic Theory of Organic Chemistry (Oxford University Press, New York, 1949). See also R. W. Taft, Jr., J. Am. Chem. Soc. 79, 1045 (1957).
⁴ L. H. Meyer, A. Saika, and H. S. Gutowsky, J. Am. Chem. Soc. 79, 4567 (1953).
¹⁵ B. P. Dailey and J. N. Schoolery, J. Am. Chem. Soc. 77, 3977 (1955).



tion to the electronegativity of an atom directly linked to the ethyl group.

E.N. =
$$0.695[\delta(CH_3) - \delta(CH_2)] + 1.71$$
.

This empirical equation first proposed for electronegativity values ranging over 2.6-3.9 was found by Baker¹⁶ to be valid approximately even for electronegativity values as small as 1.7 for lead and 1.4 for aluminum. According to this relation, the chemical shift difference $\Delta \delta$ vanishes for the electronegativity equal to 1.71. It has been shown theoretically¹⁷ that in this case I-Isplittings also disappear leading to a single sharp signal for ethyl protons, as was actually found in the present investigation.

Introducing $\Delta\delta$ equal to zero and 2.4–2.6 for BC₂H₅ and NC₂H₅ proton signals, respectively, into the aforementioned equation, one has 1.7 and 3.4-3.5 for the electronegativities of boron and nitrogen in a borazole ring. The frequency of the symmetric bending vibration of a methyl group is known to depend on the electronegativity of an atom directly bonded to the methyl group.¹⁸ The infrared absorption band of Ntrimethylborazole¹⁹ at about 1470 cm⁻¹, which is assigned to this mode of vibration, leads to the electronegativity of nitrogen equal to 3.5 in good agreement with 3.4-3.5 mentioned above. The deviation of these values beyond all conceivable errors from the accepted electronegativities of boron and nitrogen, 2.0 and 3.0 can be accounted for at least qualitatively by the electronic structure^{1,2,7,12} involving resonance among



Owing to the partial formation of donor-acceptor double bonds, the boron atoms and the nitrogen atoms of a borazole ring are presumed to be less electronegative and more electronegative, respectively.

NC₆H₅ Proton Chemical Shifts

The chemical shifts at -5.7_5 of phenyl protons in B-trimethyl-N-triphenylborazole and B-triethyl-N-

triphenylborazole are practically identical with that in benzene, -5.77. Although not all protons in a phenyl group are equivalent, the proton signals of ortho, meta, and para hydrogen atoms were not resolved in the present investigation. According to a study on the proton magnetic resonances of monosubstituted benzines,20 the proton signals are not resolved unless the substituent is NO2, CHO, COOH, NH2, etc., having a strong $\pm E$ effect or the phenyl group is bonded to fluorine showing a strong I effect. Since the phenyl groups are at right angles to the borazole ring as mentioned above, and hence π conjugation between the rings is inappreciable, and also because nitrogen is much less electronegative than fluorine, it is reasonable that the proton signals of these B-trialkyl-N-triphenylborazoles were not resolved.

Spin Coupling Constants

The spin coupling constant $J(B^{11}H) = 125$ cps was observed for N-trimethylborazole as compared with 134 cps evaluated by Phillips et al.²¹ from the B¹¹ magnetic resonance spectrum of the same compound. The value is close to 138 cps in borazole^{3,4} and also to 125 cps for the terminal protons of diborane.²² In general, the spin coupling constant J(XH) in a molecule changes with the isotopic substitution of the atom X in proportion to the nuclear g factor of the nucleus X.23 It is noteworthy that $J(B^{11}H)/g(B^{11})$ equal to 69.6 cps is considerably smaller than the corresponding ratios, 86-180 cps for C13, 113 cps for N14, 117 cps for F19, 190 cps for Si²⁹, and 81–150 cps for P³¹.

Muller and Pritchard²⁴ have measured spin coupling constants between protons and C13 nuclei for a number of hydrocarbons and interpreted the results on the basis of a simple semiempirical equation relating the coupling constant with the amount of s character of the carbon orbitals involved in the bonds. According to their theoretical calculations as well as experimental results, the ratio of the spin coupling constant J_{CH} between hydrogen and carbon directly bonded by the sp^2 hybridized atomic orbital of carbon and that between the same pair of atoms bonded by the sp^3 orbital is approximately 1.33 irrespective of the polarity of the CH bonds. The same relation holds surprisingly well also for boron compounds. The spin coupling constants J_{BH} in borazole and N-trimethylborazole involving sp^2 hybridization gives the mean value of 132 cps, whereas those in (CH₃)₂NHBH₃ and (CH₃)₃-NBH₃ equal to 94 and 97 cps, respectively,²¹ leads to

¹⁶ E. B. Baker, J. Chem. Phys. 26, 960 (1957).

 ¹⁷ See work cited in footnote 11, p. 116.
 ¹⁸ W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, J. Chem.
 Phys. 28, 777 (1958); L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (John Wiley & Sons, New York, 1958), 2nd ed., p. 25. ¹⁹ W. C.

¹⁹ W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins [Discussions Faraday Soc. 9, 131 (1950)] have reported the spectrum of this compound which is different from that recorded by the present authors [H. Watanabe, Y. Kuroda, and M. Kubo (to be published)].

²⁰ P. L. Corio and B. P. Dailey, J. Am. Chem. Soc. 78, 3043 (1956).

²¹ W. D. Phillips, H. C. Miller, and E. L. Muetterties, J. Am. ²⁴ W. D. Finings, n. C. Fining, and E. D. Endettereter, J. Theorem. Soc. 81, 4496 (1959).
 ²⁵ R. A. Ogg, Jr., J. Chem. Phys. 22, 1933 (1954).
 ²⁶ See work cited in footnote 11, p. 188.
 ²⁴ N. Muller and D. E. Pritchard, J. Chem. Phys. 31, 768 (1969).

^{(1959).}

the mean value of 96 cps for J_{BH} involving sp^3 hybridization. The ratio of the two mean values, 1.37, agrees excellently with 1.33 mentioned above.

The coupling constant $J(N^{14}H)$ was 3.0 cps across two chemical bonds in B-triethyl-N-trimethylborazole. J(HH) ranged over 7.2–8.1 cps between methyl protons and methylene protons in an ethyl group bonded to nitrogen in B-substituted N-triethylborazoles. These values are of the right order of magnitude.

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Proton Magnetic Resonance Spectra of Compounds of the Type X(C_2H_s)_n. Relative Signs of the X-H Spin Coupling Constants

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(Received August 15, 1960)

The high-resolution proton magnetic resonance spectra of phosphorus triethyl, tin tetraethyl, and lead tetraethyl have been studied at both 40 Mc and 60 Mc. The various spin-spin coupling constants (J) and the proton internal chemical shift (δ) values for these molecules have been obtained by an analysis of the spectra as A3B2 and A3B2X systems. (A denotes CH3 group protons, B the CH2 group protons, and X is a nucleus other than the proton with spin 1/2 such as P³¹, Sn¹¹⁷, Sn¹¹⁹, or Pb²⁰⁷.) In phosphorus triethyl it is found that J_{AX} and J_{BX} have opposite signs. The proton magnetic resonance spectrum of tin tetraethyl is a complex A_3B_2 type spectrum even at 60 Mc with "satellite" lines from naturally present Sn^{117} (C_2H_6)₄ (7.67%) and Sn^{119} (C_2H_6)₄ (8.68%) in the sample. Analysis of the satellite spectrum as an A_3B_2 type shows that J_{AX} and J_{BX} have opposite signs (here $X = Sn^{117}$ or Sn^{119}). The proton resonance spectrum of lead tetraethyl has been reinvestigated and it is found that the satellite lines due to Pb^{207} (C₂H₅)₄ do not show any asymmetry, in contrast with earlier observations of Baker. Probable causes for Baker's results are given and it is shown theoretically and experimentally that such an asymmetry does not truly exist. The coupling constants J_{AX} and J_{BX} are found to have opposite signs in lead tetraethyl also.

I. INTRODUCTION

'N a previous communication¹ it was shown by an A analysis of the "satellite" lines in the proton magnetic resonance spectrum of mercury diethyl that J_{AX} and J_{BX} (X = Hg¹⁹⁹) have opposite signs. (As before, we denote the protons of the CH₃ group by A and those of the CH₂ group by B.) It was further pointed out that by a study of the proton resonance spectra of compounds of the type $X(C_2H_5)n$, where the nucleus X has a spin of $\frac{1}{2}$, it might be possible to obtain the relative signs of J_{AX} and J_{BX} in favorable cases. In the present paper, we wish to deal with proton resonance spectra of three compounds of this type— $P(C_2H_5)_3$, $Sn(C_2H_5)_4$, and $Pb(C_2H_5)_4$ —to determine the relative signs of the X-H spin coupling constants in these molecules. P^{31} (natural abundance = 100%) has a nuclear spin of $\frac{1}{2}$, while tin has three naturally occurring isotopes with spin $\frac{1}{2}$. Of these three, only two isotopes, Sn^{117} (7.67%) and Sn^{119} (8.68%), occur in appreciable

abundance. Pb²⁰⁷, the isotope of lead with a spin of $\frac{1}{2}$, has a natural abundance of 21.11%. Assuming that in these molecules there is no spin interaction between protons of one ethyl group and those of another, in other words considering the ethyl groups in a given molecule to be equivalent, one might expect the proton resonance spectra of the three compounds investigated here to have the following features.

(a) Phosphorus triethyl: since the P^{31} nucleus has a spin of $\frac{1}{2}$ and since its natural abundance is 100% the proton resonance spectrum would be of the A₃B₂X type.

(b) Tin tetraethyl: the proton resonance spectrum of tin tetraethyl would be of the A_3B_2 type but the lines for $\operatorname{Sn}^{117}(C_2H_5)_4$ and $\operatorname{Sn}^{119}(C_2H_5)_4$ may show up due to the appreciable abundance of these tin nuclei. The spectra of these two species would fall under the A_3B_2X category.

(c) Lead tetraethyl: the spectrum of this compound would be of the A_3B_2 type and that due to Pb^{207} $(C_2H_5)_4$ would be of the A₃B₂X type. Earlier, Baker²

^{*} Present address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. ¹ P. T. Narasimhan and M. T. Rogers, J. Chem. Phys. 31,

^{1431 (1959).}

^{*} E. B. Baker, J. Chem. Phys. 26, 960 (1957).