4.6 mm.). It therefore appears that approximately 64% of the original non-condensable product was hydrogen. 0.825 mmole of water was added to the residue. On warming to room temperature the black solid began to turn white. The mixture was allowed to stand at room temperature for three weeks. The only volatile product obtained by distilling at $-78°$ was NH_3 (0.21 mmole; vapor pressure at $-80°$ found 37 mm., lit. value[21] 39 mm.).

On rapid heating above $200°$ BH_2CN often decomposed with explosive violence.

Results and Discussion

Diborane reacts with silyl cyanides at low temperatures according to the general equation

$$2R_3SiCN + B_2H_6 \longrightarrow 2R_3SiCN \cdot BH_3 \quad (12)$$
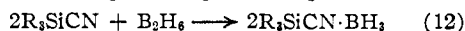
where R = H or CH_3. Available chemical evidence indicates that a borine adduct is formed. This is suggested by the reactions of $(CH_3)_3SiCN \cdot BH_3$ with HCl and $(CH_3)_3N$ as given in equations 7, 8 and 9.

Of considerable interest is the irreversible thermal decomposition of the adducts to the corresponding silane and a solid whose composition corresponds to BH_2CN, viz.

$$R_3SiCN \cdot BH_3 \longrightarrow R_3SiH + BH_2CN \quad (13)$$

The fact that silicon has available vacant 3d or-

bitals would suggest that a transfer of hydrogen from the boron to the silicon could occur readily by the means of an intermediate complex of the type

$$R_3SiCNBH_2$$
$$\vdots \quad |$$
$$H \quad H$$
$$| \quad \vdots$$
$$H_2BNCSiR_3$$
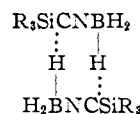
followed by the elimination of silane. This is consistent with the observation that hydrogen migration from the boron occurs more readily with the silicon derivatives than with the carbon analogs, as evidenced by the fact that some unchanged CH_3CN and B_2H_6 can be obtained on heating $CH_3CN \cdot BH_3$. Since the B–H hydrogen can presumably form a linkage more readily to the silicon in an intermediate complex than to the carbon of the CN group, it is understandable why the H migrates to the Si and not to the carbon as is the case in the formation of $(CH_2CH_2NBH)_x$ from $CH_3CN \cdot BH_3$. Reduction of the cyanide carbon only occurs on heating BH_2CN to higher temperatures.

PHILADELPHIA, PA.
AND CHICAGO, ILL.

B11 Magnetic Resonance Study of Boron Compounds

BY W. D. PHILLIPS, H. C. MILLER AND E. L. MUETTERTIES

B11 chemical shifts are presented for representative examples of most classes of boron-containing compounds. B11–H1 coupling constants are given for the boron hydrides and borane adducts. Some qualitative conclusions regarding bonding in these compounds are derived from observed chemical shifts and coupling constants. Temperature dependences of the B11 spectra of $B_2H_5 \cdot N(CH_3)_2$ and $B_{10}H_{14}$ are presented and discussed.

Introduction

The B11 magnetic resonance spectra of several boron-containing compounds already have been reported[1-10] and discussed, usually in connection with proofs of structure. However, with the exception of the work of Onak, et al.,[10] no systematic study of the nuclear magnetic resonances of this important class of compounds has been made. In the present study, boron chemical shifts and B11–H1 coupling constants for most types of boron-containing compounds are given, from which some qualitative conclusions regarding electronic struc-

(1) R. A. Ogg, Jr., J. Chem. Phys., 22, 1933 (1954).

(2) J. N. Shoolery, Disc. Faraday Soc., 19, 215 (1955).

(3) R. Schaeffer, J. N. Shoolery and R. Jones, THIS JOURNAL, 79, 4606 (1957).

(4) R. Schaeffer, J. N. Shoolery and R. Jones, ibid., 80, 2670 (1958).

(5) B. Siegel, J. L. Mack, J. U. Lowe, Jr., and J. Gallaghan, ibid., 80, 4523 (1958).

(6) R. Schaeffer, paper presented before the Division of Inorganic Chemistry, National Meeting of the A.C.S., San Francisco, California, April, 1958.

(7) R. E. Williams and I. Shapiro, J. Chem. Phys., 29, 677 (1958).

(8) A. H. Silver and P. J. Bray, ibid., 29, 984 (1958).

(9) R. E. Williams, S. G. Gibbins and I. Shapiro, ibid., 30, 320, 333 (1959).

(10) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, paper presented before the Division of Inorganic Chemistry, National Meeting of the A.C.S., Boston, Mass., April, 1959.

tures are made. In addition, some temperature dependences of the B11 spectra of $B_{10}H_{14}$ and $B_2H_5 \cdot N(CH_3)_2$ are reported and discussed.
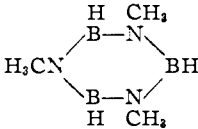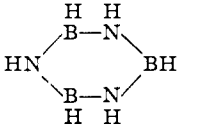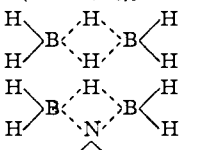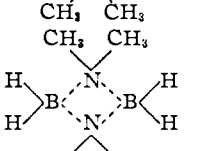
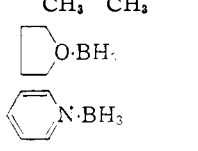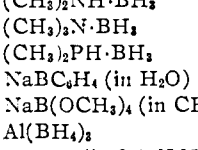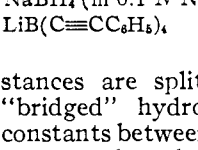## Results and Discussion

I. B11 Chemical Shifts.—An example of a B11 magnetic resonance spectrum is that of $B_2H_5 \cdot N(CH_3)_2$ shown in Fig. 1. The three main triplet components centered around 237, 367 and 497 c.p.s., arise from nuclear spin coupling between boron atoms and the two "terminal" hydrogen atoms bonded to each boron. The single "bridge" hydrogen atom splits each of the triplet components into doublets of spacing 29 c.p.s. Because of the low nuclear moment and probably weak coupling to the B11 nuclei, the "bridge" N14 nucleus with a spin of $I = 1$ only contributes to the breadth of the B11 resonance through spin-spin coupling. The B11 nucleus has a nuclear spin of 3/2 and a non-zero electric quadrupole moment; and in general, because of quadrupole relaxation effects, it exhibits resonance line widths considerably greater than those observed for hydrogen and fluorine. For this reason, coupling constants between boron and hydrogen separated by more than one bond length have not been observed. Indeed line widths of boron resonances are such that only in a few in-

TABLE I

B^{11} Chemical Shifts and B^{11}–H^1 Spin–spin Splittings in Boron Compounds

Compound	$\dfrac{H_c - H_R}{H_R} \times 10^6$	J_{B-H} (c.p.s.) Coup. constant
B(CH$_3$)$_3$	−68.2	
B(C$_2$H$_5$)$_3$	−66.6	
C$_6$H$_5$BCl$_2$	−35.9	
BF$_3$	+ 6.6	
BCl$_3$	−29.2	
BBr$_3$	−22.7	
BI$_3$	+23.3	
C$_6$H$_5$B(OH)$_2$ (in pyridine)	−15.2	
C$_6$H$_5$B(OH)$_2$ (in acetone)	−14.3	
C$_6$H$_5$B(OC$_2$H$_5$)$_2$	−10.4	
H$_3$C–N (borazine, H CH$_3$ / B–N \ BH \ B–N / H CH$_3$)	−14.3	134
HN (borazine, H H / B–N \ BH \ B–N / H H)	−12.3	136
B[N(C$_2$H$_5$)$_2$]$_3$	−12.9	
B(OCH$_3$)$_3$	0	
B(OC$_2$H$_5$)$_3$	+ 0.6	
B(O-n-C$_3$H$_7$)$_3$	+ 0.5	
B(O-n-C$_4$H$_9$)$_3$	− 0.1	
H$_2$B(H)$_2$BH$_2$ (diborane)	+ 0.5	137 (terminal) 48 (bridge)
(aminodiborane, CH$_3$ CH$_3$ N)	+36.7	130 (terminal) 29 (bridge)
(CH$_3$ CH$_3$ N)$_2$B$_2$H$_4$	+14.5	116
O·BH$_3$	+19.0	103
N·BH$_3$	+31.4	90
(CH$_3$)$_2$NH·BH$_3$	+32.8	94
(CH$_3$)$_3$N·BH$_3$	+24.9	97
(CH$_3$)$_2$PH·BH$_3$	+55.6	96
NaBC$_6$H$_4$ (in H$_2$O)	+16.1	
NaB(OCH$_3$)$_4$ (in CH$_3$OH)	+15.2	
Al(BH$_4$)$_3$	+55.1	86
NaBH$_4$ (in 0.1 N NaOH)	+61.0	81
LiB(C≡CC$_6$H$_5$)$_4$	+49.4	

stances are splittings between B^{11} and directly "bridged" hydrogen atoms observed. Coupling constants between B^{11} and "bridge" hydrogen atoms appear to be only $^1/_2$ to $^1/_5$ as great as those between B^{11} and "terminal" hydrogen atoms.

Chemical shifts are presented for several classes of boron compounds in Table I. The 130 p.p.m. range of chemical shifts for B^{11} is greater than the
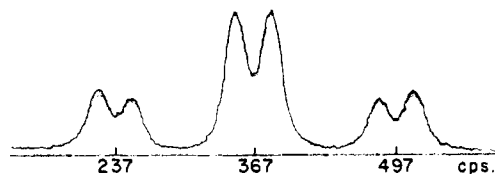

Fig. 1.—B^{11} resonance of B$_2$H$_5$·N(CH$_3$)$_2$ (−10°); 10 Mc./ sec.; ref. B(OCH$_3$)$_3$.

20 p.p.m. for H^1 [11] and less than the 300 p.p.m. for F^{19} [12] and P^{31}.[13]

Saika and Slichter[14] treated F^{19} chemical shifts in terms of a paramagnetic shift arising from the difference in electron occupancy of the bonding p_z and non-bonding p_x and p_y orbitals. Attempts have been made to correlate P^{31} chemical shifts on a similar basis.[18,15]

Qualitatively, the major features of the B^{11} chemical shifts can be accounted for on the basis of such a "paramagnetic shift." The extreme low field resonance for the compounds listed in Table I is observed for B(CH$_3$)$_3$, and the high field resonance, for BH$_4^-$. Neglecting hyperconjugation, the bonding hybrid of boron in B(CH$_3$)$_3$ should be sp^2 with a vacant p_z orbital; the bonding hybrid of boron in BH$_4^-$ should be sp^3 with full tetrahedral symmetry about boron. If such an effect dominates B^{11} chemical shifts, all B^{11} resonances would be expected to fall between those for B(CH$_3$)$_3$ and BH$_4^-$. As is seen from Tables I, II and III,

TABLE II

B^{11} Resonances of Boron Fluorides

Compound	B^{11} $\left(\dfrac{H_c - H_R}{H_R} \times 10^6\right)$
BF$_3$	+ 6.6
O·BF$_3$	+19.0
NH$_3$·BF$_3$ (H$_2$O)	+20.2
(CH$_3$)$_4$N·BF$_3$ (C$_6$H$_5$–CH$_2$OH)	+18.6
TlBF$_4$ (H$_2$O)	+18.8
AgBF$_4$ (H$_2$O)	+20.3
(C$_2$H$_5$)$_2$O·BF$_3$	+18.2
CH$_3$OH·BF$_3$	+19.1
H$_3$BO$_2$F$_2$	+18.7

such is the case for all B^{11} resonances of this study with the exception of the apex boron atom of B$_5$H$_9$. This trend also has been noted by Onak, et al.,[10] in their survey of B^{11} resonances. The B^{11} resonances of the BH$_3$ adducts with ethers and amines are consistent with this interpretation in that the reduced paramagnetic shift observed for boron in these compounds reflects presumably partial electron occupation of the boron p_z orbital as the result of donation of lone pair electrons from the oxygen and nitrogen atoms. Adduct formation is accompanied by a change of boron hybridization,

(11) L. H. Meyer, A. Saika and H. S. Gutowsky, This Journal, 76, 4567 (1953).

(12) H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys., 21, 279 (1953).

(13) N. Muller, P. C. Lauterbur and J. Goldenson, This Journal, 78, 3557 (1956).

(14) A. Saika and C. P. Slichter, J. Chem. Phys., 22, 26 (1954).

(15) J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, This Journal, 78, 5715 (1956).

Table III

B[11] Resonances of Boron Hydrides

Compound	$B^{11} \left(\frac{Hc - H_R}{H_R} \times 10^6 \right)$	J_{B-H} (c.p.s.)
	+ 0.5	137, 48
	+36.7	130, 29
$B_3H_7 \cdot O(C_2H_5)_2$	+25.8	31 ± 5
NaB_3H_8 (in H_2O)	+46.5	32
B_4H_{10}	BH_2 +25.0 BH +59.9	BH_2 132 BH 156
B_5H_9	base +30.8 apex +69.6	base 168 apex 176
$B_{10}H_{14}$	+6.9, +19.5, +53.9	124, 128, 159
$B_{10}H_{12}I_2$	+4.0, +17.6, +60.7	136, 137
B_5H_{11}	−16.2, +0.7, +49.8[a]	134, 162, 142[a]

[a] Data taken from ref. 3.

presumably from sp^2 to sp^3, which also would be expected to reduce the paramagnetic shift.

The B[11] resonances of BH_4^- and $B(C\equiv CC_6H_5)_4^-$ are similar; however, the resonance for $B(C_6H_5)_4^-$ exhibits a paramagnetic shift of 45 p.p.m. relative to BH_4^-. That such a shift is not attributable to the Pople ring current[16] observed in aromatic systems is shown by comparison of the B[11] resonances of $C_4H_9B(OH)_2$ and $C_6H_5B(OH)_2$ in which substitution of phenyl for n-butyl on boron produces a paramagnetic shift of only 0.9 p.p.m. Also, the magnitude of the $BH_4^- - B(C_6H_5)_4^-$ shift is far too large to be accounted for on the basis of a ring current shift. The large shift might largely reflect the electronegativity differences between $C_6H_5^-$ and H^-. The chemical shifts of $B(C_6H_5)_4^-$ and BF_4^- are almost identical.

The chemical shifts for boron in BCl_3, BBr_3 and BI_3 parallel the electronegativities of the halogens. However, the boron chemical shift for BF_3 is between those of BBr_3 and BI_3. A possible explanation, first proposed by Onak, $et\ al.$,[10] of this apparent anomaly is significant "back coördination" to the boron p_z orbital from the non-bonding electrons of the fluorine atoms. The n.m.r. results and interpretations are consistent with arguments for back coördination based on the shortening of B–X bond distances in BX_3[17a] and the conclusion of Brown and Holmes,[17b] among others, based on the observation that BF_3 is a weaker acceptor molecule than BBr_3 and BCl_3, at least with respect to pyridine and to nitrobenzene. The borate esters have resonances similarly shifted from the low field resonance position expected solely on electronegativity considerations. In view of this shift and since the esters do display a rather low order of acceptor character, it would appear that back coördination from the non-bonding electrons of the oxygen atoms to the boron p_z orbital is present to a significant degree in the esters.

II. Resonances of BF₃ and its Adducts.—B[11] resonances of BF_3 and BF_1^- and some adducts of

(10) J. A. Pople. $Proc.\ Roy.\ Soc.\ (London).\ A$ **239**, 550 (1957).

(17) (a) N. V. Sidgwick. "The Chemical Elements and Their Compounds." Vol. I, Oxford Univ. Press, London, 1950, p. 392; (b) H. C. Brown and R. R. Holmes, This Journal, **78**, 2173 (1956).

BF_3 with ethers and amines are presented in Table II. The B[11] resonance of BF_4^- exhibits a paramagnetic shift of about 41 p.p.m. relative to that of BH_4^-. Since both BF_4^- and BH_4^- possess tetrahedral symmetries, B[11] resonances of the two species would be expected to be the same if orbital paramagnetism were the only term affecting these chemical shifts. The chemical shifts between the two species is best ascribed to effects of the highly electronegative fluorine atoms in reducing the diamagnetic shielding about boron in BF_4^-, and so giving rise to a low field shift of the BF_4^- resonance relative to that of BH_4^-.

The boron resonances of the BF_3 adducts with ethers and amines are essentially coincident with that of BF_4^-. This suggests that the electronic configuration around the boron atom in BF_4^- and in the adducts are similar. It would appear from these results that the boron is tetrahedrally bonded in these adducts[18] (sp^3 hybrid) and that bonding between adduct components could be represented as $F_3B^- - N^+R_3$.

III. B[11]–H[1] Coupling Constants.—Gutowsky, McCall and Slichter[12] have suggested that magnitudes of coupling constants between hydrogen and other directly bonded nuclei should depend significantly on the fractional s-character of the bonding hybrid of the directly bonded nucleus. Thus, coupling constants between hydrogen and sp^2 boron should be larger than those between hydrogen and sp^3 boron.

The results of Table I suggest that such a trend exists in the boron hydrides. The bonding hybrid of boron in BH_4^- is sp^3, and for this compound a B[11]–H[1] coupling constant of 81 c.p.s. is observed. The structure[19,20] and electronic spectrum[21] of borazole indicate that the electronic configuration of boron in this molecule may be described by $pzsp^2$, with the B–H σ-bond consisting of a hydrogen 1s orbital and a boron sp^2 hybrid orbital. For borazole the B[11]–H[1] coupling constant is 136 c.p.s., and for N-trimethylborazole, 134 c.p.s. B[11]–H[1] coupling constants found in BH_3 adducts with ethers and amines (Table I) lie between the 136 c.p.s. value for borazole and the 81 c.p.s. value for BH_4^-. Configurations and boron quadrupole coupling constants in BH_3 adducts have been interpreted[22] in terms of boron hybridization intermediate between sp^2 and sp^3. The magnitudes of B[11]–H[1] coupling constants of BH_3 adducts as interpreted in terms of the s-character of the boron bonding hybrid are seen to be qualitatively consistent with conclusions regarding boron hybridization as derived from other studies.

IV. Resonances of Boron Hydrides.—B[11] chemical shifts and B[11]–H[1] coupling constants for several boron hybrides are given in Table III. The spectra of all except $B_2H_5 \cdot N(CH_3)_2$ and $B_3H_8^-$ previously have been reported and dis-

(18) X-Ray diffraction studies have, in fact, shown boron to be nearly tetrahedral in several boron halide complexes, $e.g.$, <FBF and <NBF are 107 and 112°, respectively, in (CH₃)₃NBF₃ (S. Geller and J. L. Hoard, $Acta\ Cryst.$, **4**, 399 (1951)).

(19) S. Bauer, This Journal, **60**, 524 (1938).

(20) A. Stock and R. Wierl, $Z.\ anorg.\ Chem.$, **203**, 228 (1931).

(21) C. C. J. Roothaan and R. S. Mulliken, $J.\ Chem.\ Phys.$, **16**, 118 (1948).

(22) T. P. Das, $ibid.$, **27**, 1 (1957).

cussed,[1-3,7,9,10] although in several cases calibrations were not given. In most instances, assignment[1,2] of resonances in these compounds to the proper boron atoms has followed directly from analysis of resonance intensity and multiplet structure. For $B_{10}H_{14}$[3,7] and B_5H_{11}[3,9] some ambiguity exists in analysis of the spectra in terms of the structures deduced from X-ray studies, and assignment has been made on the basis of an assumed correlation between the resonance field and calculated electron densities at boron atoms. However, as Schaeffer, Shoolery and Jones[3] have pointed out and as was suggested by the previous discussion of chemical shifts in this study, no good theoretical or experimental reasons exist for believing boron chemical shifts should be dominated by diamagnetic shieldings.

Coupling constants between boron and "conventional," i.e., non-bridged, hydrogen atoms in the boron hydrides vary between 129 and 176 c.p.s. (Table III). If B^{11}–H^1 coupling constants do reflect the s-character of the boron bonding hybrid as was suggested in the previous section, boron hybrids in the boron hydrides would appear to vary between the equivalents of sp^2 and sp hybrids. However, in view of the complexity of the electronic structures of the boron hydrides and in the absence of a quantitative treatment of B–H coupling constants and boron chemical shifts, any conclusions regarding the electronic structures of boron hydrides as derived from magnetic resonance data must be accepted with reservation.

V. Spectra of $B_3H_8^-$ and of $B_3H_7 \cdot O(C_2H_5)_2$.— The B^{11} magnetic resonance spectrum of an ether solution of NaB_3H_8 is presented in Fig. 2. The

$$NaB_3H_8 / (C_2H_5)_2O$$
$$B^{11} - 10 \text{ Mc./sec.}$$

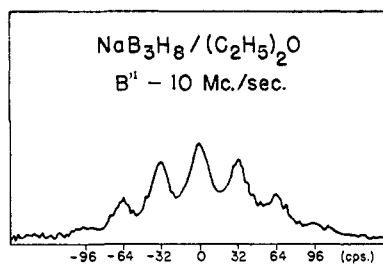-96 -64 -32   0   32   64   96 (cps.)

Fig. 2.—B^{11} resonance of $B_3H_8^-$ in ether.

spectrum appears to consist of seven components with a separation between adjacent peaks of 32 c.p.s. Quantitative intensity measurements are rendered difficult by the breadth and close spacing of the lines, but the intensities are approximately in the ratios to be expected for six hydrogen atoms coupled equally or nearly equally to each of three equivalent boron atoms. Similarly, the B^{11} spectrum of $B_3H_7 \cdot O(C_2H_5)_2$, while more diffuse than that of $B_3H_8^-$, appears to be a symmetrical sextuplet of spacing about 30 c.p.s.

A structure of $B_3H_8^-$ consistent with this spectrum is one of D_{3h} symmetry, shown in Fig. 3 in which each of three equivalent boron atoms is bonded to six "bridge" hydrogen atoms. Each of the type II hydrogen atoms would be "bridged" to three boron atoms, and the molecule would contain no "conventional" B–H bonds. The $B_3H_7 \cdot O(C_2H_5)_2$ structure would be analogous; a type
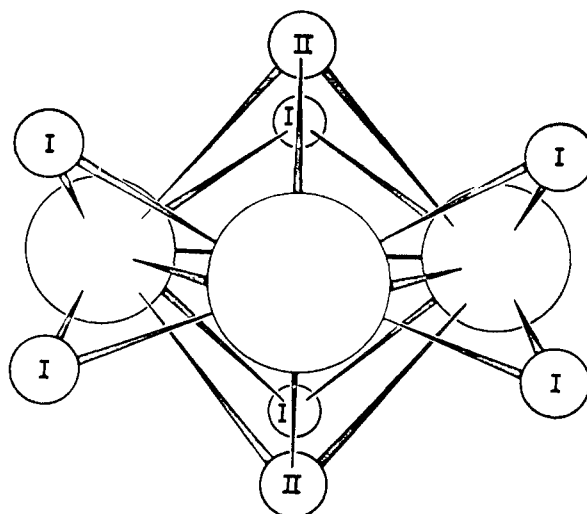
Fig. 3.—Possible structure of $B_3H_8^-$.

II hydrogen would be replaced by the oxygen atom of the ether molecule. R. W. Parry[23] has pointed out that this structure type is inconsistent with most recent X-ray work on $B_3H_7 \cdot N(CH_3)_3$ which indicates that this molecule does not possess a threefold symmetry axis in the solid state.

W. N. Lipscomb[24] has suggested that the B^{11} spectrum of $B_3H_8^-$ may actually consist of nine lines, with the outermost peaks being too weak for observation. Such an interpretation would be consistent with a more conventional structure for the anion, one containing non-equivalent boron atoms and conventional B–H hydrogen atoms as well as bridged hydrogen atoms, but with the equivalence of boron and hydrogen being achieved by some intramolecular tunnelling process. Such an interpretation previously has been invoked by Ogg and Ray[25] to account for the apparent equivalence of the hydrogen atoms of $Al(BH_4)_3$.

The H^1 spectrum of NaB_3H_8 in D_2O is rather diffuse but contains a discernible fine structure of spacing about 32 c.p.s. The B^{11} spectrum of the molecule exhibited no detectible temperature dependence to $-60°$, nor did the H^1 spectrum to $90°$. It would appear that spin saturation experiments and use of deuterium derivatives will be necessary before further progress can be made in unravelling the magnetic resonance spectrum of $B_3H_8^-$.

VI. B^{11} Temperature Dependence. a. $B_2H_5 \cdot N(CH_3)_2$.—A temperature dependence has been found in the B^{11} spectrum of $B_2H_5 \cdot N(CH_3)_2$ and is shown in Fig. 4. It is seen that, as the temperature is raised from -10 to $40°$, the B^{11} resonance is broadened and the doublet splittings almost eliminated. Such a temperature dependence is consistent with some rate process possible to the $B_2H_5 \cdot N(CH_3)_2$ molecule that results in H^1 exchange at a rate of about 10^2 sec.$^{-1}$ at $40°$. Cleavage of a bridge B–H bond could, through sequences partially diagrammed below, produce the observed temperature dependence. Identical spectral results would result through cleavage of the bridge

(23) Private communication.

(24) Private communication.

(25) R. A. Ogg, Jr., and J. D. Ray, Disc. Faraday Soc., 19, 215 (1955).

40°
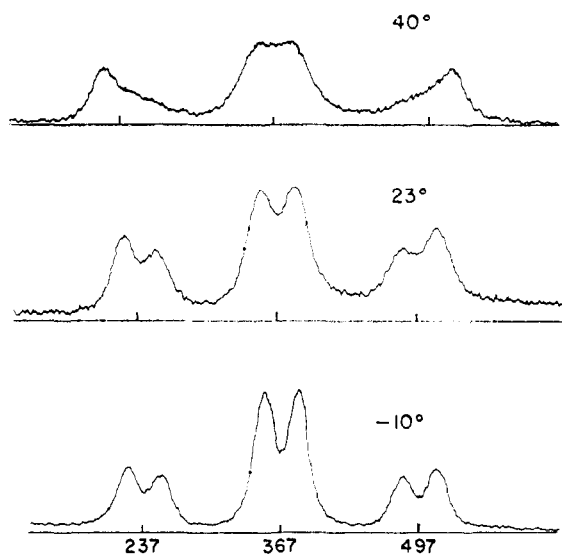
23°

−10°

237　　367　　497

Fig. 4.—Temperature dependence of B^{11} resonance of $B_2H_5 \cdot N[CH_4]_2$; 10 mc./sec.; ref. $B(OCH_3)_3$.

R_2N^- group to give an intermediate terminal R_2N group. Since this latter sequence also necessarily requires B–H bridge cleavages, the former sequence of only B–H bridge cleavage is the simpler but not necessarily the more probable of the two.[26] A quantum mechanical tunnelling similar to that proposed by Ogg and Ray[25] for $Al(BH_4)_3$ and Lipscomb[24] for $B_3H_8^-$ could also account for the observed spectra. Studies at higher temperatures will be necessary to establish the kinetic process responsible for the observed temperature dependence.
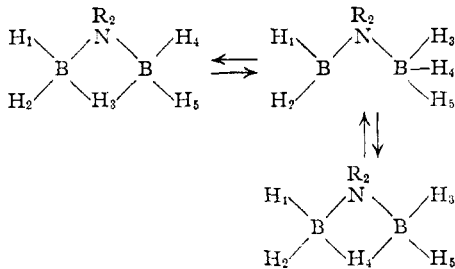
b. $B_{10}H_{14}$.—A rather striking temperature dependence was noted in the B^{11} spectra of acetone solutions of $B_{10}H_{14}$. Room temperature B^{11} spectra of $B_{10}H_{14}$ dissolved in benzene and in acetone are shown in Fig. 5. While some controversy still exists regarding assignment of the B^{11} spectrum of $B_{10}H_{14}$,[2,3,7,9] it appears to be probable that the doublet centered around 539 c.p.s. arises from a pair of equivalent boron atoms, and those centered around 70 and 193 c.p.s. from two sets of equivalent or nearly equivalent boron atoms, each set consisting of four atoms. The intensity of the peak at 131 c.p.s. is considered to result from accidental overlap of components from the 70 and 193 c.p.s. doublets.

The room temperature B^{11} spectrum of $B_{10}H_{14}$ dissolved in benzene (Fig. 5) consists of three com

(26) Bromodiborane and the alkylated diboranes have the substituent groups in terminal positions. The aminodiboranes are the only substituted diboranes in which the substituent group is known to be in a bridge position, although it is highly probable that phosphino- and alkanethiodiboranes have the substituent group in the bridge position.
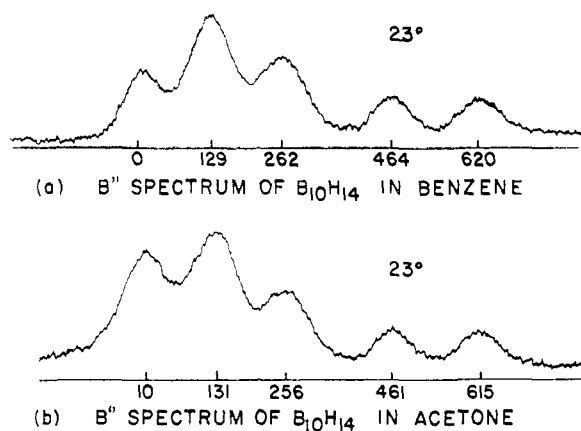
23°

0　129　262　　464　620

(a)　B^{11} SPECTRUM OF $B_{10}H_{14}$ IN BENZENE

23°

10　131　256　　461　615

(b)　B^{11} SPECTRUM OF $B_{10}H_{14}$ IN ACETONE

Fig. 5.—B^{11} resonance of $B_{10}H_{14}$ in (a) benzene, (b) acetone.

ponents of relative intensities 1:2:1 in the region between 0 and 262 c.p.s., consistent with the above interpretation of the spectrum. However, the B^{11} spectrum of $B_{10}H_{14}$ dissolved in acetone is asymmetrical in this region, with the 256 c.p.s. resonance being much weaker than the 10 c.p.s. resonance. This asymmetry is increased at reduced temperature, with the 256 c.p.s. resonance nearly vanishing and the 10 c.p.s. resonance becoming as intense as the 131 c.p.s. resonance at −50°. Conversely, at about +60°, the B^{11} spectrum of $B_{10}H_{14}$ in acetone becomes essentially identical with that of the compound in benzene.

The temperature dependence of the B^{11} spectrum of $B_{10}H_{14}$ in acetone suggests strong solvent–solute interaction. On the basis of this interpretation, the spectrum of $B_{10}H_{14}$ in benzene and in acetone at 60° would represent the non-associated molecule. The −50° spectrum of $B_{10}H_{14}$ in acetone would represent the $B_{10}H_{14}$/acetone complex. The main effect of $B_{10}H_{14}$–acetone complex formation then would be to cause the set of four boron atoms exhibiting a resonance at 193 c.p.s. in the non-complexed form to become accidentally equivalent, in the n.m.r. sense, to the set of four atoms at 70 c.p.s. If this interpretation is correct, it is interesting to note that the equilibrium is slow ($\tau >$

$$B_{10}H_{14} + \text{acetone} \rightleftharpoons B_{10}H_{14} \cdot \text{acetone}$$
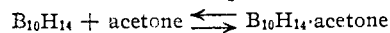
10^{-3} sec.), since separate rather than averaged resonances for complexed and non-complexed $B_{10}H_{14}$ are observed.

Experimental

Materials and Method.—The compounds examined in this study were either purchased from commercial sources or were prepared by literature procedures. In most instances, the materials were purified by standard methods.

The B^{11} magnetic resonance spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet[27] at a frequency of 10 Mc. and a field of about 7.315 gauss. Spectra were calibrated relative to the boron resonance of $B(OCH_3)_3$ using the side band technique.[28]

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(27) Varian Associates, Palo Alto, California.
(28) J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 6108 (1951).