In this connection, the N-hydrogen borazines (I and II) can be expected to take more planar structures than the N-substituted B-trivinylborazines, because the van der Waals radius of hydrogen is smaller than that of the other substituents. This expectation is supported by the ultraviolet absorption curve of B-tris(*cis*-phenylvinyl)borazine, which has a strong resemblance to that of B-tris(phenylethynyl)-N-triphenylborazine.

Further evidence is obtained by comparing the infrared spectra of the two isomers of B-tris(phenylvinyl)-N-triphenylborazine. The band at 776 $cm.^{-1}$ of the hydrogenation product (VI) and that at 991 $cm.^{-1}$ of the Grignard reaction product (VII) can readily be assigned to the characteristic out-of-plane bending vibration of *cis* and *trans* olefinic CH groups. These assignments are made on the basis[8] that the *cis* olefinic CH bending appears near 690 $cm.^{-1}$ and the *trans* one at about 960 to 970 $cm.^{-1}$. In any of the infrared spectra of the other hydrogenation products, we did not find bands assignable to the *trans* olefinic out-of-plane bending. Thus, the partial hydrogenation onto the ethynyl groups of borazine derivatives results in the *cis* addition.

The n.m.r. data given in Table II can also be adduced effectively to determine the configurations and conformations of the vinyl groups. As for a –CH=CH– group, we expect signals to appear as a single quartet for the isomers having three substituents symmetrically. On the other hand, the isomers with unsymmetrically oriented substituents would afford two quartets with a relative intensity of 1:2. In a similar way, the N-methyl protons of unsymmetrical isomers may give rise to two peaks and those of symmetric ones to a single singlet. The observations of an N-methyl singlet and a single quartet of vinyl protons indicate symmetric conformations for all the compounds in Table I.

Here, it should be mentioned that examination of the molecular model shows that internal rotation around B—C= bonds of the *trans* vinyl isomer (VII) is almost free in the sense of steric hindrance and that one might be unable to distinguish the two *trans* isomers (conformers) in Figure 1, at room temperature. The internal rotation seems to be only slightly restricted in the molecules of N-hydrogen borazines (I and II) and may average out the magnetic environment of the vinyl protons to give a single quartet. Therefore, the symmetric structure cannot be concluded from the n.m.r. data alone for these three molecules.

It is worthwhile to note that the coupling constants between the two vinyl protons are larger than those observed in the usual *cis* olefinic compounds.[9]

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(8) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York and London, 1963, p. 59.

(9) Reference 8, p. 87.

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CONTRIBUTION FROM CHEMISTRY HALL,
IOWA STATE UNIVERSITY, AMES, IOWA

# The Nuclear Magnetic Resonance Spectra of Some Boron Complexes

BY C. W. HEITSCH[1]

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Chemical shifts and coupling constants of a number of boron complexes are presented and discussed. Where available, shifts are compared with enthalpies of formation of the complexes. While $B^{11}$ resonance proves to be a poor criterion of stability, groups on the boron or groups in the ligand give shifts that can be correlated with enthalpies where available, provided the variations in structure of the compounds compared are held within narrow limits.

Many authors make reference to chemical shifts or differences in chemical shifts as a criterion of relative stability of donor–acceptor complexes. This reasoning is based on the concept that chemical shift is a measure of electron density. While the concept is frequently challenged on the basis of both theoretical and empirical grounds, the reasons for this failure are not readily understood. Precise data on a series of closely related compounds could be of assistance in this respect. Moreover, it might be possible to establish a set of limits to the variations in the structure of a series of molecules, within which limits correlations between stability and chemical shift would be valid.

Since the beginning of this work, Coyle and Stone have reported observations similar to those presented here.[2] However, since many of the compounds considered are different, and there are some variations in the conclusions, it was decided to report the present data and include the boron resonances.

## Experimental

The $BF_3$ and $B(CH_3)_3$ complexes were prepared by direct combination of the borane and ligand in a vacuum line. Triethylamine, trimethylamine, and ammonia from commercial

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[1] E. I. du Pont de Nemours and Co., Explosives Department, Experimental Station Laboratory, Wilmington, Del.

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

Table I

Chemical Shifts (in p.p.m.)[a]

| Compound | Solvent | $(\mathit{CH}_3\mathrm{CH}_2)_3\mathrm{N}$ | $(\mathrm{CH}_3\mathit{CH}_2)_3\mathrm{N}$ | $B^{11}$ | Other | |
|---|---|---|---|---|---|---|
| | | | | | Nucleus | Shift |
| $(C_2H_5)_3N$ | $CH_3CN$ | −0.95 | −2.46 | ... | ... | ... |
| $(C_2H_5)_3NBH_3$ | $CH_3CN$ | −1.13 | −2.75 | 31.7 | $H^1{}_B$ | −1.38 |
| $(C_2H_5)_3NBF_3$ | $CH_3CN$ | −1.24 | −2.93 | 18.3 | $F^{19}{}_B$ | 148.9 |
| $(C_2H_5)_3NB(CH_3)_3$ | $CH_3CN$ | −0.96 | −2.49 | 31.8 | $H^1{}_{CB}$ | −0.52[b] |
| | | $R_2$ $\mathit{H}NBX_3$ | $R_2$ $\mathit{CH}_3NBX_3$ or $(\mathit{CH}_3)_3PBX_3$ | | | |
| $(CH_3)_3PBH_3$ | $CH_3CN$ | ... | −1.29 | 55.1 | $H^1{}_B$ | −0.44 |
| $(CH_3)_3PBF_3$ | $CH_3CN$ | ... | −1.38 | 18 | $F^{19}{}_B$ | 139.0 |
| $(CH_3)_3PB(CH_3)_3$ | $CH_3CN$ | ... | −1.16 | 61.6 | $H^1{}_{CB}$ | 0.29 |
| $(CH_3)_3NBH_3$ | $C_6H_6$ | ... | −2.20 | ... | $H^1{}_B$ | −2.13 |
| $(CH_3)_3NBH_3$ | $F_2ClCCCl_2F$ | ... | −2.55 | ... | $H^1{}_B$ | −1.65 |
| $(CH_3)_3NBH_3$ | $CDCl_3$ | ... | −2.57 | ... | $H^1{}_B$ | −1.64 |
| $(CH_3)_3NBH_3$ | 1,4-Dioxane | ... | −2.56 | ... | $H^1{}_B$ | −1.62 |
| $(CH_3)_3NBH_3$ | $CH_3CN$ | ... | −2.58[b] | 25.9[c,d] | $H^1{}_B$ | −1.62 |
| $(CH_3)_3NBF_3$ | $CH_3CN$ | ... | −2.58[b] | 17.5 | $F^{19}{}_B$ | 163.5 |
| $(CH_3)_3NB(CH_3)_3$ | $CDCl_3$ | ... | −2.38[b] | ... | $H^1{}_{CB}$ | 0.34[b] |
| $(CH_3)_3NB(CH_3)_3$ | $CH_3CN$ | ... | −2.36[b] | 18.2 | $H^1{}_{CB}$ | 0.36 |
| $(CH_3)_2NHBH_3$ | $CDCl_3$ | −4.4 | −2.52 | ... | $H^1{}_B$ | −1.46 |
| $(CH_3)_2NHBH_3$ | 1,4-Dioxane | −4.7 | −2.41 | ... | $H^1{}_B$ | −1.40 |
| $(CH_3)_2NHBH_3$ | $CD_3CN$ | −4.5 | −2.46 | 32.4[c,d] | $H^1{}_B$ | −1.41 |
| $(CH_3)_2NHBF_3$ | $CH_3CN$ | −4.8 | −2.46 | 18.6 | $F^{19}{}_B$ | 158.8 |
| $(CH_3)_2NHB(CH_3)_3$ | $CDCl_3$ | −2.8 | −2.40 | ... | $H^1{}_{CB}$ | 0.38 |
| $(CH_3)_2NHB(CH_3)_3$ | $CH_3CN$ | −3.6 | −2.27 | 22.3 | $H^1{}_{CB}$ | 0.42 |
| $CH_3NH_2BH_3$ | $CDCl_3$ | −3.8 | −2.55 | ... | $H^1{}_B$ | −1.50 |
| $CH_3NH_2BH_3$ | 1,4-Dioxane | −4.2 | −2.40 | ... | $H^1{}_B$ | −1.28 |
| $CH_3NH_2BH_3$ | $CD_3CN$ | −3.9 | −2.39 | 37.0[d] | $H^1{}_B$ | −1.32 |
| $CH_3NH_2BF_3$ | $CH_3CN$ | −4.4 | −2.46 | 17.8 | $F^{19}{}_B$ | 152.7 |
| $CH_3NH_2B(CH_3)_3$ | $CDCl_3$ | −2.8 | −2.37 | ... | $H^1{}_{CB}$ | 0.37 |
| $CH_3NH_2B(CH_3)_3$ | $CH_3CN$ | −3.4 | −2.20 | 24.9 | $H^1{}_{CB}$ | 0.44 |
| $NH_3BH_3$ | 1,4-Dioxane | ... | ... | ... | $H^1{}_B$ | −1.21 |
| $NH_3BH_3$ | $CH_3CN$ | −3.6 | ... | 41.4[d] | $H^1{}_B$ | −1.29 |
| $NH_3BF_3$ | $CH_3CN$ | −4.3 | ... | 19.2[c] | $F^{19}{}_B$ | 146.5 |
| $NH_3B(CH_3)_3$ | $CDCl_3$ | −2.8 | ... | ... | $H^1{}_{CB}$ | 0.32 |
| $NH_3B(CH_3)_3$ | $CH_3CN$ | −3.2 | ... | 26.1 | $H^1{}_{CB}$ | 0.42 |
| $(NH_3)_2BH_2{}^+I^-$ | $CH_3CN$ | −5.90 ± 0.05 | ... | ... | ... | ... |
| $(NH_3)_2BH_2{}^+I^-$ | $D_2O$ | ... | ... | 32.4 ± 0.6 | $H^1{}_B$ | −2.37 ±0.01 |

[a] $H^1$ Chemical shifts are measured relative to tetramethylsilane, internal, $B^{11}$ with respect to trimethyl borate, external, and $F^{19}$ with respect to fluorotrichloromethane, internal. For all nuclei, positive shifts refer to high field. [b] Ref. 2, "ethyl shift"; $(C_2H_5)_3N$ = 1.50 p.p.m., $(C_2H_5)_3NBF_3$ = 1.73 p.p.m., $(C_2H_5)_3NBH_3$ = 1.59 p.p.m., $(C_2H_5)_3NB(CH_3)_3$ = 1.53 p.p.m., $\delta H^1$; $(C_2H_5)_3NB(\mathit{CH}_3)_3$ = −0.66 p.p.m., $(CH_3)_3NB(\mathit{CH}_3)_3$ = 0.32 p.p.m., $(\mathit{CH}_3)_3NBF_3$ = −2.60 p.p.m., $(\mathit{CH}_3)_3NBH_3$ = −2.58 p.p.m., $(\mathit{CH}_3)_3NB(CH_3)_3$ = −2.40 p.p.m. [c] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). $\delta B^{11}$, $(CH_3)_3NBH_3$ = 24.9 p.p.m., $(CH_3)_2NHBH_3$ = 32.5 p.p.m., $NH_3BF_3$ = 20.2 p.p.m.; $J_{H^1B^{11}}$, $(CH_3)_3NBH_3$ = 97 c.p.s., $(CH_3)_2NHBH_3$ = 94 c.p.s. [d] D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **86**, 1505 (1964). $\delta B^{11}$, $NH_3BH_3$ = 42.0 p.p.m., $CH_3NH_2BH_3$ = 38.7 p.p.m., $(CH_3)_2NHBH_3$ = 32.4 p.p.m., $(CH_3)_3NBH_3$ = 26.3 p.p.m.; $J_{H^1B^{11}}$, $NH_3BH_3$ = 91 c.p.s., $CH_3NH_2BH_3$ = 93 c.p.s., $(CH_3)_2NHBH_3$ = 96 c.p.s., $(CH_3)_3NHBH_3$ = 98 c.p.s.

sources were purified by storage in cylinders over drying agents ($CaH_2$ for the amines, metallic sodium for ammonia). Trimethylphosphine was prepared by the Grignard route[3] and dried over lithium aluminum hydride. Mono- and dimethylamines were obtained and recrystallized as the hydrochlorides. After liberation by base, the amines were dried and stored in cylinders over sodium. Trimethylboron and boron trifluoride were prepared and/or purified by known procedures.[4,5] The prepared complexes were purified by sublimation or distillation under vacuum.

Preparation of the salt $H_2B(NH_3)_2{}^+I^-$ is described elsewhere,[6] by a method that is essentially that of Kodama and Parry.[7]

Samples of trimethyl- and dimethylamine borane were obtained from the Callery Chemical Co. Trimethylphosphine borane and triethylamine borane were prepared by direct combination of the ligand with diborane. Procedures reported elsewhere were used for the preparation of ammonia borane[8] and methylamine borane.[9] All of the $BH_3$ complexes except $NH_3BH_3$ were purified by sublimation. The ammonia adduct was recrystallized from ethyl ether.

Most solutions were prepared in a drybox from rigorously purified solvents, although the alkylamine and phosphine borane adducts were handled in the open air. The triethylamine trimethylboron solutions were prepared in a vacuum line. The solutions were scanned on Varian instruments operating at 14.1 kgauss and the appropriate radiofrequencies. Positions of singlet methyl absorptions were determined by superposition. Posi-

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(3) H. Hibert, *Ber.*, **39**, 160 (1906).

(4) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

(5) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2934 (1950).

(6) C. W. Heitsch, Doctoral Dissertation, University of Michigan, 1959; *Dissertation Abstr.*, **20**, 670 (1959).

(7) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).

(8) S. G. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

(9) R. W. Parry, R. C. Taylor, and C. E. Nordman, "The Chemistry of Boron Hydrides and Related Hydrides," WADC Technical Report 59-207, May 1959, University of Michigan.

tions of all other peaks were determined by generation of side bands of known frequency. Tetramethylsilane was used as an internal standard for proton spectra, $FCCl_3$ (internal) for $F^{19}$ spectra, and $B(OCH_3)_3$ (external) for the $B^{11}$ spectra. Chemical shifts are reported in p.p.m. with positive values assigned to resonances at higher magnetic fields. Coupling constants are reported in c.p.s. (Table I).

## Results and Discussion

**Chemical Shifts.**—Coyle and Stone observed a decrease (increase in negative value) in the chemical shifts of protons in amine molecules as stronger acids were coordinated to the nitrogen.[2] Similar results are reported here, although the only common complexes are those of triethyl- and trimethylamine. Invariably, trimethylboron is a weaker acid than either borane or boron trifluoride. For all cases reported here, replacement of $B(CH_3)_3$ with $BF_3$ or $BH_3$ results in a decrease in the chemical shifts of groups associated with the free amine molecule. This applies to methyl groups, methylene groups, and N protons. However, in comparing $BF_3$ with $BH_3$, the situation is more complex. The relative strength of these two acids is known to vary with the reference base. Thus, with respect to dimethyl ether, $BF_3 > BH_3$,[10,11] while with respect to trimethylphosphine, $BH_3 > BF_3$.[12,13] With respect to trimethylamine, $BF_3$ and $BH_3$ seem to be acids of comparable strength. The enthalpies of dissociation of their complexes are about equal, but the reported values cover a considerable range around 30 kcal./mole.[14] Some of the discrepancies are the result of the uncertainties associated with the enthalpy of dissociation of diborane, for which values range from 28.5 kcal./mole[15] to 37 kcal./mole.[16,17] If the true value is close to the upper limit of this range then the dative bond in $(CH_3)_3NBH_3$ is 4–5 kcal. stronger than that of $(CH_3)_3NBF_3$. Moreover, while diborane (gas) will not displace $BF_3$ (gas) from $(CH_3)_3NBF_3$ (solid),[18] the reaction proceeds in ether solution, where the nearly 11 kcal./mole from the formation of $(C_2H_5)_2OBF_3$ is enough to shift the equilibrium.[19]

While differences in lattice and solvation energies will play a part in this comparison, it is probably safe to say that for the enthalpies of dissociation $\Delta H_{(CH_3)_3NBH_3} \geqslant \Delta H_{(CH_3)_3NBF_3} - 2$ kcal./mole. Since a similar situation applies in the case of pyridine,[14] one is tempted to generalize and say that $BH_3 \geqslant BF_3$ for amines in general. However, only in the case of the methyl protons in the $(CH_3)_3N$ and $(CH_3)_3P$ adducts of these two acids are their shifts equal. In all other cases, $BF_3 > BH_3$. Yet, $(CH_3)_3PBH_3$ is without a doubt more stable with respect to dissociation than is $(CH_3)_3PBF_3$.[14]

The desirability of reliable thermochemical data free of the complicating effects of lattice and solvation energies is obvious. Nevertheless, it is encouraging to note that with respect to trimethylboron on the one hand and to $BF_3$ and $BH_3$ on the other, where the differences in stabilities of complexes are much greater than uncertainties of the comparison, the chemical shifts of the groups on nitrogen are in line with the stabilities.

With respect to both the $B^{11}$ and the $H^1_B$ shifts of $BH_3$ adducts, the order of bases is $(CH_3)_3N < (CH_3)_2NH \cong (C_2H_5)_3N < CH_3NH_2 < NH_3 < (CH_3)_3P$. Gaines and Schaeffer report a similar series for ammonia and methylamines.[20] While there has been no reliable thermodynamic evidence reported to show that this is not the order of stability in this series, this sequence is not observed with any other reference acid.[21]

A single exception appears to be the work of Boyd, who has compared the heats of formation of $(CH_3)_3NBH_3$ and $(C_2H_5)_3NBH_3$ from the free amines and diborane.[22] The difference, 0.8 kcal./mole in favor of the stability of $(CH_3)_3NBH_3$, is probably not significant in view of the method or the polar nature of the solvent. However, that both values are nearly the same, 21–22 kcal./mole, conflicts with the observed chemical shift series which puts $(CH_3)_3N < (C_2H_5)_3N$. On the other hand, it is noteworthy that trimethylphosphine will displace trimethylamine from its $BH_3$ adduct.[18] Moreover, on the basis of an intensive spectral study, Taylor has determined that the B–N stretching force constant is greater for $NH_3BH_3$ than for $(CH_3)_3NBH_3$.[23] For the series $(CH_3)_{3-n}H_nNBH_3$, the difference between the dipole moment of the complex and that of the free amine increases monotonically with $n$.[9,24] This difference, at least for amines with trigonal symmetry, can be interpreted as a measure of the strength of the B–N link. Again the need for meaningful thermochemical studies is apparent.

With the $BF_3$ adducts reliable thermodynamic data are lacking for comparison. However, the order of base strength $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ would be predicted on the basis of increasing inductive effect on the nitrogen with increasing methyl substitution. Here, there is a good correlation with the $F^{19}$ chemical shifts. The subtle steric effects that permit dimethylamine to form a more stable complex with trimethylboron than does trimethylamine[25] should not be so pronounced with a strong acceptor such as

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(10) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 290 (1938).

(11) A. B. Burg, *Record Chem. Progr.*, **15**, 159 (1954).

(12) H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, **65**, 2557 (1943).

(13) A. W. Laubengayer and G. R. Finlay, *ibid.*, **65**, 884 (1943).

(14) F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958); T. D. Coyle and F. G. A. Stone, *Progr. Boron Chem.*, **1**, 83 (1964).

(15) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

(16) M. E. Garabedian and S. W. Benson, *ibid.*, **86**, 176 (1964).

(17) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 2734 (1964).

(18) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).

(19) C. W. Heitsch, *Inorg. Chem.*, **3**, 767 (1964).

(20) Table I, ref. *d*.

(21) See ref. 15. McCoy and Bauer report the results of a number of experiments wherein amines and diborane were combined directly to determine the enthalpies of formation of $BH_3$ adducts. Trimethylamine reacts with $B_2H_6$ to yield $(CH_3)_3NBH_3$ smoothly and nearly quantitatively. However, the nature of the products produced by the action of $CH_3NH_2$ and $(CH_3)_2NH$ on diborane as in the experiments of McCoy and Bauer has never been fully elucidated. They are not the simple adducts, $CH_3NH_2BH_3$ and $(CH_3)_2NHBH_3$, since they decompose at temperatures close to 0°, while the well-characterized adducts, produced by less direct methods, are stable above their melting points (58 and 37°, respectively). Thus the validity of their numbers is questionable.

(22) A. C. Boyd, Jr., Doctoral Dissertation, Purdue University, 1957; *Dissertation Abstr.*, **17**, 1908 (1957).

(23) R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p. 59.

(24) (a) H. Nöth and H. Beyer, *Ber.*, **93**, 939, 2251 (1960); (b) J. R. Weaver, S. G. Shore, and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 20 (1958).

(25) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

$BF_3$. Moreover, where enthalpies are available for comparison, the order of base strengths is $(CH_3)_3N > (C_2H_5)_3N >> (CH_3)_3P$.[22,25] Although Boyd has measured the enthalpies for the amine complexes in nitrobenzene solutions and Brown's data for the phosphine adduct are from gas phase dissociation, it is unlikely that the difference in states would be sufficient to account for the nearly 17 kcal. required to change this order.

The $B^{11}$ shifts of the $BF_3$ adducts are all essentially equal. This can be viewed as a consequence of the strong electron-withdrawing power of the fluorine atom. Any increase in charge donated to boron by a stronger base is passed on to the fluorines. Thus, even the trimethylphosphine adduct, which is particularly weak, has the same $B^{11}$ shift as the trialkylamine adducts. Enthalpies of dissociation of $BF_3$ adducts have been estimated at 35.7[22] kcal./mole for $(C_2H_5)_3N$, 38.2[12] (26.6 to 30.9)[14] for $(CH_3)_3N$, and 18.9[25] for $(CH_3)_3P$.

Among the trimethylboron complexes, the order of the chemical shifts of the B-methyl protons correlates roughly with dissociation data. Enthalpies (kcal./mole) are approximately 10 for $(C_2H_5)_3N$, 16.5 for $(CH_3)_3P$, and about 17–19 for methylamines with respect to trimethylboron as a reference acid.[25] (However, for the ammonia adduct the enthalpy is only 13.7 kcal./mole.) The $H^1$ shifts of B-methyl protons are in the order $(C_2H_5)_3N < (CH_3)_3P < NH_x(CH_3)_{3-x}$. This must be considered as a reasonable correlation, particularly since many of the differences in shifts are small and correspondingly less reliable than the differences in the hydride or in the fluoride shifts. Moreover, factors other than electron density could easily influence the order of these shifts.

The order of the $B^{11}$ shifts is $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < NH_3 < (C_2H_5)_3N << (CH_3)_3P$. Again, as in the case of $BF_3$ adducts, this sequence cannot be rationalized on the basis of any known or assumed order of complex stability. The inductive properties of the methyl group in contrast with the electron-withdrawing properties of fluorine require a different explanation of the order of shifts.

Like other $BX_3$ molecules, trimethylboron is planar when free of complexing ligands. The approach of such a ligand forces the molecule from a planar to a pyramidal configuration in which a steric stress is generated between the three methyl groups. This intramethyl stress will be passed on to the boron–carbon bonds, lengthening them and as a consequence withdrawing negative charge from the boron. An additional steric stress in the same direction arises from the interaction of groups on the ligand with those on the boron. The total of these stresses will depend on the steric requirements of the ligand and the length of the ligand–boron bond. For the amines considered here, the steric requirements can be roughly correlated to the number of carbon atoms: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N < (C_2H_5)_3N$. The position of trimethylphosphine in this series is uncertain, but presumably it would come before trimethylamine, since the P–C bonds are longer than the N–C bonds and the CPC bond angles are smaller than the CNC bond angles.[26] At the same time, the B–N length should follow the enthalpies of dissociation inversely: $(C_2H_5)_3N > NH_3 > (CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$.[25] Again the position of trimethylphosphine in the series is subject to conjecture. While the enthalpy of dissociation of $(CH_3)_3PB(CH_3)_3$ is between that of triethylamine and ammonia, the larger radius of phosphorus should permit binding over a longer distance. The result of these two factors should lead to strains in the complex molecules that diminish roughly in the order in which the observed $B^{11}$ chemical shift increases (Tables II, III, and IV).

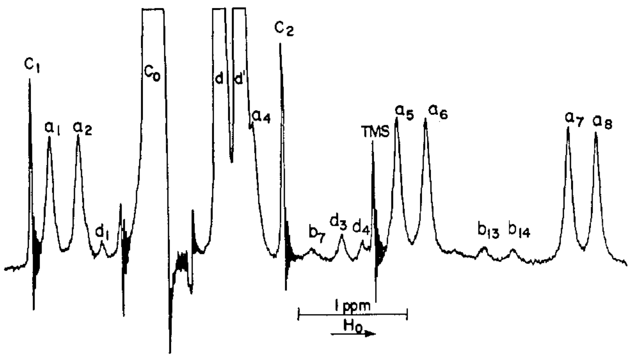

Figure 1.—$H^1$ n.m.r. spectrum of $(CH_3)_3PBH_3$ in acetonitrile: $a_x = (CH_3)_3P^{31}B^{11}H_3$; $b_x = (CH_3)_3P^{31}B^{10}H_3$; $c_0 = C^{12}H_3CN$; $C_1, C_2 = C^{13}H_3CN$; $d,d' = (C^{12}H_3)_3P^{31}BH_3$; $d_x = (C^{13}H_3)_3P^{31}BH_3$.

## Coupling Constants

Complexes of the sort discussed here are a rich source of coupling constants. In the case of trimethylphosphine borane, five out of a total of ten possible coupling constants are observed (see Figure 1). Although the relation between them and other functions of more direct chemical interest is at present obscure, coupling constants are less dependent on solvent conditions than are chemical shifts. Hence, they constitute a more profitable function from which to characterize a given compound.

Coyle and Stone state that B–F spin coupling is not observed in the $F^{19}$ spectra of several weak $BF_3$ adducts and ascribe this to the making and breaking of the donor–acceptor links.[2] Such a process can hardly account for the decoupling of boron and fluorine nuclei which remained attached. Many other processes might account for the lack of a B–F splitting pattern. One of them is an autoionization of the type $2BF_3 = BF_2^+ + BF_4^-$. However, all of the $BF_3$ complexes observed here show B–F coupling. Even in the weakest complex, that of trimethylphosphine, this coupling was observed and it was unusually large, 51 ± 1 c.p.s. In the amine complexes it varied between 13 and 18 c.p.s. with no apparent correlation with complex stability.

Coyle and Stone commented on the multiplicity of their ethyl spectra.[2] These authors reported two superimposed quartets for the methylene absorption in many

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(26) L. E. Sutton, "Tables of Interatomic Distances," The Chemical Society, Burlington House, W.1, London, 1958.

TABLE II

B–X COUPLING CONSTANTS[a]

| Compound | $J_{HB}$ | | Compound | $J_{FB}$ | |
|---|---|---|---|---|---|
| | $H^1$ | $B^{11}$ | | $F^{19}$ | $B^{11}$ |
| $\mathrm{(CH_3)_3PBH_3}$ | 94.9 | 94.6 | $\mathrm{(CH_3)_3PBF_3}$ | 52 | 50 |
| $\mathrm{(C_2H_5)_3NBH_3}$ | 96.2 | 97.3 | $\mathrm{(C_2H_5)_3NBF_3}$ | 18.4 | 16.4 |
| $\mathrm{(CH_3)_3NBH_3}$ | 96 | 95[b,c] | $\mathrm{(CH_3)_3NBF_3}$ | 13.8 | 13.8 |
| $\mathrm{(CH_3)_2NHBH_3}$ | 94 | 95.6[b,c] | $\mathrm{(CH_3)_2NHBF_3}$ | 15.5 | 15.1 |
| $\mathrm{CH_3NH_2BH_3}$ | 93 | 93.5[c] | $\mathrm{CH_3NH_2BF_3}$ | 15.7 | 16.0 |
| $\mathrm{NH_3BH_3}$ | 92 | 93.9[c] | $\mathrm{NH_3BF_3}$ | 13.8 | 13.9 |
| $\mathrm{(NH_3)_2BH_2{}^+I^-}$ | 107 | 110 | | | |

[a] All coupling constants are given in c.p.s. [b] Compare ref. *d*, Table I. [c] Compare ref. *c*, Table I.

TABLE III

COUPLING CONSTANTS[a] FROM PROTON SPECTRA

| Compound | $J_{HN}$ | $J_{HcnH}$ | Compound | $J_{HcnB}$ | $J_{HcnbF}$ |
|---|---|---|---|---|---|
| $\mathrm{(CH_3)_2NHBF_3}$ | . . . | 5.78 | $\mathrm{(CH_3)_2NHBF_3}$ | 1.79 ± 0.02 | . . . |
| $\mathrm{CH_3NH_2BF_3}$ | 45.0 | 6.2 | $\mathrm{CH_3NH_2BF_3}$ | 2.05 ± 0.04 | . . . |
| $\mathrm{(CH_3)_2NHBH_3}$ | . . . | 6.0 | $\mathrm{(C_2H_5)_3NBF_3}$ | 1.58 | 0.79 |
| $\mathrm{CH_3NH_2BH_3}$ | 45 | 6.1 | $\mathrm{(CH_3)_3NBF_3}$ | 1.54 ± 0.02 | 0.65 ± 0.02 |
| $\mathrm{NH_3BH_3}$ | 49 | . . . | | | |
| $\mathrm{(NH_3)_2BH_2{}^+I^-}$ | 53.5 | . . . | | | |
| $\mathrm{NH_3BF_3}$ | 42.3 | . . . | | | |
| | | | | $J_{PB}$[b] | $J_{PcH}$ |
| $\mathrm{(CH_3)_2NHB(CH_3)_3}$ | . . . | 1.1 | $\mathrm{(CH_3)_3PBH_3}$ | 64.3 | 10.84 |
| $\mathrm{CH_3NH_2B(CH_3)_3}$ | . . . | 5.0 | $\mathrm{(CH_3)_3PBF_3}$ | 174 | 10.6 |
| | | | $\mathrm{(CH_3)_3PB(CH_3)_3}$ | . . . | 9.5 |
| | $J_{PbH}$ | $J_{PbF}$[c] | | | |
| $\mathrm{(CH_3)_3PBH_3}$ | 26.8 | | | | |
| $\mathrm{(CH_3)_3PBF_3}$ | | 229 | | | |

[a] All coupling constants are given in c.p.s. [b] From $B^{11}$ spectra. [c] From $F^{19}$ spectra.

TABLE IV

$C^{13}$–H COUPLING CONSTANTS[a] FROM PROTON SPECTRA

| Compound | $J_{C-H}$ | Compound | $J_{C-H}$ | Compound | $J_{C-H}$ |
|---|---|---|---|---|---|
| $\mathrm{NH_3B}(CH_3)_3$ | 109.9 | $(CH_3)_3\mathrm{PB(CH_3)_3}$ | 130.7 | $(CH_3\mathrm{O})_3\mathrm{B}$ | 136.0 |
| $\mathrm{CH_3NH_2B}(CH_3)_3$ | 109.4 | $(CH_3)_3\mathrm{PBH_3}$ | 131.6 | $CH_3\mathrm{CN}$ | 136.6 |
| $\mathrm{(CH_3)_2NHB}(CH_3)_3$ | 110.6 | $(CH_3)_2\mathrm{NHB(CH_3)_3}$ | 138.5 | $(CH_3)_2\mathrm{NHBF_3}$ | 140.7 |
| $\mathrm{(CH_3)_3NB}(CH_3)_3$ | 108.3 | $(CH_3)_3\mathrm{NB(CH_3)_3}$ | 137.6 | | |

[a] All coupling constants are given in c.p.s.

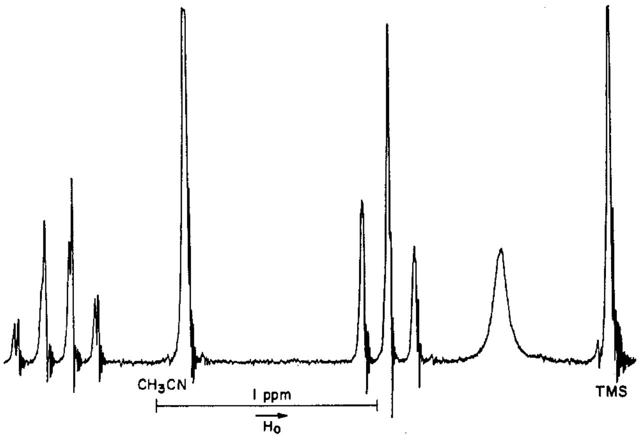

Figure 2.—$H^1$ n.m.r. spectrum of $\mathrm{(C_2H_5)_3NB(CH_3)_3}$ in acetonitrile showing second-order perturbation of the $A_2B_3$ pattern.

ethyl compounds. Similar patterns are observed here for triethylamine itself and its trimethylboron adduct (see Figure 2). Coupling of the methylene protons to both the boron and the fluorines is apparent in the spectrum of $\mathrm{(C_2H_5)_3NBF_3}$, but the doubling of the methylene quartet is unresolved if present. The methylene peaks in the $BH_3$ adduct are broader than in the free amine and again any doubling of the quartet is unresolved. This doubling of methylene quartets in ethyl groups appears to be a part of the more general $A_2B_3$ pattern. Unfortunately, analysis of these second-order effects is not practical without recourse to involved computer techniques.

The unusual patterns that develop when two or more coupling constants involving a common atom are either equal or integral multiples have been described for a number of compounds. In trialkyl phosphite boranes, $J_{BP} = J_{BH}$. The $B^{11}$ spectrum is a 1-4-6-4-1 quintuplet,[27] as it is in $\mathrm{(CH_3)_2NPF_2 \cdot BH_3}$.[28] The borohydride proton spectrum of $\mathrm{Al(BH_4)_3 \cdot N(CH_3)_3}$ is a 1-1-2-2-3-3-3-3-2-2-1-1 dodecet, apparently due to the fact that $J_{B-H} = 2J_{Al-H}$.[29] In this work, $J_{HcnB}$ and $J_{HcnH}$ in the methyl- and dimethylamine boron trifluoride complexes are related so as to give patterns

[27] J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964).

[28] Sr. Mary Albert Fleming, IHM, Doctoral Dissertation, University of Michigan, 1963; *Dissertation Abstr.*, **24**, 1385 (1963).

[29] P. C. Lauterbur, O. V. Ziebarth, R. W. King, C. W. Heitsch, and R. C. Hopkins, to be published.

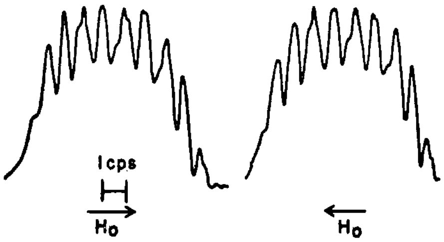

Figure 3.—$H^1$ n.m.r. spectrum of $(CH_3)_3NBF_3$ under high resolution.

of a 1-1-1-3-2-2-3-1-1-1 decet and a 1-1-1-2-1-1-1 septet, respectively, in the methyl spectra. The methyl peak of $(CH_3)_3NBF_3$ is approximately a 1-3-4-4-4-4-4-4-3-1 decet due to coupling both to the $B^{11}$ and $F^{19}$ nuclei (see Figure 3). A similar pattern prevails in the methylene absorption of $(C_2H_5)_3NBF_3$. Indeed the group III–group V donor–acceptor complexes seem to be rich in these coincidences. It is interesting to speculate that they are the result of some unknown effect causing two nearly equal coupling constants to interact to become degenerate (or integral multiples). However, the peaks in the $B^{11}$ and boron hydride $H^1$ spectra are very broad. The coupling constants obtained from them are rarely more reliable than ±2 c.p.s. Thus, it is impossible to tell if two peaks overlap anymore precisely than this rather large number. However, methyl absorptions in the methylamine–$BF_3$ complexes are quite sharp. These solutions were scanned several times under conditions favoring high resolution. For $CH_3NH_2BF_3$, $J_{\mathrm{HcnH}}$ was within 0.02 c.p.s. of $3J_{\mathrm{HcnB}}$, well within the probable error of ±0.12 c.p.s. However, in $(CH_3)_2NHBF_3$, $J_{\mathrm{HcnH}}$ is 0.44 c.p.s. greater than $3J_{\mathrm{HcnB}}$, while the probable error in these quantities is ±0.05 c.p.s. Also, for $(CH_3)_3NBF_3$, $J_{\mathrm{HcnB}}$ is 0.24 c.p.s. greater than $2J_{\mathrm{HcnbF}}$ while the probable error is ±0.04 c.p.s. Thus, the apparent precise overlap in many cases is the result of a near integral relationship between the two coupling constants, the breadth of the peaks obscuring the fact that the patterns do not overlap exactly.[30]

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(30) NOTE ADDED IN PROOF.—Since the submission of this article, Banister and Greenwood have reported their observation of $J_{\mathrm{HcnB}}$ in $[(CH_3)_2NBX_2]_2$: 3.3 c.p.s. where X = Br and 3.1 c.p.s. where X = Cl.[31] These authors also refer to Miller and Onyszchuck, who report values for $J_{\mathrm{HcnB}}$ of 2.8 c.p.s. for $(CH_3)_3NBBr_3$, 2.7 c.p.s. for $(CH_3)_3NBCl_3$, and 2.8 c.p.s. for $(C_2H_5)_3NBCl_3$ (methylene protons).[32] The latter did not observe this quantity for $BF_3$ and $BH_3$ adducts, however. Since $J_{\mathrm{HcnB}}$ was observed here for both $(CH_3)_3NBF_3$ and $(C_2H_5)_3NBF_3$, the apparent lack of splitting would seem to be a function of spectrometer sensitivity, at least in some cases. In other instances it may be an intrinsic property of the molecule. Which of these alternatives is true of $(CH_3)_3NBH_3$ is difficult to decide at this moment. However, these instances, as well as the observation here of several $H^1N^{14}$ couplings, serve to re-emphasize the caution required in the face of a negative result. This is most particularly true in the case of n.m.r. spectroscopy. Miller and Onyszchuck report chemical shifts in $CHCl_3$ solutions for the methyl protons in $(CH_3)_3NBH_3$ (−2.66 p.p.m.) and in $(CH_3)_3NBF_3$ (−2.62 p.p.m.).[32] These values are in good agreement with those reported in Table I and in ref. 2.

(31) A. J. Banister and N. N. Greenwood, *J. Chem. Soc.*, 1534 (1965).

(32) J. M. Miller and M. Onyszchuck, *Can. J. Chem.*, **42**, 1518 (1964).