

**Liquid Phase Pyrolysis of Hexamethylborazole.**—An ampoule was charged with 318.5 mg. (19.4 mmoles) of hexamethylborazole and sealed as usual. The tube was then heated to 400°, and a major portion of the material was observed to be in the liquid phase; heating was continued at 385–405° for 24 hr. When the tube was cooled and opened, no gases were evolved. Sublimation of the solid at 100° (0.8 mm.) produced 296.8 mg. of hexamethylborazole, m.p. 96–100°.

**Relative Thermal Stabilities of Borazoles.**—The ampoules were charged and sealed as described earlier, then heated for 3 hr. in a fused salt bath maintained at 450 ± 2°. The cooled tubes were opened into an evacuated system containing a -196° trap, manometer and molecular weight bulb. The temperature of the trap was raised to -78°, and the pressure increase due to liberated methane (infrared identification) in the 131-ml. system was recorded.

**I. B-Triphenyl-N-trimethylborazole.**—A sample of 478.8 mg. (1.365 mmoles) of B-triphenyl-N-trimethylborazole produced 0.212 mmole of noncondensable gas after pyrolysis. Increasing the trap temperature to -78° liberated 0.25 mmole of methane. Sublimation of the reaction solids at 200° (0.1 mm.) produced a non-volatile clear yellow glass, 86 mg., and a white volatile solid. Recrystallization procedures on the latter fraction produced only wide-melting materials, and no unreacted starting material was isolated. A clear liquid, 15.5 mg., was collected in a trap maintained at -78° during the sublimation. On the basis of its odor and the results of a previous experiment (see above), this liquid was assumed to be benzene (0.199 mmole).

**II. Hexaphenylborazole.**—On opening a sample of 178 mg. (0.332 mmole) of hexaphenylborazole after pyrolysis, 0.028 mmole of gas was obtained. The -78° trap in the vacuum line contained 7.0 mg. of liquid (0.09 mmole, assuming benzene as before). The solid, 120 mg., was recrystallized from tetrahydrofuran-petroleum ether to give 40 mg. of powder, m.p. 385–397°. The infrared spectrum matched that of hexaphenylborazole.

**III. B-Trimethyl-N-triphenylborazole.**—Pyrolysis of B-trimethyl-N-triphenylborazole, 301.9 mg. (0.861 mmole) produced a total of 0.106 mmole of gas. Sublimation of the solid at 185–195° (0.1 mm.) left 9.0 mg. of a clear yellow glassy residue. The sublimate, m.p. 230–255°, was recrystallized from benzene to give 80 mg. of B-trimethyl-N-triphenylborazole, m.p. 260–265°.

**IV. B-Triphenylborazole.**—No gases were evolved from the ampoule after reaction of 340.8 mg. (1.104 mmoles) of B-triphenylborazole under the conditions described above. The solid was sublimed at 200° (0.1 mm.) giving 290 mg. of sublimate, m.p. 177–180° (85.4% recovery). In a second trial, 235.6 mg. (0.746 mmole) of B-triphenylborazole produced a total of 0.11 mmole of gas. Sublimation of the solid at 180° (0.1 mm.) gave 20½ mg. of sublimate, m.p. 175–180° (87% recovery). A small amount of clear yellow resin remained as a residue.

**V. Hexamethylborazole.**—A sample of hexamethylborazole, 162.5 mg. (2.96 mmoles) produced 0.018 mmole of gas and 171.4 mg. of solid, m.p. 95.8–98.6° (105% recovery).

**VI. N-Trimethylborazole.**—Pyrolysis of a 209.5-mg. sample (1.71 mmoles), b.p. 128–130°, lit.<sup>18</sup> b.p. 134°, produced a total of 0.0776 mmole of gas.

**VII. B-Trimethylborazole.**—A 224.2-mg. sample (1.835 mmoles) of this borazole, b.p. 128–129°, m.p. 31.4–32.2°, lit.<sup>19</sup> b.p. (extrap.) 129°, m.p. 31.5°, produced no gaseous material, and 218 mg. of solid, m.p. 32–33° (97.3% recovery), was obtained.

**Acknowledgments.**—The authors wish to thank Messrs. H. Goldsmith and P. D. Faurote, who prepared many of the compounds studied herein.

(18) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 1296 (1938).

(19) H. I. Schlesinger, L. Horvitz and A. B. Burg, *ibid.*, **58**, 409 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## Molecular Addition Compounds of Boron. V. Proton Chemical Shifts and the Stability of Adducts<sup>1,2</sup>

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The proton chemical shifts in some boron-containing addition compounds of Lewis bases in which the donor atom has an ethyl substituent have been measured in an attempt to correlate the separation of the absorptions due to the methylene and methyl protons of the ethyl groups with the stability of the addition compounds. The n.m.r. spectra of a number of other molecular addition compounds of boron were also examined in order to try to correlate the chemical shifts of methyl protons in adducts of methyl substituted bases, and the chemical shifts of B-methyl protons of adducts of trimethylboron, with the strengths of the donor-acceptor bonds in the various complexes. The results show that the chemical shift criterion is not uniformly successful in predicting the stabilities of addition compounds.

The simple qualitative description of the formation of molecular addition compounds by electron donor-acceptor interactions implies that the electron-attracting power of the donor and acceptor atoms in an adduct will be somewhat different from that in the free Lewis base and acid, and will depend in part upon the strength of the coordinate bond. On these grounds, the empirical relationship<sup>4</sup> between the electronegativity of substituents and the internal chemical shifts<sup>5</sup> in ethyl deriva-

tives was applied recently to an investigation of the triethyl derivatives of aluminum and gallium and their diethyl etherates.<sup>6</sup> The results of that study indicated that the apparent electronegativity of the Group III acceptor atom is diminished by complex formation and that the electronegativity of the donor atom is increased with increasingly strong coordination.

These results, if generally applicable, suggest that the internal chemical shift might provide a welcome new technique for establishing the relative stabilities of molecular addition compounds, applicable to those cases in which the acid or base, or both, are ethyl-substituted. Furthermore, the relation between electronegativity and chemical group and is taken as positive when the methyl absorption is at higher applied field.

(6) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, *J. Am. Chem. Soc.*, **81**, 3826 (1959).

(1) Previous paper, T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

(2) The work described in this paper was made possible by the award of a grant (G14610) from the National Science Foundation.

(3) Edwin W. Rice, Jr., Fellow of the General Educational and Charitable Fund, 1959–1961.

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

(5) The term internal chemical shift refers to the separation of the absorptions due to the methylene and methyl protons of an ethyl

shifts in methyl derivatives<sup>7</sup> might provide a similar means of evaluating relative stabilities in methyl-substituted addition compounds.

In view of the many factors known to influence proton chemical shifts, it is perhaps optimistic to expect that the variations in electron distribution in a series of related adducts will result in a direct correlation between chemical shifts and addition compound stabilities. It is of some interest, however, in view of the relation observed in the diethyl etherates of triethylaluminum and triethylgallium, to consider in more detail the extent to which chemical shift-electronegativity correlations can be applied to the problem of determining molecular addition compound stabilities. We have accordingly measured the internal chemical shifts of ethyl groups and the chemical shifts of methyl groups for a series of molecular addition compounds of boron for which stabilities are known or can be reasonably inferred.

### Experimental

The preparation and/or purification of most of the Lewis acids and bases used in this study have been described in earlier papers of this series. All manipulations were carried out by conventional high vacuum techniques. Samples for nuclear magnetic resonance measurements were prepared by combining equivalent quantities of acid and base, measured as gases, in 5 mm. (o.d.) Pyrex tubes. Dry dichloromethane was added to bring the final concentration of addition compound to 10%.

Nuclear magnetic resonance spectra were measured at room temperature (*ca.* 23°) using a Varian V4300-B high-resolution spectrometer equipped with superstabilizer and field homogeneity control coils and operating at 60 Mc.p.s. Line separations were measured to  $\pm 0.5$  c.p.s. by direct superposition of sidebands, or, in a few cases, by calibration of recorder traces. In these latter instances, at least six traces were used to establish the measured separations. Except as noted below, the multiplets due to the methylene and methyl protons of the ethyl groups were sufficiently separated to allow analysis of the spectrum according to first-order theory, and the internal shifts were taken as equal to the separations of the multiplet centers.

### Results and Discussion

**Internal Chemical Shifts in Adducts of Ethyl-substituted Bases.**—The internal chemical shifts in some adducts of triethylamine, ethyldimethylamine, diethyl ether, methyl ethyl ether and diethyl sulfide are given in Table I. Internal shifts are also given for the free bases, except for ethyldimethylamine, which reacts rapidly with dichloromethane solvent, precipitating a white crystalline solid presumed to be a quaternary ammonium salt.

Since it is known that aluminum alkyls form more stable etherates than gallium alkyls<sup>8</sup> the n.m.r. results obtained for the diethyl etherates of triethylaluminum and triethylgallium<sup>6</sup> suggest that the internal shifts in the adducts of a given base should be greatest in the strongest adducts. We might thus hope, for the series of adducts in Table I, to relate the observed shift sequences to the known stability of the adducts.

In the case of the triethylamine adducts, the internal shifts are in the order  $\text{BF}_3 > \text{BH}_3 > \text{BMe}_3$ . Calorimetric studies<sup>9</sup> have shown that the enthalpy

(7) A. L. Allred and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 5361 (1957).

(8) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958), and references cited therein.

(9) A. C. Boyd, Jr., Ph.D. Thesis, Purdue University (1957).

TABLE I

INTERNAL CHEMICAL SHIFTS IN ADDUCTS OF ETHYL-SUBSTITUTED BASES

Compound <sup>a</sup>	Chemical shift (p.p.m.)	Compound <sup>a</sup>	Chemical shift (p.p.m.)
Et <sub>3</sub> N	1.50	Et <sub>2</sub> O	2.45
Et <sub>3</sub> N·BF <sub>3</sub>	1.73	Et <sub>2</sub> O·BF <sub>3</sub>	2.83
Et <sub>3</sub> N·BH <sub>3</sub>	1.59	Et <sub>2</sub> O·BH <sub>3</sub> <sup>b</sup>	2.28
Et <sub>3</sub> N·BMe <sub>3</sub>	1.53	Et <sub>2</sub> O·BMe <sub>3</sub> <sup>b</sup>	2.28
EtMe <sub>2</sub> N·BF <sub>3</sub>	1.75	EtMeO	2.25
EtMe <sub>2</sub> N·BH <sub>3</sub>	1.63	EtMeO·BF <sub>3</sub>	2.83
EtMe <sub>2</sub> N·BMe <sub>3</sub>	1.77	EtMeO·BMe <sub>3</sub> <sup>b</sup>	2.25
Et <sub>2</sub> S	1.31		
Et <sub>2</sub> S·BF <sub>3</sub>	1.42		
Et <sub>2</sub> S·BH <sub>3</sub>	1.32		
Et <sub>2</sub> S·BMe <sub>3</sub> <sup>b</sup>	1.32		

<sup>a</sup> The following abbreviations are used in this and succeeding tables: Me = CH<sub>3</sub>, Et = C<sub>2</sub>H<sub>5</sub>, Vi = CH<sub>2</sub>:CH-.  
<sup>b</sup> For convenience formulas of addition compounds are used although for this acid-base pair dissociation may be nearly complete under conditions of measurement.

of dissociation of the boron trifluoride adduct ( $\Delta H = 35.7$  kcal. mole<sup>-1</sup>) is about equal, under comparable conditions, to that of the borane adduct ( $\Delta H = 35.2$  kcal. mole<sup>-1</sup>, taking the enthalpy change in the reaction  $\frac{1}{2}\text{B}_2\text{H}_6(\text{g}) = \text{BH}_3(\text{g})$ <sup>10</sup> as 14.2 kcal. mole<sup>-1</sup>). Gas phase dissociation studies<sup>11</sup> indicate that the trimethylboron adduct is considerably weaker ( $\Delta H = \sim 10$  kcal. mole<sup>-1</sup>). We should thus have expected the internal shift values for the first two adducts to lie closer together, if the electronegativity correlation is in fact applicable to these systems.

No data are available for the enthalpies of dissociation of the adducts of ethyldimethylamine, except in the case of the trimethylboron adduct ( $\Delta H = 13.8$  kcal. mole<sup>-1</sup>).<sup>12</sup> It is clear, however, from all available data concerning the base strengths of triethylamine and trimethylamine,<sup>8</sup> that we may expect the boron trifluoride and borane adducts to be of roughly comparable strength and that both will be stronger than the trimethylboron adduct. Since the internal shifts are in the order  $\text{BMe}_3 > \text{BF}_3 > \text{BH}_3$ , it is evident that the proposed chemical shift-adduct stability correlation is not applicable to this system. Because of reduction in the steric requirements of the base, the trimethylboron adduct may be expected to be closer in stability to the boron trifluoride adduct when ethyldimethylamine is the reference base than when triethylamine is the reference base. The values of the internal shifts may reflect this tendency, but other factors are evidently more important in determining the magnitude of the internal shift.

The diethyl ether adduct of boron trifluoride is a well-known compound ( $\Delta H = 10.9$  kcal. mole<sup>-1</sup> 13a;  $\Delta H = 11.93$  kcal. mole<sup>-1</sup> 13b). The corresponding borane adduct is known to exist only at low temperatures, while it may be inferred, from the non-

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

(11) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947).

(12) H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960).

(13) (a) H. C. Brown and R. M. Adams, *ibid.*, **65**, 2557 (1943).

(b) D. E. McLaughlin and M. Tamres, *ibid.*, **82**, 5618 (1960).

existence of the adduct  $\text{Me}_2\text{O}\cdot\text{BMe}_3$ ,<sup>14</sup> that the adduct  $\text{Et}_2\text{O}\cdot\text{BMe}_3$  does not form. The internal shifts for the three etherates given in Table I are thus consistent with the known stability of the etherates. It should be noted, however, that the internal shift for diethyl ether in the presence of an equivalent amount of diborane or trimethylboron is smaller than that observed for the solution of the ether alone. Such a shift implies a lower apparent electronegativity in the presence of the Lewis acid. A similar decrease in the internal shift is noted in the formation of the etherates of triethylaluminum and triethylgallium and has been attributed to changes in the magnetic anisotropy resulting from reduction of the number of unshared electron pairs on the donor atom upon coordination.<sup>6</sup> The occurrence of any change under conditions where no association is expected, however, suggests the occurrence of some sort of specific interaction between the acid and base.

Our value for the internal shift in diethyl ether differs slightly from that reported previously (2.50 p.p.m.<sup>6</sup>) and may reflect differences in solution conditions.<sup>15</sup> It is of interest that our value for the internal shift in  $\text{Et}_2\text{O}\cdot\text{BF}_3$  (2.83 p.p.m.) is greater than that reported<sup>6</sup> for  $\text{Et}_2\text{O}\cdot\text{AlEt}_3$  (2.25 p.p.m.) or  $\text{Et}_2\text{O}\cdot\text{GaEt}_3$  (2.12 p.p.m.). Precise stability data are not available to permit exact assessment of the relative stabilities in this case, but it is certain that triethylaluminum is the strongest Lewis acid of the three.<sup>8</sup> Thus the acidity order  $\text{BF}_3 > \text{AlEt}_3 > \text{GaEt}_3$  predicted by consideration of our chemical shift data together with the data reported elsewhere<sup>6</sup> is quite likely in error. We must assume that there is a strong dependence upon solution conditions or that the method is not applicable when the Lewis acids are markedly dissimilar in structure.

The results for the two adducts of methyl ethyl ether are in accord with those for diethyl ether and do not provide any further information.

The complexes of diethyl sulfide clearly demonstrate that the internal shift criterion for adduct stability is not generally applicable. It is known that the order of acidity toward diethyl sulfide is  $\text{BH}_3 > \text{BF}_3 > \text{BMe}_3$ ,<sup>14,16</sup> yet the internal shift sequence is  $\text{BF}_3 > \text{BH}_3 = \text{BMe}_3$ . The stability of the  $\text{BH}_3$  adduct has been attributed to "back donation" of electron density from the  $\text{BH}_3$  group into the vacant d-orbitals of the sulfur atom,<sup>14</sup> and such an effect might be expected to reduce the internal shift in the  $\text{BH}_3$  adduct. In view of the demonstrated deficiencies of the simple electron-density picture in explaining other internal shifts, however, it would seem injudicious to attribute the shift sequence to this effect.

**Internal Shifts in Ethyl-substituted Boron Compounds and their Adducts.**—The proton spectra of ethylboron compounds are characterized by small internal shifts and by broadening due to quadrupole relaxation of the boron nucleus. Detailed analysis is therefore difficult. It is possible, how-

ever, to draw certain qualitative conclusions from the general appearance of the spectra.

The spectrum of ethylboron dichloride shows two broad, poorly resolved multiplets. It is apparent from the relative intensities that the internal shift is positive, and its magnitude is about 0.3 p.p.m. In ethylboron difluoride, the internal shift is even smaller and the spectrum appears as a single broad multiplet. These results indicate, on the basis of the Dailey-Shoolery rule,<sup>4</sup> that the electronegativity of the boron atom is greater in the chloride than in the fluoride. A similar conclusion follows from the relative chemical shifts of the methyl protons in methylboron dichloride and methylboron difluoride. In 10% solution in chlorotrifluoromethane, the shifts, relative to tetramethylsilane (internal reference) are:  $\text{CH}_3\text{-BF}_2$ , -0.48 p.p.m.; and  $\text{CH}_3\text{BCl}_2$ , -1.25 p.p.m. These results, while unexpected in terms of inductive effects of the halogens, are in accord with conclusions based on addition compound stabilities,<sup>17</sup> infrared data,<sup>18</sup> boron and fluorine chemical shifts<sup>1,18</sup> and a molecular orbital treatment,<sup>19</sup> that  $\pi$ -bonding between boron and fluorine is considerably more significant than the analogous interaction between boron and chlorine.

Upon formation of the trimethylamine adducts, the internal chemical shifts are diminished in both ethyl compounds. The two multiplets in the chloride coalesce to a single broad multiplet in the adduct, while the fluoride adduct shows two multiplets with an internal shift of about -0.5 p.p.m. The influence of coordination upon the internal shift is similar to that observed for the triethylaluminum and triethylgallium etherates.

**Chemical Shifts of Methyl Protons in Adducts of Methyl-substituted Bases.**—Allred and Rochow<sup>7</sup> have shown that the electronegativity of substituents may be correlated under certain conditions with chemical shifts in methyl derivatives and have used this correlation to establish a qualitative scale of substituent electronegativities. Although the importance of magnetic anisotropy effects must be considered in such systems, the empirical correlation is nonetheless a useful one. It would seem that the same arguments used to relate the Dailey-Shoolery equation with electron distribution in addition compounds<sup>6</sup> could be used to infer from methyl proton shifts the stabilities of adducts in which the acid or base or both bear methyl groups. Accordingly, the validity of such a procedure appeared worthy of investigation.

The chemical shifts of the methyl protons in the adducts of some methyl-substituted bases are summarized in Table II. The most complete series is that of the trimethylamine adducts. A number of investigations have demonstrated that the order of acidity of the boron compounds toward trimethylamine is  $\text{BF}_3 \sim \text{BH}_3 > \text{BF}_2\text{Et} \sim \text{BF}_2\text{Vi} > \text{BMe}_3$ .<sup>1,8</sup> The chemical shift sequence agrees with this order of acidity, the N-methyl protons being least shielded in the strongest adducts. The position of ethylboron dichloride in the stability

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

(15) Solution conditions were not specified in ref. 6.

(16) T. D. Coyle, H. D. Kaesz and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 2989 (1959).

(17) H. C. Brown and R. R. Holmes, *ibid.*, **78**, 2173 (1956).

(18) T. D. Coyle, S. L. Stafford and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(19) F. A. Cotton and J. R. Leto, *J. Chem. Phys.*, **30**, 993 (1959).

TABLE II  
CHEMICAL SHIFTS OF METHYL PROTONS IN ADDUCTS OF  
METHYL-SUBSTITUTED BASES

Compound	Chemical shift <sup>a</sup> (p.p.m.)	Compound	Chemical shift <sup>a</sup> (p.p.m.)
Me <sub>3</sub> N·BCl <sub>2</sub> Et	2.53	Me <sub>2</sub> S	3.25
Me <sub>3</sub> N·BF <sub>3</sub>	2.73	Me <sub>2</sub> S·BF <sub>3</sub>	3.05
Me <sub>3</sub> N·BH <sub>3</sub>	2.75	Me <sub>2</sub> S·BH <sub>3</sub>	3.12
Me <sub>3</sub> N·BF <sub>2</sub> Et	2.88	Me <sub>2</sub> S·BMe <sub>3</sub> <sup>b</sup>	3.25
Me <sub>3</sub> N·BF <sub>2</sub> Vi	2.88	EtMeO	2.05
Me <sub>3</sub> N·BMe <sub>3</sub>	2.93	EtMeO·BF <sub>3</sub>	1.55
EtMe <sub>2</sub> N·BF <sub>3</sub>	2.81	EtMeO·BMe <sub>3</sub> <sup>b</sup>	2.05
EtMe <sub>2</sub> N·BH <sub>3</sub>	2.83		
EtMe <sub>2</sub> N·BMe <sub>3</sub>	3.04		

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> internal standard. <sup>b</sup> See Table I, footnote b.

sequence is less clear, although a recent study of the acidity of the methylboron chlorides<sup>20</sup> suggests that Me<sub>3</sub>N·BCl<sub>2</sub>Me should be of comparable stability to Me<sub>3</sub>N·BF<sub>3</sub>. On this basis, the greater stability of Me<sub>3</sub>N·BCl<sub>2</sub>Et implied by the chemical shift data seems somewhat anomalous.

The more limited data for the adducts of ethyl-dimethylamine and of methyl ethyl ether, listed in Table II, are also in the order that would be predicted on the basis of a direct relation between donor-atom electronegativity and the strength of the dative bond. In the dimethyl sulfide sequence, however, the stability order predicted by the chemical shift result is Me<sub>2</sub>S·BF<sub>3</sub> > Me<sub>2</sub>S·BH<sub>3</sub>, yet the latter is well known to be the more stable.<sup>14,16</sup> The shift sequence may be related to the occurrence of "back bonding," but it seems best to accept this explanation with considerable caution.

**Chemical Shifts of B-Methyl Protons in Adducts of Trimethylboron.**—The chemical shifts of the B-methyl protons in trimethylboron and a number of its adducts are summarized in Table III. The shifts for the amine adducts parallel the known stabilities of the compounds.<sup>12,21</sup> Without doubt, the ether and sulfide adducts listed in Table III are either non-existent or, at most, very unstable. Chemical shifts for these acid-base pairs are essentially the same as the value found for a solution of trimethylboron, with some indication that the interaction between trimethylboron and dimethyl sulfide is the strongest of the four.

TABLE III  
CHEMICAL SHIFTS OF B-METHYL PROTONS IN TRIMETHYL-  
BORON ADDUCTS

Compound	Chemical shift <sup>a</sup> (p.p.m.)	Compound	Chemical shift <sup>a</sup> (p.p.m.)
Me <sub>3</sub> B	4.57	Et <sub>2</sub> O·BMe <sub>3</sub> <sup>b</sup>	4.57
Et <sub>3</sub> N·BMe <sub>3</sub>	4.67	EtMeO·BMe <sub>3</sub> <sup>b</sup>	4.56
EtMe <sub>2</sub> N·BMe <sub>3</sub>	5.63	Et <sub>2</sub> S·BMe <sub>3</sub> <sup>b</sup>	4.57
Me <sub>3</sub> N·BMe <sub>3</sub>	5.65	Me <sub>2</sub> S·BMe <sub>3</sub> <sup>b</sup>	4.62

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> internal standard. <sup>b</sup> See Table I, footnote b.

The correlation of chemical shifts with addition compound formation prompted by the earlier work<sup>6</sup> tests a hypothesis based on two assumptions:

1. In a series of molecular addition compounds,

(20) N. E. Miller, *Diss. Abstr.*, **18**, 1972 (1958).

(21) H. C. Brown, M. D. Taylor and M. Gerstein, *J. Am. Chem. Soc.*, **66**, 431 (1944).

the electron-withdrawing power of the donor atom increases and that of the acceptor atom diminishes, as they become involved in stronger adducts.

2. A direct relation exists between the electron-withdrawing power of an atom and the magnetic shielding of protons on substituent groups.

It is evident from the results given here that these considerations only provide a qualitative explanation of variations in chemical shifts in a few addition compounds. The chemical shift criterion, and particularly the application of the relationship between electronegativity and internal shifts in ethyl groups, is not uniformly successful, perhaps because of magnetic anisotropy effects. Unfortunately, the demonstrated deficiencies of this correlation reduce its value as a tool for elucidating relative stabilities of compounds that have not been investigated by other techniques.

**Qualitative Features of the Spectra.**—The spectra of most of the addition compounds investigated are relatively simple and offer no difficulty in interpretation. In the case of Et<sub>2</sub>S·BH<sub>3</sub>, however, a complex multiplet is observed in the methylene region, in contrast to the quartet usually shown by ethyl groups. Under moderate resolution, the spectrum appears to consist of two overlapping quartets, the total intensity being approximately two-thirds that of the sharp methyl triplet. Under higher resolution, additional structure is observed. The separations are enhanced in the pure liquid and reduced in the 40 Mc. spectrum.

These observations are qualitatively similar to the results reported by Finegold<sup>22</sup> for the proton spectrum of diethyl sulfite and attributed by him to non-equivalence between the two ethyl groups. More recently a similar effect has been observed in the n.m.r. spectrum of cyclopropylmethylcarbinyl ethyl ether and other compounds, and it has been shown that the spectrum of the methylene group can be interpreted as the AB portion of an ABC<sub>3</sub> system.<sup>23</sup> The non-equivalence is clearly between the two protons of the individual methylene group and is attributed to the influence of the asymmetric carbon atom favoring a particular rotational conformation about the C-O bond.

In the case of diethyl sulfide-borane, the disposition of the three groups and the lone pair about the sulfur atom is undoubtedly close to tetrahedral. In this case, the individual protons of either methylene group in general will be non-equivalent even in the case of fast rotation about the C-S bond, although the average chemical shift of a given proton on one methylene carbon corresponds to that of one of the protons on the other methylene group.

We have investigated a number of other compounds in an effort to establish the generality of this effect. In diethyl sulfoxide, the structure of which is closely analogous to the sulfide adduct Et<sub>2</sub>S·BH<sub>3</sub>, the methylene group gives rise to a pattern that is strikingly similar to the multiplet depicted elsewhere.<sup>23</sup> Again, non-equivalence is to be expected as a consequence of the stereochemistry. The effect is also noted in ethyliso-

(22) H. S. Finegold, *Proc. Chem. Soc.*, 283 (1960).

(23) P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **47**, 49 (1961).

propyl sulfoxide, but not in ethyl sulfate, ethyl sulfone or ethylisopropyl sulfone, where there is greater symmetry about the sulfur atom. The non-equivalence is not confined to ethyl-sulfur derivatives but is shown also in the salt  $\text{Et}_2\text{MeNHI}$ . In this case, the difference in chemical shift of the two methylene protons is particularly pronounced, being 0.54 p.p.m. for the compound measured in saturated solution in dichloromethane. In this case, two distinct quartets are observed, overlapped by the strong absorption of the N-methyl groups.

It is particularly noteworthy that the spectrum of the adduct  $\text{Et}_2\text{S}\cdot\text{BF}_3$  is quite simple, showing no evidence of non-equivalence of the methylene protons. Since non-equivalence would be expected, even in the case of rapid rotation about the C-S bond, and since it is observed in the analogous  $\text{BH}_3$  adduct, this result suggests strongly that some sort of averaging process, perhaps an exchange of

the  $\text{BF}_3$  group between the two lone-pair positions, is occurring. A study of the temperature dependence of this spectrum would be welcome.

NOTE ADDED IN PROOF.—Since the submission of this article, Waugh and Cotton<sup>24</sup> have reported their observation that the protons of the single methylene group in  $\text{C}_6\text{H}_5\text{S}(\text{O})\text{OC}_2\text{H}_5$  are non-equivalent. Their conclusion that the low molecular symmetry is the source of this non-equivalence is in accord with our interpretation of the spectrum of the somewhat analogous  $\text{Et}_2\text{S}\cdot\text{BH}_3$ .

A further indication that exchange of the Lewis acid groups is responsible for the absence of similar effects in the spectrum of  $\text{Et}_2\text{S}\cdot\text{BF}_3$  is the observation that the resonance due to the B-H hydrogen atoms in the borane adduct is split into a quartet of broad lines by spin coupling to the  $^{11}\text{B}$  nucleus. In the  $^{19}\text{F}$  spectra of a number of weak  $\text{BF}_3$  adducts (and of several addition compounds of other metal fluorides<sup>25</sup>), B-F spin coupling is not observed, presumably because of the effects of rapid breaking and reforming of the donor-acceptor links. Any similar exchange processes in the  $\text{BH}_3$  adducts are therefore, in all probability, slower.

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## Stability of the Mixed Complex $\text{FeSCNF}^+$

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Evidence was obtained from potentiometric and spectrophotometric experiments for the formation of  $\text{FeSCNF}^+$  in solutions containing iron(III), thiocyanate and hydrofluoric acid.

Rabinowitch and Stockmayer<sup>1</sup> were the first to suggest the existence of the mixed complex,  $\text{FeSCNCl}^+$ , in the iron(III)-thiocyanate-chloride system. Spectrophotometric evidence for this complex<sup>2</sup> as well as for  $\text{FeSCNBr}^+$ ,  $\text{FeSCNOH}^+$ ,  $\text{FeSCNSO}_4$  and related complexes has been obtained by Lister and Rivington.<sup>2</sup> The purpose of this paper was to investigate the iron(III)-thiocyanate-fluoride system spectrophotometrically for evidence for the formation of  $\text{FeSCNF}^+$ . In addition the system was investigated potentiometrically using the ferrous-ferri cell.<sup>3-5</sup>

As a check on the experimental procedures the formation constants of  $\text{FeF}^{++}$ ,  $\text{FeF}_2^+$ ,  $\text{FeSCN}^{++}$  and  $\text{Fe}(\text{SCN})_2^+$  were determined potentiometrically while the formation constant of  $\text{FeSCN}^{++}$  was determined spectrophotometrically. All measurements were made on solutions containing 0.5 M perchloric acid and the ionic strength of these solutions varied from 0.51 to 0.53. Under these conditions the variation in ionic strength can be ignored; the dimerization of iron(III),<sup>6</sup> the hydrolysis of iron(II)<sup>7</sup> and the formation of  $\text{HF}_2^{-3}$  are negligible; and the hydrolysis of iron(III)<sup>6</sup>

and the ionization of hydrofluoric acid<sup>8</sup> is less than 0.5%. Although iron(III) perchlorate ion pairs<sup>9</sup> may be present, their formation is not dependent upon the hydrogen ion concentration, and they will not affect the results obtained significantly. Finally the concentrations of iron(III), fluoride and thiocyanate were chosen so as to prevent complications due to the formation of  $\text{FeF}_3^4$  and  $\text{Fe}(\text{SCN})_3$ .<sup>10</sup>

### Experimental

**Reagents.**—Ferric perchlorate monohydrate was prepared by dissolving freshly precipitated ferric hydroxide in dilute perchloric acid and crystallizing the salt from hot concentrated perchloric acid. The salt was white when hot and lilac when cold. Ferric hydroxide was prepared by precipitation with ammonia vapors from hot solutions of ferric nitrate. The precipitate was washed by decantation with hot water until the washings were nitrate free. Stock solutions of ferric perchlorate were prepared by dissolving the salt in 1M perchloric acid. When they contained less than 0.01 M iron, the perchloric acid solutions had no absorbance in the visible region.

Ferrous perchlorate was prepared by reducing perchloric acid solutions of ferric perchlorate with analytical grade iron wire. These solutions were found to be stable in air for periods up to two weeks. Ammonium thiocyanate solutions were prepared from freshly opened bottles of C.P. A.C.S. grade ammonium thiocyanate and stored in the dark. All other reagents were also of C.P. A.C.S. grade. Solutions containing fluoride were stored in polyethylene bottles and hydrofluoric acid solutions were measured with calibrated polyethylene burets. All solutions were carefully filtered before diluting to final volume and then analyzed by standard volumetric procedures.

**Potentiometric Measurements.**—All measurements were made at  $26.7^\circ \pm 0.1$  with Leeds and Northrup type K poten-

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