

equilibrium shift increases the concentration of the common conjugate acid of the acetylated aldose, thus increasing the rates of both reactions 3 and 4 to comparable extents. The latter steps, involving no O-H bond fission, should not be subject to a deuterium isotope effect. It is interesting to note that the anomerization rate isotope effect in pure acetic anhydride (No. 11) is only about 78% as great as the corresponding isotope effect (No. 5) in 1:1 acetic acid-acetic anhydride, an observation which suggests that acetic anhydride is more basic than acetic acid to H<sub>2</sub>SO<sub>4</sub>.

The essentially similar rates of C1 exchange and C1 inversion for 1,2-*cis* anomers (No. 3) as well as the enhanced rate of exchange over inversion for 1,2-*trans* anomers (No. 1) find their parallels in the present deuterated systems (Nos. 4 and 2, resp.) to practically equivalent extents. More significant mechanistically are the similarities in values for the deuterium isotope effects in all C1 acetoxy inversion and exchange rates. Table II reveals that the kinetic isotope effects for  $k_{\text{exch-}\beta}$  (No. 6),  $k_{\beta}$  (No. 7),  $k_{\text{exch-}\alpha}$  (No. 8) and  $k_{\alpha}$  (No. 9) are all identical within experimental error<sup>10</sup> under similar environmental conditions. To us these similarities argue strongly for a common type of conjugate acid precursor, that of the acetylated aldose, in both the C1 exchange and inversion reactions. This observation is thus in accord with mechanism 3 but, in itself, does not exclude mechanism 2.

The similarities in the values of  $(k_{\text{exch-}\beta}/k_{\beta})_{\text{H}}$  in 1:1 acetic acid-acetic anhydride (No. 1) and 100% acetic acid (No. 14) suggest that this ratio is not particularly sensitive to changes in solvent composition. With the limited data at hand,

(10) Cf. Ref. 7 for a discussion of the errors involved, particularly with respect to specific rate constants for inversion.

however, it is not possible to determine if the rather different value for this ratio in 100% acetic anhydride (No. 12) is due to a difference in solvent composition or in catalyst concentration.

### Experimental

**Deuterio-Sulfuric Acid.**—Liquid sulfur trioxide (Sulfam) (10.092 g.) was weighed into a small glass-stoppered flask. The stopper was replaced by a rubber stopper equipped with a small vent slit and a hypodermic syringe. The flask was chilled in an ice-bath and the calculated volume (2.34 ml.) of 99.5% deuterium oxide was added to the sulfur trioxide through the hypodermic needle very slowly with swirling and cooling. The resulting deuterio-sulfuric acid, having  $d^{20}$  1.868 was used directly in the anomerization and exchange experiments described below. As a control, unlabeled sulfuric acid,  $d^{20}$  1.834, was made in an identical fashion by the action of water on sulfur trioxide. Use of this sulfuric acid as catalyst in anomerization experiments gave results identical within experimental error to those obtained with commercial C.P. sulfuric acid.<sup>2,4</sup>

**Deuterio-acetic acid** was prepared typically as follows. Acetic anhydride (15.6 ml.) was treated with a drop of the above deuterio-sulfuric acid. The calculated volume of 99.5% deuterium oxide (3.08 ml.) was added dropwise with swirling and cooling. After standing in a glass-stoppered vessel for several days the mixture was treated with anhydrous sodium acetate (ca. 1 g.) and the product was distilled through a small Claisen head, b.p. 117°.

**Anomerization experiments** were conducted at 25° under the solvent and catalyst conditions listed in Table I in the manner fully described previously.<sup>2,4,7</sup> Equilibrium constant data previously published<sup>4,7</sup> have been used to calculate the individual inversion rate constants given in Table I.

**C1 acetoxy exchange experiments** were performed at 25° under the indicated solvent and catalyst conditions in Table I according to the procedures which we have described previously.<sup>2</sup> For these exchange experiments the anomers of tetra-*O*-acetyl-D-glucopyranosyl acetate-C<sup>14</sup>, prepared as described before,<sup>2</sup> were employed. The exchange rate constants shown are the averages of those calculated on the basis of products isolated from 4 to 6 aliquots taken at different times from each reaction mixture. The precision in the exchange rate constants in Table I was about the same as that previously reported.<sup>2</sup>

[CONTRIBUTION FROM THE RESEARCH LABORATORY, NATIONAL ENGINEERING SCIENCE COMPANY, PASADENA, CALIFORNIA]

## B<sup>11</sup> N.m.r. Chemical Shifts. II. Amine-borate Ester Complexes, Alkoxydifluoroborane Trimers and Tetrahaloborate Ions<sup>1,2</sup>

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The B<sup>11</sup> nuclear magnetic resonance spectra of BF<sub>2</sub>Cl and BCIF<sub>2</sub> have been obtained but no B<sup>11</sup>-F<sup>19</sup> spin coupling could be observed. Some amine addition compounds of triethyl and triallyl borates have been prepared and the B<sup>11</sup> chemical shifts are found to be dependent on reactant concentrations. Thus borate-amine exchange is taking place. Evidence that the compounds produced from the reaction of one mole of various borate esters and two moles of boron trifluoride are alkoxydifluoroborane cyclic trimers rather than the previously suggested coordination complexes is presented. Chemical shifts for tetrahalo and tetrapseudohalo borate ions prepared in nitrobenzene are presented.

In the previous paper,<sup>1</sup> B<sup>11</sup> chemical shifts for a large variety of boron compounds were presented and correlations were made between shift values and bonding in the compounds. Another group of compounds has been reported by Phillips and co-workers<sup>3</sup> and where there was overlap there is reasonably good agreement.

(1) Paper I; T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(2) This paper was presented at the 138th Meeting of the American Chemical Society, New York, September 1960.

(3) W. D. Phillips, H. C. Miller and E. L. Muettterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

Additional B<sup>11</sup> shift values ( $\delta$ ) are shown in Table I. There is noted a large shift to high field in the change from sp<sup>2</sup> bonding in boron triethyl to sp<sup>3</sup> in boron triethyl dimethyl amine complex. Also of interest is the effect of phenyl groups in triphenyl boron as compared to triethyl boron. Here the resonance effect of the phenyl groups permits greater shielding and a shift to higher field. Shifts for the complexes of boron triiodide are at highest field yet observed for boron compounds.

**Boron-Fluorine Coupling.**—Boron-fluorine spin coupling in B<sup>11</sup> spectra has not been observed either

TABLE I<sup>a</sup>  
 B<sup>11</sup> CHEMICAL SHIFTS

|  |         |
|--|---------|
| BI <sub>3</sub> :PCl <sub>3</sub>  | +65     |
| BI <sub>3</sub> :C <sub>6</sub> H <sub>5</sub> N   | +60 ± 5 |
| ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> NH:B(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> | + 6.5   |
| BBr <sub>3</sub> :C <sub>6</sub> H <sub>5</sub> N  | + 6.2   |
| BBr <sub>3</sub> :(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O  | + 6.1   |
| BF <sub>3</sub> :PCl <sub>3</sub>  | 0.0     |
| BF <sub>3</sub> :H <sub>2</sub> O  | - 0.2   |
| B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> :(CH <sub>3</sub> ) <sub>2</sub> NH                         | - 4.0   |
| BCl <sub>3</sub> :C <sub>6</sub> H <sub>5</sub> N  | - 9.0   |
| BCl <sub>3</sub> :(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O  | -10.5   |
| (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> BBr   | -18.5   |
| (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> B  | -60     |

<sup>a</sup>  $\delta = \frac{H_s - H_r}{H_r} \times 10^6$ , BF<sub>3</sub>:O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>,  $\delta = 0$ . Shift spacings are determined using B(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,  $\delta = -85$  and BCl<sub>3</sub>,  $\delta = -45.6$  as internal standards.

because quadrupole broadening of B<sup>11</sup> prevents such observations or because resolution is not high enough. Another possible reason might have been intermolecular exchange processes which would quench spin coupling. It was postulated that if a mixture of boron trifluoride and boron trichloride were prepared in which separate resonances for BF<sub>2</sub>Cl and BCl<sub>2</sub>F could be observed, this latter possibility could be substantially eliminated. The separate resonances were observed for BF<sub>2</sub>Cl at  $\delta = -20$ , and BCl<sub>2</sub>F at  $\delta = -31.2$  (BF<sub>3</sub> is at  $\delta = -9.4$  and BCl<sub>3</sub> at  $\delta = -45.6$ ). The possibility that in this mixture BF<sub>2</sub>Cl exchanges only with BF<sub>2</sub>Cl is extremely improbable as is the possibility of BCl<sub>2</sub>F exchanging only with BCl<sub>2</sub>F. Since these observations were made, Coyle and Stone<sup>4</sup> have observed spin-coupling in F<sup>19</sup> spectra of the chloro and bromo fluoroboranes. This definitely rules out exchange processes being the cause of our not observing spin-coupling in B<sup>11</sup> spectra. The observation of separate resonances also rules out the possibility that the mixture constituents are present as dimers at room temperature unless this is also restricted to a single species which is unlikely. In addition, dimerization would give tetrahedral boron and shifts to higher fields than observed. Dibromochloroborane and dichlorobromoborane also show separate resonances positioned between boron trichloride and boron tribromide resonances.

**Borate Ester-Amine Adducts.**—Crystalline amine complexes of methyl borate have been reported<sup>5</sup> with strongly basic unhindered amines and amine adducts of aryl borates are well known.<sup>6</sup> Urs and Gould observed heat effects when ethyl borate and some amines were mixed but observed no crystalline compounds.

Chemical shifts and melting points for some amine-borate complexes at 1:1 mole ratios are shown in Table II. It is noteworthy that where the complex is stable and soluble, the chemical shift for

(4) T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, **32**, 1892 (1960).

(5) S. U. Urs and E. S. Gould, *J. Am. Chem. Soc.*, **74**, 2948 (1952). H. Horn and E. S. Gould, *ibid.*, **78**, 5772 (1956). J. Goubeau and U. Bohn, *Z. anorg. u. allgem. Chem.*, **266**, 161 (1951). J. Goubeau and R. Link, *ibid.*, **267**, 27 (1952). J. Goubeau and E. Ekhoft, *ibid.*, **268**, 145 (1952).

(6) M. F. Lappert, *Chem. Revs.*, **56**, 973 (1956).

boron surrounded by three oxygens and a nitrogen is found to be in the same region ( $\delta =$  approx. 0) as for tetrahedral boron in fluoborate ion, boron trifluoride ether, amine, sulfide, phosphorous triphenyl and trichloride complexes and tetralkoxyborate and tetrahydroxyborate ions. It was also noted that a single resonance is observed but its chemical shift value changes and is dependent upon the relative concentrations of the amine and the borate ester. This indicates equilibrium between the borate ester, amine and adduct; the exchange process is rapid enough that only one peak is present in the spectrum. Equilibrium is attained rapidly, generally before the sample is introduced into the spectrometer, since only small changes are observed upon standing. Association of these borates with other bases such as benzyl amine and diethyl amine does occur, but equilibria are far to the dissociated side.

 TABLE II  
 CHEMICAL SHIFTS AT 1:1 RATIOS AND MELTING POINTS<sup>a</sup>  
 OF BORATE ESTER-AMINE COMPLEXES  
 $\delta$  (RO)<sub>2</sub>B = -18.1

|   | (CH <sub>3</sub> O) <sub>2</sub> B | (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> B | (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> O) <sub>2</sub> B |        |
|---|------------------------------------|--|---|--------|
| N <sub>2</sub> H <sub>4</sub>                                   | 79-80°                             | - 4.25 <sup>b</sup>                              | -4.0  | 41-42° |
| C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>                   | 67-69°                             | -13.7 <sup>b</sup>                               | -7.2 <sup>b</sup>   |        |
| Pyrrolidine   | 74-75°                             | -12.7 <sup>c</sup>                               | -3.7 <sup>b</sup>   |        |
| Piperidine  | 75° <sup>d</sup>                   | -9.6 <sup>c</sup>                                | -3.8  | 44-45° |
| H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> | 81-82° <sup>d</sup>                | -9.3 <sup>b</sup>                                | -2.2  | 31-33° |

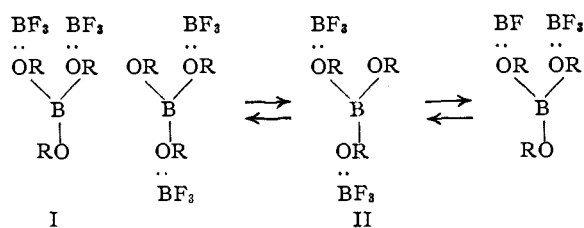
<sup>a</sup> Melting points in sealed tubes. <sup>b</sup> Crystals observed but not isolated. <sup>c</sup> No crystals observed. <sup>d</sup> S. U. Urs and E. Gould, ref. 5.

As an example of the sensitive steric requirements, methyl borate ( $\delta = -18$ ) shifts to  $\delta = -14$  in the presence of unsymmetrical dimethyl hydrazine indicating only slight association. Complete association would give a  $\delta$  value of about zero. There is no evidence of even this much association with higher borates. The unsymmetrical dimethyl hydrazine is a stronger base than hydrazine which forms crystalline compounds ( $\delta =$  approx. 0) with both ethyl and allyl borates. Amorphous solids are formed when *n*-propyl, *n*-butyl, *n*-amyl and *n*-hexyl borates are mixed with hydrazine. These were not investigated. It was noted that complexes of allyl borate with the amines listed in Table II were more stable than ethyl borate complexes and formed with greater ease. Models predict that the steric requirements of both esters are approximately equivalent.

**Alkoxydifluoroborane Trimers.**—The compounds formed from one mole of borate ester and two moles of boron trifluoride were recently described<sup>7</sup> as borate ester-boron trifluoride complexes. Presumably these would be static adducts (I) though the dynamic system (II) with BF<sub>3</sub>'s migrating from oxygen to oxygen would also be considered a complex.

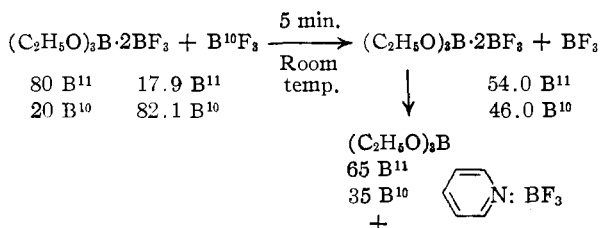
In the structure II boron trifluoride molecules are exchanging all ester oxygens. Since in either

(7) P. A. McCusker and M. L. Kilzer, *J. Am. Chem. Soc.*, **82**, 372 (1960).



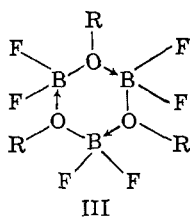
structure, ester and fluoride borons are not equivalent, the  $B^{11}$  NMR spectrum expected would consist of two peaks. One, at  $\delta = 0$  where boron trifluoride-oxygen complexes have been found, would be twice the area of one at  $\delta = -18$  where ester borons have been found. Possibly the latter peak should be at even lower field since the inductive effect of the boron trifluorides should lessen the interaction of unbonded oxygen electron pairs with the vacant  $P_z$  orbital of the borate ester boron atom.

The spectrum observed was a sharp singlet at  $\delta = 0$  showing only one type boron present, and this apparently in a tetrahedral configuration. To confirm the equivalence of boron atoms the compound was exchanged with  $B^{10}$  enriched boron trifluoride and exchange was found to take place more rapidly than in the boron trifluoride-boron trifluoride etherate system. As seen, the ethyl



borate liberated from the compound after removing the exchanged boron trifluoride was enriched in  $B^{10}$ . This confirms the equivalence of boron atoms and is in agreement with the n.m.r. data.

The structure in agreement with these data is the cyclic alkoxydifluoroborane trimer, III. A dimer is ruled out by the molecular weights of the



compounds.<sup>7</sup> Other possible structures involving fluorine bridging or alternate oxygen-fluorine bridging were ruled out when  $F^{19}$  NMR showed only one narrow peak, that is, only one type of fluorine is present. The peak width was less than 6 cycles per second. This is less than the 15 c.p.s. observed for fluorine-boron coupling by Coyle and Stone<sup>4</sup> and indicates if there is spin-coupling in this compound it is less than 2-3 c.p.s.

With structure III established, it is possible to consider the arguments advanced for I and II.<sup>7</sup> The major evidence for coordination structures were dipole moments of the same magnitude as

boron trifluoride etherates. Cyclic alkoxydifluoroborane trimers were said to have small dipoles. This might be true if structures were planar, but with oxygen-boron coordination to form a ring, there is an approach to tetrahedral configuration for both boron and oxygen and the resultant cyclohexane like structure would be expected to have a dipole moment.

Consideration of boiling points of the compounds as compared to boron trifluoride etherates also would cast doubts on coordination structures. The compound from ethyl borate and boron trifluoride has a boiling point of  $82.5^\circ$  and a molecular weight of 252, while boron trifluoride etherate boils at  $127^\circ$  and has a molecular weight of 142. Though there is a large degree of dissociation in the vapor for both compounds, this inverse ratio suggests more symmetry in the compounds than a coordination complex would have.<sup>8</sup>

The exchange data and the low temperature reaction of the compound with amines to form boron trifluoride amine complexes indicate the compound III can possibly dissociate to borate ester and boron trifluoride. The dissociation course cannot be followed in the n.m.r. at room temperature. Possibly the first step in the dissociation and exchange is formation of the alkoxydifluoroborane monomer which then exchanges through fluorine bridging with boron trifluoride or reacts with amines to form unstable alkoxydifluoroborane amine adducts. These latter then disproportionate to boron trifluoride adducts and the ester. The alkoxydifluoroborane adducts are not known so it is possible that they do disproportionate. A consideration of reactivity of the alkoxydichloroboranes suggests this is so. The latter compounds, in ether, disproportionate to dialkoxychloroboranes<sup>9</sup> and the etherate of boron trichloride. The amine adducts of alkoxydichloroboranes disproportionate on heating to amine, borate ester and boron trichloride-amine adducts.<sup>10</sup> Boron-chlorine compounds are stronger acids than boron-fluorine compounds,<sup>11</sup> so it would not be unreasonable that the alkoxydichloroborane amine adduct requires heat for disproportionation while the alkoxydifluoroborane amine adduct would be entirely unstable.

The greater acceptor strength of boron trichloride compared to boron trifluoride should have led to a more stable complex with borate esters for boron trichloride if I or II were correct structures. Models indicate boron trichloride could complex with methyl borate, but the reaction actually gives dichloroalkoxy or chlorodialkoxyboranes. Boron tribromide, an even stronger acceptor, also gives dialkoxybromoboranes. The possible reason for the cyclization of alkoxydifluoroboranes, while alkoxydichloroboranes remain as monomers,<sup>1</sup> is steric crowding in the chloro compounds.

**Tetrahaloborates.**—Recently the preparation of cesium tetrachloroborate in nitrobenzene was re-

(8) Referee II states that in his opinion "Boron-oxygen bond strength differences could cause volatility effects (but) not molecular symmetry."

(9) H. Ramser and E. Wiberg, *Ber.*, **63**, 1136 (1930).

(10) M. F. Lappert, *J. Chem. Soc.*, 667 (1953).

(11) H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, **78**, 2173 (1956).

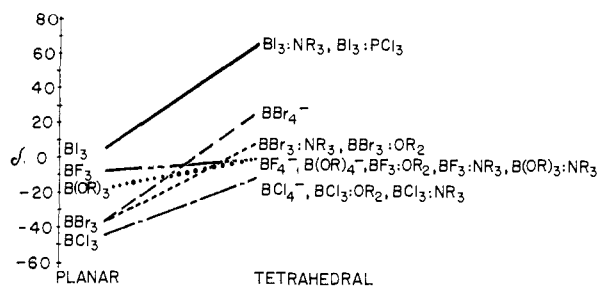
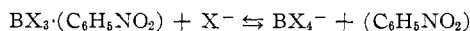


Fig. 1.—Chemical shifts of planar and tetrahedral boron compounds.

ported.<sup>12</sup> Potassium tetrachloroborate also formed but was less stable. Boron trichloride Lewis base complexes have chemical shifts of  $\delta = -9$  or  $-10$ . The tetrachloroborate ion chemical shift is at  $\delta = -11$  or  $-12$  and the shift is chloride ion dependent. Thus the chemical shift may be at lower field than  $\delta = -12$ . Tetrabromoborate ion prepared from cesium of potassium bromide and boron tribromide in nitrobenzene had a chemical shift at  $\delta = +26$  while Lewis base adducts of boron tribromide are at  $\delta = +6$  to  $+10$ . The  $B^{11}$  shift was at lower field than  $\delta = +26$  if lower concentrations of bromide ion were used. It appears that the rapid exchange process



is occurring. The actual shift value for  $BBr_4^-$  may then be slightly higher than  $\delta = +26$  since a higher concentration of bromide ion might give more of the tetrabromoborate ion in equilibrium with the boron tribromide or its nitrobenzene adduct.

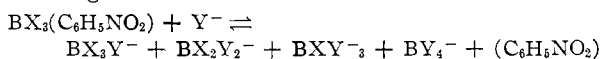
Exchange is also observed in boron tribromide-nitrobenzene with chloride ion: all possible ions are apparently produced rapidly. When iodide ion was added to the boron halides in nitrobenzene, black products with feeble boron signals were obtained. The reaction of boron iodide with nitrobenzene was vigorous and gave insoluble black products possibly containing iodine; no boron signal was obtained from these mixtures.

The chemical shifts of planar boron compounds have been compared in Fig. 1. The slopes of lines connecting the shifts of planar compounds with the shift found for the corresponding tetrahedral complexes show some relation to the amount of "back coordination" in the planar compounds.<sup>13</sup>

(12) E. L. Muetterties, *J. Inorg. Nuclear Chem.*, **12**, 355 (1960).

Where the back coordination is great, the difference between shielding in the planar and tetrahedral compounds is small. Thus, the slope is least for the boron trifluoride-boron trifluoride complex and for borate ester-ester complex lines and greater for boron trichloride-boron trichloride complexes and tetrachloroborate ion are close, but boron tribromide and tetrabromoborate ion diverge with the increased shielding of a bromine compared to a complexing atom. It would be expected that there would be even greater divergence in comparing boron triiodide complexes and tetraiodoborate ion; the increased shielding of a fourth iodine would give a chemical shift of over  $+100\delta$  for the tetraiodoborate ion. This greatly enhanced shielding in tetraiodoborate ion is also suggested by a plot of halogen electron affinities<sup>14</sup> against tetrahaloborate ion chemical shifts. Here again, though the exact values of tetrahaloborate ion shifts are not known with certainty in exchanging systems, a shift value of over  $+100$  is predicted for tetraiodoborate ion.

Other ions besides halide ions take part in exchange with the boron halides in nitrobenzene. Pseudo halides such as cyanide, cyanate, thiocyanate and azide ions added to boron trichloride in nitrobenzene all show chemical shifts at higher field than boron trichloride in nitrobenzene. With potassium cyanide a series of peaks at  $\delta = -5$ ,  $+0.6$  and  $+4.5$  were seen immediately on mixing with the boron trichloride-nitrobenzene. After five days a broad exchange peak was seen centered at  $\delta = 0$  with a small shoulder at  $\delta = -5$ . These data indicate formation of such ions as  $BCl_3CN^-$ ,  $BCl_2(CN)_2^-$ ,  $BCl(CN)_3^-$ ,  $B(CN)_4^-$  which slowly exchange



**Instrument.**—All spectra were obtained with a Varian V-4300 high resolution n.m.r. spectrometer operating at 12.83 Mc. for boron and at 40 Mc. for fluorine.

**Acknowledgment.**—The assistance of Mr. C. A. Burns in obtaining these data is gratefully acknowledged.

(13) Exact values for chemical shifts are found in ref. 1 and in Tables I and II.

(14) A. Von Hippel, "Molecular Science and Molecular Engineering," The Technology Press of M.I.T. and John Wiley and Sons, Inc., New York, N. Y., 1959, p. 30.