

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

**Donor-Acceptor Bonding. I. Etherates of Boron Trifluoride<sup>1</sup>**BY A. W. LAUBENGAYER AND G. R. FINLAY<sup>2</sup>

The formation of addition compounds by the union of two substances, whose molecules apparently already have the normal valence requirements of their constituent atoms satisfied, has long been established. The classical example is ammonia-boron trifluoride,  $\text{H}_3\text{N}:\text{BF}_3$ , discovered in 1809 by Gay-Lussac and Thenard. The suggestion that the bond formed between the two component molecules probably is of the covalent shared-electron-pair type<sup>3</sup> seems reasonable. Such a shared-electron-pair bond may be considered to be established by donor-acceptor action,<sup>4</sup> an atom in the donor molecule having an unshared pair of electrons in the valence shell which it can donate for sharing with an atom in the acceptor molecule which has a suitable unoccupied orbital.<sup>5</sup>

In spite of the prevalence of such bonding in systems such as the Grignard reagent and the Friedel-Crafts intermediates, and the fact that numerous other important cases of catalytic action may reasonably be accounted for by assuming addition compound formation very little attention has been given to the quantitative aspects of donor-acceptor action.

The formation of a donor-acceptor bond between two molecules should have a number of important consequences.

1. The coordination numbers of both the donor atom and the acceptor atom are increased by one unit. In general, an increase in coordination number demands a change in bond angles. This should be more serious for the acceptor than for the donor molecule. The donor atom, prior to addition, already has a pair of unshared elec-

trons in the coordination position, and so no great change in its electronic environment will be produced by the formation of the bond, and no great changes of bond angles are to be expected. On the other hand, the acceptor atom acquires a share of a pair of electrons and its electronic environment is greatly changed, which should cause a considerable change in its configuration. Thus a change in the coordination number of an acceptor atom from three to four would probably involve a change of configuration from planar to tetrahedral.

2. If an asymmetrical atom is produced, the increase in coordination number may give rise to optical isomers.

3. The bonds of the original molecules should be weakened and probably the bond distances should become greater.

4. The donor-acceptor bond distance should approximate that of the normal covalent bond for the same coordination numbers, allowance being made for the effect of separation of charge.

5. The donor-acceptor bond energy should approximate that of the normal covalent bond for the same coordination number. The heat of formation observed for the addition compound should be the algebraic sum of the energy required to bend and stretch the bonds of the system in accord with the increased coordination number, and the energy of the donor-acceptor bond itself.

6. Since two independent molecules combine to form one, the system loses three degrees of freedom of translation and three of rotation, and gains five of vibration and one of internal rotation.

7. The donor may be considered as losing some interest in a pair of electrons and so acquires a positive charge, while the acceptor acquires a negative charge. This separation of charge should give the bond a dipole moment which would be very large if the electrons were equally shared. The dipole moment for the addition complex will depend upon not only the moment for the donor-acceptor bond but also upon the moments of the other bonds in the donor and acceptor molecules. These latter should be quite different from those in the molecules prior to addition and their di-

(1) Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September 9, 1942.

(2) Present address: Norton Company, Chippawa, Ontario, Canada.

(3) Langmuir, *THIS JOURNAL*, **41**, 868 (1919).

(4) Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1929, p. 116.

(5) The nomenclature associated with this kind of covalent bonding is confused. Lowry has spoken of a "mixed bond" and Sugden introduced the term "semi-polar double bond," arguing that it is made up of one covalent and one electrovalent bond. The term "dative bond" was proposed by Menzies but this term has not been much used. Sidgwick has described the link as "coordinate covalent" but this term is confusing because in many cases other mechanisms also probably are involved in binding the groups coordinated to a central atom. We shall use the term donor-acceptor bond because this clearly describes the electronic rearrangement suggested by Sidgwick without introducing unfortunate connotations.

reactions should be changed, due to the changes which have occurred in the configurations of the donor and acceptor molecules.

This paper reports the first of a series of investigations which have been initiated in an effort to obtain quantitative data on the changes which take place when donor-acceptor bonding occurs. Such data should throw more light on the nature of this bond, which has been largely a matter of conjecture, and on its relation to the physical and chemical properties of the compounds which contain it.

The addition compounds of boron trifluoride with dimethyl, diethyl and methyl ethyl ethers have been selected for study because they seemed especially suitable for obtaining extensive quantitative data. Boron trifluoride is one of the strongest acceptor systems known and the ethers show good donor activity. Previous workers<sup>6,7,8</sup> had shown that  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$  are volatile enough to allow extensive study in the gas phase. The present authors have investigated  $\text{Me}_2\text{O}:\text{BF}_3$  in detail, and have considered the variations in properties in the homologous series, particularly with respect to constitutive properties.

### Experimental

**Preparation.**—The etherates of boron trifluoride were prepared by mixing the respective ether vapors with boron trifluoride gas in a one-liter three-necked flask. A vertical glass tube, about a foot in length and drawn to a jet at the end, provided a means of escape for excess gases. The flask was cooled, as desired, with ice-water. The reaction vessel was first swept out with ether vapor, and then a slow flow of this vapor was maintained and boron trifluoride was admitted at such a rate that a trace of it exhausted through the jet. Since the boron trifluoride fumed immediately on contact with damp air, it acted as its own indicator. Vigorous combination in one-to-one mole ratios occurred, and the etherates which collected in the flask were purified by fractionation *in vacuo* and subsequently handled in the absence of air.<sup>10</sup> They were colorless liquids which fumed in moist air due to hydrolysis, but they could be stored without decomposition by sealing in glass.

The etherates were analyzed for boron and fluorine. Hydrolysis of boron trifluoride and of its addition products produces an equilibrium mixture of hydrofluoric, fluoboric

and boric acids and this greatly complicates the analytical problem. The fluorine must be removed before the boron is determined. A modification of the method described by Pflaum and Wenzke<sup>11</sup> was used. The sample was decomposed by alkaline hydrolysis in a glass-stoppered flask, the fluorine was precipitated and weighed as calcium fluoride, and the boron was finally determined by titration with sodium hydroxide in the presence of mannitol. In the case of  $\text{MeEtO}:\text{BF}_3$ , the fluorine analysis was carried out by titration with zirconium oxychloride, using sodium alizarin sulfonate as indicator.<sup>12</sup> Although the accuracy of these methods is not great, they establish the identity of the compounds.

**Anal.** Calcd. for  $\text{Me}_2\text{O}:\text{BF}_3$ : F, 50.1; B, 9.5. Found: F, 49.5, 50.2; B, 10.3, 9.4. Calcd. for  $\text{MeEtO}:\text{BF}_3$ : F, 44.6; B, 8.5. Found: F, 44.3, 45.2; B, 8.0, 8.8. Calcd. for  $\text{Et}_2\text{O}:\text{BF}_3$ : F, 40.1; B, 7.7. Found: F, 39.2, 40.2; B, 8.8, 9.2.

**Physical Constants.**—The melting point, boiling point, refractive index and density were determined for each etherate and are given in Table I.

TABLE I

	$\text{Me}_2\text{O}:\text{BF}_3$	$\text{MeEtO}:\text{BF}_3$	$\text{Et}_2\text{O}:\text{BF}_3$
M. p., °C.	-14	-98	-60.4
B. p., °C. <sup>a</sup>	126.6	127	125.7
$d_{25}^{25}$	1.239	1.176	1.125
$n_D^{20}$	1.302	1.327	1.348

<sup>a</sup> Obtained from saturation vapor pressure data by extrapolation. Since dissociation is known to occur in the vapor phase the values here are not to be considered the true boiling points of the etherates.

The data for  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$  agree well with those previously reported.<sup>7,8</sup> The boiling points fail to give the trend usual for an homologous series but show a surprisingly close coincidence. The possibility that  $\text{MeEtO}:\text{BF}_3$  might disproportionate to form  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$  was considered, but the physical constants for  $\text{MeEtO}:\text{BF}_3$  were found to be noticeably different from those of an equimolar mixture of the symmetrical etherates. The unsymmetrical etherate should be optically active in consequence of its containing an asymmetric oxygen atom. Since the formation gives the *dl* mixture, this optical activity cannot be shown experimentally until a method for resolving the mixture can be worked out. However, the low melting point may be considered to be supporting evidence.

**Molar Volumes, Molar Refraction, Surface Tension and Parachor.**—The changes in the molar volumes of the systems when donor-acceptor bonding occurs have been calculated. Ruff and Bretschneider<sup>13</sup> have reported the value 42.5 for the molar volume of boron trifluoride at its boiling point. By adding to this value the respective molar volumes for the ethers, determined at their boiling points, the sums of the

(6) Gasselin, *Ann. chim. phys.*, [7] **3**, 1, 14 (1894).

(7) Sugden and Waloff, *J. Chem. Soc.*, 1492 (1932).

(8) Wiberg and Mäthling, *Ber.*, **70B**, 690 (1937).

(9) The excellent scheme suggested by Davidson and Brown, *THIS JOURNAL*, **64**, 317 (1942), for formulating donor-acceptor complexes is adopted here, since it is a logical extension of the accepted rules for formula writing. The donor molecule is written first and the donor-acceptor bond is indicated by the pair of dots connecting the donor and acceptor atoms.

(10) Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

(11) Pflaum and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **4**, 392 (1932).

(12) de Boer and Basart, *Z. anorg. allgem. Chem.*, **152**, 213 (1926).

(13) Ruff and Bretschneider, *ibid.*, **206**, 59 (1932).

molar volumes of the component molecules were obtained. The densities of the etherates were extrapolated to their boiling points and the observed molar volumes were calculated. The data are summarized in Table II. In all cases there are contractions in molar volume when addition occurs, the amount of contraction increasing in the homologous series. Several factors must contribute to changes in molar volume when donor-acceptor action occurs.

TABLE II

	Me <sub>2</sub> O:BF <sub>3</sub>	MeEtO:BF <sub>3</sub>	Et <sub>2</sub> O:BF <sub>3</sub>
Observed molar volume for etherate	102.1	120.7	139.9
Sum of molar vol. obsd. for component molecules	103.5	126.0	148.5
Decrease in molar vol. upon addn.	1.4	5.3	8.6
Observed parachor for etherate	220.6 <sup>7</sup>	256.2	294.6 <sup>7,8</sup>
Sum of parachors observed for component molecules	...	...	297.0
Decrease in parachor upon addition	...	...	2.4
Observed molar refrac. for etherate	17.60	22.04	26.63
Sum of molar refrac. obsd. for component molecules	...	...	28.46
Decrease in molar refractivity upon addition	...	...	1.83

The increase in coordination number for oxygen and boron and the changes in bond angles and probable lengthening of the bond distances should tend to increase the volume. But the interpenetration of the component molecules due to the formation of the oxygen-boron bond should give a decrease in volume, and this appears to be the predominating effect. The contraction in molar volume increases as the ethers increase in complexity.

The decreases in volume produced by donor-acceptor bonding should be accompanied by corresponding decreases in other constitutive properties, such as parachor and molar refractivity, which are functions of molar volume. The parachors of Me<sub>2</sub>O:BF<sub>3</sub> and Et<sub>2</sub>O:BF<sub>3</sub> have been reported.<sup>7,8</sup> We measured the surface tension of MeEtO:BF<sub>3</sub> by the maximum bubble pressure method in the apparatus already described<sup>14</sup> and found it to be 30.80 dynes per cm.

(14) Sidgwick and Laubengayer, *THIS JOURNAL*, **54**, 948 (1932).

at 25°. This gives a parachor of 256.2. In Table II the observed parachors for the etherates are listed and, in the one case when sufficient data on the component molecules are available, that of Et<sub>2</sub>O:BF<sub>3</sub>, it is seen that there is a decrease in parachor for the system when donor-acceptor bonding occurs.

Meerwein and Pannwitz<sup>15</sup> have observed that the refractivities of Me<sub>2</sub>O:BF<sub>3</sub> and Et<sub>2</sub>O:BF<sub>3</sub> are less than would be calculated using the accepted constants, indicating a decrease in polarizability when bonding is realized. The values observed for the molar refractivities of the etherates are given in Table II. In the case of Et<sub>2</sub>O:BF<sub>3</sub>, where the value for the etherate can be compared with the sum of the molar refractivities for the component molecules, a contraction in refractivity for the system is observed when addition occurs.

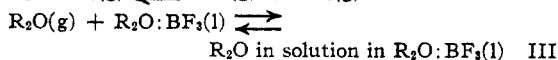
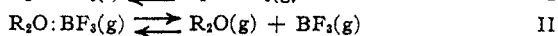
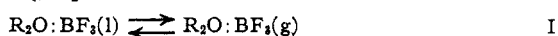
#### Saturation Vapor Pressure Measurements.—

These were made for all three etherates with an isotensiscopes<sup>10</sup> having a volume of 4 cc., samples of about 1 cc. of liquid being used. Readings were taken during both heating and cooling to insure the attainment of equilibrium values and to see whether any irreversible secondary decomposition occurred. Such irreversible decomposition was observed for MeEtO:BF<sub>3</sub> above 103° and for Et<sub>2</sub>O:BF<sub>3</sub> above 92°, but not for Me<sub>2</sub>O:BF<sub>3</sub> up to 130°. Saturation vapor pressure data were obtained which give approximately straight lines for the plot of log *p* against 1/*T*. The characteristic equations, heats of vaporization, and Trouton's constants were calculated and are given in Table III.

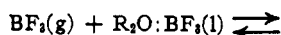
TABLE III

	log <i>p</i> (mm. Hg)	<i>L</i> , kcal.	Trouton constant
Me <sub>2</sub> O:BF <sub>3</sub>	-2650/ <i>T</i> + 9.58	12.2	30.5
MeEtO:BF <sub>3</sub>	-2860/ <i>T</i> + 10.05	13.2	33.0
Et <sub>2</sub> O:BF <sub>3</sub>	-2845/ <i>T</i> + 10.02	13.1	32.8

The high values for the Trouton constants indicate dissociation of the etherates in the vapor phase and such reversible dissociation has been confirmed by vapor density measurements. The pressures observed in the system therefore are not due alone to R<sub>2</sub>O:BF<sub>3</sub> molecules, and the following equilibria must be involved



(15) Meerwein and Pannwitz, *J. prakt. Chem.*, **141**, 123 (1934).



$\text{BF}_3$  in solution in  $\text{R}_2\text{O}:\text{BF}_3(\text{l})$  IV

Processes III and IV are affected by the relative volumes of liquid and vapor and should be appreciable when the volume of liquid is comparatively large, as was the case in the isotensiscopic measurements. It is curious that the plots of  $\log p$  against  $1/T$  are approximately linear, but perhaps in these experiments processes III and IV somewhat counteracted the effects of process II. Data secured in the large vapor density cell described below, where a relatively small volume of liquid was present, indicated that in the low temperature range below  $50^\circ$  the relationship is not linear.

**Vapor Density and Heat of Dissociation of  $\text{Me}_2\text{O}:\text{BF}_3$ .**—When all of the etherate has been vaporized process II as described above is the only one which need be considered. Vapor density measurements were made on  $\text{Me}_2\text{O}:\text{BF}_3$  in a large all-glass cell (700 cc. volume) employing a "sickle" pressure gage.<sup>16</sup> The dissociation was studied between  $40$  and  $130^\circ$  and the data are given in Table IV.

TABLE IV

Sample No.	Temp., °C.	Press., mm.	Degree of dissoc.	$K_{\text{dissoc.}}$ atm.	$\Delta F_{\text{dissoc.}}$ kcal.
1,	90	142.8	0.475	0.055	2.09
0.3482 g. in	100	166.0	.672	.180	1.27
718 cc. volume	110	179.0	.755	.312	0.89
	120	189.8	.811	.483	.57
	130	198.6	.852	.701	.29
Sample No. 2,	50	16.1	.287	.002	4.8
0.0507 g. in	60	21.2	.642	.020	2.6
718 cc. volume	80	25.6	.871	.107	1.6
	100	27.6	.914	.180	1.27

From the graph of  $K_p$  plotted against  $1/T$  the heat of dissociation in the range  $100$ – $130^\circ$  was found to be 13 kcal.

Measurements of the dissociation of the other etherates were not carried out, since the irreversible secondary reactions noted previously limited the range of such measurements so that the accuracy of the data would not have been great.

**Calorimetric Studies of the Heats of Formation.**—The calorimetric measurements were made in a Bunsen ice calorimeter such as has been described by Hieber and Mühlbauer.<sup>17</sup> The cell used fitted into a four-liter Dewar cylinder which was packed with crushed ice and covered with a felt jacket to minimize heat transfer. The gases

(16) Laubengayer and Schirmer, *THIS JOURNAL*, **62**, 1578 (1940).

(17) Hieber and Mühlbauer, *Z. anorg. allgem. Chem.*, **166**, 97 (1930).

were added to the reaction vessel through a capillary jet from a mercury gas buret. The addition of 100 cc. of gas to 20 cc. of liquid gave a heat change which could be measured with reasonable accuracy. During the course of a run the liquid was stirred mechanically. Corrections were made for the heat of stirring and for the heat leak for the system.

The heats of solution of boron trifluoride in a number of solvents at  $0^\circ$  were determined. Since the boron trifluoride was added from a buret at room temperature, a correction was made for the heat evolved on reducing this gas to  $0^\circ$ . The heats of solution of  $\text{Me}_2\text{O}:\text{BF}_3$  in water and of  $\text{Et}_2\text{O}:\text{BF}_3$  in diethyl ether were also measured. The heats of vaporization of  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$  were calculated from their Trouton constants. Using these values and data from Bichowsky and Rossini,<sup>18</sup> the heats of formation of  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$  were calculated. The thermal data are summarized in Table V. The value 13.9 kcal. for the heat of formation of  $\text{Me}_2\text{O}:\text{BF}_3$  checks well with the value 13 kcal. derived for the heat of dissociation from vapor density data. The methyl etherate appears to be slightly more stable than the ethyl etherate.

TABLE V  
HEATS OF SOLUTION AT  $0^\circ$ 

	$H$ in kcal.
$\text{BF}_3(\text{g})$ in water	$21.9 \pm 0.2$
$\text{BF}_3(\text{g})$ in diethyl ether	$17.3 \pm .4$
$\text{Me}_2\text{O}:\text{BF}_3(\text{l})$ in water	$7.5 \pm .5$
$\text{Me}_2\text{O}(\text{g})$ in water	$8.3^{18}$
$\text{Et}_2\text{O}:\text{BF}_3(\text{l})$ in diethyl ether	$2.7 \pm .5$

HEATS OF VAPORIZATION

$\text{Me}_2\text{O}:\text{BF}_3$	8.8
$\text{Et}_2\text{O}:\text{BF}_3$	8.8
$\text{Et}_2\text{O}$	$6.2^{18}$

HEATS OF FORMATION

$\text{Me}_2\text{O}:\text{BF}_3(\text{g})$ from $\text{Me}_2\text{O}(\text{g})$ and $\text{BF}_3(\text{g})$	$13.9 \pm 0.7$
$\text{Et}_2\text{O}:\text{BF}_3(\text{g})$ from $\text{Et}_2\text{O}(\text{g})$ and $\text{BF}_3(\text{g})$	$12.5 \pm 1.0$

**Molecular Weight Determinations in Benzene.**—Measurements were made cryoscopically on solutions of  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{MeEtO}:\text{BF}_3$  in benzene. The results summarized in Table VI indicate that in dilute solutions these substances are monomeric.

TABLE VI

	$\text{Me}_2\text{O}:\text{BF}_3$	$\text{MeEtO}:\text{BF}_3$
Grams solute/1000 g. solvent	7.01	15.2
Molecular wt., found	$120 \pm 5$	$137 \pm 5$
Molecular wt., calcd.	114	128

(18) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

**Dipole Moments and Bond Moments.**—The dipole moments of the etherates were measured in benzene, using a heterodyne oscillator operating at a frequency of 1.57 megacycles. A precision condenser was connected in parallel with the measuring cell which was of the type described by Smyth.<sup>19</sup> The thiophene-free benzene employed was dried over sodium wire and distilled over sodium. It boiled at 80.1° and its  $d^{25}_4$  was 0.8722.

The etherate samples were distilled *in vacuo* into ampules which were sealed off, weighed, and then broken in a glass-stoppered flask containing a known amount of benzene. Even with these precautions the solution became faintly cloudy, indicating some hydrolysis. The solution fumed in air and therefore exposure was kept to a minimum. The measurements were made at  $25 \pm 0.05^\circ$  and the results are listed in Table VII. The agreement is not good, due no doubt to hydrolysis, but with the apparatus available it was impossible to eliminate this difficulty. The dipole moments were calculated from the average values for the molar polarization.

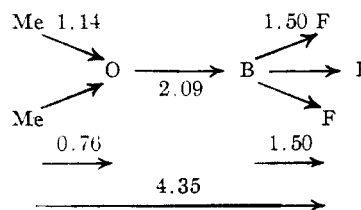
TABLE VII  
DIPOLE MOMENTS IN BENZENE AT 25°

$\epsilon$	$d$	$P_2$	$P_{\text{orientation}}$	$\mu$
Benzene				
2.2727	0.8722			
$\text{Me}_2\text{O}:\text{BF}_3$				
0.00148	2.3096	0.8730	392	394
0.00556	2.4296	.8736	433	
$\text{MeEtO}:\text{BF}_3$				
0.00213	2.3529	0.8730	573	
0.00426	2.4178	.8736	531	535
0.00756	2.5647	.8750	566	
$\text{Et}_2\text{O}:\text{BF}_3$				
0.00119	2.3212	0.8728	630	
0.00187	2.3223	.8731	422	503
0.00501	2.4509	.8744	539	

It is difficult to break down the dipole moments of the etherates so that an estimate of the moment associated with the O-B donor-acceptor bond may be obtained. However, it is possible to attempt this in the case of  $\text{Me}_2\text{O}:\text{BF}_3$ , where we have data available on the molecular structure as the result of an electron diffraction investigation which is being reported.<sup>20</sup>

In the structure which best fits the electron diffraction patterns, we have the methyl ether por-

tion of the molecule substantially unchanged while the boron atom is tetrahedrally bonded to the fluorine and oxygen atoms. The methyl groups are considered to rotate freely about the O-B axis. Using values for the dipole moments of the various bonds taken from Sidgwick<sup>21</sup> or estimated from his tables, and resolving these moments along the O-B axis, we obtain the results indicated below.



This gives an apparent moment for the O-B bond of 2.09 debyes. This, however, cannot be the true moment of the bond because the contribution of the ether and boron trifluoride systems have been calculated without taking into account the fact that when the etherate is formed the oxygen will become more electropositive and the boron more electronegative. This should reduce the contributions of the ether and boron trifluoride to the total moment, and therefore it is likely that the O-B bond moment is greater than 2.09. The value calculated for this bond moment if the pair of donated electrons is equally shared is 7.4 debyes, and therefore the observed dipole moment for  $\text{Me}_2\text{O}:\text{BF}_3$  seems surprisingly small. The oxygen atom must retain the larger interest in the donated electron pair.

### Summary

1. It has been shown that the compounds of boron trifluoride are good examples for the study of donor-acceptor bonding.
2. The consequences of the formation of such bonds have been considered.
3.  $\text{MeEtO}:\text{BF}_3$  has been prepared and its properties have been compared with those of  $\text{Me}_2\text{O}:\text{BF}_3$  and  $\text{Et}_2\text{O}:\text{BF}_3$ .
4. A decrease in molar volume has been observed when donor-acceptor bonds are formed, and the effect of this decrease upon the constitutive properties has been discussed.
5. Saturation vapor pressure measurements on the three etherates have been made. Vapor density measurements have been made on  $\text{Me}_2\text{O}:$

(19) Smyth, *THIS JOURNAL*, **50**, 1547 (1928).

(20) Bauer, Finlay and Laubengayer, *ibid.*, **65**, 889 (1943).

(21) Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933.

$\text{BF}_3$ , leading to a value of 13 kcal. for its heat of dissociation.

6. The heat of formation of  $\text{Me}_2\text{O}:\text{BF}_3$  has been determined calorimetrically as 13.9 kcal. and that of  $\text{Et}_2\text{O}:\text{BF}_3$  as 12.5 kcal. The heats of solution of boron trifluoride in water and diethyl ether have been determined.

7. Molecular weight determinations made

cryoscopically in benzene indicate that the etherates are monomeric.

8. Dipole moment measurements on these etherates have been carried out in benzene. The results indicate that the contribution of the donor-acceptor bond to the total dipole moment is small.

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## Donor-Acceptor Bonding. II. An Electron Diffraction Investigation of the Structure of Dimethyl Ether-Boron Trifluoride

BY S. H. BAUER, G. R. FINLAY AND A. W. LAUBENGAYER

With the establishment of the correct molecular formula by the vapor density method<sup>1</sup> for the product of the reaction  $\text{BF}_3(\text{g}) + (\text{CH}_3)_2\text{O}(\text{g})$ , an investigation of the structure of that association product became possible. The apparent molecular weight of the gaseous dimethyl ether-boron trifluoride has been determined over the temperature range 25–130°. At the lower portion of this interval the molecules present do have a molecular weight very near to 114 units; together with the analytical data this leads to the formula  $(\text{CH}_3)_2\text{O}:\text{BF}_3$ . Below 40° the extent of dissociation is under 10%.

In this report we are presenting electron diffraction data obtained on the vapor of the associated compound at about 40°. The photographs permitted a structure determination.

### The Photographs

For the electron diffraction studies the clear liquid of density 1.246 (20°), b. p. 126.6° (760 mm.),  $n_D$  1.302, was heated to about 65° during the run, so that sufficient vapor be available. However, condensation took place in the long lead tube to the electron diffraction nozzle; it is, therefore, doubtful whether the temperature of the vapor at the point of diffraction was much above 40°. The construction of the nozzle is such as to maintain the pressure at the instant of diffraction as high as possible over a very small volume.<sup>2</sup> Thus, although it is difficult to estimate the actual pressure at the point of diffraction, we can safely state that the amount of dissociation was negligible. This assumption

is in agreement with our previous experience, and was borne out by the resulting electron diffraction photographs. Both light and dense pictures were obtained, the latter showing six maxima. The visual appearance of the pattern is sketched as curve Vis, Fig. 2; the  $s_0$  values for the maxima and minima and their relative intensities as determined visually from five of the best photographs are given in Table I.

TABLE I  
DIMETHYL ETHER-BORON TRIFLUORIDE

Max.	Min.	$s_0$	$I_{av.}$	$s_0(\text{calcd.})/s_0(\text{obs.})$		$V_a$												
				IVb	IVc													
1		3.22	7	1.012	1.020	1.056												
	2	4.44	— 5	0.991	0.990	1.016												
2		5.76	10	1.005	1.010	1.024												
	3	7.61	— 6	1.012	1.016	1.016												
3		8.88	4.2	1.033	1.038	1.036												
	4	10.07	— 3	1.025	1.031	1.029												
4		11.32	3.5	1.003	1.012	1.007												
	5	12.68	— 2.8	1.006	1.018	1.019												
5		14.08	2.2	1.004	1.012	1.018												
	6	15.24	— 1.5	1.015	1.020	1.043												
6		16.43	1	1.003	1.020	1.075												
Average				1.010	1.017	1.031												
Mean deviation				0.0086	0.0082	0.0158												
Interatomic distances deduced, Å. — { <table> <tr> <td>B-F</td> <td>1.404</td> <td>1.414</td> <td>1.433</td> </tr> <tr> <td>B-O</td> <td>1.555</td> <td>1.505</td> <td>1.485</td> </tr> <tr> <td>C-O</td> <td>1.434</td> <td>1.444</td> <td>1.464</td> </tr> </table>							B-F	1.404	1.414	1.433	B-O	1.555	1.505	1.485	C-O	1.434	1.444	1.464
B-F	1.404	1.414	1.433															
B-O	1.555	1.505	1.485															
C-O	1.434	1.444	1.464															

A radial distribution calculation<sup>3</sup> resulted in the curve R.D. of Fig. 1; the indicated distances are

- 1.40 Å. interpreted as a superposition of B-F, C-O, B-O
- 2.36        interpreted as a superposition of F-F, B-C, C-C
- 2.84        interpreted as a superposition of variable F-C,
- 3.61        C-H, B-H
- 4.58        possibly due to the longer F-H and stray maxima arising from the incomplete integration.

(1) A. W. Laubengayer and G. R. Finlay, *THIS JOURNAL*, **65**, 884 (1943).

(2) Nozzle design similar to that described by E. H. Eyster, R. H. Gillette and L. O. Brockway, *ibid.*, **62**, 3236 (1940).

(3) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940)