tween alcohols and amines. Numerous other applications of the method suggest themselves, but the pressure of other work will prevent pursuing the problem further at present.

Summary

When a mixture of MeOH and BuOD is fractionated, it is found that MeOH and MeOD are both present in the recovered methanol and that BuOH and BuOD are both present in the recovered butanol. It is concluded that the intermolecular hydrogen bonds involve the actual transfer of protons between molecules. Extension of the present study to include other compounds is suggested.

The Structures of Dimethyl Boron Fluoride and Methyl Boron Difluoride

BY S. H. BAUER AND J. M. HASTINGS

The structures of boron trifluoride and boron trimethyl as determined by Lévy and Brockway[1] were among the first items of information to suggest that rather artificial explanations may be necessary in some cases to make the observed interatomic distances harmonize with the Pauling and Huggins[2] table of covalent radii and with the postulate of the dependence of bond order on the distances between the atoms in a molecule.[3] The suggestion of Schomaker and Stevenson[4] that as a next best approximation the electronegativity difference between the atoms be considered in computing the separation for normal covalent bonding was a welcomed one since it permitted a reasonable interpretation of data otherwise not readily accounted for; it removed the necessity for the artificial postulates applied to various boron compounds.[5] The structures of the methyl boron fluorides discussed in this paper furnish critical tests for the applicability of the table of atomic radii as revised by them and of the use of their equation

$$r_{ab} = r_a + r_b - 0.09|x_a - x_b| \qquad (1)$$

Both the methyl boron difluoride and the dimethyl boron fluoride were furnished by Dr. Anton B. Burg.[6] We wish to acknowledge his coöperation and to thank him sincerely for this and other compounds he gave us.

The Apparatus and Photographs

The present electron diffraction apparatus re-

sembles the latest model constructed by Brockway.[7] A simple but highly effective voltage regulator[8] and voltmeter have been set up so that the net voltage fluctuations have been reduced to a few hundredths of one per cent. The apparatus was designed to be flexible and special provision made for the incorporation of a rotating sector,[9] the assembly of which has now been completed. A more detailed description of this unit will be given in a future paper.

The photographs were taken with electrons having a wave length near 0.06 Å., and with the nozzle–plate distance equal to 13.69 cm. The visual appearance of the photographs is that indicated by curves V, Figs. 2 and 4; the $s_0 = \left[\frac{4\pi}{\lambda}\sin\theta_0/2\right]$ values for the maxima and minima as determined by the usual visual technique, and their relative intensities above or below the estimated backgrounds (lines through curves V) are given in Tables II and III.

Analysis of the Data

Because of their relative simplicity, considerable information regarding the structures of these molecules can be obtained from their radial distribution curves. These were computed according to the method of Walter and Beach,[10] and are plotted in Fig. 1. The results are summarized in Table I. To facilitate the interpretation of these curves and to show the resolution which might be expected under ideal conditions, "synthetic" radial distribution curves for various

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(3) For references, L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Chapter V, 1940.

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(9) P. P. Debye, Physik. Z., **40**, 404 (1939).

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

models are also included in Fig. 1. The approximate equations given by Debye[11] were used, as was also an average value for the temperature factor, a_{ij} ($=0.042$). The synthetic D(r)'s thus computed for planar models, boron valence angles equal to 120°, with B–C = 1.56 Å. and B–F = 1.30 Å., agree very well with the experimentally determined R. D. curves. It is clear that only slight distortions of these basic models (Table I) would be needed to obtain the best quantitative check between the calculated and observed patterns.

TABLE I
B(CH₃)₂F

Peaks at Å.	Interpreted as	Ratios
0.95	C–H	
1.29	B–F	
1.55	B–C	B-C/B-F = 1.204
2.49	C–F	B-C/C-F = 0.623
		∠CBF = 122° indicated

BCH₃F₂

Peaks at Å.	Interpreted as	Ratios
1.01	C–H	
1.31	B–F	B-F/F-C = 0.512
2.23	F–F	B-F/F-F = 0.586
2.55	C–F	F-F/F-C = 0.874
		∠CBF = 121½° indicated

To begin with, we considered models with 120° valence angles, varying the B–C/F–B ratio. The intensity curves, calculated in the usual manner, are shown in Figs. 2 and 4, with the description of the corresponding models given in the legends. In order to restrict the total number of computations for configurations with unequal boron valence angles, we made use of the following argument. If

$$I(s) = \sum_{ij}' Z_i Z_j \frac{\sin l_{ij}s}{l_{ij}s}$$

then

$$\frac{\partial I(s)}{\partial P_n} = \sum_{ij}' Z_i Z_j \frac{\partial}{\partial l_{ij}} \left[\frac{\sin l_{ij}s}{l_{ij}s} \right] \frac{\partial l_{ij}}{\partial P_n} \qquad (2)$$

where P_n is a given structure parameter. Furthermore

$$\frac{\partial l_{ij}}{\partial} \left[\frac{\sin l_{ij}s}{l_{ij}s} \right] = \frac{1}{2\epsilon} \left[\frac{\sin s(l_{ij} + \epsilon)}{s(l_{ij} + \epsilon)} - \frac{\sin s(l_{ij} - \epsilon)}{s(l_{ij} - \epsilon)} \right] - \frac{\epsilon^2 s^2}{2 l_{ij}} \frac{\sin l_{ij}s}{l_{ij}s} \qquad (3)$$

to the approximation $\sin s\epsilon = s\epsilon$; $\cos \epsilon s = 1 - s^2\epsilon^2/2$; and $\epsilon^2 \ll l_{ij}^2$. Since with the available $\sin x/x$ strips, ϵ can be made as small as 0.01, equations 2 and 3 are quite accurate. Hence it is a simple matter to estimate the effect an increment

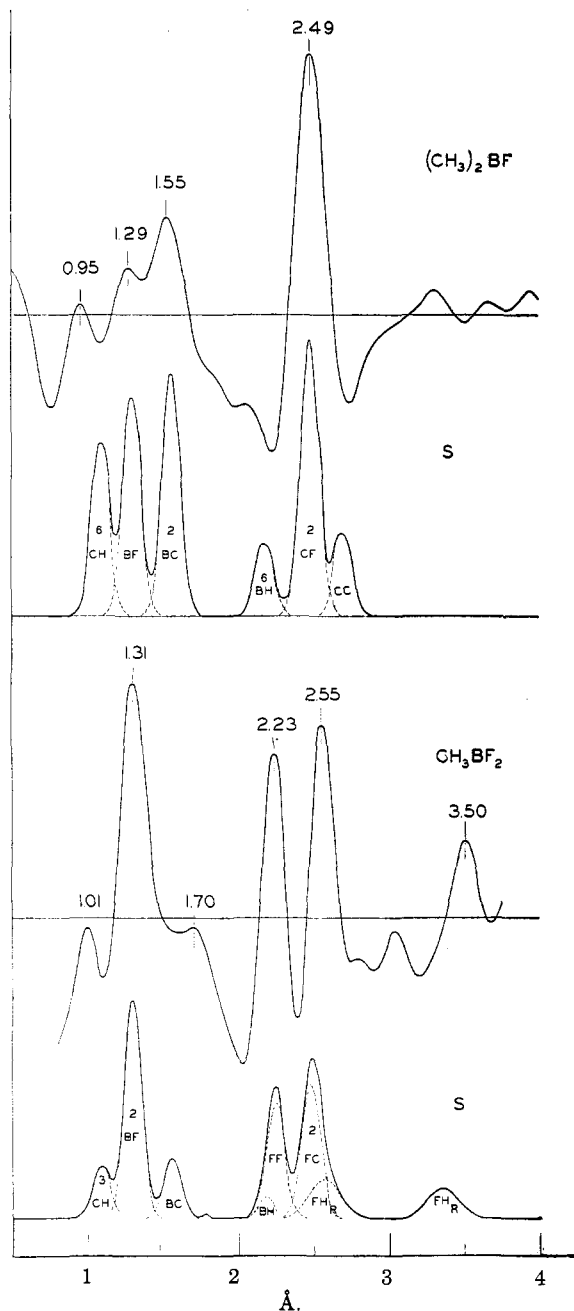(11) P. Debye, *J. Chem. Phys.*, **9**, 55 (1941).

Fig. 1.—Radial distribution curves for methyl boron fluorides. Those marked "S" are synthetic curves for boron valence angles equal to 120°, B–C = 1.56 Å., B–F = 1.30 Å., C–H = 1.09 Å., a_{ij} = 0.042. The other curves were computed from the data quoted in Tables II and III, using the method of Walter and Beach.

in a particular structure parameter will have on the intensity pattern over any given interval of s. Knowing such trends is of considerable aid in deducing a configuration which is satisfactory. However, of greater value is the possibility thus presented of deducing the effects of increments

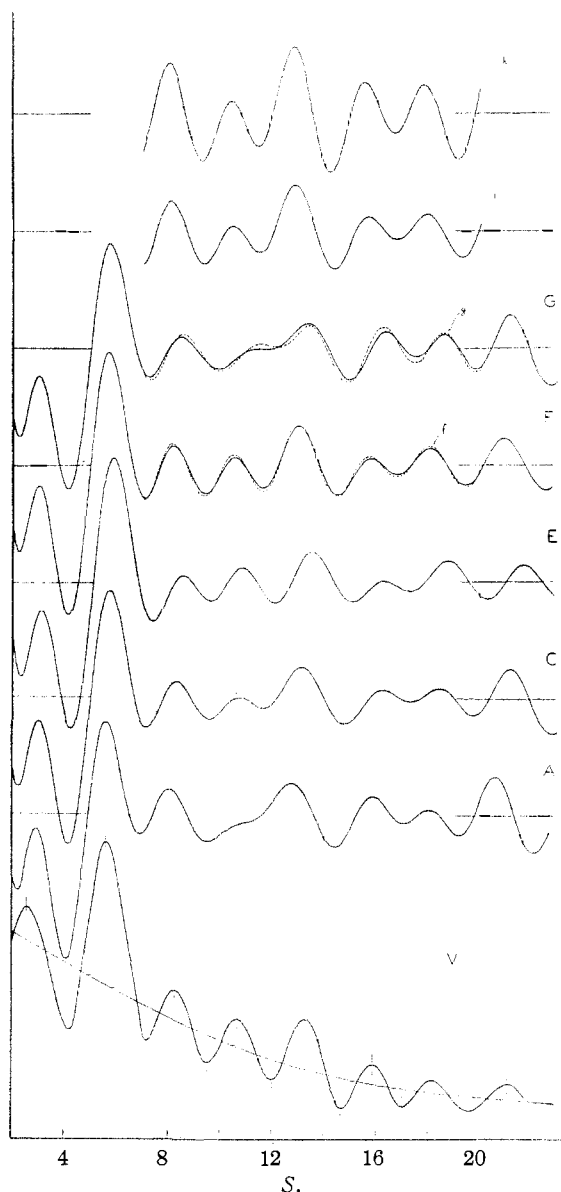in several parameters at once. Were one to start

Fig. 2.—Intensity curves for dimethyl boron fluoride. Curve V is a sketch of the visual appearance of the pattern; the dashed curve is the supposed background above and below which our relative intensity estimates were made. For the computed curves, C–H = 1.09 Å., carbon valence angles tetrahedral (assumed); B–F = 1.29 Å., boron valences in a plane, and

B–C = 1.61 Å., ∠CBF = 120° Curve A
1.55	120	C
1.49	120	E
1.55	122	F (usual method), f (eq. 4)
1.55	118	G (usual method), g (eq. 4)
1.58	122	i (eq. 4)
1.61	124	k (eq. 4)

with a satisfactory model and values for $\partial I(s)/\partial P_n$ covering the critical regions, he can quickly estimate the effects of any combination of increments, if these are reasonably small, from

$$I(s)_{\text{new config.}} = I(s)_{\text{original}} + \sum_{P_n} \frac{\partial I(s)}{\partial P_n} \Delta P_n \quad (4)$$

and thus conclude which combinations will still lead to satisfactory models. Limits on these increments are imposed by the radial distribution curve.

Dimethyl boron Fluoride.—The critical points of comparison are the intensities of the fourth and seventh peaks relative to the maxima on either side of these. For configurations with 120° boron valence angles six curves were computed, with the B–C/B–F ratio varying from 1.61/1.29 to 1.49/1.29. Of these, curves A and E, Fig. 2, are the extremes. The curve marked C, for which B–C/B–F = 1.202, and B–C/C–F = 0.630, appears to be quite satisfactory, both qualitatively and quantitatively (Tables I and II). A change of 0.03 Å. in the B–C separation introduces features not experimentally observed in the photographs.

TABLE II

DIMETHYL BORON FLUORIDE

Max.	Min.	$s_{\text{obs.}}$	I	C	$s_{\text{calcd.}}/s_{\text{obs.}}$ i	k
1		2.54	10	(1.181)		
	2	4.20	− 9	0.986		
2		5.59	18	1.020		
	3	7.19	−12	0.992		
3		8.24	10	1.004*	0.982	0.972
	4	9.51	− 5	1.002*	.982	.975
4		10.67	5	1.001*	.978	.975
	5	12.01	− 4	0.965*	.958	.952
5		13.29	5	0.983*	.967	.962
	6	14.65	− 2	1.006*	.978	.969
6		15.85	3	1.022*	.989	.980
	7	16.99	− 1	1.018*	.989	.982
7		18.15	1	1.012*	.986	.982
	8	19.61	− 1	1.003*	.983	.977
8		21.03	1	1.003*		
Average			1.001	1.002	0.979	0.973
Mean deviation			0.011	0.011	0.0072	0.0070
Distances and angle deduced	B–F		1.291	1.293	1.263	1.255
	B–C		1.552	1.553	1.547	1.566
	C–F		2.462	2.465	2.457	2.491
	∠CBF		120°	120°	122°	1.24°

The radial distribution curve suggests a small distortion in the boron valence angles. However, instead of calculating a whole series of curves covering a range in B–C/B–F ratio for various angles in the vicinity 120°, we computed $\partial I(s)/$
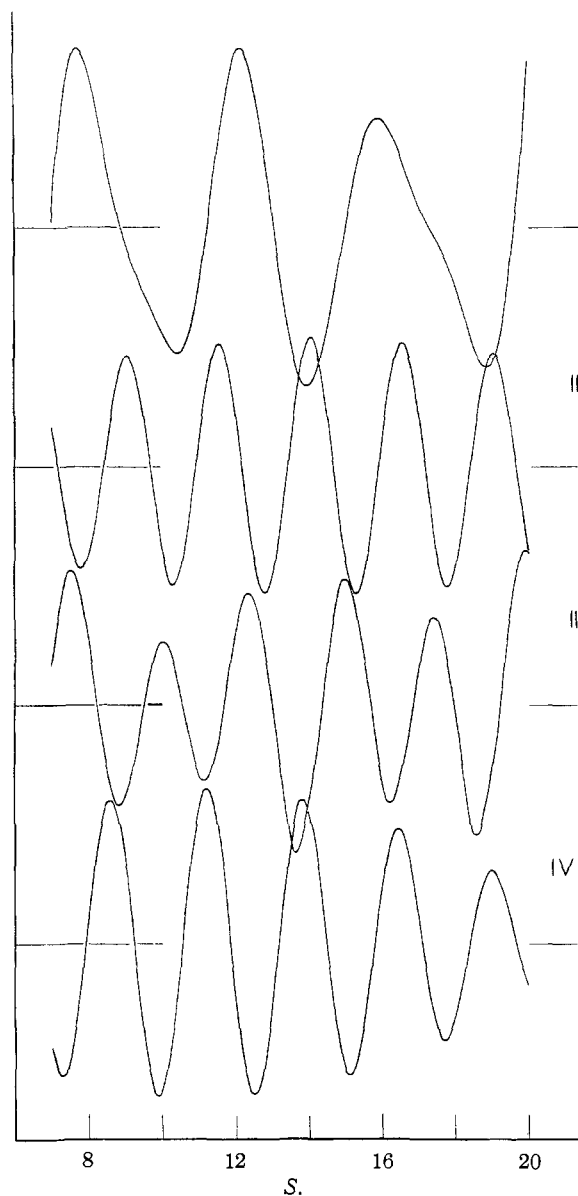
Fig. 3.—The variation of the intensity curves with distance and angle parameters, $(CH_3)_2BF$, curves I and II: $\partial I(s)/\partial(B-C)$ and $\partial I(s)/\partial(\angle CBC/2)$, respectively. CH_3BF_2, curves III and IV: same distance parameter, while angle parameter is $\angle FBF/2$.
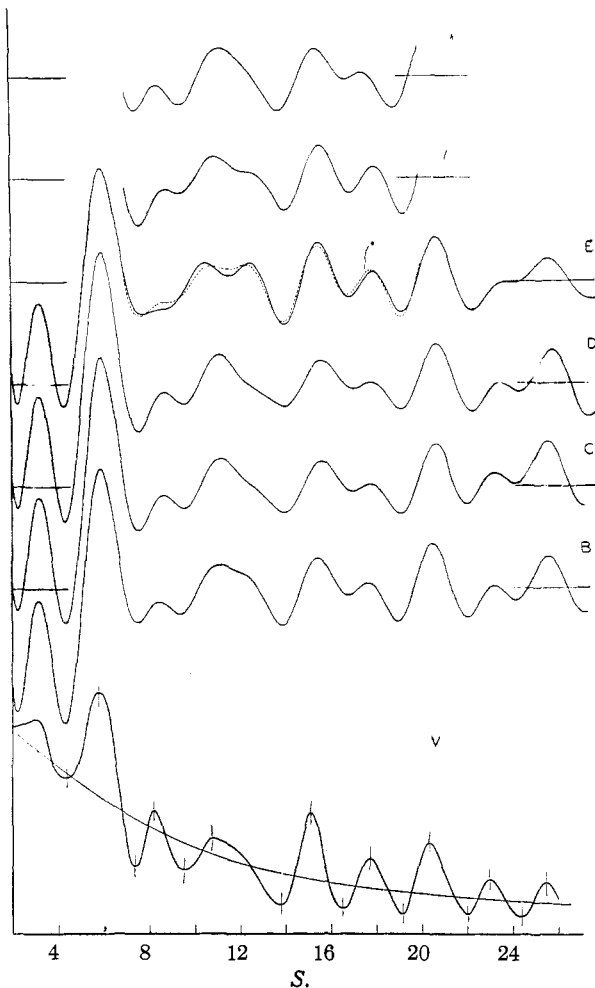

Fig. 4.—Intensity curves for methyl boron difluoride. Curve V is a sketch of the visual appearance of the pattern; the background curve is included. Once more, for the computed curves, C–H = 1.09 Å., carbon valence angles tetrahedral (assumed); B–F = 1.29 Å., boron valences in a plane, and

B–C	$\angle$CBF	Curve
1.61 Å.,	120°	B
1.58	120	C
1.56	120	D
1.58	122	E (usual method),
		e (eq. 4)
1.55	122	f (eq. 4)
1.625	119	h (eq. 4)

∂(B–C) and $\partial I(a)/\partial a$, where $a = \angle$ CBC/2, using curve C as our basic model (Fig. 3, curves I and II, respectively). We then made use of equation 4 to obtain subsequent models, some of which are included in Fig. 2, f–k. The accuracy of the method can be judged from a comparison of curves F and G with f and g, the former two being computed in the usual manner, with B–C/ B–F Δa = 1.202 and $\angle$ CBF = 122 and 118°, respectively, while the latter were obtained from

eq. 4 (curve II, Fig. 3) with = −2 and +2°, respectively.

It soon became evident that in general increments in either parameter alone lead to unacceptable curves, the fit being least disturbed for Δa negative. However, the combination of positive increments in B–C and negative ones in a resulted in a series of curves having the proper form (typical ones are i, k, Fig. 2); however, due to the good resolution obtained in the R. D. curves,

TABLE III
METHYLBORON DIFLUORIDE

Max.	Min.	$S_{obs.}$	I	B	C	D	f	h
						$S_{calcd.}/S_{obs.}$		
1		(3.2)	5	(0.991)	(0.997)	(0.997)		
	2	4.35	−14	0.986	0.993	0.991		
2		5.73	20	1.024	1.030	1.033		
	3	7.33	−1	1.025	1.027	1.027	1.040	1.015
3		(8.16)	1	(1.032)	(1.059)	(1.071)	(1.083)	(1.032)
	4	(9.50)	−1	(0.981)	(1.007)	(1.007)	(0.993)	(0.994)
4		(10.70)	3	(1.034)	(1.044)	(1.037)	(1.028)	(1.045)
	5	13.79	−8	1.004	1.012	1.015	1.022	1.001
5		15.06	5	1.024	1.036	1.039	1.039	1.024
	6	16.47	−2	1.021	1.032	1.036	1.032	1.019
6		17.67	2	1.001	1.005	1.008	1.019	0.990
	7	19.14	−2	0.990	0.996	1.000	1.008	0.987
7		20.29	3	1.008	1.016	1.020		
	8	22.00	−1	1.001	1.000	1.012		
8		22.93	1	1.013	1.014	1.026		
	9	24.39	−1	0.991	0.990	1.000		
9		25.44	1	1.006	1.006	1.015		
Average				1.007	1.012	1.017	1.027	1.006
Mean deviation				0.011	0.013	0.012	0.010	0.013
Distances and angles deduced	B–F			1.29_9	1.30_5	1.31_2	1.32_5	1.29_8
	B–C			1.62_1	1.59_9	1.58_7	1.59_2	1.63_5
	C–F			2.53_8	2.52_0	2.51_2	2.55_7	2.53_5
	F–F			2.25_6	2.26_7	2.27_8	2.24_9	2.22_3
	∠CBF			120°	120°	120°	122°	119°

not all of these are acceptable. On weighing the various data, we concluded that dimethyl boron fluoride is a planar molecule, B–F = 1.29 ± 0.02 Å.; B–C = 1.55 ± 0.02 Å.; C–F = 2.48 ± 0.03 Å.; C–H =1.09 Å. and tetrahedral carbon valence angles were assumed. The above combination of distances leads to ∠CBF = 121¹⁄₂°.

Methylboron Difluoride.—The critical region extends from $s = 7$ to 19. Due to the steeply decreasing background and the presence of a broad fourth maximum, the exact shape of the pattern in the interval $s = 8$ to 13 could not be clearly determined. Again, using 120° valence angles for boron, four curves were computed for the B–C/B–F ratio ranging from 1.66/1.29 to 1.56/1.29, with the best qualitative and quantitative fit being somewhere between curves B and C (Fig. 4 and Table III) B–C/B–F = 1.61/1.29 and 1.58/1.29, respectively.

With model B as a base, $\partial I(s)/\partial(\text{B–C})$ and $\partial I(s)/\partial\beta$ where $\beta = \angle$ FBF/2 (Fig. 3, III and IV, respectively) were obtained. It is clear that positive or negative increments in the two parameters would cancel each other except in the range $s = 8$ to 11. Thus, although the R. D. curve suggests that ∠ CBF is greater than 120°, a negative increment in β leads to unacceptable curves (E and e, Fig. 4), as do increments in either

parameter alone. However, small positive increments both in B–C and in β lead to several acceptable curves (h, Fig. 4 is typical), as do small negative increments in both (f of Fig. 4). One may conclude that methyl boron difluoride is a planar molecule, B–F =1.30 ± 0.02 Å.; B–C 1.60 ± 0.03 Å.; C–F = 2.53 ± 0.03 Å.; C–H = 1.09 Å. and tetrahedral carbon valence angles assumed. The above combination of distances leads to ∠ CBF = 121°.

Discussion

The electron diffraction results of Lévy and Brockway[1] coupled with the data obtained in this investigation show that the molecules comprising the series $B(CH_3)_3$, $B(CH_3)_2F$, BCH_3F_2, and BF_3 have the same configuration, and essentially the same interatomic distances. For quantitative comparison we have compiled Table IV. All but one of the reported B–C separations are equal to that expected for normal covalent bonding; at present writing we are unable to propose a theory which would account for the small increase in the B–C distance in BCH_3F_2 and which would not introduce difficulties for the remaining data. Empirically, the difference between the B–F separations observed in the methyl boron fluorides and those in $(CH_3)_2O:BF_3$, etc., may be

TABLE IV

Compound	B–C distance, Å.	B–F distance, Å.	Reference
H_3BCO	1.57 ± 0.03		12
$(CH_3BO)_3$	1.57 ± .03		5
$B(CH_3)_3$	1.56 ± .02		1
$B(CH_3)_2F$	1.55 ± .02	1.29 ± 0.02	B and H
BCH_3F_2	1.60 ± .03	1.30 ± .02	B and H
BF_3		1.30 ± .02	1
		1.29	13
$(CH_3)_2O:BF_3$		1.41 ± .02	14
Alkali fluoborates		1.43	15
Expected, for bonds of unit order: S and S	1.57	1.39	4, 5

ascribed to the transition in the coördination of boron from three to four, although reasoning on the basis of this postulate would lead one to expect a somewhat larger B–C distance in H_3BCO, wherein the boron atom is tetrahedrally bonded, than in the other compounds.

Introduction of the assumption of the dependence of bond distance on bond type always raises the question as to the interatomic distance one should select for a unit bond. Assuming that no distinction need be made between sp^2 and sp^3 type bonds (Table IV), it follows that the B–C linkages are all of unit order, whereas the B–F bonds in boron trifluoride are of an order higher than unity; i. e., that the three excited structures $F_2B^-::F^+::$ contribute appreciably to the ground state. This is borne out by a rough comparison of the bond strengths in BF_3 and BF_4^- as deduced from their heats of formation,[16] and is further

supported by the low parachor value which must be assigned to boron in BF_3 (8 as compared with about 15 in the other trihalides).[17]

If the postulate of sp^2 plus graphite type resonance presented above for boron trifluoride is extended to the methylboron fluorides, the fact that the B–F separation is the same for the three compounds appears to be fortuitous. Thus one has to assume that a bond order of about 1.2 may result either from the normal $(CH_3)_2B:F:::$ plus the single excited structure $(CH_3)_2B^-::F^+::$, or from the normal $F_2B:F:::$ plus the three excited structures $F_2B^-::F^+::$, in which each $B^-::F^+$ link is on the average only one-third double bond. Clearly, resonance among the latter three equivalent structures lowers some of the levels and raises others, so that the consequent resonance with the ground state is not strictly parallel to the case for dimethyl boron fluoride.

Finally one might point out the difference between the effects of successive substitutions of fluorine atoms on carbon and on boron. In CH_2F_2 the C–F separation is around 0.05 Å. less than in the monosubstituted methane,[18] whereas all the observed B–F distances are equal in the series BF_3, BF_2CH_3, $BF(CH_3)_2$.

Summary

An electron diffraction study of dimethyl boron fluoride and methyl boron difluoride leads to the following: the molecules are planar, $B(CH_3)_2F$: B–F = 1.29 ± 0.02 Å.; B–C = 1.55 ± 0.02 Å.; C–F = 2.48 ± 0.03 Å. BCH_3F_2: B–F = 1.30 ± 0.02 Å.; B–C = 1.60 ± 0.03 Å.; C–F = 2.53 ± 0.03 Å.

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