

the very small number of parallel layers per group, few groups containing more than two layers.

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Structures of Molecular Addition Compounds.

I. Monomethyl Amine-Boron Trifluoride, $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$

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X-ray data obtained from crystals of $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ lead to a monoclinic unit of structure with $a = 5.06$, $b = 7.28$, $c = 5.81$ A., $\beta = 101^\circ 31'$, containing two stoichiometric molecules. All of the X-ray data are consistent with the space group $P2_1/m$. Approximate positions of the atoms (other than hydrogen) were determined by the use of various Patterson syntheses, and the parameters refined by means of various Fourier syntheses.

There are several important and interesting features of the structure of $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$. The B-N bond is 1.58 A., 0.09 A. longer than the value predicted on the basis of Pauling's covalent radii with application of a correction for difference of electronegativity between boron and nitrogen. Yet the compound is stable at ordinary temperatures. The nitrogen atom does not form four equivalent tetrahedral bonds in $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ ($\angle \text{B}-\text{N}-\text{C} = 114^\circ$). The methyl group and fluorine atoms are in the staggered configuration.

The deviations of the F-B-F angle (111°) and the F-B-N angle (108°) from the tetrahedral value ($109^\circ 28'$), of the value for the B-F bond (1.37 A.) from the predicted value, 1.39 A. (Schomaker & Stevenson, 1941; Bauer & Beach, 1941), and of the C-N bond (1.50 A.) from 1.47 A. cannot be said to be very significant since the limits of error may be such as to make these differences unreal. On the other hand, there is some evidence from the results of the X-ray diffraction investigation of $\text{H}_3\text{CCN}-\text{BF}_3$ (the second paper in this series) and of the electron diffraction investigation of $(\text{H}_3\text{C})_2\text{O}-\text{BF}_3$ that indicates that these differences are possible. The results of the former study leave little doubt that the boron atom need not form four equivalent tetrahedral bonds, whereas the results of the latter give some indication that the stretching of the C-N bond in $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ is probable.

All of the important interatomic distances have been calculated and the packing arrangement of the molecules in the crystal is discussed.

Introduction

The discovery, in recent years, of many new boron compounds, and of interesting and important properties of both old and new compounds, has led to increased study of them.

It is generally considered that in molecules such as the boron trihalides or trimethyl boron, boron has a strong

tendency to complete its octet of valency electrons by forming a fourth bond. It is also postulated that the nitrogen atom in NH_3 and in substituted ammonias possesses a pair of unshared electrons which tend to form a fourth bond. In this investigation, the particular interest is in the compound formed by the reaction in equimolar ratio of BF_3 and H_3CNH_2 . In this

combination, the unshared pair of electrons from the nitrogen atom completes the octet of boron valency electrons with the formation of a B-N 'donor-acceptor' bond.

Several questions immediately present themselves. What is the nature of this 'donor-acceptor' bond? Can the length of this bond be predicted by the usual empirical method? What happens to the configuration of the BF_3 or 'acceptor' part of the molecule? What happens to the configuration of the H_3CNH_2 or 'donor' part of the molecule?

Other questions arising from the answers to some of the above questions might be anticipated. For example, what would the effect be on the B-N bond and on the configurations of the donor and acceptor parts of the molecule of changing the substituents on the boron and/or on the nitrogen atoms? It would also be of interest to know whether there are any differences in the structure of such donor-acceptor compounds in different states of aggregation.

Some of the above questions are answered by the results of this study; others can be answered only on the basis of further experimental and theoretical investigations.

The most interesting aspect of the results of this study is that they are contrary to those predicted by the usual empirical method. The B-N bond in $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ is apparently a strong one since the compound is stable at ordinary temperatures. Yet the length of the bond is 1.58 Å, 0.09 Å longer than the predicted value. As expected, the configuration of the BF_3 part of the new molecule differs from the planar configuration of the free BF_3 , the B-F bonds being stretched and directed toward the apices of a trigonal pyramid. But corresponding to the long B-N distance, the F-B-F angles are greater than tetrahedral ($109^\circ 28'$), and the B-F bonds are shorter than the predicted value. That is, the boron atom does not form 'equivalent' tetrahedral bonds in this compound.

Changes also occur in the configuration of the H_3CNH_2 when it combines with BF_3 to form $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$. The C-N bond is stretched and there is some evidence that the H-N-C and H-N-H angles become smaller, indicating that the nitrogen atom also does not form 'equivalent' tetrahedral bonds in this compound. Such changes in the H_3CNH_2 would seem to indicate that it is less stable in the combined than in the free state.

There is conclusive evidence from an unpublished investigation in this Laboratory of $\text{H}_3\text{CCN}-\text{BF}_3$ that different substituents on the nitrogen atom can affect radically the B-N bond length and the configuration of the BF_3 .

It can thus be seen that the nature of the donor-acceptor bond is complex. The results of this investigation only present some of these complexities. Undoubtedly, in order to explain them, much further study is indicated.

Determination of the structure

Purified samples of monomethyl amine-boron trifluoride were obtained from Prof. A. W. Laubengayer and E. W. Heiderich of this Laboratory.

Small crystals were cut away from conglomerates and adhering particles removed with a small camel's hair brush. These crystals were coated with polystyrene and mounted on goniometer heads. It did not seem practicable to attempt to make these crystals cylindrical since the compound is deliquescent and brittle. The crystals of $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ are translucent and colorless.

Oscillation photographs with the application of the Hendershot (1937) corrections were used to align the crystals for Weissenberg photographs. Complete sets of Weissenberg equi-inclination photographs were obtained about the three principal axes of the unit cell. The Weissenberg camera diameter is 57.3 mm. The Cu $K\alpha$ radiation used for the Weissenberg photographs was obtained from a North American Philips hot-cathode vacuum tube operating at 35 kV. and 18 mA., using Ni foil as a filter.

The symmetry of the X-ray diffraction effects is C_{2h}^2-2/m and reflections of the type $(0k0)$, k odd, are absent. These data indicate that the space group is either $C_{2h}^2-P2_1$ or $C_{2h}^2-P2_1/m$ (*Internationale Tabellen*). All of the Patterson functions evaluated in this study gave results consistent with the space group $C_{2h}^2-P2_1/m$.

The monoclinic unit of structure has

$$a = 5.06, b = 7.28, c = 5.81 \text{ \AA. (each accurate to within } 0.01 \text{ \AA.)}, \beta = 101^\circ 31' \pm 10',$$

and contains two stoichiometric molecules. These lattice constants were obtained from the Weissenberg photographs. The angle β was determined by the method of angular lag described by Buerger (1942, p. 377). Corrections for film shrinkage and error in film radius were made using the reflections from a very well-aligned and very thin NaCl crystal as standard. The NaCl reflections were recorded on films on which also were registered the reflections from the $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ crystals, and proper correction factors were thereby obtained.

The relative intensities of all reflections were estimated visually by comparison with a carefully prepared intensity scale. The relative intensities of the spots on this intensity scale were:

$$3 : 6 : 8 : 9 : 14 : 17 : 24 : 28 : 33 : 36 : 39 : 40 : 43 : 54 : \\ 56 : 62 : 71 : 76 : 88 : 94 : 104 : 108 : 110.$$

The spot labelled 3 was just visible, whereas that labelled 110 was near saturation. Three simultaneous Weissenberg photographs were taken of each layer line. The ratios of the intensities on the three successive films were approximately 9 : 3 : 1. Compaction and extension of reflections on layer lines other than zero were carefully considered in estimating the relative intensities.

The estimated relative intensities were divided by

the Lorentz and polarization factors and multiplied by the Tunell (1939) rotation factor to obtain the relative values of the squares of the reflection amplitudes, $|F_{hkl}|^2$, for each layer-line photograph taken about each rotation axis. Then by a method of cross calibration, the relative $|F_{hkl}|^2$'s were all based on one reference film. The film chosen for reference is the 23 min. exposure zero-layer-line photograph taken about the b axis. In the cases that reflections (hkl) occur in two or three of the three sets of films (all the films taken about a given axis being considered a set), the $|F_{hkl}|^2$ values obtained from each set when based on the reference film compare very well generally. This seems to be ample justification for neglecting the absorption correction.

The thicknesses of the specimens used were as follows:

Rotation axis	Thickness range (mm.)
a	0.9–1.0
b	0.4–0.5
c	0.35–0.45

The value of the linear absorption coefficient for $H_3CH_2N-BF_3$ is 18.9 cm.^{-1} , giving for the optimum cross-sectional diameter for X-ray work, 1.06 mm.

The final relative observed $|F_{hkl}|^2$ values are the averages of the corresponding relative $|F_{hkl}|^2$ values from the three sets of films obtained as described above.

In order to determine the approximate positions of the atoms, several Patterson functions were evaluated:

$$p(X, Y) = \sum_h \sum_k |F_{h00}|^2 \cos 2\pi(hX + kY),$$

$$p(Y, Z) = \sum_k \sum_l |F_{0kl}|^2 \cos 2\pi(kY + lZ),$$

$$P(0, Y, 0) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi kY,$$

$$P(X, \frac{1}{2}, Z) = \sum_h \sum_k \sum_l (-1)^k |F_{hkl}|^2 \cos 2\pi(hX + lZ),$$

$$P(X, 0, Z) = \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hX + lZ).$$

$p(X, Y)$ and $p(Y, Z)$ were most valuable in leading to approximate parameters for the fluorine atoms in fourfold positions. $P(0, Y, 0)$ gave a closer approximation to the y parameter of these fluorine atoms. $P(X, \frac{1}{2}, Z)$ is quite complex for the $P2_1/m$ case, since peaks appear not only for equivalent atoms related by the twofold axis, but also for non-equivalent atoms lying in the planes of symmetry $y = \frac{1}{4}$ and $y = \frac{3}{4}$. However, $P(X, 0, Z)$ gave the orientation of the molecules in the unit cell, and with this information $P(X, \frac{1}{2}, Z)$ became very useful. When the exact structure was finally obtained, every peak in each of the Patterson functions was accounted for. However, some peaks that should appear do not. The B–B peak, for example, does not appear in $P(X, \frac{1}{2}, Z)$. A few other peaks due to vectors between unlike atoms do not appear in $p(X, Y)$ and in $p(Y, Z)$. This is to be expected in these latter cases particularly, since reflections with visible intensity from only 44 $hk0$ and only 47 $0kl$ forms were recorded. It

should also be noted, and it will be shown more clearly later, that the amplitudes of the thermal vibrations of the atoms in the lattice are large. Initial evidence for this was the rapid dropping off of intensity of the reflections with increasing $\sin \theta$.

As a result of the consideration of the above Patterson functions, approximate parameters were obtained for all of the atoms in the unit cell excluding the hydrogen atoms. Because of the initial complexity of $P(X, \frac{1}{2}, Z)$, and because $p(X, Y)$ and $p(Y, Z)$ did not prove very useful in the determination of the parameters for atoms occupying twofold positions, most of the parameters obtained from a consideration of the Patterson functions were very rough for these atoms. The parameters obtained for the fluorine atoms occupying fourfold positions were reasonably accurate. Also, the z parameters obtained for the twofold fluorine and boron atoms were reasonably accurate. The use initially of the approximate parameters derived from consideration of the Patterson functions led ultimately to very accurate values of the parameters as will now be shown.

In order to determine the parameters more accurately, several Fourier syntheses were made. These were the Fourier projections of relative electron density on (100), on (001) and on (010); the Fourier projection along the b axis on (010) of the relative electron density of the lower half of the unit cell (this giving the projection of just one molecule on the (010) face); the Fourier section, $\rho(x, \frac{1}{4}, z)$, i.e. the relative electron density at all points in the plane $y = \frac{1}{4}$, and finally the relative electron density along the line $x = -0.244$, $z = 0.129$ or $\rho(-0.244, y, 0.129)$.

The Fourier syntheses were performed in the order shown above, those requiring least data being done first, so that when the section was first evaluated only few changes of phase occurred after the new parameters so obtained were used to recalculate the reflection amplitudes. The Fourier section and half-cell projection were corrected for all changes in phase of the reflection amplitudes, and the reflection amplitudes recalculated. This procedure was continued until no further changes of phase occurred.

The final x and z parameters of the fourfold fluorine atom were obtained from the half-cell Fourier projection. These parameters are $x = -0.244$ and $z = 0.129$. The synthesis $\rho(-0.244, y, 0.129)$ was performed to check the accuracy of the y parameter which had been obtained from the Fourier projections on (100) and on (001). This synthesis gave $y = 0.095$, exactly the value obtained previously. The final parameters of the atoms occupying twofold positions were obtained from the Fourier section. The accurate parameters for $H_3CH_2N-BF_3$ are given in Table 1.

The important parts of the Fourier syntheses from which the above parameters were obtained are shown in Figs. 1, 2 and 3.

All summations described above were carried out using Beavers & Lipson (1936) strips.

Table 1. Atomic co-ordinates in $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$

Atom	Position	Atomic co-ordinates		
		x	y	z
Nitrogen	2 (e)	-0.180	$\frac{1}{2}$	0.152
Carbon	2 (e)	-0.252	$\frac{1}{2}$	0.415
Boron	2 (e)	0.134	$\frac{1}{2}$	0.050
Fluorine	2 (e)	0.172	$\frac{1}{2}$	-0.190
Fluorine	4 (f)	-0.244	0.095	0.129

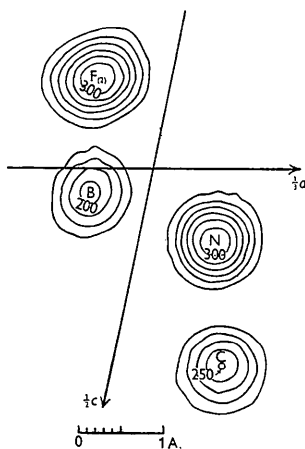


Fig. 1. Part of Fourier section $\rho(x, \frac{1}{2}, z)$ used to determine accurate positions of atoms occupying twofold positions. Contours differ by 50 arbitrary units.

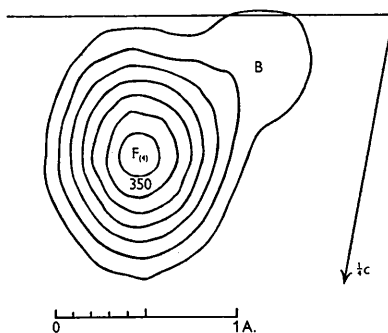


Fig. 2. Part of projection of relative electron density of half the cell on (010) used to determine the x and z parameters of fluorine atoms occupying fourfold positions. Contours differ by 50 arbitrary units.

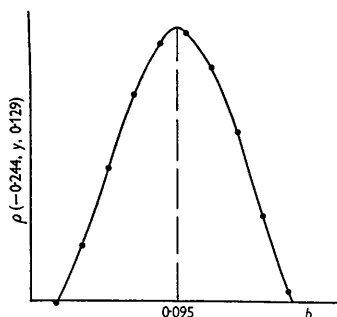


Fig. 3. The relative electron density along the line $x = -0.244$, $z = 0.129$, used to determine the y parameter of the fluorine atoms occupying fourfold positions.

A determination of the dynamical scattering powers of the atoms in this structure would at the very least be an extremely arduous task, one which is not essential to the purpose of an investigation such as that described here. If, therefore, we wish to find a means of comparing observed and calculated values of the reflection amplitudes, it seems reasonable to assume an isotropic temperature factor which, of course, cannot be correct, but can be the best mean value of the B_{hkl} . The value of the temperature factor and of the scale factor (by which the $|F_{\text{obs.}}|$ were multiplied to put them on the same basis as the $|F_{\text{calc.}}|$) were obtained by the method of least squares using the $(hk0)$, $(h0l)$, $(0kl)$ data (124 forms in all) as representative of the whole. The value of B so obtained is $2.33 \times 10^{-16} \text{ cm.}^2$, definite evidence that the thermal vibrations in crystals of $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ are large. The values of $F_{\text{calc.}}$ multiplied by the corresponding temperature factors,

$$\exp[-2.33(\sin \theta_{hkl}/\lambda)^2 \times 10^{-16}],$$

and the values of $|F_{\text{obs.}}|$ multiplied by the scale factor (1.74) are shown in Table 2.

Using $\text{Cu } K\alpha$ radiation, it is possible for 500 forms to be recorded on the various Weissenberg films. Out of these, five $(0k0)$, k odd are absent because of space-group extinctions, and 103 other forms were not observed. For these it is not really possible to ascertain how important is the deviation of $F_{hkl(\text{calc.})}$ (temperature factor included) from the value zero without calculating the relative intensities the corresponding reflections should have on a given film. This was done for these reflections. The expression for calculating such relative intensities is

$$I_{hkl} = \frac{(F_{hkl(\text{calc.})} T)^2}{K^2} \times \frac{LP}{D_e} C,$$

in which

$K = 1.74$ (the scale factor derived by least-squares method),

$L =$ Lorentz factor,

$P =$ polarization factor,

$T =$ temperature factor,

$D_e =$ Tunell rotation factor,

$C =$ film calibration factor.

Owing to the nature of the approximations made in this investigation, it can be said that none of the discrepancies for the unobserved reflections is serious. Of the 103 reflections observed to have zero relative intensity, 88 have calculated intensities below the minimum observable value of 3. Of the remaining 15, only four have values greater than 6, the greatest being 11. From an examination of Table 2, together with consideration of the above treatment of reflections too weak to be observed, it will be seen that the agreement between calculated and observed reflection amplitudes is very good and gives definite confirmatory evidence of the correctness of the parameters.

Table 2. Comparison of calculated with observed reflection amplitudes

Amplitude			Amplitude			Amplitude			Amplitude			Amplitude		
(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.
080	3.8	7.2	241	2.9	0.7	502	3.8	4.8	414	2.4	2.0	451	0	1.3
060	15.1	-19.7	231	8.4	6.4	083	0.7	-2.2	404	6.1	-7.6	441	9.8	-12.1
040	3.0	7.6	221	7.8	5.0	073	3.8	6.7	065	0	-0.8	431	4.9	-3.2
020	22.3	-26.3	211	14.3	12.9	063	5.2	7.9	055	0.7	-0.5	421	13.7	13.4
190	3.5	-2.8	201	24.6	-24.2	053	5.2	-7.3	045	3.5	6.5	411	7.8	-4.5
180	1.7	2.7	371	1.7	2.8	043	1.7	-0.6	035	3.5	6.2	401	4.5	-4.4
170	4.9	-5.4	361	5.5	5.2	033	2.4	1.4	025	5.2	-6.9	561	1.7	1.9
160	4.9	-4.9	351	3.5	-1.9	023	7.7	5.3	015	0	1.6	551	2.4	-0.1
150	2.4	2.2	341	2.4	2.6	013	17.7	-18.2	005	3.8	1.1	541	3.0	1.3
140	7.3	8.6	331	7.7	-3.6	003	23.0	-24.9	165	0	-0.2	531	4.9	-4.4
130	22.2	18.3	321	0	-0.4	183	0	-1.0	155	0	-0.4	521	2.4	-0.5
120	13.2	-13.1	311	8.0	-6.7	173	1.7	3.8	145	3.5	6.5	511	3.5	-2.1
110	13.6	10.9	301	14.7	-13.1	163	2.4	-1.5	135	0	-3.2	501	5.8	-4.2
100	16.7	17.6	461	0	-1.9	153	0	-2.7	125	6.8	-6.4	631	0.9	-0.1
280	1.7	-3.5	451	0	-1.7	143	5.4	-6.4	115	0	-2.0	621	4.9	-5.2
270	0	-2.6	441	3.7	-2.2	133	5.8	-4.8	105	3.8	-0.4	611	4.4	3.2
260	9.9	11.8	431	5.6	-3.8	123	7.6	6.2	255	0	1.0	601	0	1.3
250	3.5	4.0	421	0	1.0	113	8.9	-9.5	245	0	-1.0	182	0	0.4
240	5.2	-0.6	411	6.1	-5.3	103	2.5	5.1	235	2.4	-5.4	172	3.0	-0.5
230	3.5	-3.4	401	7.0	5.4	273	3.0	-4.3	225	0	0.4	162	7.0	5.2
220	8.0	7.2	551	0	0.6	263	4.3	-7.2	215	1.7	-0.2	152	4.7	1.3
210	8.9	9.3	541	0	-0.7	253	3.8	4.0	205	3.5	3.7	142	11.5	11.1
200	32.6	-41.0	531	3.0	1.7	243	1.7	1.3	335	0	0.4	132	2.4	-1.5
380	1.7	-3.6	521	0	-0.7	233	0	0.6	325	1.7	2.1	122	11.5	-12.3
370	2.4	1.3	511	1.7	2.1	223	5.6	-4.3	315	1.7	2.3	112	4.9	5.4
360	5.8	6.4	501	6.8	6.6	213	8.4	8.6	305	2.4	2.5	102	19.0	-17.9
350	3.5	2.3	611	0	1.2	203	16.0	16.5	056	0	1.2	282	0	1.7
340	7.8	-8.3	601	1.2	-0.2	363	2.4	-2.3	046	0	0.3	272	3.8	-2.9
330	15.8	-14.9	082	0	-0.3	353	2.4	3.1	036	0	3.1	262	0	-3.2
320	12.7	11.9	072	6.3	4.2	343	6.3	8.1	026	0	-0.6	252	0	-0.5
310	3.5	-2.2	062	2.4	1.3	333	0	1.7	016	2.4	4.1	242	4.4	5.4
300	18.5	-14.8	052	4.4	0.3	323	9.2	-8.9	006	1.7	1.9	232	15.5	14.8
470	2.4	1.0	042	1.7	-1.7	313	7.7	6.8	146	1.7	3.4	222	9.6	-9.2
460	3.0	-2.7	032	15.8	-18.1	303	7.8	3.9	136	1.7	-0.5	212	8.7	8.3
450	0	-1.0	022	1.7	3.3	453	0	-0.2	126	2.4	-2.7	202	10.8	9.9
440	8.0	-5.9	012	9.9	-12.3	443	1.4	1.9	116	3.0	2.0	382	0	1.3
430	1.7	-0.4	002	3.5	-2.9	433	0	-2.4	106	1.4	-3.5	372	1.7	0.6
420	6.4	4.8	182	0	-0.6	423	0	-1.1	236	0.7	-1.8	362	4.9	-6.6
410	1.7	-2.5	172	2.4	2.0	413	1.7	-1.3	226	0	-0.7	352	4.4	-1.1
400	8.7	6.8	162	6.1	-4.1	403	3.5	-4.9	216	1.7	-3.4	342	6.1	-3.2
550	0	-2.2	152	3.0	-2.6	523	3.8	4.8	206	0	-0.3	332	1.7	2.4
540	0	1.3	142	11.2	-12.2	513	1.7	-2.2	027	0	0.2	322	3.0	0.2
530	7.3	8.3	132	2.4	2.5	503	3.8	-3.0	017	1.0	1.8	312	1.0	-1.9
520	0	-2.1	122	15.3	13.4	074	0	0.6	007	1.4	1.1	302	17.6	17.7
510	0	-1.0	112	9.9	-8.0	064	3.8	6.0	191	1.7	0.3	472	0	1.4
500	4.7	3.9	102	10.3	10.1	054	1.2	-1.6	181	1.7	4.9	462	1.7	1.7
630	2.4	2.0	282	0	-0.9	044	1.7	3.0	171	6.5	6.3	452	2.4	0.3
620	3.0	-3.1	272	3.8	-2.9	034	2.4	3.3	161	0	-3.6	442	3.5	-3.6
610	2.4	-1.1	262	0	1.0	024	2.4	-0.6	151	5.8	-4.8	432	11.0	-8.2
600	0.9	-1.3	252	3.8	-0.5	014	3.0	-2.7	141	22.4	-20.3	422	5.6	4.3
091	1.2	1.5	242	2.9	-3.1	004	12.5	-14.9	131	11.5	-7.7	412	4.4	-3.5
081	2.4	2.2	232	11.5	13.3	174	0	2.3	121	31.0	-28.8	402	2.5	-3.6
071	6.4	4.5	222	6.6	4.2	164	1.7	-4.3	111	22.1	-18.4	552	0	0.6
061	8.0	-8.2	212	5.6	5.8	154	0	0.3	101	15.5	12.4	542	0	-1.5
051	5.6	-1.5	202	5.6	-2.6	144	5.8	7.8	281	0	2.0	532	0	-1.5
041	4.9	-2.4	372	2.4	-2.2	134	6.3	-8.7	271	5.2	-2.1	522	3.0	3.8
031	11.7	-15.6	362	2.9	3.1	124	10.3	-9.2	261	4.9	1.1	512	0	0.6
021	3.5	-2.0	352	5.6	2.6	114	2.4	-3.8	251	1.7	-0.7	502	11.8	-11.8
011	16.4	-14.4	342	5.5	6.3	104	9.9	8.3	241	12.2	12.3	632	6.5	3.9
001	22.6	30.6	332	3.5	-1.7	264	2.4	-7.9	231	11.7	13.1	622	0	0.1
191	1.7	0.1	322	7.0	-5.6	254	0	1.1	221	15.7	-14.0	612	1.5	2.0
181	1.7	-1.6	312	4.9	4.2	244	3.0	2.4	211	9.1	6.0	602	0	-1.1
171	3.8	-6.0	302	6.8	-7.0	234	2.4	-0.2	201	8.5	-7.5	183	0	-0.8
161	6.6	-2.0	462	0	-1.8	224	8.2	-5.4	381	1.2	-3.1	173	1.7	-1.4
151	2.4	5.6	452	0	1.6	214	1.7	2.5	371	4.4	-2.8	163	4.9	5.0
141	11.9	-13.0	442	2.9	4.1	204	15.2	15.9	361	2.4	2.0	153	3.8	-1.4
131	8.5	4.0	432	6.3	-7.7	354	0	1.5	351	4.4	0.5	143	3.0	2.6
121	16.7	15.7	422	5.6	-4.7	344	0	-0.9	341	12.9	-12.5	133	12.0	11.7
111	24.4	19.9	412	0	-0.2	334	1.7	3.0	331	9.4	8.6	123	1.7	0.4
101	8.0	7.1	402	4.9	3.3	324	0	0.8	321	14.3	13.6	113	1.7	2.7
281	0	-2.0	542	1.7	-1.8	314	3.8	4.8	311	7.3	3.6	103	12.9	-14.4
271	4.4	-5.2	532	1.0	-0.2	304	0	0.9	301	3.8	-3.3	283	0.7	0.4
261	5.6	7.2	522	0	-0.9	434	0	-0.6	471	3.0	2.3	273	1.4	-4.8
251	4.9	3.6	512	2.4	-1.2	424	1.7	2.3	461	0	2.8	263	3.5	-4.1

Table 2 (cont.)

Amplitude			Amplitude			Amplitude			Amplitude			Amplitude		
(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.	(hkl)	Obs.	Calc.
253	2.4	4.2	513	4.4	1.6	334	8.0	-11.3	235	0	-2.4	106	3.0	6.5
243	4.4	-3.7	503	4.5	-3.8	324	3.5	-2.8	225	8.4	9.7	256	0	-1.0
233	5.6	2.3	623	1.4	2.3	314	1.7	0.9	215	4.5	-5.5	246	1.7	-0.5
223	2.4	1.6	613	1.0	1.9	304	3.5	3.0	205	5.6	-4.0	236	2.4	-3.3
213	11.0	12.2	603	1.0	0.4	444	3.0	5.6	365	1.7	4.3	226	1.4	0.5
203	12.4	12.7	174	0	0.1	434	4.4	-5.6	355	1.7	-1.3	216	1.7	-3.8
373	1.2	1.3	164	3.5	5.4	424	4.5	-5.0	345	0	-0.9	206	1.7	-1.1
363	3.8	-3.8	154	2.4	-4.1	414	4.9	5.8	335	0	-2.4	346	1.0	-0.2
353	2.4	0.9	144	7.0	-8.7	404	3.0	-3.1	325	1.7	2.4	336	0	0.2
343	3.0	-2.4	134	12.0	15.8	544	0	1.1	315	3.8	-3.5	326	1.7	1.8
333	8.4	-7.7	124	12.4	11.3	534	3.5	3.3	305	6.1	-8.8	316	0	0.2
323	1.7	0.2	114	5.2	-2.3	524	0	-1.2	445	2.4	4.4	306	5.2	-8.1
313	0	-1.6	104	13.7	-11.7	514	3.5	2.8	435	0	0.2	436	3.0	3.1
303	11.8	12.1	274	1.7	1.8	504	0	0.8	425	2.4	-4.3	426	0	1.6
463	2.4	1.2	264	2.4	-1.6	604	1.7	3.3	415	2.4	4.6	416	1.0	2.2
453	2.4	-0.8	254	4.4	-2.9	165	0	-1.4	405	1.0	-0.2	406	0	-1.8
443	3.8	4.0	244	5.6	-8.8	155	0	-0.6	535	0	1.2	137	1.7	-5.3
433	7.3	-4.4	234	4.4	3.0	145	3.5	-4.8	525	1.7	-2.9	127	0	0.6
423	3.0	-3.5	224	7.0	7.3	135	2.4	5.5	515	3.0	5.3	117	2.4	1.8
413	2.4	-3.5	214	4.5	-4.2	125	4.9	4.0	505	3.5	6.4	107	0.7	2.2
403	4.5	-2.8	204	4.5	5.4	115	0	1.0	156	0	-1.2	227	1.7	-0.4
553	0	-0.4	374	1.7	0.3	105	2.4	3.7	146	0	-2.1	217	0.9	-0.2
543	0	2.2	364	1.4	-1.6	265	1.7	2.8	136	0	0.5	207	1.0	-3.3
533	0	3.1	354	0	2.8	255	1.7	-1.9	126	0	0.8	317	0	0.2
523	0	-1.3	344	3.0	2.1	245	5.6	-9.2	116	0	-1.3	307	1.0	-2.0

There are, of course, a few minor discrepancies other than those involving reflections too weak to be observed. There are several cases (e.g. F_{200} , F_{020} , F_{001}) for which the calculated reflection amplitudes are much greater than the observed. This may be partially explained by noting that the intensities of very intense reflections are often under-estimated. In addition, these reflections are probably affected by extinction. It happens also that the intensities of very light reflections are often overestimated. Other discrepancies may be due to errors in calculated reflection amplitudes of small magnitude, which result from differences of several large terms or from trigonometric functions in the region of greatest sensitivity. The use of an isotropic temperature factor, the spherical symmetry approximation used in the determination of the atomic scattering powers, and possibly errors due to absorption, also contribute to the discrepancies.

The index of reliability,

$$R = \frac{\sum | |F_{\text{obs.}}| - |F_{\text{calc.}}| |}{\sum |F_{\text{obs.}}|}$$

was calculated in three ways. Excluding $|F_{\text{calc.}}|$ values for reflections too weak to be observed, $R=0.26$. Including $|F_{\text{calc.}}|$ values for reflections too weak to be observed, and assuming the corresponding $|F_{\text{obs.}}|$ equal to zero, $R=0.32$. Including $|F_{\text{calc.}}|$ values, and assuming that if the corresponding reflections were observed the $|F_{\text{obs.}}|$ would be exactly equal to the corresponding $|F_{\text{calc.}}|$, $R=0.25$. Therefore, the true value of R lies somewhere between 0.25 and 0.32, and probably closer to 0.25 than to 0.32.

It is the opinion of the authors that too much emphasis should not be put on the value of R alone as a test of the structure since the errors described above may contribute largely to R . Also it seems possible to

obtain a relatively low value of R for an erroneous structure.

Discussion of the structure

In order to simplify this discussion, the following notation will be used:

- $F_{(2)}$, fluorine atom occupying a twofold position,
- $F_{(4)}$, fluorine atom occupying a fourfold position,
- $H_{(4)}^{(N)}$, hydrogen atom occupying a fourfold position bonded to nitrogen atom,
- $H_{(2)}^{(C)}$, hydrogen atom occupying twofold position bonded to carbon atom,
- $H_{(4)}^{(C)}$, hydrogen atom occupying fourfold position bonded to carbon atom.

No method thus far proposed for the determination of limits of error is applicable to this compound since there is no sharp cutoff of the series, and since, as has been shown, an accurate assessment of the values of the temperature factors is not feasible (Cruickshank, 1949). Thus no attempt has been made to calculate limits of error. However, we may hazard the opinion that the probable error in the bond distances is ± 0.02 Å., and in interbond angles $\pm 2^\circ$. The probable error in other distances and angles, particularly those involving hydrogen atoms, would be somewhat larger.

We propose to study other molecular addition compounds involving the B-N bond. With such further information, it should be feasible to assess the accuracy with which the structural constants of such molecules can be established.

Table 3 lists intramolecular interatomic distances and bond angles in $H_3CH_2N-BF_3$.

The distance of the boron atom from the plane of the three fluorine atoms is 0.43 Å. The angles that the line

joining the boron and nitrogen atoms makes with the altitude of the equilateral fluorine triangle dropped from $F_{(2)}$ to the base of the triangle (the line joining the two $F_{(4)}$ atoms) is 89.8° .

Table 3. *Distances and angles*

Interatomic distances (A.) between bonded atoms:

B-F ₍₂₎	= 1.37
B-F ₍₄₎	= 1.38
B-N	= 1.58
C-N	= 1.50

Bond angles ($^\circ$):

F ₍₂₎ -B-F ₍₄₎	= 110.9
F ₍₄₎ -B-F ₍₄₎	= 110.1
F ₍₂₎ -B-N	= 108.1
F ₍₄₎ -B-N	= 108.5
B-N-C	= 113.9

Interatomic distances (A.) between non-bonded atoms:

F ₍₂₎ -F ₍₄₎	= 2.26
F ₍₄₎ -F ₍₄₎	= 2.26
F ₍₂₎ -N	= 2.39
B-C	= 2.58
F ₍₄₎ -C	= 2.95
F ₍₄₎ -N	= 2.40

Admittedly the $F_{(4)}$ atoms are not required by symmetry to be equivalent to the $F_{(2)}$ atom, but there is other evidence (for example, in $(H_3C)_3N-BF_3$ there is discussed in a paper to be published in the near future) that would lead to the belief that all the B-F bonds should be equivalent. The angle that the B-N line makes with the altitude of the fluorine triangle is certainly close enough to 90° to be considered so. It is also seen that very small changes in the B-F₍₄₎ component in the plane of symmetry produce appreciable changes in the $F_{(4)}$ -B-F₍₄₎ angle. The difference between the lengths of the B-F₍₄₎ and B-F₍₂₎ bonds is 0.01 A. Yet this difference is sufficient to make the $F_{(4)}$ -B-F₍₄₎ angle 0.8° less than the $F_{(2)}$ -B-F₍₄₎ angle. (If the B-F₍₂₎ and B-F₍₄₎ bonds were both 1.37 A., the F-B-F angles would be 111.4° .) It is also seen that the N-F₍₄₎ distance and the $F_{(4)}$ -B-N angle are not so sensitive to changes in the B-F₍₄₎ component in the symmetry plane. The N-F₍₄₎ distance differs from the N-F₍₂₎ distance by 0.01 A., and the $F_{(4)}$ -B-N angle differs from the $F_{(2)}$ -B-N angle by only 0.4° .

Now the final parameters of the fourfold fluorine atoms were obtained from the half-cell projection and from $\rho(-0.244, y, 0.129)$ described previously. All the other parameters were obtained from the Fourier section $\rho(x, \frac{1}{4}, z)$. It can be said that the accuracy of the parameters obtained from the section is greater than the accuracy of the parameters obtained from the projection, and therefore that distances and angles in the plane calculated from the parameters obtained from $\rho(x, \frac{1}{4}, z)$ are more reliable than those obtained from the half-cell projection. It seems safe to conclude, therefore, that within experimental error all of the B-F distances are the same, and so it would follow that the N-F distances are all equal, the F-B-N angles are all equal, and the F-B-F angles are all equal. The B-F distance may be taken as 1.37 A.; the F-B-F angle as 111° ; the

F-B-N angle as 108° ; and the F-N distance as 2.39 A. The interatomic distances and angles are summarized in Fig. 4.

The results obtained for the bond lengths and bond angles in $H_3CH_2N-BF_3$ are indeed very interesting. The B-N bond distance is 0.09 A. longer than the distance predicted from Pauling's table of tetrahedral radii with application of the correction for the difference of electronegativity between the boron and nitrogen atoms. Another type of comparison can, however, be made on the basis of the following considerations. In the graphite structure, the C-C bond distance is 1.42 A. In the diamond structure, the C-C bond distance is 1.54 A., an increase of 0.12 A. Now BN crystallizes with the graphite structure with alternate B and N atoms arranged in layers, and with a B-N distance of

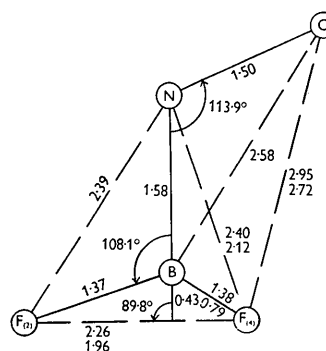


Fig. 4. Summary of important intramolecular interatomic distances and bond angles. Solid lines indicate bonded atoms. For distances which are out of the plane of the figure, the total distances are written above the components of these distances in the plane; thus for B-F₍₄₎ 1.38 A. is the bond distance, 0.79 A. is the component of 1.38 A. in the plane of the figure.

1.45 A. If BN crystallized also in one of the SiC forms which are structurally related to diamond, it seems reasonable to expect an increase in the B-N distance comparable to that for carbon in going from the graphitic to the diamond structure. If this increase is assumed to be 0.12 A., the B-N distance would be 1.57 A. Thus the value which should be attributed to the B-N bond when of the sp^3 type is somewhat in doubt.

It would seem, however, that the B-F bonds are stronger than partially ionic single bonds, and the F-B-F angles are larger than tetrahedral ($109^\circ 28'$). The condition of minimum potential energy for the compound formed from the BF_3 and H_3CNH_2 does not necessarily require the boron atom to possess four equivalent tetrahedral bond orbitals. In fact, there is some indication here that the bonds formed by the boron atom may vary with the donor molecule and even with the atoms linked to the boron. There is further indication that such is the case by the results of the investigation of $H_3CCN-BF_3$ in which the B-N bond has been found to be longer, the B-F bonds shorter, and the F-B-F angles larger than in $H_3CH_2N-BF_3$. The

results obtained for $\text{H}_3\text{CCN}-\text{BF}_3$ are consistent with observations that this compound is very unstable at ordinary temperatures and completely dissociated in the vapor state at 50°C . (Laubengayer & Sears, 1945). $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$, on the other hand, is quite stable at ordinary temperatures.

The stability of $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ gives rise to further comment on the B-N bond. Since very small increases in bond distances are accompanied by a pronounced weakening of the bonds, it is very interesting indeed to note that in spite of the large deviation of the B-N bond distance in $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ from the predicted value, it still remains a comparatively strong bond. The nature of this B-N 'donor-acceptor' bond is far from clear and thus the importance of further study of similar compounds and of further attempts to determine the structure of elementary boron is evident.

Now the free BF_3 molecule has a planar configuration, the three fluorine atoms being linked to the boron at distances of 1.30 A. and F-B-F angles of 120° . When the BF_3 molecule combines with a donor molecule, the fluorine atoms move away from the boron atom in the direction of motion of the approaching donor molecule. It might then be expected that changes in configuration and in bond distances of donor molecules would also occur in such combinations.

The structure of monomethyl amine has not as yet been determined. However, an electron diffraction study (Brockway & Jenkins, 1936) of $\text{N}(\text{CH}_3)_3$ gave for the C-N distance 1.47 ± 0.02 A., and for the C-N-C angle $108 \pm 4^\circ$. The value 108° was also obtained for the H-N-H angle in NH_3 by spectroscopic studies (Dennison & Uhlenbeck, 1932). It is therefore reasonable to assume that the C-N distance in H_3CNH_2 is 1.47 ± 0.02 A. and the H-C-N angle about 108° .

There is evidence that the configuration and bond distances in the combined and free H_3CNH_2 molecule differ. If the two N-H bonds and the C-N bond are assumed to be directed toward the apices of a trigonal pyramid, the value obtained for the C-N-H angle is 105° , somewhat smaller than 108° . Because the limits of error of the value given for the C-N-C angle in $\text{N}(\text{CH}_3)_3$ are large, and because the assumption made above may not be accurate, the value calculated for the C-N-H angle may not be sufficiently conclusive evidence of change of configuration. However, there is a 2% increase in the length of the C-N bond in the combined molecule, and although the limits of error may be such as to permit the C-N distances in $(\text{H}_3\text{C})_3\text{N}$ and in the combined $\text{H}_3\text{CH}_2\text{N}$ to be the same, it seems that the atoms on the nitrogen move away from that atom when the H_3CNH_2 molecule combines with the BF_3 molecule. This means that the donor part of the $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ molecule should be somewhat less stable than it is in the free state, and therefore that $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ might be a good methylating agent. This possibility arises by comparison with results obtained

from an electron-diffraction study of dimethyl ether-boron trifluoride by Bauer, Finlay & Laubengayer (1943) (see also Dunderman & Bauer (1946)). In this molecule, it was found that the C-O distance is 0.03 A. greater than in the free dimethyl ether molecule, and it is known that dimethyl ether-boron trifluoride is a good methylating agent.

In order to determine how the molecules pack into the crystal, it is necessary to calculate distances between atoms in neighboring molecules along the three principal axes of the unit cell. It is also of importance to calculate, at least approximately, the positions of the hydrogen atoms which cannot be determined by the methods discussed earlier.

A list of distances between closest neighboring atoms of adjacent molecules is given in Table 4.

Table 4. Distances between closest neighboring atoms of adjacent molecules

Along the <i>a</i> axis:		
C-F ₍₄₎		3.48 A.
H ₍₄₎ ^(N) -F ₍₂₎		3.63
H ₍₄₎ ^(N) -F ₍₄₎		2.41
H ₍₄₎ ^(C) -F ₍₄₎		3.09
Along the <i>b</i> axis:		
C-F ₍₂₎		3.87 A.
N-F ₍₄₎		3.04
H ₍₄₎ ^(N) -F ₍₄₎		2.16
H ₍₄₎ ^(C) -F ₍₂₎		3.52
Along the <i>c</i> axis:		
C-F ₍₂₎		3.44 A.
F ₍₄₎ -F ₍₂₎		4.06
N-F ₍₂₎		4.53
H ₍₂₎ ^(C) -F ₍₂₎		2.35
C-H ₍₄₎ ^(N)		4.11
H ₍₂₎ ^(C) -H ₍₄₎ ^(N)		3.42

The distance between the carbon atom in one molecule and the F₍₂₎ atom in the nearest molecule in the direction of the short diagonal is 4.07 A.

The van der Waals' radii of atoms important in this discussion are:

$$\text{H } 1.2 \text{ A.}, \quad \text{F } 1.35 \text{ A.}$$

From an examination of the lists of intermolecular interatomic distances it can be seen how the molecules build up the crystal. Along the *a* axis, the H₍₄₎^(N) atoms of one molecule are in contact with the closest neighboring F₍₄₎ atoms of the adjacent molecule. Along the *b* axis, the H₍₄₎^(N) atom above the mirror plane $y = \frac{1}{4}$ is in contact with the F₍₄₎ atom below the plane $y = \frac{3}{4}$, and the F₍₄₎ atom above the plane $y = \frac{1}{4}$ is in contact with the H₍₄₎^(N) atom below the plane $y = \frac{3}{4}$. Along the *c* axis, the H₍₂₎^(C) atom of one molecule is in contact with the F₍₂₎ atom of the adjacent molecule. An idea of the packing arrangement along the *a* and *c* axes may be got from Fig. 5.

The molecules are bound most tightly along the *b* axis, probably accounting for the ease with which the crystals cleave along this direction.

Hydrogen parameters

In the calculation of the $H_{(4)}^{(N)}$ parameters, the following assumptions were made:

1. The two N-H bonds and the N-C bond are directed toward the apices of a trigonal pyramid (making the C-N-H and the H-N-H angles 105°).

2. The N-H distance is 1.02 Å. (0.01 Å. longer than in NH_3). The parameters obtained for $H_{(4)}^{(N)}$ based on these assumptions are:

$$x=0.279, \quad y=0.13 \quad \text{and} \quad z=0.102.$$

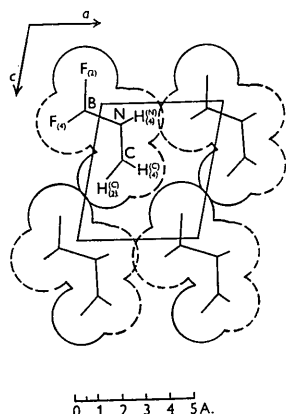


Fig. 5. Packing arrangement of the molecules in $y = \frac{1}{4}$.

Before calculating the parameters for the methyl hydrogen atoms, it is necessary to determine the most probable orientation of these atoms. If the space-group conditions are to be satisfied, one of the hydrogen atoms must lie in the plane of symmetry, and the other two must be mirror images of each other in the plane of symmetry. An examination of the interatomic distances between the carbon atom and neighboring fluorine atoms belonging to adjacent molecules shows that the C-H₍₂₎^(C) bond should most likely be in the general direction of the c axis rather than of the a axis. The former orientation of the methyl hydrogen atoms puts these atoms closer to neighboring fluorine atoms than does the latter orientation. Moreover, the latter orientation would not link the molecules in the c axis direction since, for that orientation, the F₍₂₎-H₍₄₎^(C) distances would be appreciably larger than 2.55 Å., the sum of the van der Waals' radii of fluorine and hydrogen.

Having determined the probable orientation of the methyl hydrogen atoms the following additional

assumptions were made in determining the positions of these atoms:

(1) The C-N bond is perpendicular to the plane determined by the centers of the three hydrogen atoms.

(2) The N-C-H angles are 114° (making the H-C-H angles 105°).

(3) The C-H distances are all equal to 1.10 Å.

The parameters obtained for the methyl hydrogen atoms based on the above assumptions are,

$$\text{for } H_{(2)}^{(C)}: \bar{x}=0.150, \quad y=\frac{1}{4} \quad \text{and} \quad z=0.565;$$

$$\text{and for } H_{(4)}^{(C)}: x=0.374, \quad y=0.130 \quad \text{and} \quad z=0.487.$$

The intermolecular interatomic distances involving hydrogen atoms were determined, using the calculated hydrogen parameters shown above. These parameters were also used to calculate contributions of the hydrogen atoms to the reflection amplitudes with $\sin \theta/\lambda \leq 0.3$. In several cases these contributions were by no means insignificant, and their inclusion resulted in a general improvement between calculated and observed reflection amplitudes.

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