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Structures of Molecular Addition Compounds. IV. Trimethylamine–Boron Trifluoride, $(H_3C)_3N–BF_3$

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Trimethylamine–boron trifluoride, $(H_3C)_3N–BF_3$, crystallizes in a one-molecule rhombohedral unit having $a = 5{\cdot}76$ A., $\alpha = 108°\ 16'$ and space group $C_{3v}^5–R3m$. All of the X-ray diffraction data obtainable with Cu $K\alpha$ radiation were utilized in Patterson, Fourier and differential syntheses to attain maximum accuracy in the determination of atomic positions. Corrections for finite-series termination are especially important in this structure, amounting in the case of the B–N bond to fully 0·04A. The accuracy of the structure determination seems at best to be inferior to that attained for other compounds studied in this series, and perhaps the principal interest of this investigation is associated with the analysis of the various factors leading to this conclusion. Bond distances within trimethylamine–boron trifluoride as given by the study, nevertheless, are in rather good agreement with the results obtained for related molecules. Detailed comparisons are presented in the succeeding paper of this series.

Introduction

Although the structural type in which trimethylamine–boron trifluoride crystallizes is of almost trivial simplicity, the determination of atomic positions with an accuracy even fairly comparable with that attained for other structures studied in this series has been a task out of all proportion to the apparent difficulties of the problem. The assignment of complex phases to the experimental amplitudes of reflection has proved to be a slowly converging process, and the accuracy of the final set of phases is open to question, since it seems impossible to achieve better than fair agreement between what are believed to be excellent experimental amplitudes and those calculated from the usual type of model. Corrections for finite-series termination are particularly important for $(H_3C)_3N–BF_3$; failure to include such corrections, in fact, would lead to definitely misleading conclusions. It is clear, nevertheless, that the study has been most illuminating, and it seems possible to account in part for some of the apparent anomalies which were encountered and to foresee their probable effects in future studies.

Determination of the structure

Our sample of trimethylamine–boron trifluoride was purified by successive sublimations under reduced pressure. One crystal providing excellent X-ray data was grown in a thin-walled glass cylindrical capillary by subliming the compound from a reservoir in one end of a long evacuated tube kept at 110° C. into the capillary tip at the other end kept at 105° C. Oscillation photographs with the application of Hendershot (1937) corrections were used to align this crystal for Weissenberg photographs. The axis of rotation was the unique threefold axis of the rhombohedral unit cell. Examination of the crystal with a polarizing microscope showed that this rational direction was very closely parallel to the axis of the capillary.

To obtain complete data, it was desirable to align a crystal with the hexagonal a axis as rotation axis. Repeated attempts to grow a specimen having this orientation within a glass capillary always yielded crystals oriented as before. The following procedure led finally to the desired result. Some of the purified compound was put into a glass tube which was then evacuated and sealed off. This glass tube was held in an oil bath which was heated to the melting-point of the compound, and then allowed to cool slowly. The tube was opened and a small crystal, cut from the crystalline mass, was mounted on a goniometer head and coated with Canada balsam. Oscillation photographs again were employed to align the specimen.

Complete Weissenberg equi-inclination photographic data were obtained with Cu $K\alpha$ radiation from a North American Philips hot-cathode vacuum tube operating at 35 kV. and 18 mA., using nickel foil as a filter.

Crystals of $(H_3C)_3N–BF_3$ are translucent, soft and colorless. A positive test for pyroelectricity was obtained.

The hexagonal unit of structure has

$$a = 9{\cdot}34 \pm 0{\cdot}02, \quad c = 6{\cdot}10 \pm 0{\cdot}02\ \text{A.},$$

but the data are also consistent with a rhombohedral unit of structure having

$$a = 5{\cdot}76\ \text{A.}, \quad \alpha = 108°\ 16'.$$

As the hexagonal unit of structure contains three stoichiometric molecules, the rhombohedral unit contains but one. In terms of rhombohedral indices there

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are no special vanishings. The symmetry of the photographs is that of the point group D_{3}^{d}–$\bar{3}m$, so the possible space groups are $R\bar{3}m$, $R32$, $R3m$, of which the centrosymmetric group is ruled out by the positive test for pyroelectricity. The molecule can hardly possess the twofold axes required by $R32$; thus $R3m$ is uniquely indicated as the space group.

The intensities of all reflections were estimated visually by comparison with a carefully prepared scale having relative intensities of

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 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 for each layer-line photograph taken about each rotation axis. Then, by a technique of cross-calibration, the relative $|F_{HK.L}|^2$ were all based on one reference film. The film chosen for reference was that with $(HK.0)$ reflections. Since the crystal oriented for rotation about the hexagonal c axis was cylindrical and so well aligned with the axis of the glass capillary, the character of the reflections recorded on the films produced by this crystal was especially good for intensity estimation. Wherever possible, the values for $|F_{HK.L}|^2$ were those obtained from these films. It was found that corrections for variation of absorption with $\sin\theta$ could be neglected.

The Patterson function

$$P(0, Y, 0) = \sum_{H}\sum_{K}\sum_{L} |F_{HK.L}|^2 \cos 2\pi KY$$

was evaluated to obtain the approximate x parameters of the carbon and fluorine atoms. If the co-ordinates for atoms occupying the ninefold positions in $R3m$ (see *Internationale Tabellen*) are examined, it will be seen that such atoms should produce peaks at $Y = 3x$ in $P(0, Y, 0)$. A smooth peak occurred at $Y = 0{\cdot}242$ and, aside from the peak at the origin, there were no others. It is therefore clear that the F–F and C–C peaks overlap, and that the absolute values of the carbon and fluorine x parameters must both be near 0·081.

In order to obtain approximate values of the remaining parameters, a sharpened Patterson function

$$P_s(X, 0, Z) = \sum_{h}\sum_{k}\sum_{l} |F_{hkl}|^2 \exp\,[5(\sin\theta/\lambda)^2 \times 10^{-16}] \times \cos 2\pi(hX + lZ)$$

was evaluated, where h, k, l are orthohexagonal indices, used to simplify the calculations. The (010) face of the orthohexagonal cell lies in a plane of symmetry normal to a secondary hexagonal axis. $P(X, 0, Z)$ should give the approximate parameters of all of the atoms (excluding hydrogen) since all lie in the planes of symmetry. $P(X, 0, Z)$ (Fig. 1) shows peaks at $X \doteq 0, Z \doteq 0{\cdot}27$; $X \doteq 0{\cdot}083, Z \doteq 0{\cdot}067$; $X \doteq 0{\cdot}083$, $Z \doteq 0{\cdot}340$; $X \doteq 0{\cdot}172$, $Z \doteq 0{\cdot}400$; $X \doteq 0{\cdot}160$, $Z \doteq 0{\cdot}267$. The first peak could arise only from the B–N vector. The second represents C–N and B–F vectors, and the third B–C and N–F vectors. The fourth peak is associated with an intramolecular C–F vector, and the fifth with the vector between the carbon atom of one molecule and the fluorine atom (in the plane) of the adjacent molecule. Approximate parameters in the orthohexagonal cell as derived from $P(X, 0, Z)$ are given in Table 1.

Table 1. *Approximate orthohexagonal atomic co-ordinates in* $(H_3C)_3N$–BF_3

	x	z
F	−0·081	−0·067
C	0·09	0·34
N	0	0·270
B	0	0·000

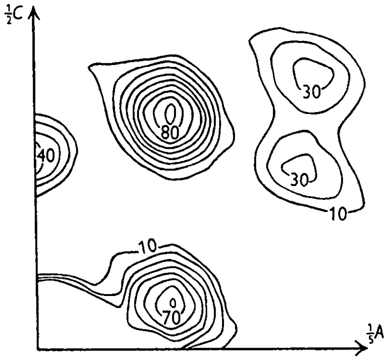

Fig. 1. $P(X, 0, Z)$, Patterson density in the orthohexagonal (010) plane. Contours differ by ten arbitrary units. Zero contour and contours for peak at origin not shown.

Refinement of the parameter data given in Table 1 was carried out in several stages. In the first step the approximate parameters as derived from $P(X, 0, Z)$, together with atomic form factors from the *Internationale Tabellen*, were used to calculate a set of phases for all reflection amplitudes. Following the usual procedure the calculated phases were applied to the observed amplitudes, and the Fourier section $\rho(x, 0, z)$ in orthohexagonal co-ordinates was evaluated with the aid of the Beevers & Lipson (1936) strips. Positions as given by this section were employed to recalculate phases which, for the most part, showed only small changes from the first set. The next stage of refining parameters was carried out by the differential-synthesis method (Booth, 1946). The values thus obtained (orthohexagonal co-ordinates) are presented as 'trial' parameters in Table 3, and may be compared with the data given by $P(X, 0, Z)$ in Table 1.

Two stages of refinement having produced a change of only 0·006 at most in the value of any parameter, it might seem plausible to take the 'trial' parameters, after correction for finite-series termination, as the final values. Further refinement, however, does result in small yet quite significant changes in the phases to be attributed to the final structure. It was decided to carry out further calculations utilizing the 'n-shift' rule as applied by Shoemaker, Donohue, Schomaker & Corey (1950) and by Donohue (1950) to the structures of L-threonine and DL-alanine, respectively.

The formula most convenient for calculation contains both the correction of phases to the final values (by application of the n-shift rule) and, to a sufficient approximation, the correction for finite-series termination. If x_0 represent the true parameter, x_1 that of the 'trial' structure, x_2 and x_3 respectively the parameters obtained from observed and calculated syntheses (both using the phases of the 'trial' structure), then

$$x_0 = x_1 + n(x_2 - x_3),$$

in which $1 \leqslant n \leqslant 2$. With only real amplitudes, $n=1$, and with only complex amplitudes, $n=2$. In trimethylamine–boron trifluoride only 30 reflections of a possible total of 1384 are real, so presumably n is very near 2.

The phases of the 'trial' structure were used to calculate two further differential syntheses using observed (F_o) and calculated (F_c) amplitudes, i.e. to give parameters corresponding to x_2 and x_3. The shifts in peak positions, $x_2 - x_1$, thus obtained are given in columns 3 and 4 of Table 2. As a check on the applicability of the double-shift rule, corrections obtained from the original differential synthesis using observed amplitudes (leading to the 'trial' parameters) are listed in column 2. Were the double-shift rule exactly obeyed, then each shift of parameter in column 5 of Table 2 would be just twice the corresponding shift in column 6 (both values having been corrected for finite-series termination). Where the corrections are still substantial the rule seems to be very roughly obeyed. Failure to get closer agreement is not surprising, since the distribution of atoms within the very simple structure is probably too specialized to satisfy the general conditions under which the rule was derived.

A comparison of the various sets of parameters which are most pertinent to the selection of the final values is given in Table 3. There are included the 'trial' parameters (column 2), the set (column 3) which results from the final differential synthesis of F_o amplitudes without application of the double-shift rule or correction for finite-series termination, the set (column 4) with $n=1$ which corresponds to correction for finite-series termination while assuming that the phases have already converged to their final values, the set (column 5) which corresponds to simultaneous application of the double-shift rule and correction for finite-series termination, and the final values (column 6). Comparison of column 3 and 4 shows that corrections for finite-series termination are quite significant in most cases. Comparison of columns 4 and 5 indicates that, excepting only boron, the additional shifts implied by the double-shift rule are virtually negligible, but it would appear preferable to take the value for $n=1$ in any case for which the shift (corrected for finite series) given by the successive syntheses is oscillating in sign. This last is true of the corrections to z_{F} and z_{N}. The comparison of corrected shifts, 0·056 and 0·034 A. (columns 5 and 6 of Table 2), in the position of boron given by the successive differential syntheses indicates that the true value of the parameter is closer to 0·011 than to 0·006. For 0·056 and 0·068, respectively, taken as 'doubled shifts' one obtains 0·0092 and 0·0111 as the corresponding parameters. The rounded-off mean value, 0·010, is taken as the final parameter for boron.

A comparison of calculated amplitudes containing the isotropic temperature factor

$$\exp\left[-2{\cdot}5(\sin\theta/\lambda)^2 \times 10^{-16}\right]$$

and based on the 'trial' parameters with the observed amplitudes is given in Table 4. Of the reflections too weak to be observed there are only three, (64 . 1), (51 . 2), and (54 . 5), which, on the basis of the calculated ampli-

Table 2. *Corrections obtained from differential syntheses*

(Values in Ångström units)

(1) Parameter corrected	(2) First (F_o)	(3) Second (F_o)	(4) Second (F_c)	(5) First ($F_o - F_c$)	(6) Second ($F_o - F_c$)
z_{B}	0·033	0·011	−0·023	0·056	0·034
z_{N}	0·008	0·024	0·020	−0·012	0·004
x_{F}	0·014	0·003	−0·008	0·022	0·011
z_{F}	0·006	0·000	0·005	0·001	−0·005
x_{C}	−0·013	−0·020	−0·027	0·014	0·007
z_{C}	0·000	−0·007	−0·007	0·007	0·000

Table 3. *Comparison of parameters* (*orthohexagonal co-ordinates*)

(1) Parameter	(2) Trial	(3) F_o	(4) $n=1$	(5) $n=2$	(6) Final
z_{B}	0·000	0·002	0·0055	0·011	0·010
z_{N}	0·269	0·273	0·270	0·270	0·270
x_{F}	−0·081	−0·081	−0·080	−0·080	−0·080
z_{F}	−0·072	−0·072	−0·073	−0·074	−0·073
x_{C}	0·089	0·088	0·090	0·090	0·090
z_{C}	0·334	0·333	0·334	0·334	0·334

tudes, should have been observed. In the worst case, (54.5), the calculated value is about three times the observable minimum.

When we exclude those unobserved reflections which are also calculated as too weak to be observed, the reliability index for the data of Table 4 is 0·23. This is approximately equal to the values obtained for the centrosymmetric structures of H_3N–BF_3 (Hoard, Geller

Table 4. *Comparison of calculated with observed reflection amplitudes*

HK.L	$\lvert F_c \rvert$	$\lvert F_o \rvert$	α (°)
03.0	14·3	12·9	230
06.0	6·9	12·0	241
09.0	4·5	0	83
11.0	60·4	64·8	0
14.0	14·9	10·1	254
17.0	4·2	9·2	116
22.0	7·2	16·6	180
25.0	19·6	20·7	352
28.0	2·6	0	100
33.0	26·4	22·1	0
36.0	12·0	12·0	14
44.0	34·6	24·4	0
47.0	0·8	0	180
55.0	9·7	6·5	0
66.0	0·4	0	0
01.1	36·5	36·8	32
04.1	44·2	39·2	219
07.1	17·6	13·8	57
0,10,.,1	6·9	3·7	77
12.1	16·8	13·8	229
15.1	5·4	6·1	205
18.1	12·7	6·5	68
20.1	45·7	41·0	43
23.1	10·4	11·1	186
26.1	12·0	13·8	41
29.1	2·4	2·3	175
31.1	41·5	41·0	68
34.1	11·7	12·9	32
37.1	3·3	0	237
42.1	20·1	20·7	61
45.1	9·0	6·5	7
50.1	29·5	33·6	73
53.1	10·6	9·2	19
56.1	1·2	0	246
61.1	5·8	0	208
64.1	9·3	0	26
72.1	2·3	0	259
80.1	16·0	9·2	222
83.1	9·7	4·6	57
91.1	2·4	4·6	164
02.2	24·3	23·7	269
05.2	14·2	13·8	188
08.2	15·8	9·2	89
10.2	51·4	47·4	280
13.2	16·4	16·5	192
16.2	8·5	6·4	110
19.2	2·2	0	261
21.2	17·8	21·6	91
24.2	13·7	11·1	247
27.2	5·1	0	66
32.2	11·3	18·4	104
35.2	13·6	11·1	286
38.2	0·6	0	239
40.2	41·3	36·4	88
43.2	19·4	14·3	281
46.2	6·0	0	242
51.2	8·8	0	75
54.2	11·0	9·2	287
62.2	6·9	9·2	268
65.2	3·4	4·6	87
70.2	2·6	6·4	207
73.2	5·2	4·6	104
81.2	4·8	0	192
10,0,.,2	5·5	2·9	237
00.3	65·9	51·0	304
03.3	23·0	20·3	155
06.3	2·0	7·8	237
09.3	7·3	4·6	0
11.3	25·0	29·0	305
14.3	16·2	12·9	155
17.3	7·6	7·8	339
22.3	3·3	6·4	100
25.3	12·0	14·2	311
28.3	2·2	0	66
30.3	18·4	15·2	348
33.3	13·9	14·3	328
36.3	6·9	6·4	314
41.3	15·6	19·3	358
44.3	21·0	15·2	312
52.3	11·2	15·2	325
55.3	6·7	4·6	301
60.3	4·9	12·9	84
63.3	8·6	6·5	299
71.3	8·5	6·5	151
82.3	1·2	0	114
90.3	3·5	0	151
01.4	9·0	14·3	253
04.4	12·4	6·5	153
07.4	17·4	11·1	13
12.4	2·6	4·6	54
15.4	4·2	7·8	71
18.4	11·8	7·8	13
20.4	18·2	18·0	0
23.4	4·8	11·1	87
26.4	7·5	9·2	4
31.4	30·4	29·0	13
34.4	1·7	0	214
37.4	1·2	0	259
42.4	10·1	13·8	13
45.4	3·4	0	264
50.4	23·9	23·0	12
53.4	2·0	0	247
61.4	0·7	6·5	60
64.4	6·4	4·6	352
72.4	1·7	0	26
80.4	5·2	4·6	159
02.5	2·7	6·5	151
05.5	12·5	14·3	80
08.5	6·0	1·8	42
10.5	18·5	20·7	231
13.5	13·8	16·5	71
16.5	4·4	4·6	75
21.5	7·5	11·1	51
24.5	3·0	6·5	164
32.5	5·1	11·1	45
35.5	10·2	4·6	233
40.5	12·1	12·0	39
43.5	10·3	6·5	235
51.5	5·3	0	24
54.5	6·3	0	229
62.5	1·3	0	170
70.5	8·1	4·6	58
00.6	8·0	9·2	246
03.6	12·0	11·1	107
06.6	0·9	0	284
11.6	4·4	6·5	240
14.6	9·5	7·8	100
22.6	0·9	0	343
25.6	0·5	0	333
30.6	12·3	11·1	284
33.6	2·6	4·6	298
41.6	10·5	11·1	294
52.6	1·7	0	277
60.6	1·1	4·6	355
01.7	6·0	6·4	156
04.7	4·2	6·4	5
12.7	3·9	6·4	338
20.7	3·8	4·6	323
23.7	3·6	4·6	0
31.7	11·3	12·0	327

& Cashin, 1951) and H_3CN_2H–BF_3 (Geller & Hoard, 1950).

In at least two cases, monomethylamine–boron trifluoride and trimethylamine–boron trifluoride, it seems rather certain that the disappointingly high values of the reliability index are not primarily a consequence of inadequate estimation and cross-calibration of the experimental intensities. These operations were carried out with the greatest care at every stage of the work. It appears rather that the assumption of spherically symmetric atomic form factors (including temperature factor) is not good. The data of Table 4 show outstanding discrepancies between calculated and observed amplitudes even for the particularly simple and experimentally reliable $(HK.0)$ reflections. Especially notable is (22.0) with a real structure factor, the calculated value being less than half that observed. The correct ranges within narrow limits for the x parameters of carbon and fluorine were considered in trial-and-error calculations at the outset of the analysis, and it was the impossibility of achieving really satisfactory agreement for $(HH.0)$ reflections which prompted the use of the straightforward Patterson analysis which otherwise would have been quite unnecessary.

Inadequacy of the model based on spherically symmetric atom distributions, at least in principle, is more serious for non-centrosymmetric than for centrosymmetric structures. For the latter, provided Fourier analysis be used, the model need only be good enough to give correct signs to the experimental amplitudes. But in the non-centrosymmetric case the model is inextricably involved in the determination of the detailed phases to be assigned to the experimental amplitudes. Even though the phases thus determined represent a unique set resulting from a convergent process they are not necessarily a good approximation to the real set unless the real structure is adequately represented by the model, i.e. in the usual case, by a superposition of spherically symmetric atom distributions.

Cruickshank's (1949, 1950) treatment of the accuracy of electron-density maps gives the estimated standard deviation of atomic co-ordinates in a non-centrosymmetric structure twice the value which an otherwise comparable centrosymmetric structure would have, the difference arising from the fact that the phases are considered as certain in the latter case but as subject to random errors in the non-centrosymmetric structure. The differences, $F_o - F_c$, are taken as a measure of the random errors associated with the amplitudes of reflection. We believe that Cruickshank's treatment would overestimate the uncertainties in the atomic coordinates for the centrosymmetric structures studied in this series, since it seems that the F_o's should give a considerably more reliable representation of the structure than would the F_c values. But we feel that it would be unsafe to assume that Cruickshank's method overestimates the uncertainties in trimethylamine–boron trifluoride, since the final phases are dependent on the probably inadequate model. Additional grounds supporting this conclusion will be discussed later.

We have not carried out detailed calculations of the standard deviations in atomic positions or in bond distances by Cruickshank's method, but if we take on the average a value 50 % larger than that found for dibenzyl (representing rough proportionality with the value of the reliability index), then we estimate for the average standard deviation in any bond length about 0·015 A. for H_3N–BF_3 and H_3CH_2N–BF_3, and, of course, 0·03 A. for $(H_3C)_3N$–BF_3. The internal consistency within the series and the correlation of the structural data with the thermodynamic stabilities of the compounds (presented in the succeeding paper) indicates that the foregoing estimates are conservatively large.

With N atoms, all of the same kind and randomly distributed within a primitive cell, Hughes (1949) and Wilson (1949) find $1/\sqrt{N}$ for the root-mean-square value of the unitary structure factor for reflections (hkl). In comparing two otherwise similar structures of quite different N it is our intuitive feeling that larger corrections for finite-series termination should be expected for the structure having the smaller number of atoms; for in this case not only is the average value of the unitary structure factor larger but the fraction of amplitudes beyond cut-off showing a significant departure from the average is also larger.

A comparison between trimethylamine–boron trifluoride and ammonia–boron trifluoride, this latter crystallizing in an eight-molecule orthorhombic unit of space group *Pbca*, is of interest in this connection. Corrections (in Ångström units) indicated by differential syntheses of calculated amplitudes are:

$(H_3C)_3N$–BF_3: B, 0·023; C, 0·028; N, 0·020; F, 0·009.
H_3N–BF_3: B, 0·008; N, 0·011; F (av.), 0·015.

These limited data indicate that there may be a rather small yet significant dependence of the average correction to an atomic position on the number of atoms in the primitive unit.

The effects on calculated corrections to *bond distances* of departures from a random distribution of atoms within the unit cell seem to be rather more important. The approximation to a random distribution of atoms in trimethylamine–boron trifluoride is poor, but apparently is good in ammonia–boron trifluoride. This latter appears to be achieved through a combination of no required symmetry for the arbitrary grouping of any atom and its immediate neighbors together with a dense packing of molecules. At any rate the approximate symmetry of the molecule of H_3N–BF_3, is not effective in determining the directions of the corrections to atomic positions. No bond length is altered by more than 0·010 A., the average absolute value of the correction to a bond length is only 0·005 A., and the overall size of the molecule is not appreciably altered.

In trimethylamine–boron trifluoride, on the other hand, the correction to the B–N bond is 0·043 A. In consequence of the large effect of rippling the Patterson section $P(X, 0, Z)$ gives a high value for the B–N separation, and the rate of convergence in the cyclic approximation process of assigning complex phases is slow. Use of the n-shift rule from the outset should obviate this difficulty.

Corrections for finite-series termination also have been calculated for a majority of the atoms in methyl cyanide–boron trifluoride (four molecules in the primitive orthorhombic unit, *Pnma* (Hoard *et al.* 1950) and in monomethylamine–boron trifluoride (two molecules in the primitive monoclinic unit, $P2_1/m$). In both cases the average correction to an atomic position lies between the average values for $\mathrm{(H_3C)_3N{-}BF_3}$ and $\mathrm{H_3N{-}BF_3}$, but is closer to that of the latter compound. Presumably in consequence of the effectively greater symmetry of $\mathrm{H_3CCN{-}BF_3}$, the corrections to atomic positions have a slightly greater effect on bond distances for this molecule. However, no correction alters a bond distance by more than 0·025 A. in either compound.

Since the B–N bond length is of primary interest in this series, we list the values finally obtained (to the nearest 0·005 A.) together with the values (in parentheses) uncorrected for finite series termination:

$\mathrm{H_3NBF_3}$: 1·60 A. (1·61)
$\mathrm{(H_3C)_3N{-}BF_3}$: 1·585 A. (1·63)
$\mathrm{H_3CH_2N{-}BF_3}$: 1·565 A. (1·58)
$\mathrm{H_3CCN{-}BF_3}$: 1·635 A. (1·64)

Omission of the finite series correction for $\mathrm{(H_3C)_3N{-}BF_3}$ would place it structurally with the very unstable $\mathrm{H_3CCN{-}BF_3}$ rather than with the quite stable $\mathrm{H_3CH_2N{-}BF_3}$, which latter it closely resembles.

Were it feasible to make correction for finite-series termination with complete confidence in the results, then the preceding considerations would indicate the special urgency of making such corrections only for any structure of particularly small unit cell or of poor approximation to a random distribution of atoms. But one may question the accuracy of a large correction based on an inadequate model as indicated, for instance, by an unsatisfactory value of the reliability index.

Discussion of the structure

Interatomic distances and angles within the molecule, as calculated from the final parameter data of Table 3, are given in Table 5.

Table 5. *Interatomic distances and angles within the molecule of* $\mathrm{(H_3C)_3N{-}BF_3}$

B–N	1·585 A.	C–B	2·45 A.
B–F	1·39	∠F–B–F	107°
C–N	1·50	∠N–B–F	112
F–F	2·24	∠C–N–C	114
N–F	2·46	∠C–N–B	105

The detailed comparison of these data with the results obtained for other compounds studied in this series will be reserved for the succeeding paper (in which corrections for finite series termination will be applied to the already published data for $\mathrm{H_3CH_2N{-}BF_3}$ and $\mathrm{H_3CCN{-}BF_3}$). It may be remarked, however, that whereas the bond distances in $\mathrm{(H_3C)_3N{-}BF_3}$ are in good agreement with those found in the comparably stable compounds, $\mathrm{H_3N{-}BF_3}$ and $\mathrm{H_3CH_2N{-}BF_3}$, there are notable variations in interbond angles. It would seem that mutual repulsive forces operative between the methyl groups are responsible for the rather large C–N–C angle of 114° and the correspondingly small C–N–B angle of 105°. Brockway & Jenkins (1936), in their electron-diffraction study of free trimethylamine, obtained 1·47 ± 0·02 A. for the C–N bond distance and 108 ± 4° for the angle C–N–C.

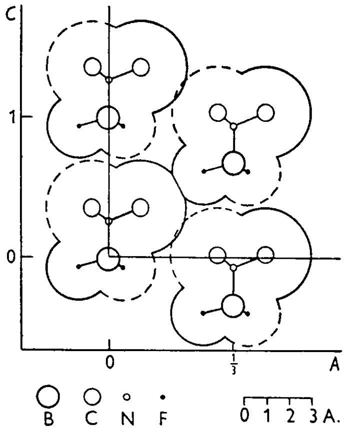

Fig. 2. Packing arrangement in the orthohexagonal (010) plane. Broken lines indicate pairs of fluorine atoms or of methyl groups not lying in the plane.

There are two possible orientations for the methyl groups within the molecule consistent with symmetry: the plane passing through six hydrogen atoms and normal to the threefold axis may lie either away from or toward the center of gravity. In the first orientation the distance between hydrogen atoms attached to adjacent carbon atoms is calculated to be approximately 1·8 A., 0·4 A. less than the normal van der Waals separation. In the second orientation the corresponding distance is approximately 2·5 A., and, moreover, the remaining hydrogen atoms of the molecule are well placed with respect to fluorine atoms of neighboring molecules. Parameters based on the latter orientation were used to calculate contributions of hydrogen for reflection amplitudes having $\sin\theta/\lambda \leqslant 0{\cdot}30$. It was found that agreement between calculated and observed amplitudes was improved for (01.1) and (22.0), was made less satisfactory for (00.3), and was not significantly affected for other reflections.

The packing arrangement of molecules in a plane of symmetry normal to a secondary hexagonal axis (i.e. in the (010) face of the orthohexagonal cell) is shown in Fig. 2. Envelopes of molecules have been drawn with the use of conventional van der Waals radii. The closest approach between carbon and fluorine atoms of adjacent molecules within the structure occurs in the symmetry plane, and there is indication of extremely weak hydrogen bonding. This distance of closest approach is 3·1 A., about 0·25 A. less than the sum of the van der Waals radii for fluorine and methyl.

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Structures of Molecular Addition Compounds. V. Comparison of Four Related Structures.

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As a preliminary to presenting detailed comparisons of the structural results obtained for four related compounds of formula H_3CH_2N–BF_3, H_3CCN–BF_3, H_3N–BF_3 and $(H_3C)_3N$–BF_3, corrections to atomic positions arising from finite termination of Fourier series are made to the published data for the two compounds first listed. It is then shown that the structural data form a self-consistent pattern which correlates well with the limited available information on the relative stabilities of the addition compounds. The quite unstable methyl cyanide–boron trifluoride molecule contains significantly longer B–N and shorter B–F bond distances than the values characterizing the three relatively stable amine-boron trifluorides. The shortest B–N distance observed, 1·57 A., is 0·07 A. larger than the value predicted by the Schomaker & Stevenson rule.

Introduction

The four structures to be compared are those of the compounds monomethylamine–boron trifluoride, H_3CH_2N–BF_3 (Geller & Hoard, 1950), methyl cyanide–boron trifluoride, H_3CCN–BF_3 (Hoard, Owen, Buzzell & Salmon, 1950), ammonia–boron trifluoride, H_3N–BF_3 (Hoard, Geller & Cashin, 1951), and trimethylamine–boron trifluoride, $(H_3C)_3N$–BF_3 (Geller & Hoard, 1951). The two papers of the series first published did not contain corrections for finite termination of series. As such corrections are of prime importance for $(H_3C)_3N$–BF_3, we have deemed it advisable to compute them for H_3CH_2N–BF_3 and H_3CCN–BF_3, in order to make our comparisons of structural data as meaningful as possible.

H_3CH_2N–BF_3 crystallizes in a two-molecule monoclinic unit of space group $P2_1/m$. Four of the six (excluding hydrogen) atoms of the molecule lie in a symmetry plane, and corrections for finite series termination for these atoms were derived from the section of a three-dimensional Fourier synthesis in this plane using amplitudes calculated from the positions given by the final syntheses of observed data. H_3CCN–BF_3 crystallizes in a four-molecule orthorhombic unit of space group *Pnma*. Five of the seven (excluding hydrogen) atoms of the molecule lie in a mirror plane, and corrections for these atoms were obtained from differential syntheses of calculated amplitudes. Parameter data (rounded off to the nearest 0·001) for these structures are given in Table 1; the values in parentheses are those already published without corrections.

Limitations of time have not permitted us to calculate the complete finite series corrections for fluorine

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