

Structures of Molecular Addition Compounds.

III. Ammonia-Boron Trifluoride, $\text{H}_3\text{N}-\text{BF}_3$

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X-ray diffraction data from single crystals of ammonia-boron trifluoride lead to an eight-molecule orthorhombic unit with $a = 8.22$, $b = 8.11$, $c = 9.31$ Å. and the space group $Pbca$. The approximate structure, derived with the aid of numerous Patterson syntheses, was confirmed by three pinacoidal Fourier projections. Further refinement of parameters, including corrections for finite-series termination, was achieved by means of three-dimensional differential syntheses. Finite-series corrections to bond distances are almost negligible.

Averaged bond distances and angles are as follows: B-N, 1.60; B-F, 1.38 Å.; $\angle \text{N-B-F}$, 107° ; $\angle \text{F-B-F}$, 111° . These data are closely similar to the corresponding values for monomethylamine-boron trifluoride (Geller & Hoard, 1950). The low volatility of $\text{H}_3\text{N}-\text{BF}_3$ is correlated with electrostatic interactions, i.e. generally unlocalized hydrogen bonding between molecules.

Introduction

The considerable interest which attaches to the structures of the amine-boron trifluoride series of molecular addition compounds was adequately discussed in the paper dealing with monomethylamine-boron trifluoride (Geller & Hoard, 1950). The investigation to be described shows that the structure of ammonia-boron trifluoride, $\text{H}_3\text{N}-\text{BF}_3$, fits into a consistent pattern with the results obtained for the related compounds $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$, $(\text{H}_3\text{C})_3\text{N}-\text{BF}_3$ (Geller & Hoard, 1951), and $\text{H}_3\text{CCN}-\text{BF}_3$ (Hoard, Owen, Buzzell & Salmon, 1950). The length of the boron-nitrogen bond in the thermodynamically rather stable amine-boron trifluoride series of compounds is significantly less than in the quite unstable methyl cyanide-boron trifluoride. In all cases, however, the B-N separation is at least 0.07 Å. greater than the sum of the covalent radii corrected for partial ionic character (Schomaker & Stevenson, 1941).

Determination of structure

The ammonia-boron trifluoride used in our study was prepared as described by Laubengayer & Condikey (1948), and was recrystallized from aqueous solution. Specimens were made cylindrical by rolling on a ground-glass plate, and were aligned by means of oscillation photographs using the Hendershot (1937) correction technique. Complete sets of equi-inclination Weissenberg photographs were obtained about each of the three principal axes of the orthorhombic crystal, using $\text{Cu } K\alpha$ radiation filtered through nickel foil.

The symmetry of the X-ray photographs is that of $D_{2h}-mmm$ and reflections of the type $(hk0)$, h odd; $(h0l)$, l odd; and $(0kl)$, k odd are absent. The space group

thus uniquely indicated is $D_{2h}^{15}-Pbca$. The orthorhombic unit cell has

$$a = 8.22 \pm 0.03, \quad b = 8.11 \pm 0.03, \quad c = 9.31 \pm 0.03 \text{ Å.},$$

and contains eight stoichiometric molecules.

Relative intensities of all reflections were estimated visually. Lorentz, polarization, and Tunnell corrections were applied to obtain relative $|F|^2$ for each film. All data were then placed on the same basis by careful cross-calibration. The value of the linear absorption coefficient for $\text{Cu } K\alpha$ in $\text{H}_3\text{N}-\text{BF}_3$ is 24.8 cm.^{-1} . As the thickness of all three specimens (cylindrical along the crystal axes) was 0.5 mm., it was unnecessary to make correction for variations in absorption with angle.

Numerous Patterson projections and sections were used in conjunction with packing considerations to give the approximate structure. The parameters thus obtained were used to assign phases to all prism reflections, and the three pinacoidal Fourier projections were constructed. These projections confirmed the approximate structure with only small changes in parameters and provided a basis for further refinement.

As all atoms in the unit cell occupy general positions the differential synthesis method for refinement of parameters (Booth, 1946) is particularly suitable. Because computational errors so easily creep into the differential syntheses we found it desirable to carry out two successive (three-dimensional) syntheses and to compare the two term by term. We feel assured that the final synthesis of observed amplitudes is virtually free of computational error.

Table 1 lists parameter data as obtained at three stages of the investigation. The columns headed P contain values as given by the three pinacoidal projections; under FO are listed values obtained from the final differential synthesis of observed amplitudes; and under Fin are given the final parameter data after

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Table 1. *Parameter data for H₃N-BF₃*

Atom	<i>x</i>			<i>y</i>			<i>z</i>		
	<i>P</i>	<i>FO</i>	<i>Fin</i>	<i>P</i>	<i>FO</i>	<i>Fin</i>	<i>P</i>	<i>FO</i>	<i>Fin</i>
F _I	0.077	0.078	0.078	-0.042	-0.040	-0.040	0.168	0.168	0.167
F _{II}	0.304	0.305	0.305	0.093	0.093	0.094	0.092	0.092	0.093
F _{III}	0.188	0.191	0.188	0.158	0.155	0.156	0.307	0.307	0.308
N	0.048	0.046	0.046	0.238	0.242	0.241	0.095	0.095	0.095
B	0.157	0.160	0.160	0.108	0.104	0.105	0.166	0.168	0.169

correction (as described below) for finite series termination.

On the whole the positions of fluorine atoms are given with fair accuracy by the Fourier projections. Subsequent corrections to the positions of nitrogen and especially boron are considerably larger. Corrections for finite-series termination, however, actually are largest for fluorine.

A comparison of some 650 calculated and observed amplitudes of reflection gave a reliability index

$$R \equiv \Sigma ||F_o| - |F_c|| \div \Sigma |F_o| = 0.24.*$$

Calculated amplitudes include an isotropic temperature factor having $B = 1.4 \times 10^{-16} \text{ cm.}^2$. To put observed amplitudes on an absolute basis it was found necessary to multiply the original relative values by the scale factor 3.7. Numerical values for B and for the scale factor were obtained from the straight line (fitted by least squares) best representing the data on a plot of $\log K |F_o/F_c|$ against $(\sin \theta/\lambda)^2$. All observed data, excepting only a few quite erratic values, were employed. Atomic form factors from the *International Tables* were used. In computing R only those unobserved reflections were excluded which have calculated amplitudes below the limit of observation on our photographs. As $R = 0.24$ is about as good a value as we have been able to obtain for any of the compounds studied in this series, we again are led to the conclusion that the model constructed by superposition of spherically symmetric atomic distributions (including temperature factor) is rather inadequate as a representation of the real structure.

A differential synthesis of calculated amplitudes, based on the same parameter values as used for the final synthesis of observed amplitudes, was made as a basis for correction for finite-series termination. The differences, $\epsilon_o - \epsilon_c$, in the shift indicated, respectively, by the differential syntheses of observed and calculated amplitudes gives the corrections to be applied to the parameters (used in calculating the syntheses) to obtain the final values. The same result to a sufficient approximation is obtained by applying the correction, $-\epsilon_c$, directly to the parameter (*FO*) given by the final differential synthesis of observed amplitudes.

* *Editorial note.* A full list of the observed and calculated intensities was submitted to the Editors and has been deposited, with the author's agreement, at the American Documentation Institute, 1719 N Street, Northwest, Washington 6, D.C., U.S.A., under reference 3218. It can be obtained from there in microfilm or in photocopy at a charge of \$1.00.

The magnitudes in Ångström units of ϵ_c for the various atoms are as follows: B, 0.0075; N, 0.011; F_I, 0.014; F_{II}, 0.010; F_{III}, 0.021; F (average), 0.015.

Despite the fact that the average correction to an atomic position is 0.013 Å., the apparent size of the molecule is almost unaffected. One B-F bond length is increased by 0.01 Å., the two others are unchanged (<0.005 Å.), and the B-N separation actually is decreased by 0.01 Å. This is in contrast with Cruickshank's (1949) results for dibenzyl, in which case the finite-series corrections produce an appreciable expansion in the apparent dimensions of the molecule.

There are forty atoms (excluding hydrogen) occupying general positions within H₃N-BF₃, the cell contains no true axes or planes of symmetry, and (as pointed out later) the molecules are rather densely packed as a result of extensive electrostatic interactions. The corrections for finite series termination tend to be random in direction and quite unpredictable on the basis of the approximate molecular symmetry.

Discussion of the structure

Table 2 contains dimensional data for the molecule of H₃N-BF₃, calculated from the final corrected parameters of Table 1.

Table 2. *Molecular dimensions of H₃N-BF₃*

B-N:	1.60 Å.	N-F _{II} :	2.44 Å.
B-F _I :	1.36	N-F _{III} :	2.40
B-F _{II} :	1.39	$\angle F_I-B-N$:	106°
B-F _{III} :	1.38	$\angle F_{II}-B-N$:	109
F _I -F _{II} :	2.26	$\angle F_{III}-B-N$:	107
F _{II} -F _{III} :	2.28	$\angle F_I-B-F_{II}$:	111
F _I -F _{III} :	2.26	$\angle F_{II}-B-F_{III}$:	111
N-F _I :	2.37	$\angle F_I-B-F_{III}$:	111

A list of distances between a nitrogen atom (x, y, z) and neighboring fluorine atoms in adjacent molecules is given in Table 3. Included also are the angles between the line joining boron and nitrogen atoms of the same molecule and the lines joining this nitrogen to the fluorine atoms of neighboring molecules.

Table 3. *Data pertaining to hydrogen bonding in H₃N-BF₃*

N-F _I ($\bar{x}, \bar{y}, \bar{z}$)	= 3.10 Å.	$\angle B-N-F_I$	= 100°
N-F _I ($\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$)	= 3.02 Å.	$\angle B-N-F_I$	= 107°
N-F _{II} ($\frac{1}{2} - x, \frac{1}{2} + y, z$)	= 3.11 Å.	$\angle B-N-F_{II}$	= 112°
N-F _{II} ($x - \frac{1}{2}, \frac{1}{2} - y, \bar{z}$)	= 2.98 Å.	$\angle B-N-F_{II}$	= 163°
N-F _{III} ($x, \frac{1}{2} - y, z - \frac{1}{2}$)	= 3.03 Å.	$\angle B-N-F_{III}$	= 110°
N-F _{III} ($x - \frac{1}{2}, y, \frac{1}{2} - z$)	= 3.15 Å.	$\angle B-N-F_{III}$	= 106°

The data of Table 3 indicate that strong localized hydrogen bonds are not formed in ammonia-boron

trifluoride. If, however, a staggered configuration of the hydrogen atoms with respect to fluorine be assumed (as is indicated by analogy with $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ and $(\text{H}_3\text{C})_3\text{N}-\text{BF}_3$), together with an N-H bond distance of 1.02 Å. and a B-N-H bond angle of about 107° , then hydrogen atoms would occupy the approximate positions

H_I	0.11	0.35	0.10
H_{II}	-0.06	0.25	0.15
H_{III}	0.025	0.20	-0.01

Inclusion in the calculated amplitudes for $\sin \theta/\lambda < 0.30$ of hydrogen contributions based on these values seems in general to improve slightly the agreement with observed amplitudes.

The assumed position for one hydrogen atom, H_I , places it very nearly on the line connecting the nitrogen with a fluorine atom, F_{II} ($\frac{1}{2} - x, \frac{1}{2} + y, z$), with H-F = 2.1 Å. This represents the nearest approximation to a localized hydrogen bond, but there are four other H-F distances which are 0.15–0.4 Å. less than the sum of the van der Waals radii, 2.55 Å. Several other H-F separations range from 2.6 to 3.0 Å., and there would appear to be sufficient electrostatic energy to account for the involatile character of the crystalline material.

A minimum value of 3.0 Å. is obtained for F-F contacts between molecules.

Calculations of the standard deviations of the bond lengths within a molecule, following Cruickshank (1949), have not been carried out. By comparison with Cruickshank's treatment of dibenzyl, and allowing for the difference in the reliability coefficients, we conclude that a value of about 0.015 Å. should represent a fair estimate on the average of the standard deviation in any bond length in $\text{H}_3\text{N}-\text{BF}_3$. On this basis the indicated variations, 1.36–1.39 Å., in the B-F bond distances are of doubtful significance. The range of values for the N-F separation within a molecule is larger, 2.37–

2.44 Å., and it seems quite probable that there are real variations in consequence of the rather close packing of the structure and the strong but unsymmetrical electrostatic interactions.

The structural data for the molecule, $\text{H}_3\text{N}-\text{BF}_3$, fit into a consistent pattern with the results obtained for the three other related compounds which have been studied. It seems more satisfactory, however, to present the detailed comparisons in a separate communication (V in this series) in which corrections for finite series termination to the already published structural data for two compounds, $\text{H}_3\text{CH}_2\text{N}-\text{BF}_3$ and $\text{H}_3\text{CCN}-\text{BF}_3$, also will be incorporated.

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