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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The final stages of refining the structure were carried out during the period, 1949–50, in which Seymour Geller was duPont Post-Doctorate Fellow in Chemistry.

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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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Table 1. *Parameter data for* H_3CH_2N–BF_3 *and* H_3CCN–BF_3

H_3CCN–BF_3			H_3CH_2N–BF_3		
Atom	x	z	Atom	x	z
F	0·270 (0·270)	0·473 (0·471)	F	0·172 (0·172)	−0·193 (−0·190)
B	0·392 (0·391)	0·358 (0·359)	B	0·131 (0·134)	0·051 (0·050)
N	0·571 (0·573)	0·461 (0·460)	N	−0·180 (−0·180)	0·152 (0·152)
C_{CN}	0·696 (0·698)	0·529 (0·530)	C	−0·254 (−0·252)	0·416 (0·415)
C_{CH_3}	0·859 (0·860)	0·616 (0·615)			

Table 2. *Comparison of molecular configurations of four related compounds*

	H_3N–BF_3	H_3CH_2N–BF_3	$(H_3C)_3N$–BF_3	H_3CCN–BF_3
N–B	1·60 A.	1·57 A.	1·585 A.	1·635 A.
B–F	1·38	(1·39)	1·39	(1·33)
F–F	2·27	(2·27)	2·24	(2·23)
N–F	2·40	(2·40)	2·46	(2·34)
N–C_{CH_3}	—	1·50	1·50	—
∠F–B–F	111°	(110·5°)	107°	(114°)
∠F–B–N	107	(108·5)	112	(103)
∠B–N–C	—	114	105	—
∠C–N–C	—	—	114	—
∠C–N–B	—	114	105	—

atoms in the general positions of H_3CCN–BF_3 and H_3CH_2N–BF_3. Since, however, the y component of the B–F separation is considerably larger than the component parallel to the symmetry plane, presumably it is primarily important to compute corrections to the y co-ordinates of fluorine. Such corrections were obtained from the line syntheses

$$\rho(0{\cdot}398, y, 0{\cdot}273) \quad \text{and} \quad \rho(-0{\cdot}244, y, 0{\cdot}129)$$

of calculated amplitudes for, respectively, H_3CCN–BF_3 and H_3CH_2N–BF_3. The corrected y parameters (to the nearest 0·001) are 0·096 (instead of 0·097) in H_3CCN–BF_3 and 0·094 (instead of 0·095) in H_3CH_2N–BF_3. The B–F separation is thereby increased by 0·010 A. in the first compound and 0·007 A. in the second.

To produce an additional change in the B–F distance of as much as 0·010 A. the uncomputed corrections to the x and z parameters of fluorine would need to give a properly oriented shift of magnitude approximately as large as the maximum total correction found for any fluorine atom of the four compounds studied. Thus the averaged B–F separations in H_3CCN–BF_3 and H_3CH_2N–BF_3 each should be correct to better than 0·010 A. in so far as finite-series corrections are concerned.

Interatomic distances and interbond angles within the molecule are compared for the four structures in Table 2. Wherever chemically identical atoms are not required to be structurally equivalent the corresponding distances or angles represent averaged values. Values in parentheses depend in varying degree on the positions of those fluorine atoms for which finite-series corrections were made only in part.

By comparison with Cruickshank's (1949, 1950) treatment of dibenzyl we estimate (assuming rough proportionality with the reliability index) the following values for the standard deviation in any bond length: 0·015 A. for H_3N–BF_3 and H_3CH_2N–BF_3, 0·02 A. for H_3CCN–BF_3, and 0·03 A. for the non-centrosymmetric $(H_3C)_3N$–BF_3. There is convincing internal evidence that the model of spherically symmetrical atomic distributions is rather inadequate as a representation of any of the structures. Hence the use of calculated amplitudes as quantitative criteria of accuracy is questionable, and we believe the estimated standard deviations to be conservatively large for the three centrosymmetric structures (except perhaps where corrections for finite series termination were incomplete).

Existing data bearing on the relative stabilities of these compounds are rather incomplete but in a general way correlate with our structural data. All three amine compounds are stable in aqueous solution, and H_3N–BF_3 in solution has been shown to be inappreciably dissociated (Laubengayer & Condike, 1948). Above 125° C. solid H_3N–BF_3 undergoes disproportionation to give the very stable substances, boron nitride and ammonium fluoroborate. The irreversible vapor pressure *v.* temperature curves of H_3CH_2N–BF_3 have been interpreted (Nichols, 1947) as implying the onset of a disproportionation reaction at 260° C., but products were not identified. The vapor density of $(H_3C)_3N$–BF_3 at 230° C. corresponds to just the theoretical formula without dissociation (Burg & Green, 1943); at lower temperatures the density corresponds to a varying degree of association of $(H_3C)_3N$–BF_3 molecules. The data appear to be too limited to ensure that the interpretation is unique with any considerable probability. Thus it is certain that the thermal stability of H_3N–BF_3 is less than that of the substituted amine–boron trifluorides but, as few of the data bear on the dissociation reaction involving the breaking only of the B–N bond, no real criteria of the relative strength of this bond in the three compounds are evident.

The strength of the B–N bond in H_3CCN–BF_3, however, certainly is much less than in the amine–boron trifluorides. The vapor of H_3CCN–BF_3 is virtually completely dissociated at 50° C. (Laubengayer & Sears, 1945). The compound, moreover, immediately hydrolyzes when brought into contact with water vapor.

Some quantitative data also are available at 0° C. for the reaction, $AB(s)=A+B$, in which $AB(s)$ represents the solid addition compound, A and B the gaseous component molecules. The ΔH values for this reaction are: H_3CCN–BF_3, 26,500 cal.; H_3N–BF_3, 42,000 cal.; H_3CH_2N–BF_3, 42,700 cal. With approximately the same allowance for vaporization of the solid to give undissociated vapor, the residual ΔH of disrupting the B–N bond would be much smaller for H_3CCN–BF_3. One might expect the considerable hydrogen bonding in H_3N–BF_3 to make the ΔH of vaporization of this compound appreciably larger than for H_3CH_2N–BF_3, which would mean a smaller ΔH of dissociation for H_3N–BF_3 and imply a weaker B–N bond.

The similarity in the B–N and B–F bond distances for the three amine-boron trifluorides is quite striking. The maximum difference of 0·03 A. in the B–N separation as between H_3N–BF_3 and H_3CH_2N–BF_3 is not highly significant in terms of the estimated standard deviations, yet some such difference perhaps is implied by the sketchy thermodynamic data. It is to be noted that a distance of 1·50 A. is obtained for the C–N bond in both of the two substituted amine-boron trifluorides, and that this figure represents almost exactly the average value obtained for this type of bond in several recent accurate determinations.

Interbond angles in H_3N–BF_3 and H_3CH_2N–BF_3 are closely similar. The large C–N–C angle (114°) in $(H_3C)_3N$–BF_3 presumably is a result of mutual repulsion of the methyl groups attached to nitrogen, and naturally produces a smaller C–N–B angle (105°) than is found in H_3CH_2N–BF_3 (114°). The F–B–F and F–B–N angles in $(H_3C)_3N$–BF_3 also are found to be somewhat different from those in H_3N–BF_3 and H_3CH_2N–BF_3. Whether this is solely a consequence of different packing relations is not clear.

The difference between the average value, 1·585 A., of the B–N distance in the three amine–boron trifluorides and that, 1·635 A., in H_3CCN–BF_3 clearly is significant, and correlates with the relative stabilities. An almost equally significant difference is found for the B–F bond distance. The boron trifluoride molecule, indeed, undergoes much less alteration in configuration and in bond distance in forming the addition compound with methyl cyanide than with any of the amines. Free boron trifluoride is planar with a B–F separation of 1·30 ± 0·02 A. (Levy & Brockway, 1937).

The minimum B–N bond distance observed in any of the addition compounds is 0·07 A. greater than the value, 1·50 A., predicted by the Schomaker & Stevenson (1941) rule. In the more stable compounds the B–F separation approaches the value, 1·39 A., predicted by Bauer & Beach (1941).

Some further data for H_3CCN–BF_3 resulting from the corrections for finite-series termination may be given. The figure, 1·13 A., given by the original study for the triple bond separation $C\equiv N$, surprisingly, is decreased by 0·005 A. when the finite-series correction is applied. The resulting bond distance is 0·02–0·03 A. less than that expected from other investigations. The C–C bond distance is increased from 1·44 to 1·46 A. to give closer agreement with the figure, 1·49 ± 0·03 A., obtained in the electron-diffraction study of methyl cyanide (Pauling, Springall & Palmer, 1939).

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