Crystal and molecular structures of three trimethylamine–boron halide adducts: $(CH_3)_3NBCl_3$, $(CH_3)_3NBBr_3$, and $(CH_3)_3NBI_3$*

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Abstract

X-ray diffraction data from single crystals of the trimethylamine complexes of the three boron halides, BCl_3, BBr_3, and BI_3, lead to a $P2_1/m$ monoclinic cell containing two molecules for each complex. The unit cell dimensions are $a = 6\cdot68(1)$, $b = 10\cdot247(3)$, $c = 6\cdot502(6)$ Å, $\beta = 116\cdot2(1)°$ (chloro); $a = 6\cdot86(1)$, $b = 10\cdot612(4)$, $c = 6\cdot737(6)$ Å, $\beta = 115\cdot8(1)°$ (bromo); $a = 6\cdot92(2)$, $b = 10\cdot86(1)$, $c = 7\cdot147(6)$ Å, $\beta = 93\cdot9(1)°$ (iodo). The structures were solved by three-dimensional sharpened Patterson functions and show only the chloro and bromo compounds to be isomorphous. Refinement of 662, 718 and 954 observed reflexions for the chloro, bromo and iodo complexes, respectively, using anisotropic thermal parameters yielded conventional R factors of 0·045, 0·087 and 0·054.

The molecules are shown to possess a B—N dative bond, a staggered conformation, and effective $3m$ (C_{3v}) symmetry. Average C—N bond lengths are 1·52(1) Å for all three complexes. Boron–halogen bond lengths average 1·864(4), 2·04(2) and 2·28(2) Å, while B—N bond distances are 1·609(6), 1·60(2) and 1·58(3) Å, respectively, for the chloro through iodo compounds. Bond angles are approximately tetrahedral with the C—N—C angle decreasing by several degrees in the Cl → Br → I series.

Introduction

Although there has been considerable interest in Lewis complexes, particularly with respect to correlations between chemical properties and dative bond lengths (Bent, 1968), for many years the only data available in the trimethylamine-boron halide series were the rather old results of Geller & Hoard (1951) for the BF_3 complex. Recently, however, Hess (1969) has reported the results of an X-ray study of the BCl_3 complex, and Bryan & Kuczkowski (1971) have carried out a microwave investigation of the BF_3 complex. In the latter case, a value for the B—N distance was found which was significantly longer than the early value of Geller and Hoard. This difference may be due to the difference in physical state, but the X-ray result does not compare with modern work with regard to accuracy. Part of the difference, therefore, may not be real. The paper by Hess appeared shortly after the completion of the present study. Although there is general agreement for most of the results, a

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disparity in the B—N distance existed which was greater than the sum of the stated errors. In view of the interest in this particular distance, further analysis of the available data was made and the source of the discrepancy appears to have been identified. The B—N distances from the present investigation on the chloro, bromo and iodo complexes appear more compatible with the B—N distance from the microwave study of the BF_3 complex than with the early X-ray result.

Experimental

Unit cell parameters and space group. Single, prismatic crystals of the three complexes were obtained by slow evaporation of chloroform solutions. The preparations of the complexes were carried out by standard methods and have been described elsewhere (Clippard, 1969).

Precession photographs ($h0l$, $h1l$, $hk0$, and $hk1$) showed that each crystal system was monoclinic and that the only systematic absences were $0k0$ for odd k. The space group of all three compounds is therefore $P2_1/m$ or $P2_1$; the structure determination verified the space group to be the centrosymmetric one. Approximate densities determined by flotation gave $Z = 2$. Unit cell dimensions at room

Table 1. *Unit cell parameters for trimethylamine-BX_3 complexes, with esd's in parentheses*

	$(CH_3)_3NBCl_3$	$(CH_3)_3NBBr_3$	$(CH_3)_3NBI_3$*
a (Å)	6·677(12)	6·862(12)	6·919(16)
b	10·247(3)	10·612(4)	10·862(12)
c	6·502(6)	6·737(6)	7·147(6)
β (°)	116·18(10)	115·83(10)	93·87(10)
V_c (Å^3)	399·2(7)	441·6(8)	536·0(14)
D_m (g cm^{-3})	1·47(1)	2·32(2)	2·9(1)
D_c (g cm^{-3}) ($Z = 2$)	1·467(3)	2·328(4)	2·792(7)

* Previous data in the literature (Muetterties, 1960) based on powder X-ray diffraction results give an orthorhombic unit cell with $Z = 8$ and a, b and c values inconsistent with those listed above.

temperature were calculated by direct measurements on the $h0l$ and $hk0$ precession photographs, and the b and c lengths were refined using results from diffractometer measurements of large θ values. Cu $K\alpha$ radiation was used for the choro- and bromo- compounds and Mo $K\alpha$ for the iodo compound. Table 1 summarizes the experimental and calculated results for the parameters and densities.

Collection and treatment of intensity data. For each adduct, the crystal was mounted with the a axis coincident with the crystal rotation axis. Intensity data were collected on a 0·01° incrementing Weissenberg-geometry automated diffractometer (Charles Supper Co.) which utilized a Phillips scintillation counter and a Datex Corp. programmer. A fixed counter, moving crystal method (Hanson, 1969), was used with the crystal scan range broken into ten scan and counter steps. The background was based on a least-squares line through all steps in the background region. Seven nets of data, $0kl...6kl$, were collected for each of the crystals. Standard reflexions, one per net, were selected and periodically monitored. A total of 706, 767 and 1108 independent reflexions for the chloro, bromo, and iodo complexes, respectively, were collected and used in the structure determinations; of these, 662, 718 and 954 had $|F_o|^2 > 3\sigma(|F_o|^2)$ and were included in the refinement.

A balanced filter technique was used to filter the radiation, with Ni and Co foil for the Cu source and Zr and Y for the Mo. Integrated intensities were corrected for Lorentz, polarization and absorption effects. Linear absorption coefficients for the three complexes were 96, 182 and 88 cm^{-1} in

the order Cl → Br → I. Calculations of the absorption corrections were carried out using a subroutine modified from Burnham's original program (Burnham, 1966); values for reflexions in the $0kl$ level gave transmission factors in the range of 0·14 to 0·27 (chloro), 0·012 to 0·10 (bromo) and 0·16 to 0·33 (iodo).

The chloro crystal sublimed slowly during the data collection. However, the decrease in raw counts for a given reflexion at the start and at the end of the data collection was only about 10%, and was compensated to a large extent by an absorption correction based on average size. The bromo and iodo compounds did not sublime, but the iodo compound proved somewhat unstable when exposed to high energy radiation. Therefore data were collected as rapidly as possible with only one of a pair of symmetry equivalent reflexions being measured.

Structure determination and refinement

Atomic scattering factors for neutral atoms were those of Cox & Bonham (1967). Form factors for each element were generated by computer from Cox's functions. For each compound, a scale factor was calculated by the Wilson method, to put the relative intensities on an absolute basis, after which sharpened three-dimensional Patterson functions with the origin peak removed were computed. From these, all non-hydrogen peaks were located.

Table 2. *Computed R factors*

Crystal	Using isotropic temperature factors	Using anisotropic temperature factors	Final values (H atoms included)
$(CH_3)_3NBCl_3$	0·19	0·067	0·055
$(CH_3)_3NBBr_3$	0·24	0·091	0·087
$(CH_3)_3NBI_3$	0·15	0·060	0·059

Table 3. *Fractional atomic coordinates for* $(CH_3)_3NBX_3$ *crystals, with esd's in parentheses*

	Atom	x	y	z
$(CH_3)_3NBCl_3$	B	0·3840(7)	$\frac{1}{4}$	0·2465(7)
	C_1	0·6909(8)	$\frac{1}{4}$	0·1112(8)
	C_2	0·7568(6)	0·1302(4)	0·4554(7)
	N	0·6480(5)	$\frac{1}{4}$	0·3196(5)
	Cl_1	0·3422(2)	$\frac{1}{4}$	0·5090(2)
	Cl_2	0·2545(1)	0·1037(1)	0·0769(2)
$(CH_3)_3NBBr_3$	B	0·3994(27)	$\frac{1}{4}$	0·2568(25)
	C_1	0·7022(22)	$\frac{1}{4}$	0·1281(21)
	C_2	0·7605(19)	0·1375(14)	0·4613(20)
	N	0·6550(17)	$\frac{1}{4}$	0·3294(16)
	Br_1	0·3494(3)	$\frac{1}{4}$	0·5332(2)
	Br_2	0·2561(2)	0·0970(1)	0·0794(2)
$(CH_3)_3NBI_3$	B	0·3504(30)	$\frac{1}{4}$	0·2961(21)
	C_1	0·6384(30)	$\frac{1}{4}$	0·0928(27)
	C_2	0·6769(22)	0·1407(16)	0·3851(23)
	N	0·5786(23)	$\frac{1}{4}$	0·2883(19)
	I_1	0·2670(2)	$\frac{1}{4}$	0·5983(2)
	I_2	0·2193(1)	0·0813(1)	0·1524(1)

Table 4. *Thermal parameters* for* $(CH_3)_3NBX_3$ *compounds, with esd's in parentheses*

Atom	β_{11}	β_{22}	β_{33}	β_{12}†	β_{23}†	β_{13}
$(CH_3)_3NBCl_3$						
B	0·0266(13)	0·0077(4)	0·0236(12)	0	0	0·0118(19)
C_1	0·0357(14)	0·0146(6)	0·0342(15)	0	0	0·0374(24)
C_2	0·0379(13)	0·0121(4)	0·0445(13)	0·0105(10)	0·0167(12)	0·0196(21)
N	0·0279(10)	0·0072(3)	0·0239(10)	0	0	0·0139(15)
Cl_1	0·0374(4)	0·0188(2)	0·0305(4)	0	0	0·0319(7)
Cl_2	0·0389(4)	0·0100(1)	0·0427(4)	−0·0119(2)	−0·0125(2)	0·0167(6)
$(CH_3)_3NBBr_3$						
B	0·0347(50)	0·0078(13)	0·0226(37)	0	0	0·0161(68)
C_1	0·0270(39)	0·0148(18)	0·0222(34)	0	0	0·0279(59)
C_2	0·0383(37)	0·0111(12)	0·0350(33)	0·0071(32)	0·0095(35)	0·0180(56)
N	0·0276(31)	0·0083(10)	0·0174(24)	0	0	0·0149(44)
Br_1	0·0385(6)	0·0187(3)	0·0258(5)	0	0	0·0255(8)
Br_2	0·0407(5)	0·0094(1)	0·0366(4)	−0·0103(3)	−0·0102(3)	0·0108(7)
$(CH_3)_3NBI_3$						
B	0·0194(49)	0·0081(18)	0·0052(29)	0	0	0·0080(47)
C_1	0·0189(49)	0·0108(21)	0·0155(38)	0	0	0·0183(60)
C_2	0·0146(34)	0·0117(17)	0·0251(37)	0·0062(35)	0·0041(39)	−0·0093(46)
N	0·0231(41)	0·0045(11)	0·0111(28)	0	0	0·0066(44)
I_1	0·0296(4)	0·0114(2)	0·0110(2)	0	0	0·0072(4)
I_2	0·0251(3)	0·0063(1)	0·0202(2)	−0·0047(2)	−0·0064(2)	−0·0008(4)

* The β_{ij} are defined in the following anisotropic temperature factor expression

$$\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13}).$$

† From symmetry requirements, β_{12} and β_{23} were 0 for atoms lying on the mirror plane.
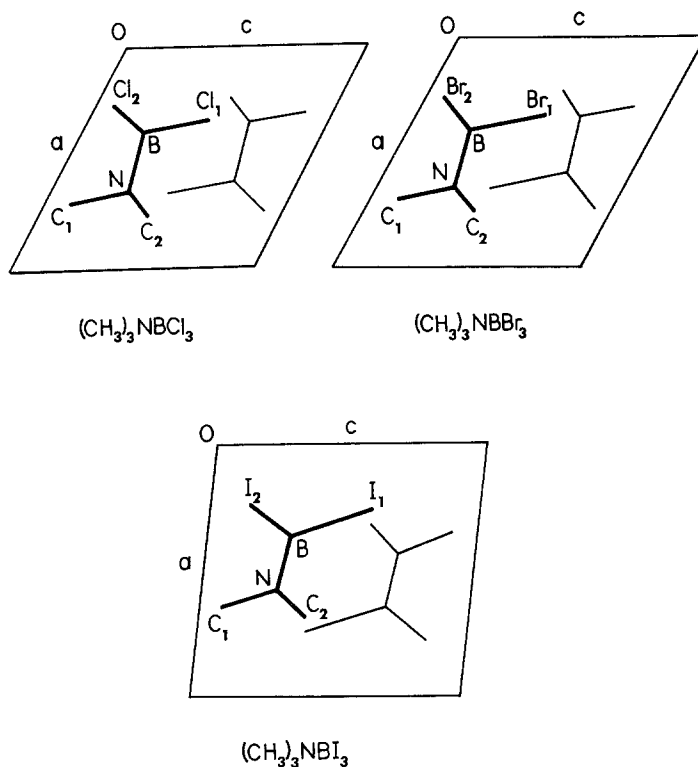

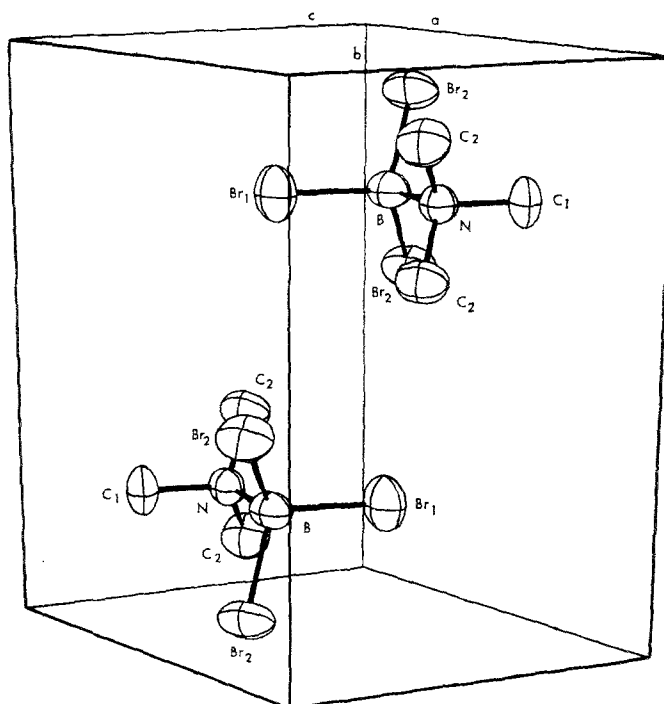Fig. 1. Unit cells of $(CH_3)_3NBX_3$ in parallel projection (mean positions: $\frac{1}{4}b$; $\frac{3}{4}b$).

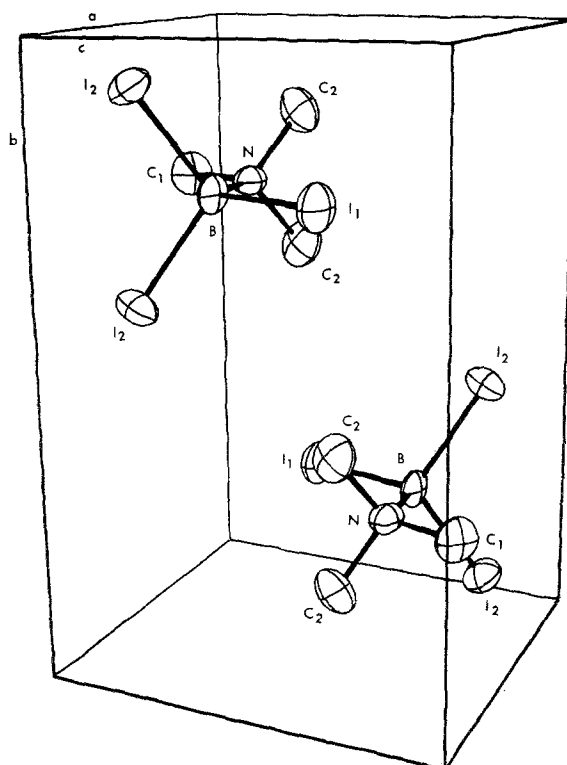Fig. 2. A unit cell of $(CH_3)_3NBBr_3$. Thermal ellipsoids are scaled to include 50% probability. Methyl hydrogen atoms are omitted.

Fig. 3. A unit cell of $(CH_3)_3NBI_3$. Thermal ellipsoids are scaled to include 50% probability. Methyl hydrogen atoms are omitted.

Since all atoms except hydrogen were found by the Patterson method, a full-matrix least-squares refinement (Busing, Martin & Levy, 1962; Schilling, 1968) of the initial atomic coordinates and temperature factors was carried out without recourse to preliminary difference Fourier syntheses. The weighting scheme was that originally suggested by Hughes (1941), namely, $w = 1$ if $|F_o| < 4|F_{min}|$, $w = 4|F_{min}|/|F_o|$ if $|F_o| > 4|F_{min}|$. Values of $4|F_{min}|$ (unscaled) were 100, 50 and 90 for the Cl, Br, and

Table 5. *Molecular parameters for crystalline* $(CH_3)_3NBX_3$ *compounds, with esd's in parentheses*

	$(CH_3)_3NBCl_3$		$(CH_3)_3NBBr_3$		$(CH_3)_3NBI_3$	
	Uncorr.	Corr.*	Uncorr.	Corr.*	Uncorr.	Corr.*
Bond distances (Å)						
B—N	1·610(6)	1·611(6)	1·603(21)	1·606(21)	1·584(25)	1·586(26)
C_1—N	1·504(6)	1·523(6)	1·525(15)	1·539(16)	1·484(21)	1·496(22)
C_2—N	1·500(4)	1·528(4)	1·475(13)	1·501(15)	1·513(17)	1·530(18)
B—X_1	1·847(5)	1·869(5)	2·035(16)	2·052(16)	2·273(15)	2·282(15)
B—X_2	1·836(3)	1·858(3)	2·002(9)	2·019(10)	2·261(11)	2·274(11)
Bond angles (°)						
X_1—B—X_2	109·4(2)		108·2(6)		108·2(5)	
X_2—B—X_2	109·5(2)		108·4(7)		108·3(8)	
X_1—B—N	108·6(3)		108·6(9)		110·6(10)	
X_2—B—N	110·0(2)		111·7(6)		110·8(6)	
C_1—N—C_2	107·2(2)		107·3(8)		106·6(11)	
C_2—N—C_2	109·9(4)		108·0(12)		103·5(15)	
C_1—N—B	110·7(3)		110·9(9)		112·0(14)	
C_2—N—B	110·9(2)		111·6(7)		113·7(10)	

* A 'riding' correction to allow for the effect of thermal motion on bond distances has been applied to these data.

Table 6. *Non-bonded intramolecular contacts* (Å), with esd's in parentheses*

	$(CH_3)_3NBCl_3$	$(CH_3)_3NBBr_3$	$(CH_3)_3NBI_3$
C_1—C_2	2·417(6)	2·417(16)	2·402(23)
C_2—C_2	2·455(9)	2·387(29)	2·375(35)
X_1—X_2	3·005(3)	3·269(3)	3·672(3)
X_2—X_2	2·999(2)	3·248(2)	3·664(4)
C_1—X_2	3·196(6)	3·353(13)	3·481(18)
C_2—X_1	3·185(6)	3·288(14)	3·516(18)
C_2—X_2	3·177(7)	3·320(14)	3·535(16)

* Not corrected for thermal motion.

I compounds, respectively, which gave unit weight to 26, 28, and 31 % of the observed reflexions. The function $\sum w(|F_o| - |F_c|)^2$ was minimized.

Initially, the overall scale factor, the isotropic temperature factors and the positional coordinates of all non-hydrogen atoms were refined. The isotropic temperature factors were then converted to anisotropic ones and the refinement continued. After additional cycles, difference Fourier maps were obtained in an attempt to locate the methyl hydrogen atoms, but approximate hydrogen

positions were obtained only for the chloro adduct. For the bromo and iodo compounds, spurious maxima and minima, perhaps arising from anomalous dispersion, were observed around the halogen atom positions and no information regarding the hydrogens could be obtained. Near the end of the refinement, methyl hydrogen atoms were introduced at positions expected from a model based on C_{3v} symmetry, since such a conformation was indicated by the difference Fourier map in the chloro compound. Standard parameters were assumed and the methyl group orientations were fixed to minimize steric interactions with each other and with the halogen atoms. These positions and the assumed isotropic temperature factors ($B = 5 \cdot 0$ Å) of the hydrogen atoms were held constant during the last cycles. For each compound, a secondary extinction correction was included as a variable parameter during the final cycles. It is of interest to note that the anisotropic thermal parameters of the skeletal atoms in no way suggested that the actual space group was $P2_1$.

Table 7. *Intermolecular contacts less than* $4 \cdot 5$ Å *in* $(CH_3)_3NBX_3$ *crystals, with esd's in parentheses*

(CH$_3$)$_3$NBCl$_3$			(CH$_3$)$_3$NBBr$_3$			(CH$_3$)$_3$NBI$_3$		
Dist. (Å)*,†	Code‡	Pair	Dist. (Å)	Code	Pair	Dist. (Å)	Code	Pair
3·565(7)	1B	C$_1$...X$_1$	3·670(14)	1B	C$_1$...X$_1$	4·023(6)	3G	X$_2$...X$_2$
3·750(5)	3G	X$_2$...X$_2$	3·802(6)	3G	X$_2$...X$_2$	4·115(16)	3C	C$_2$...X$_2$
3·893(2)	4B	C$_1$...X$_2$	3·993(5)	4B	C$_1$...X$_2$	4·150(9)	4B	C$_1$...X$_2$
3·899(4)	3C	C$_2$...X$_2$	4·011(13)	3C	C$_2$...X$_2$	4·227(23)	1B	C$_1$...X$_1$
3·949(7)	1D	C$_2$...X$_2$	4·036(15)	1A	C$_2$...X$_1$	4·255(19)	1A	C$_2$...X$_2$
3·959(9)	1A	C$_1$...X$_1$	4·075(16)	1A	C$_1$...X$_1$	4·262(18)	3C	C$_2$...X$_1$
3·962(8)	1A	C$_2$...X$_1$	4·093(13)	1D	C$_2$...X$_2$	4·310(37)	3C	C$_2$...C$_2$
3·976(5)	3C	C$_2$...X$_1$	4·184(15)	3C	C$_2$...X$_1$	4·396(4)	1B	X$_1$...X$_2$
4·043(9)	3E	C$_2$...C$_2$	4·255(26)	3E	C$_2$...C$_2$	4·412(21)	1A	C$_1$...X$_2$
4·147(8)	1A	C$_1$...X$_2$	4·276(14)	1A	C$_1$...X$_2$	4·423(17)	1A	C$_2$...X$_1$
4·183(6)	3F	C$_2$...X$_2$	4·318(4)	1B	X$_1$...X$_2$			
4·258(4)	1B	X$_1$...X$_2$	4·372(14)	3F	C$_2$...X$_2$			
4·377(6)	3F	X$_2$...X$_2$	4·439(6)	3F	X$_2$...X$_2$			

* Not corrected for thermal motion.
† H, B, and N atoms not included.
‡ Code: Symmetry operations, (1) identity, (2) reflexion, (3) inversion, (4) screw. Translations: *A*, along *x*; *B*, along *z*; *C*, along *y*; *D*, along *x* and *z*; *E*, along *x* and *y*; *F*, along *y* and *z*; *G*, along *x*, *y* and *z*.

A summary of the *R* factors at various stages of the refinement is compiled in Table 2, where $R = \sum ||F_o| - |F_c||/\sum |F_o|$. The poorness of the bromo results compared to the other two can be attributed to the magnitude of the absorption corrections necessary for that compound. Final fractional atomic coordinates for the three compounds are given in Table 3 and the final temperature factors in Table 4. A schematic drawing of the asymmetric unit of a $(CH_3)_3NBX_3$ molecule is given in Fig. 1 to show the atom numbering while unit cells of the bromo and iodo compounds are illustrated in Figs. 2 and 3. The refined atomic parameters together with a variance-covariance matrix of the associated errors were used to calculate interatomic distances and angles and their errors (Busing, Martin & Levy, 1964). A rigid body 'riding' correction for the effect of librational thermal motion (Busing & Levy, 1964) was applied to the bonded distances and found to be negligible for the B—N distances but significant (0·01–0·03 Å) for the C—N and B—X distances. Corrections assuming independent motions of the atoms appeared unreasonably large. The sizeable librational motions of the carbon atoms could easily account for the poorly defined H positions. The molecular parameters are listed in Tables 5, 6, and 7.

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Discussion

The high values for the uncertainties in the atomic positions of the light atoms in the bromo and iodo compounds (Table 3) are not surprising since these atoms constitute only a small percentage of the total scattering matter in the unit cell. This factor may be responsible in part for the discrepancies in the pairs of experimental bond angles shown in Table 5. In addition, several carbon–halogen and halogen–halogen intermolecular distances in the three complexes (Table 7) are shorter than, or approximately equal to, the methyl–halogen van der Waals distances of 3·80, 3·95 and 4·15 Å, and the halogen–halogen van der Waals distances of 3·60, 3.90 and 4·30 Å for the chloro, bromo and iodo compounds, respectively. The repulsions engendered by these close contacts may also contribute to the slight angular distortions from true C_{3v} symmetry.

Although there is a systematic shortening of the B—N distance from the chloro to the iodo compound which is suggestive of a slight increase in the strength of the dative bond, the trend is not striking and the uncertainties in the distances in comparison with this trend preclude any very positive conclusions.

Of more interest are comparisons with the values for the B—N dative bond in the literature for the same or related molecules. The only other datum for any of the compounds studied here is the value for the B—N distance in the BCl₃ complex reported recently by Hess (1969). His value is 1·575 Å which, as was mentioned previously, differs by more than the sum of the standard errors from the present result of 1·609 Å. In an effort to identify the source of this disagreement, his observed data were subjected to the same analysis as that used for the data obtained in this research. We found that by using his weighting system with our $|F_o|$ values, we obtained essentially his reported B—N distance. Conversely, using his $|F_o|$ data and our weighting scheme (Hughes, 1941), we obtained our reported value. A discussion of the merits and appropriateness of various weighting schemes is beyond the scope of this paper. However, the values of weighted residuals over various scattering ranges were compared for the two schemes to provide additional information. It was found that the residuals for Hughes' scheme were consistent over the ranges examined whereas a systematic trend of decreasing residuals with increasing scattering angle was found for the other. The evidence, thus, indicates that Hughes' scheme is preferable for this particular molecule.

The other molecule in the trimethylamine series, which was not studied in the present work, is the BF₃ complex. Two values are available for the B—N distance in this molecule, the X-ray value of 1·58 Å (Geller & Hoard, 1951) being significantly shorter than the recent microwave value of 1·636 Å (Bryan & Kuczkowski, 1971). Despite the uncertainty introduced by the different physical states involved, the microwave value is more compatible with the present results for the other halogen members of the series in that it gives a regular variation in the B—N distance down the series. The older X-ray value gives an irregular progression. Unfortunately, the data available for other related series are quite few, such that the existence, or non-existence, of similar trends cannot be cited. However, data have recently been provided for the BF₃ and BCl₃ complexes of acetonitrile (Swanson, Shriver & Ibers, 1969) in which the B—N bond length in the BCl₃ complex was found to be significantly (0·068 Å) shorter than in the fluorine compound. This result thus indicates that the microwave value may provide a better value for comparison with the B—N values in the trimethylamine series than the X-ray value of Geller and Hoard. The rather large decrease in the B—N distance in the acetonitrile complexes is not unexpected in view of the rather marked difference in stability of the two compounds; the complex, CH₃CN:BF₃, dissociates readily at room temperature whereas the BCl₃ complex is undissociated and comparable in stability to the trimethylamine complexes, all of which are stable and undissociated under normal conditions. The value for the B—N distance in CH₃CN:BCl₃, 1·562 Å, is appreciably shorter than the value of 1·609 Å found here for (CH₃)₃N:BCl₃. It is well known, however, that bonds adjacent to triple bonds often are considerably shorter than normal, and consequently this comparison does not appear to be significant even though the comparison of relative values in the two series is useful. An additional complicating feature of the trimethylamine

series is the fact that the molecules are sterically quite crowded. This is evident from a comparison of the intramolecular non-bonded distances in Table 6 with the sum of the van der Waals radii. Indeed, this factor may be largely responsible for the small change in the B—N distance in the series which otherwise might reflect to a greater degree the differences in acid strength of the three Lewis acids.

Acknowledgement

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