Refinement of the Structure of Orthorhombic Ammonium Tetrafluoroborate, NH$_4$BF$_4$

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The orthorhombic structure of ammonium tetrafluoroborate has been refined with three-dimensional visually estimated data by the full-matrix least-squares method. The results include a mean value of 1·406 (4) Å for the B–F bond length. Thermal vibration ellipsoids and the components of the T and L tensors in a rigid-body analysis are also presented. The largest root mean square libration for the fluoroborate ion is 9·5 (0·9)° about the normal to the crystallographic and molecular mirror plane.

Introduction

The crystal structure of orthorhombic ammonium tetrafluoroborate, NH$_4$BF$_4$, was determined by Hoard & Blair (1935) with assumed B–F bond lengths of 1·43 Å. The room temperature structure of several other tetrafluoroborate salts has also been studied: RbBF$_4$ (Hoard & Blair, 1935), KBF$_4$ (Bellanca & Sgarlata, 1950), and NaBF$_4$ (Bellanca, 1946, 1948; Weiss & Zohner, 1967). However, either the B–F bond lengths were assumed, were not reported, or were inconsistent with published coordinates and lattice constants. Furthermore, none of these structures was refined with anisotropic temperature factors so that no thermal motion analysis could be made although there is ample spectroscopic evidence (Pendred & Richards, 1955; Caron, Huettner, Ragle, Sherk & Stengle, 1967; Huettner, Ragle, Sherk, Stengle & Yeh, 1968) that the BF$_4^-$ ion is undergoing, at room temperature, large librations with rapid reorientations.

Thus, it was thought of value to reinvestigate the structure of a fluoroborate salt hoping to obtain more reliable atomic distances and some information on rigid-body motions of the BF$_4^-$ ion. The ammonium

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salt was chosen as it offers the added possible feature of hydrogen bonding.

Experimental

A sample of NH$_4$BF$_4$ purchased from Alfa Inorganics was recrystallized slowly in a mixture of water and methanol at room temperature. The lattice constants were previously determined by the powder method with a Debye–Scherrer camera (Caron, Ragle, Yorke & Yeh, 1968). The values of these constants, together with other crystallographic data, are given in Table 1.

Two crystals were used to collect intensities by the equi-inclination Weissenberg method (Cu $K\alpha$). One short needle measuring $0·4 \times 0·25 \times 0·15$ mm was chosen to record data around b ($k=0, 1, 2, 3$) and a wedge-shaped crystal measuring $0·4 \times 0·3 \times 0·3$ mm provided intensity data around a ($h=0, 1, 2, 3, 4, 5$).

The intensities were estimated visually, corrected with Lp factors and correlated by Rae's (1965, 1966) method using unit weights (this corresponds to assuming that the percentage error in the intensities is constant). No absorption correction was made ($\mu R < 0·5$). Of the 466 non-extinguished unique reflections within the Cu $K\alpha$ sphere, 40 were inaccessible, 71 were recorded as 'unobserved', and 355 had a measurable intensity. The average deviation between the two independent sets of observed structure factors was 8·8%.

Table 1. *Crystal data*

	a	b	c
Ammonium tetrafluoroborate NH$_4$BF$_4$	F.W.: 104·86 $F(000) = 208$		
Orthorhombic; space group *Pnma* [F(1), F(2), B and N in 4(c); F(3) in 8(d)]			
Hoard & Blair (1935)	9·08 Å	5·65 Å	7·24 Å
Swanson, Morris, Evans & Ulmer (1964); 26°C	9·063 (1)	5·686 (1)	7·252 (1)
Caron, Ragle, Yorke & Yeh, (1968); 23°C [λ(Cu $K\alpha_1$) = 1·54050 Å]	9·077 (3)	5·679 (2)	7·279 (3)
$V = 375$ Å^3	$D_m = 1·851$ g.cm^{-3}		
$Z = 4$	$D_x = 1·856$ g.cm^{-3}		

Refinement of the structure

Refinement of the heavy atoms

The refinement of the structure was carried out by the full-matrix least-squares method with a computer program devised by Palenik (1962). The assumed partial charges for the atoms were those suggested by Pauling (1960) as well as Weiss & Zohner (1967): $F^{-0.5}$, $B^{+1.0}$, $N^{+0.2}$, $H^{+0.2}$. The corresponding scattering factors were estimated by the interpolation of the appropriate curves given in *International Tables for X-ray Crystallography* (1962). The quantity minimized was $\sum w(F_o - F_c)^2$ and the weighting scheme was: $\sqrt{w} = 1/\Delta_o$, where Δ_o is the average deviation between two equiv-

alent structure factors from each data set. Only those reflections of observable intensity were included in the calculations.

Initially, the structure was refined to convergence with four isotropic least-squares cycles using, as starting heavy-atom coordinates, the first set of values given by Hoard & Blair (1935). At this point, R had reached a value of 13.8%. Refinement was resumed with anisotropic temperature factors and no hydrogen contributions for four additional cycles. Convergence was attained $(R = 7.8\%,\ R' = 2.5\%,$ where $R = \sum|F_o| - |F_c|/\sum|F_o|$, $R' = (\sum w|F_o - F_c|^2/\sum wF_o^2)^{1/2})$ and all parameter shifts were less than one-hundredth of the corresponding estimated standard deviations.

Table 2. *Observed and calculated structure factors*

The headings of the subcolumns are from letf to right: h, k, l, $10F_o$, and $10F_c$. Negative F_o are 'unobserved'.

Table 3. *The final parameters of the nonhydrogen atoms and their standard deviations (in parentheses) for a pair of ions at $y=\frac{1}{4}$*

All values $\times 10^4$. The temperature factor is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(1)	10752 (3)	2500	6111 (3)	112 (5)	505 (14)	301 (5)	—	197 (7)	—
F(2)	8283 (3)	2500	5637 (2)	159 (5)	368 (11)	139 (2)	&	−118 (5)	—
F(3)	9241 (2)	517 (3)	8030 (1)	139 (3)	237 (7)	163 (1)	14 (6)	−7 (3)	78 (5)
B	9403 (4)	2500	6931 (4)	95 (8)	238 (17)	107 (3)	—	5 (7)	—
N	3140 (5)	2500	3360 (2)	72 (5)	274 (13)	118 (3)	—	−4 (5)	—

The hydrogen atoms

A difference Fourier synthesis did not reveal unambiguously the hydrogen atoms as the maximum peak heights at the anticipated positions varied from 0·1 to 0·4 e.$Å^{-3}$ while there were spurious peaks of comparable height. No doubt this lack of resolution is due in great part to large librations undergone by the NH_4^+ ion; the smearing of the 'hydrogen peaks' around the nitrogen periphery attests to this fact. In spite of these shortcomings, hydrogen contributions were introduced in the least-squares calculations. This was done by selecting a number of plausible positions, refining hydrogen isotropic temperature factors alone, and rejecting those positions with diverging B values. In this fashion, an acceptable set of coordinates (N–H = 1 Å; H–N–H = 110°) was obtained and refined together with the heavy atom parameters for four cycles while the temperature factors of the hydrogen atoms were held constant at 6 $Å^2$. In the end, the parameter shifts of the heavy atoms were less than one-thirtieth and of the hydrogen atoms less than one-half of the corresponding e.s.d.'s.

The final values for R and R' are 6·1 and 2·0%, respectively. A list of the corresponding observed and calculated structure factors is given in Table 2. The final values of the atomic parameters appear in Tables 3 and 4.

Table 4. *Hydrogen atom coordinates for the molecule given on Table 3 at $y = \frac{1}{4}$*

All values have been multiplied by 10^3 and standard deviations are in parentheses.

	x	y	z
H(1)	225 (10)	250	346 (8)
H(2)	327 (7)	250	234 (9)
H(3)	346 (5)	121 (10)	372 (7)

Systematic errors

An inspection of the B–F bond lengths revealed a spread of about 0·03 Å as compared to e.s.d.'s of

0·005 Å or less. Since the BF_4^- ion would be expected, *a priori*, to have equivalent bond lengths within experimental error, the discrepancy raised the issue of systematic errors.

A number of possible sources of systematic errors were therefore carefully investigated. However, it had to be concluded that absorption, extinction, radiation damage to the crystals by the X-rays, partial charge assignment, layer scaling method and the choice of a weighting scheme could not be responsible for the bond length discrepancies. It was also ascertained that the structure was not disordered, that the space group was correct and that the crystal used did not contain amounts of NH_4BF_3OH detectable by the nuclear magnetic resonance method (Kuhlmann & Grant, 1964). Thus, it would appear that the bond length differences are meaningful and are most likely due to thermal motion, the one cause of systematic error unmentioned heretofore.

Discussion

Thermal motions

The amplitudes and the direction cosines of the principal axes of the vibrational ellipsoids are presented in Table 5. It may be noted that the amplitudes of the fluorine atoms are large as compared to those of the boron atom and that their magnitude is in reverse order to that of the uncorrected B–F bond lengths. Also, the longest axes of the fluorine ellipsoids are parallel to the mirror plane and nearly perpendicular to the B–F directions: 95° for F(1), 110° for F(2), and 101° for F(3). The second largest axes are similarly oriented with respect to the B–F directions: 90° for F(1) and F(2) (required by symmetry), and 91° for F(3). In contrast, the shortest axes are nearly parallel to the bond directions: 5° for F(1), 20° for F(2), and 11° for F(3).

Thus, all the above features of the atomic thermal ellipsoids suggest strongly that the BF_4^- ion is librating and that the origin of the librational axes is near the

Table 5. *Ellipsoids of vibration: square amplitudes and direction cosines of the principal axes*

	i	$B(Å^2)$	q_{ia}	q_{ib}	q_{ic}
F(1)	1	7·97	−0·5211	0	−0·8535
	2	6·51	0	1	0
	3	2·10	−0·8535	0	0·5211
F(2)	1	6·04	−0·8930	0	0·4500
	2	4·75	0	1	−0·8066
	3	2·16	−0·4500	0	0·5895
F(3)	1	4·59	0·9962	0·0765	−0·0426
	2	3·92	0·0108	−0·5910	−0·8066
	3	2·57	0·0869	−0·8031	0·5895
B	1	3·12	−0·9971	0	−0·0755
	2	3·07	0	1	0
	3	2·27	−0·0755	0	0·9971
N	1	3·54	0	1	0
	2	2·53	−0·2892	0	0·9573
	3	2·34	−0·9573	0	−0·2892

boron atom. Since the BF_4^- ion would be expected to be fairly rigid, it was therefore considered appropriate to subject the thermal parameters to a rigid-body analysis. The calculations were made with a program written by Coulter, Gantzel & Trueblood (1962) and the origin for the translational and librational axes was assumed to be at the boron position. Results are shown in Tables 6 and 7.

Table 6. *Translational amplitudes and direction cosines of the principal axes*

$T(\text{Å}^2)$	q_{ia}	q_{ib}	q_{ic}
0·040 (5)	0	1	0
0·036 (5)	−0·8868	0	−0·4622
0·025 (6)	−0·4622	0	0·8868

Table 7. *Librational amplitudes and direction cosines of the principal axes*

$L(\text{deg}^2)$	q_{ia}	q_{ib}	q_{ic}
90 (16)	0	1	0
52 (15)	−0·6131	0	−0·7900
25 (15)	−0·7900	0	0·6131

The librational amplitudes are large, particularly the one parallel to the mirror plane which has a value $9 \cdot 5 \pm 0 \cdot 9°$. It may also be noted that the two minor librational axes are nearly parallel to the $B-F(1)$ and $B-F(2)$ directions as the corresponding angles have values $11 \cdot 8°$ for L_2 and $9 \cdot 4°$ for L_3.

The S tensor (Schomaker & Trueblood, 1968), which in this case retains only two cross terms, was not included in the rigid-body analysis. It is felt that this omission should not materially alter the results and that the uncertainty of the temperature factors did not warrant the more refined calculation. An important contribution to this uncertainty is directly related to the uncertainty in the assignment of partial charges to the boron and fluorine atoms.

The molecular structure

After corrections for rigid-body librations (Cruickshank, 1961; Caron & Donohue, 1964) the B–F bond lengths are equal within experimental error (see Table 8); the mean B–F bond length has a value of 1·406 (4) Å. Thus, it would appear that the differences in uncorrected B–F bond lengths are due principally to thermal motion. This is further supported by Brunton's (1969) results on the structure of isomorphous KBF_4 which exhibits, within experimental error, the same uncorrected bond lengths: $B-F(1)=1 \cdot 378$ (5), $B-F(2)=1 \cdot 382$ (4) and $B-F(3)=1 \cdot 391$ (3) Å. Besides lending credence to the present results, this close agreement implies that the BF_4^- ion is undergoing similar thermal motions in both crystals. This is in line with Trueblood's (1969) observation that 'librational patterns are remarkably similar' for related molecules in different structures.

Table 8. *Distances and angles for the BF_4^- ion*

A Not corrected for librations
B Corrected for librations

Distances	A	B
B–F(1)	1·362 (5) Å	1·392 (7) Å
B–F(2)	1·386 (4)	1·410 (6)
B–F(3)	1·389 (2)	1·410 (4)
B–F$_{mean}$	1·382 (6)	1·406 (4)
F(1)···F(2)	2·267 (4)	2·312 (8)
F(1)···F(3)	2·258 (3)	2·302 (7)
F(2)···F(3)	2·249 (2)	2·286 (6)
F(3)···F(3)	2·253 (3)	2·279 (8)
F······F$_{mean}$	2·257 (4)	2·295 (7)

Angles	A	B
F(1)–B–F(2)	111·2 (0·2)°	111·2 (0·2)°
F(1)–B–F(3)	110·3 (0·2)	110·5 (0·2)
F(2)–B–F(3)	108·3 (0·2)	108·3 (0·2)
F(3)–B–F(3)	108·3 (0·2)	107·9 (0·2)

Most of the F–B–F angles are found to differ significantly from the ideal tetrahedral value as they range from 108·3 (0·2)° to 111·2 (0·2)°, even after librational corrections; possibly such distortions are caused by packing forces. Two angles, F(1)–B–F(2) and F(1)–B–F(3), have values very close to the corresponding ones in KBF_4 (Brunton, 1969): 111·4 (0·2)° and 108·5 (0·4)°, respectively. However, the remaining KBF_4 angles, F(2)–B–F(3) and F(3)–B–F(3) with values of 109·4 (0·2)° and 108·5 (0·4)° differ significantly from the present ones.

The mean N–H apparent bond length is quite short, 0·80 (2) Å, indicating that the NH_4^+ ion must have large librational amplitudes (see Table 9). All the H–N–H angles are equal to 110° within the standard deviations.

Table 9. *Distances and angles for the NH_4^+ ion*

N–H(1)	0·81 (9) Å
N–H(2)	0·75 (7)
N–H(3)	0·83 (5)
H(1)–N–H(2)	104 (6)°
H(1)–N–H(3)	109 (3)
H(2)–N–H(3)	105 (4)
H(3)–N–H(3)	124 (7)

Packing and hydrogen bonding

The packing can be characterized by focusing only on the anion–cation contacts since the shortest interionic F···F distance is 3·233 (2) Å as opposed to Pauling's (1960) value of 2·70 Å for the fluorine van der Waals diameter; also, there are no NH_4^+ van der Waals contacts. The NH_4^+ ion is surrounded by 12 fluorine atoms: two within the mirror plane and ten above and below the plane. The corresponding values for the uncorrected N···F distances vary from 2·912 (2) to 3·428 (2) Å (see Tables 10 and 11). If it is assumed that the motions of the NH_4^+ and BF_4^- ions are uncorrelated, these distances should be corrected upward by about 0·022 to 0·013 Å (Busing & Levy, 1964). Hoard &

Table 10. *Shortest nitrogen–fluorine and hydrogen–fluorine intermolecular distances*

Standard deviations are in parentheses.

	Relative position of second atom		Uncorrected distance	Corrected distance	Multiplicity
N······F(1,A)	$x-1$,	$\frac{1}{4}$, z	2·951 (4) Å	2·973 Å	1
N······F(1,B)	$\frac{1}{2}-x$,	$-\frac{1}{4}$, $z-\frac{1}{2}$	3·428 (2)	3·446	2
N······F(2,C)	$x-\frac{1}{2}$,	$\frac{1}{4}$, $\frac{1}{2}-z$	2·912 (2)	2·930	1
N······F(2,D)	$1-x$,	$-\frac{1}{4}$, $1-z$	3·204 (2)	3·220	2
N······F(3,D)	$1-x$,	$\bar{y}$, $1-z$	2·938 (4)	2·951	2
N······F(3,B)	$\frac{1}{2}-x$,	$\bar{y}$, $z-\frac{1}{2}$	2·940 (4)	2·953	2
N······F(3,E)	$x-\frac{1}{2}$,	y, $\frac{3}{2}-z$	3·029 (2)	3·043	2
H(1)···F(1,A)	$x-1$,	$\frac{1}{4}$, z	2·36 (7)	—	1
H(2)···F(2,C)	$x-\frac{1}{2}$,	$\frac{1}{4}$, $\frac{1}{2}-z$	2·16 (7)	—	1
H(3)···F(3,B)	$\frac{1}{2}-x$,	$\bar{y}$, $z-\frac{1}{2}$	2·36 (5)	—	2
H(3)···F(3,E)	$x-\frac{1}{2}$,	y, $\frac{3}{2}-z$	2·50 (5)	—	2

Blair (1935) have noted that the F(1,A)–N–F(2,C) angle of 135·3 (0·2)° is close to the value of a tetrahedral angle and that therefore there probably is hydrogen bonding along these two directions. Indeed, the difference Fourier synthesis as well as the structural refinement of the isomorphous NH₄ClO₄ (Venkatesan, 1957) tend to support this conclusion. However, since the F(1,A)–N–F(2,C) angle is larger than 110°, it is possible that one of the two in-plane hydrogen bond is favored over the other. There are in fact some indications that the N–H(2)···F(2,C) bond is favored over the N–H(1)···F(1,A) bond as the thermal vibrations of F(1,A) are larger than those of F(2,C), the N···F(1,A) distance, 2·951 (4) Å, is larger than the N···F(2,C) distance, 2·912 (2) Å, and it would appear that the N–H(1)–F(1,A) angle, 130 (6)°, departs significantly from 180°.

Table 11. *Anion–cation angles*

The symmetry code is as given in Table 10.

F(1,A)–N–F(2,C)	135·3 (0·2)°
F(1,A)–N–F(3,B)	130·5 (0·1)
F(1,A)–N–F(3,E)	72·1 (0·1)
F(2,C)–N–F(3,B)	83·2 (0·1)
F(2,C)–N–F(3,E)	71·9 (0·1)
N–H(1)–F(1,A)	130 (6)
N–H(2)–F(2,C)	171 (6)
N–H(3)–F(3,B)	128 (4)
N–H(3)–F(3,E)	122 (4)

It is difficult to find suitably positioned fluorine atoms for the bonding of the out-of-plane H(3) atoms. In effect, the two closest fluorine atoms, F(3,B) and F(3,E) are so positioned that both N–H(3)···F(3) contacts depart from linearity by about 55°.

It should be added that it is believed that hydrogen bonding contributes negligibly to the lattice energy of this crystal because of the following considerations:

(1) The uncorrected N···F distances are long compared with values of 2·62 (2) Å for N₂H₄.2HF (Kronberg & Harker, 1942), 2·69 Å for NH₄F (Plumb & Hornig, 1955), and 2·797 (2) and 2·822 (2) Å for NH₄HF₂ (McDonald, 1960).

(2) Rubidium tetrafluoroborate and NH₄BF₄ are isomorphous. Since the rubidium ion has no strong

angle requirements for its coordination, it would be a rather remarkable coincidence if the same structure could fit the angular requirements of the NH₄⁺ ion for ideal hydrogen bonding.

(3) Finally, the thermal motions are so large that the hydrogen bonds could not be very effective. Thus, the first and the second axes of libration are nearly perpendicular to the N–H(1)···F(1,A) direction while the first and the third axes are nearly perpendicular to the N–H(2)···F(2,C) direction. In addition, there is ample independent evidence that both the NH₄⁺ and BF₄⁻ ions are undergoing rapid reorientations. For example, Stephenson, Orehotsky & Smith (1968) conclude from heat capacity measurements that the NH₄⁺ ion is essentially a classical rotor with three degrees of freedom at room temperature. Also, nuclear spin-lattice relaxation measurements show that the tumbling rate of the BF₄⁻ ion is about 10^8 sec⁻¹ at room temperature (Caron, Huettner, Ragle, Sherk & Stengle, 1967). This rate increases until at 199 °C the crystal transforms to a face-centered cubic phase in which the BF₄⁻ ions are disordered (Finbak & Hassel, 1936).

From these arguments, it cannot be concluded that in some way the bonding state of the fluorine atoms precludes effective hydrogen bonding, since the identical situation arises with the isomorphous NH₄ClO₄ (Venkatesan, 1957). Rather, the ionic charges, the smallness of the ions, and their near perfect spherical symmetry cause the hydrogen bonding forces to be overwhelmed by Coulombic forces from ion–ion interactions.

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The Crystal Structure of Sodium 5,5-Diethylbarbiturate (Sodium Barbital)

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The crystal structure of sodium 5,5-diethylbarbiturate $NaC_8N_2O_3H_{11}$ (sodium barbital) has been determined from X-ray diffraction data measured on an automatic diffractometer. $R = 0.025$. The crystal data are: $P2_12_12_1$, $a = 6.724$ (1), $b = 11.950$ (2), $c = 12.129$ (2) Å, $Z = 4$, $D_m = 1.408$ g.cm^{-3}. The conformation of the barbital ion is similar to that of the barbital molecule. Deprotonization of the pyrimidine ring at N(3) decreases the internal bond angle at N(3) by 7° and increases those at the neighbouring atoms C(2) and C(4) by 5°. The greater part of the formal negative charge seems to be equally distributed between the two oxygen atoms O(2) and O(4). The molecules are hydrogen bonded (NH$\cdots$O = 2.84 Å) to form ribbons along the a axis. The sodium atom is tetrahedrally coordinated by barbital oxygen atoms, with tetrahedra sharing corners to form columns parallel to a.

Introduction

We report the crystal structure determination of sodium 5,5-diethylbarbiturate (sodium barbital, Fig. 1) as part of a program for studying and comparing the tautomeric form, stereochemistry and intermolecular interactions of simple barbituric acids and their salts. A series of crystal structures have been determined, including barbituric acid (Bolton, 1963), its dihydrate (Jeffrey, Ghose & Warwicker, 1960) and ammonium salt (Craven, 1963); 5-ethylbarbituric acid (Gatehouse & Craven, 1971) and the $\frac{2}{3}$ hydrate of its potassium salt (Gartland, Craven & Gatehouse, 1971); and 5,5-diethylbarbituric acid or barbital (Craven, Vizzini & Rodrigues, 1969) and its sodium salt presently reported).

Barbituric acid and 5-ethylbarbituric acid have at least one hydrogen atom at C(5), whereas barbital has none. It is of interest to note that the crystal structures of salts of barbituric acid and 5-ethylbarbituric acid show the formation of carbanions, *i.e.* proton loss is from C(5), whereas in the case of barbital, proton loss is necessarily from an imine nitrogen atom. Barbital is a weaker acid than barbituric acid, as shown by the acid dissociation constants ($pK_a = 7.86$, 3.90 respectively; Doornbos & de Zeeuw, 1969). The pK_a value for 5-ethylbarbituric acid has not been reported.

The crystal structure determination of potassium barbital, based on photographic X-ray intensity data, was reported by Berthou, Rérat & Rérat (1965). The sodium salt was described as isomorphous (Berthou, Cavelier, Marek, Rérat & Rérat, 1962). In order to