

## The Crystal and Molecular Structures of Ammonium Fluoroacetate, $C_2H_6FNO_2$ , and Ammonium Difluoroacetate, $C_2H_5F_2NO_2$

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(Received 7 July 1975; accepted 17 February 1976)

Ammonium fluoroacetate (II),  $C_2H_6FNO_2$ , crystallizes in the monoclinic system with  $a=11.755$  (3),  $b=10.900$  (3),  $c=6.788$  (2) Å,  $\beta=92.67$  (2)°,  $D_m=1.451$ ,  $D_x=1.454$  g cm<sup>-3</sup>,  $Z=8$ ; the space group is  $C2/c$ . Ammonium difluoroacetate (III),  $C_2H_5F_2NO_2$ , crystallizes in the orthorhombic system with  $a=7.486$  (4),  $b=9.271$  (3),  $c=6.570$  (2) Å,  $D_m=1.644$ ,  $D_x=1.647$  g cm<sup>-3</sup>,  $Z=4$ ; the space group is  $P2_12_12_1$ . The X-ray intensities were measured with a Picker FACS-I automatic diffractometer, Mo  $K\alpha$  radiation, and  $\theta-2\theta$  scans: (II) 772 unique data for  $2\theta \leq 50^\circ$  (580 'observed'); (III) 653 unique data for  $2\theta \leq 55^\circ$  (482 'observed'). The parameters were refined by full-matrix least squares to final  $R$  values of 0.050 for both structures. The structures of (II) and (III) are different from each other and from those reported in space group  $P2_1/c$  for ammonium acetate (I) and  $P2_1/a$  for ammonium trifluoroacetate (IV). All four structures exhibit extensive hydrogen-bonding networks, but in (II) two H atoms appear to be involved in bifurcated hydrogen bonds. Molecules (II) and (III) are packed more densely than expected if they formed structures similar to (I) and (IV).

### Introduction

Single crystals of the title compounds are currently being studied by ESR techniques (Rogers & Schoening, 1974). The crystal and molecular structure determinations of ammonium fluoroacetate (II) and ammonium difluoroacetate (III) were undertaken to further elucidate the results from the ESR studies, to reveal the hydrogen-bonding networks in the crystals, and to complete the series of fluoro derivatives of ammonium acetate [ammonium acetate (I), Nahringbauer (1967), and ammonium trifluoroacetate (IV), Cruickshank, Jones & Walker (1964)].

### Experimental

Ammonium fluoroacetate (II) and ammonium difluoroacetate (III) were prepared by R. C. Schoening by the neutralization of the acids with  $NH_4OH$  and recrystallized from ethanol-water solutions. A single crystal of ammonium fluoroacetate (II) of approximate dimensions  $0.13 \times 0.36 \times 0.52$  mm [ $\mu$  for Mo  $K\alpha=1.06$  cm<sup>-1</sup>] was sealed in a glass capillary tube to prevent contact with moisture. The diffraction conditions  $hkl: h+k=2n$ ,  $h0l: l=2n$  ( $h=2n$ ), and  $0k0: (k=2n)$ , the absence of other conditions, and the monoclinic symmetry indicate the space groups  $C2/c$  and  $Cc$ . The density, determined by flotation in a mixture of tetrachloroethylene and 1,2,4-trichlorobenzene, is  $1.451$  g cm<sup>-3</sup>. For  $Z=8$ , the calculated density is  $1.454$  g cm<sup>-3</sup>.

A single crystal of ammonium difluoroacetate (III) of approximate dimensions  $0.13 \times 0.25 \times 0.25$  mm [ $\mu$  for Mo  $K\alpha=1.37$  cm<sup>-1</sup>] was sealed in a glass capillary tube to prevent contact with moisture. The diffraction con-

ditions  $h00: h=2n$ ,  $0k0: k=2n$ , and  $00l: l=2n$ , the absence of other conditions, and the orthorhombic symmetry establish the space group as  $P2_12_12_1$ . The density, determined by flotation in a mixture of carbon tetrachloride and methylene bromide, is  $1.644$  g cm<sup>-3</sup>. For  $Z=4$ , the calculated density is  $1.647$  g cm<sup>-3</sup>.

Diffraction data were measured at 23°C with a Picker FACS-I automatic diffractometer using zirconium-filtered Mo  $K\alpha$  radiation. Precise unit-cell parameters for (II) and (III) were determined by a least-squares fit to the setting angles ( $2\theta, \omega, \chi, \phi$ ) of 12 reflections each in the range  $35 \leq 2\theta \leq 45^\circ$  for which the  $\alpha_1\alpha_2$  doublet was clearly resolved [ $\lambda$  for Mo  $K\alpha_1=0.70926$  Å]. The crystal data are listed in Table 1. The intensity data were collected by  $\theta-2\theta$  scans [ $2^\circ(2\theta)$  min<sup>-1</sup>, 10 s backgrounds at the start and end of each scan, and scan ranges of  $1.2^\circ(2\theta)$  for (II) and  $1.8^\circ(2\theta)$  for (III) plus the  $\alpha_1-\alpha_2$  divergence] using zirconium-filtered Mo  $K\alpha$  radiation. The intensities of three standard reflections, monitored during data collection, showed no systematic variations and were used to scale the raw intensities. There was no evidence of radiation damage to the crystals. For (II), 772 unique intensities in the  $+h+k \pm l$  region were collected for  $2\theta \leq 50^\circ$ . For (III), 653 unique intensities in the  $+h+k+l$  octant were collected for  $2\theta \leq 55^\circ$ .

### Calculation of standard deviations and weights

The raw intensity of a reflection (RAWI) is calculated as  $RAWI = COUNT-TIME \times (B1+B2)/(2 \times CT)$  and the standard deviation of the raw intensity (SIGI) as  $SIGI = (COUNT + SIGBKG^2)^{1/2}$  where  $SIGBKG = SIGB12 \times TIME/(2 \times CT)$ ;  $SIGB12$  is the greater of  $(B1+B2)^{1/2}$  and  $|B1-B2| \times 1.414$ ;  $B1$  and  $B2$  are

Table 1. *Crystal data*

	(II) Ammonium fluoroacetate C <sub>2</sub> H <sub>6</sub> FNO <sub>2</sub>	(III) Ammonium difluoroacetate C <sub>2</sub> H <sub>5</sub> F <sub>2</sub> NO <sub>2</sub>
F.W.	95.07	113.06
<i>F</i> (000)	400	232
System	Monoclinic	Orthorhombic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i>	11.755 (3) Å	7.486 (4) Å
<i>b</i>	10.900 (3)	9.271 (3)
<i>c</i>	6.788 (2)	6.570 (2)
$\beta$	92.67 (2)°	(90°)
<i>V</i>	868.8 Å <sup>3</sup>	456.0 Å <sup>3</sup>
<i>D<sub>m</sub></i>	1.451 g cm <sup>-3</sup>	1.644 g cm <sup>-3</sup>
<i>D<sub>x</sub></i>	1.454	1.647
<i>Z</i>	8	4

background counts measured at the ends of the scan for CT s each and COUNT is the counts recorded while scanning for TIME s. Factors are applied to RAWI and SIGI to correct for Lorentz-polarization, scaling (decay), and absorption (if necessary) and one obtains the square of the structure factor (FSQ) and its standard deviation (SIGFSQ).

Any equivalent and/or duplicate data are combined to give averaged values for FSQ and SIGFSQ for the unique reflection:

$$FSQ_{av} = \left( \sum_{i=1}^N FSQ_i \right) / N$$

$$SIGFSQ_{av} = \left[ \sum_{i=1}^N (SIGFSQ_i)^2 \right]^{1/2} / N,$$

where *N* is the number of data averaged. The scatter (SCATTER) of the data from the averaged value (FSQ<sub>av</sub>) is calculated as

$$SCATTER = \left\{ \left( \sum_{i=1}^N |FSQ_i - FSQ_{av}|^2 \right) / [(N-1)N] \right\}^{1/2}.$$

When SCATTER is greater than SIGFSQ<sub>av</sub> by a factor NBOP (typically 4) or more, SCATTER is used for SIGFSQ<sub>av</sub> for this reflection.

SIGFSQ can be modified further in the full-matrix least-squares program by using the factors *P* and *Q*:

$$SIGFSQ_{mod} = [SIGFSQ^2 + (P \times FSQ)^2 + Q^2]^{1/2}.$$

The structure factor (FOBS; FOBS = FSQ<sup>1/2</sup>) can be corrected for extinction by using the extinction factor (EF): FOBS<sub>cor</sub> = (1 + EF × RAWI) × FOBS. The standard deviation of the structure factor (SIGMA) is defined as:

$$SIGMA = SIGFSQ^{1/2} \text{ for } RAWI \leq SIGI,$$

and

$$SIGMA = FOBS - (FSQ - SIGFSQ)^{1/2} \text{ for } FSQ \geq SIGFSQ;$$

the weight of a structure factor used in least-squares refinement is 1/SIGMA<sup>2</sup>.

For the present two structures, absorption and extinction corrections were not applied, *P* was set at 0.02, and *Q* was set at zero.

Table 2. *Atomic parameters for ammonium fluoroacetate and ammonium difluoroacetate*

Fractional coordinates are × 10<sup>4</sup> (× 10<sup>3</sup> for H). Thermal parameters are in Å<sup>2</sup>. Anisotropic temperature factor is in the form exp [−½∑<sub>i,j</sub>(a<sub>i</sub><sup>2</sup>h<sub>i</sub><sup>2</sup>+h<sub>i</sub>h<sub>j</sub>B<sub>ij</sub>)], where a<sub>i</sub><sup>2</sup> is a reciprocal cell edge and h<sub>i</sub> is one of the Miller indices.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub> ( <i>B</i> <sub>iso</sub> )	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Ammonium fluoroacetate									
F	1374 (1)	9578 (1)	1108 (3)	6.5 (1)	2.6 (1)	6.5 (1)	0.1 (1)	−1.3 (1)	−0.9 (1)
O(1)	855 (1)	6486 (1)	−89 (3)	4.3 (1)	2.6 (1)	4.3 (1)	−0.1 (1)	−0.1 (1)	−0.6 (1)
O(2)	1749 (2)	7359 (2)	2500 (3)	6.3 (1)	4.1 (1)	3.8 (1)	−1.3 (1)	−2.1 (1)	1.2 (1)
N	3416 (3)	9077 (3)	4133 (4)	3.7 (1)	2.7 (1)	3.4 (1)	−0.3 (1)	−0.0 (1)	−0.2 (1)
C(1)	1196 (2)	7381 (2)	904 (3)	2.3 (1)	2.7 (1)	2.7 (1)	0.0 (1)	0.2 (1)	0.3 (1)
C(2)	902 (3)	8605 (2)	27 (5)	4.5 (2)	2.6 (1)	3.9 (1)	0.4 (1)	−1.4 (1)	−0.4 (1)
H(1)	3 (3)	869 (2)	−4 (4)	5.4 (7)					
H(2)	112 (2)	863 (2)	−147 (5)	5.0 (7)					
H(3)	342 (2)	864 (3)	545 (5)	5.5 (8)					
H(4)	270 (3)	884 (3)	342 (5)	5.6 (8)					
H(5)	352 (2)	988 (3)	432 (4)	4.4 (8)					
H(6)	404 (4)	877 (4)	334 (6)	8.0 (11)					
Ammonium difluoroacetate									
F(1)	4246 (5)	993 (3)	7291 (3)	7.8 (2)	4.9 (1)	2.7 (1)	−0.5 (1)	−2.0 (1)	0.9 (1)
F(2)	4428 (4)	−217 (2)	4471 (4)	6.0 (1)	3.1 (1)	4.9 (1)	1.8 (1)	0.4 (1)	0.2 (1)
O(1)	3229 (5)	3315 (2)	5271 (4)	8.3 (2)	2.1 (1)	2.8 (1)	0.7 (1)	1.2 (1)	0.1 (1)
O(2)	3511 (4)	2100 (3)	2378 (3)	4.2 (1)	3.6 (1)	2.1 (1)	0.5 (1)	0.4 (1)	0.4 (1)
N	3091 (5)	6246 (3)	4240 (5)	3.7 (2)	2.6 (1)	2.0 (1)	0.1 (1)	0.6 (1)	0.4 (1)
C(1)	3419 (5)	2216 (3)	4257 (5)	2.8 (1)	2.5 (1)	2.2 (1)	−0.0 (1)	0.3 (1)	0.2 (1)
C(2)	3462 (6)	799 (3)	5458 (5)	3.7 (2)	2.2 (1)	2.5 (1)	0.1 (1)	−0.1 (1)	0.2 (1)
H(1)	217 (6)	41 (4)	571 (6)	2.6 (7)					
H(2)	424 (7)	672 (5)	391 (6)	3.0 (9)					
H(3)	305 (4)	530 (4)	456 (5)	2.0 (7)					
H(4)	245 (5)	644 (4)	316 (7)	2.0 (8)					
H(5)	257 (5)	676 (4)	544 (7)	2.8 (8)					

## Structure solution and refinement

Both crystal structures were solved with the program *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study include *ORTEP* (Johnson, 1965), the entire system of Allan Zalkin's programs (Zalkin, 1974), and programs written and/or modified locally. Computations were performed on a CDC 6500 computer.

The scattering factors of Doyle & Turner (1968) were used for the non-H atoms, those of Stewart, Davidson, and Simpson (1965) for H, the anomalous scattering factors of Cromer & Liberman (1970) for the non-H atoms, and anomalous scattering factors of zero were assumed for H.

The structure of (II) was refined by full-matrix least squares. Three additional cycles of full-matrix least-squares refinement using the polar complex H scattering factors as described by Templeton, Olson, Zalkin & Templeton (1972) led to  $R_1 = (\sum |F_o - F_c|) / \sum F_o = 0.050$ ,  $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2} = 0.038$ ,  $R_1 = 0.077$  including the 171 zero-weighted data for which  $I \leq \sigma(I)$  and the standard deviation of an observation of unit weight = 1.245. In the same fashion, (III) was refined to  $R_1 = 0.050$ ,  $R_2 = 0.036$ , the standard deviation of an observation of unit weight = 0.879 and  $R_1$  [including the 192 zero-weighted data for which  $I \leq \sigma(I)$ ] = 0.079. The atomic parameters for (II) and (III) are listed in Table 2.\*

The final difference maps do not appear to indicate missing or incorrectly positioned atoms; the maximum and minimum residual densities for (II) are 0.16 and  $-0.13 \text{ e } \text{Å}^{-3}$ , and for (III) are 0.37 and  $-0.37 \text{ e } \text{Å}^{-3}$ . The maximum and average shift-to-error ratios on the final cycle of least-squares refinement were 0.413 and 0.054 for (II) and 0.287 and 0.039 for (III).

## The structures and hydrogen bonding

All the atoms lie in general positions. The structure of the ions in (II) and (III) are similar (apart from the replace-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31814 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

ment of one H by a F atom) as can be seen from a comparison of the interatomic distances and angles listed in Table 3. Extensive hydrogen bonding in three dimensions is observed in (II) and (III) involving both O atoms and all four ammonium H atoms. The hydrogen-bonding distances and angles are given in Table 4 for (II) and Table 5 for (III). The packing diagrams, Fig. 1 for (II) and Fig. 2 for (III), indicate possible hydrogen bonds by fine solid lines.

Table 3. Bond distances (Å) and angles (°)

Ammonium fluoroacetate			
C(1)-C(2)	1.495 (3)	O(1)-C(1)-O(2)	127.0 (2)
C(1)-O(1)	1.242 (3)	O(1)-C(1)-C(2)	115.0 (2)
C(1)-O(2)	1.238 (2)	O(2)-C(1)-C(2)	118.0 (2)
C(2)-F	1.391 (3)	F-C(2)-C(1)	113.0 (2)
C(2)-H(1)	1.03 (4)	F-C(2)-H(1)	109 (2)
C(2)-H(2)	1.06 (3)	F-C(2)-H(2)	112 (1)
N-H(3)	1.02 (4)	C(1)-C(2)-H(1)	108 (2)
N-H(4)	0.99 (4)	C(1)-C(2)-H(2)	110 (1)
N-H(5)	0.89 (4)	H(1)-C(2)-H(2)	104 (3)
	0.99 (5)	H(3)-N-H(4)	106 (3)
		H(3)-N-H(5)	110 (3)
		H(3)-N-H(6)	111 (4)
		H(4)-N-H(5)	116 (4)
		H(4)-N-H(6)	107 (4)
		H(5)-N-H(6)	108 (4)
Ammonium difluoroacetate			
C(1)-C(2)	1.533 (4)	O(1)-C(1)-O(2)	128.3 (3)
C(1)-O(1)	1.226 (4)	O(1)-C(1)-C(2)	115.8 (3)
C(1)-O(2)	1.241 (4)	O(2)-C(1)-C(2)	115.9 (3)
C(2)-F(1)	1.352 (4)	F(1)-C(2)-C(1)	110.8 (3)
C(2)-F(2)	1.353 (4)	F(2)-C(2)-C(1)	111.2 (3)
C(2)-H(1)	1.04 (5)	F(1)-C(2)-F(2)	106.7 (3)
N-H(2)	0.99 (5)	C(1)-C(2)-H(1)	111 (2)
N-H(3)	0.90 (4)	F(1)-C(2)-H(1)	108 (2)
N-H(4)	0.87 (5)	F(2)-C(2)-H(1)	109 (2)
N-H(5)	1.00 (5)	H(2)-N-H(3)	121 (5)
		H(2)-N-H(4)	102 (5)
		H(2)-N-H(5)	107 (4)
		H(3)-N-H(4)	112 (5)
		H(3)-N-H(5)	106 (4)
		H(4)-N-H(5)	109 (4)

Table 4. Hydrogen bonding in ammonium fluoroacetate

	O...H	O...N	O...H-N
O(1) <sup>ii</sup> ...H(5)-N	1.96 (4) Å	2.828 (3) Å	164 (1)°
O(1) <sup>iii</sup> ...H(6)-N	2.24 (4)	2.978 (3)	131 (1)
O(1) <sup>iv</sup> ...H(6)-N	2.36 (4)	2.956 (3)	118 (1)
O(2)...H(4)-N	2.05 (4)	2.893 (3)	143 (1)
O(2) <sup>i</sup> ...H(3)-N	1.78 (4)	2.783 (3)	168 (1)

Table 4 (cont.)

O(1) <sup>ii</sup> ...N...O(1) <sup>iii</sup>	107.8 (1)°	N <sup>v</sup> ...O(1)...N <sup>iii</sup>	85.6 (1)°
O(1) <sup>ii</sup> ...N...O(1) <sup>iv</sup>	82.6 (1)	N <sup>v</sup> ...O(1)...N <sup>vi</sup>	97.5 (1)
O(1) <sup>ii</sup> ...N...O(2)	151.8 (1)	N <sup>v</sup> ...O(1)...C(1)	121.2 (2)
O(1) <sup>ii</sup> ...N...O(2) <sup>i</sup>	111.4 (1)	N <sup>iii</sup> ...O(1)...N <sup>vi</sup>	96.4 (1)
O(1) <sup>iii</sup> ...N...O(1) <sup>iv</sup>	78.7 (1)	N <sup>iii</sup> ...O(1)...C(1)	124.2 (2)
O(1) <sup>iii</sup> ...N...O(2)	74.5 (1)	N <sup>vi</sup> ...O(1)...C(1)	123.1 (2)
O(1) <sup>iii</sup> ...N...O(2) <sup>i</sup>	132.5 (1)		
O(1) <sup>iv</sup> ...N...O(2)	124.6 (1)	N...O(2)...N <sup>i</sup>	96.9 (1)
O(1) <sup>iv</sup> ...N...O(2) <sup>i</sup>	80.8 (1)	N...O(2)...C(1)	129.9 (2)
O(2)...N...O(2) <sup>i</sup>	83.1 (1)	N <sup>i</sup> ...O(2)...C(1)	132.6 (2)
		Sum about O(2)	359.4

Symmetry code: (i)  $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} - x, \frac{3}{2} - y, -z$ ; (iv)  $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (v)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (vi)  $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ .

Ammonium fluoroacetate (II) contains a bifurcated hydrogen bond involving the ammonium H(6) atom.

As expected for this type of hydrogen bond, the  $O \cdots H$  and  $O \cdots N$  distances are longer and the  $O \cdots H-N$  angle more acute than are usual for a hydrogen bond to only one acceptor atom. A second possible bifurcated hydrogen bond involves the ammonium H(4) atom. Table 4 lists the distances and angles of this bond to O(2). The distances and angles of the possible bond to the F atom are  $F \cdots H(4)$  2.30 (4),  $F \cdots N$  3.133 Å,  $F \cdots H(4)-N$  141, and  $C(2)-F \cdots N$  119.2°. The longer

Table 5. *Hydrogen bonding in ammonium difluoroacetate*

	$O \cdots H$	$O \cdots N$	$O \cdots H-N$
$O(1) \cdots H(3)-N$	1.91 (4) Å	2.802 (4) Å	174°
$O(1)^I \cdots H(4)-N$	1.98 (5)	2.818 (5)	161
$O(2)^{II} \cdots H(2)-N$	1.92 (5)	2.869 (5)	160
$O(2)^{III} \cdots H(5)-N$	1.84 (5)	2.836 (4)	172

Table 5 (cont.)

$O(1) \cdots N \cdots O(1)^I$	112.1 (2)°	$O(1)^I \cdots N \cdots O(2)^{II}$	85.9 (1)°
$O(1) \cdots N \cdots O(2)^{II}$	108.9 (1)	$O(1)^I \cdots N \cdots O(2)^{III}$	116.5 (2)
$O(1) \cdots N \cdots O(2)^{III}$	111.4 (1)	$O(2)^{II} \cdots N \cdots O(2)^{III}$	119.7 (1)
$N \cdots O(1) \cdots N^{III}$	94.1 (2)	$N^I \cdots O(2) \cdots N^{IV}$	104.8 (2)
$N \cdots O(1) \cdots C(1)$	132.8 (3)	$N^I \cdots O(2) \cdots C(1)$	130.7 (3)
$N^{III} \cdots O(1) \cdots C(1)$	131.6 (3)	$N^{IV} \cdots O(2) \cdots C(1)$	116.2 (3)
Sum about O(1)	358.5	Sum about O(2)	351.7

Symmetry code: (i)  $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$ ; (ii)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ ; (iv)  $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$ .

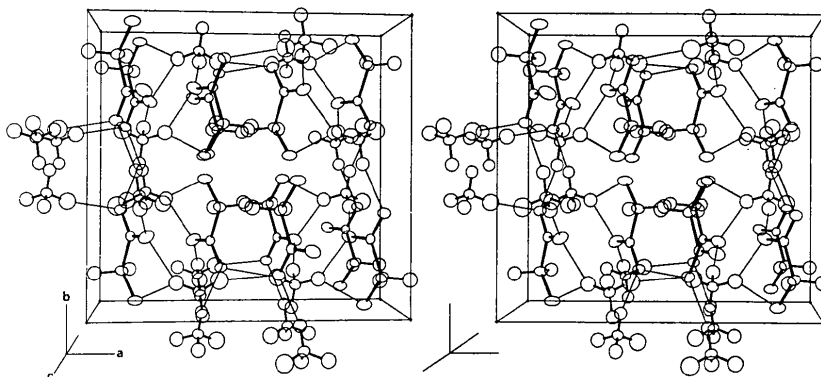


Fig. 1. Packing diagram for ammonium fluoroacetate viewed down the [001] direction [ORTEP, Johnson (1965)].

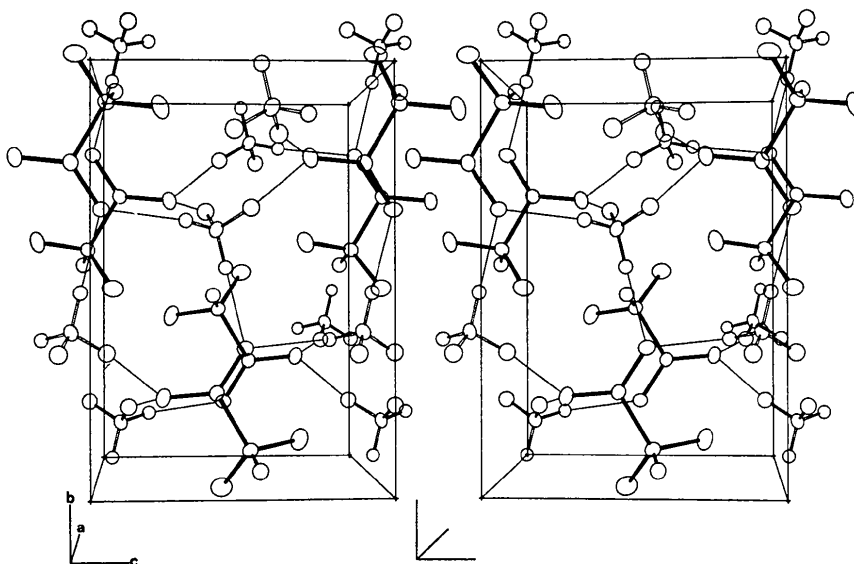


Fig. 2. Packing diagram for ammonium difluoroacetate viewed down the  $[100]$  direction [ORTEP, Johnson (1965)].

distances to F compared with the distances to O(2) indicate a weaker interaction between F and H(4) than between O(2) and H(4). The similar angles about F and about O(2), the essentially equal angles about H(4) (see Fig. 1, also), the  $F \cdots H(4)$  distance less than the sum of the van der Waals radii (Bondi, 1964) of 2.6 Å, and the geometry of the  $N-H(4) \cdots O(2)$  hydrogen bond (longer distances and more acute angle than are usual for a hydrogen bond to only one acceptor atom) together indicate that H(4) may participate in a bifurcated hydrogen bond involving O(2) and F. This possible hydrogen bond is indicated in Fig. 1.

The ammonium ions in (II) and (III) are tetrahedral to within about two standard deviations of the angles. The ammonium ion in (II) is associated with one F and five O atoms in an irregular arrangement. Two O atoms are associated with the N atom by normal hydrogen bonds involving H(3) and H(5). A bifurcated hydrogen bond involving H(6) associates two additional O atoms with the N atom; the preceding paragraph indicates that it may be a second bifurcated hydrogen bond, involving H(4), which associates the fifth O atom and the F atom with the N atom. The irregular arrangement around the ammonium ion in (II) can best be understood by studying Fig. 1.

The ammonium ion in (III) is associated with four O atoms in an approximately regular tetrahedral arrangement. The O atoms are associated with the N atom by regular hydrogen bonds which appear, on the basis of similar distances and angles, to be similar in strength. The arrangement around the ammonium ion in (III) is clearly shown in Fig. 2.

In the fluoro- and difluoroacetate ions the four atoms O(1), O(2), C(1), C(2) lie very close to a plane,

with C(1) showing the largest deviation from the least-squares plane [(II) 0.002, (III) 0.015 Å]. The fluoroacetate ion (in II) has the fluoromethyl group rotated so that the F atom lies within 0.10 Å of the plane of C(1), C(2), O(1) and O(2). The F atoms of the difluoroacetate ion (in III) lie on the same side of the C(1), C(2), O(1), O(2) plane and at nearly equal distances from it [F(1) at 0.67, F(2) at 0.61 Å].

The O atoms of the fluoroacetate ion (in II) are associated with five N atoms by normal and bifurcated hydrogen bonds. The three N atoms associated with O(1) are arranged so that the C–O bond approximates a threefold axis relating the N atoms. One association is by a normal hydrogen bond and the other two by parts of bifurcated hydrogen bonds. The two N atoms associated with O(2) lie in an arrangement which, including the adjacent C atom, is nearly planar. One association is by a normal hydrogen bond and the other by part of a possible bifurcated hydrogen bond.

The O atoms of the difluoroacetate ion (in III) are each associated with two N atoms by normal hydrogen bonds in arrangements which, including the adjacent C atoms, are nearly planar.

### Comparison

Ammonium acetate (I) (Nahringbauer, 1967) and ammonium trifluoroacetate (IV) (Cruickshank, Jones & Walker, 1964) are isostructural but the crystal structures of ammonium fluoroacetate (II) and ammonium difluoroacetate (III) are considerably different from each other and from those of (I) and (IV). The space groups and cell parameters of (II) and (III) are different, the hydrogen-bonding networks are different [especially so

Table 6. Comparison of ammonium acetate and its fluoro derivatives

	C <sub>2</sub> H <sub>7</sub> NO <sub>2</sub> (I)	C <sub>2</sub> H <sub>6</sub> FNO <sub>2</sub> (II)	C <sub>2</sub> H <sub>5</sub> F <sub>2</sub> NO <sub>2</sub> (III)	C <sub>2</sub> H <sub>4</sub> F <sub>3</sub> NO <sub>2</sub> (IV)
Unit-cell parameters				
<i>a</i> (Å)	4.787	11.755	7.486	<i>c</i> = 4.83
<i>b</i> (Å)	7.742	10.900	9.271	<i>b</i> = 8.20
<i>c</i> (Å)	12.015	6.788	6.570	<i>a</i> = 12.65
$\beta$ (°)	100.76	92.67	(90)	100.6
<i>V</i> (Å <sup>3</sup> )	437.5	868.8	456.0	492.5
<i>V</i> mol <sup>-1</sup> (Å <sup>3</sup> )	109.4	108.6	114.0	123.1
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
Bond angles (°) and distances (Å)*				
O–C–O	123.6	127.0 (2)	128.3 (3)	128.0
C–C–O	118.2	116.5 (2)	115.8 (2)	116.0
C–C–F	—	113.0 (2)	111.0 (2)	111.6
F–C–F	—	—	106.7 (3)	107.2
C–O	1.251	1.240 (2)	1.233 (2)	1.257
C–C	1.504	1.495 (3)	1.533 (4)	1.535
C–F	—	1.391 (3)	1.352 (2)	1.334
Hydrogen-bond angles (°) and distances (Å)*				
O $\cdots$ H	1.92	2.08	1.91	1.99
O $\cdots$ N	2.816	2.888	2.831	2.90
O $\cdots$ H–N	179	145	167	169
O $\cdots$ N $\cdots$ O	109.4	102.8	109.1	109.3
(C, N) $\cdots$ O $\cdots$ N	119.5	111.9	118.4	119.8

\* The angles and distances have been averaged for an individual structure where this is appropriate. The estimated standard deviations then apply to the average value of the angle or distance.

for (II) where two H atoms appear to participate in bifurcated hydrogen bonds], and the packing of the molecules in the unit cells is different. In spite of the differences between the four crystal structures, corresponding angles and distances within the ions are similar, as is shown in Table 6. No systematic trends are observed among (I), (II), (III) and (IV) in the C-C or average C-O distances or in the O-C-O or average C-C-O angles.

The C-F bonds in (II), (III) and (IV) show a uniform decrease in length with an increase in the number of H atoms replaced by F atoms; this effect has been reviewed thoroughly by Yokozeki & Bauer (1975) for molecular structures in the gas phase and the average C-F bond lengths in the crystalline ammonium fluoroacetates are in excellent agreement with their tabulated values. In addition, the departures of the C-C-F and F-C-F angles from the tetrahedral value of  $109.5^\circ$ , as reported by Cruickshank, Jones & Walker (1964) for (IV), are also observed in (II) and (III); again, in agreement with Yokozeki & Bauer (1975). The average C-F distances and C-C-F and F-C-F angles are listed in Table 6.

The volume occupied by one molecule in each structure is listed in Table 6. The molecular volumes of (II) and (III) are less than those expected from a linear interpolation between the molecular volumes of the other two members of the series. The denser packing of the molecules in (II) and (III) reflects the departure from the  $P2_1/c$  space group and the ammonium acetate structures for these two members of the series. The denser packing may also reflect the different hydrogen-bonding networks in (II) and (III).

The suggestion was made that the hydrogen-bond N...O distances in (IV) are longer than in (I) because the greater electronegativity of the  $-CF_3$  group relative to  $-CH_3$  makes the O atoms less negative (Nahringbauer, 1967). As shown in Table 6, the N...O distances in (I), (II), (III) and (IV) do not correspond closely to the number of F atoms; this indicates that the

effective electronegativity of the O atoms is not the major factor affecting N...O distances in these structures. The average N...O distance in (II) is longer because of the bifurcated hydrogen bond(s). The average N...O distance in (III) is only 0.015 Å longer than in (I) and 0.069 Å shorter than in (IV). Lingafelter (1976) suggests that the N...O distance in (IV) is longer than in (I) because the larger van der Waals radius of F relative to H creates packing effects [in the  $P2_1/c$  ammonium acetate type structures of (I) and (IV)] which prevent a close N...O distance without squeezing F atoms in (IV). Thus it appears that the differences between the hydrogen-bonding networks in (I), (II), (III) and (IV) are primarily due, not to the number of H atoms replaced by F atoms, but to the different crystal structures themselves (see Table 6 to compare space groups and unit-cell parameters).

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