

## The Crystal and Molecular Structure of Difluoroacetamide

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The structure of difluoroacetamide has been determined from three-dimensional counter-measured data. Libration corrections have been applied to the full-matrix least-squares refined parameters. The principal interatomic distances are C-C 1.543 (7), C-F 1.361 (9) and 1.364 (9), C-N 1.334 (8), and C-O 1.247 (8) Å.

The determination of the structure of difluoroacetamide forms part of a general series of investigations on the structure and hydrogen bonding of some simple amides related to acetamide. One particular aspect is a comparison of members of the series  $\text{CH}_3\text{CONH}_2$ ,  $\text{CH}_2\text{FCONH}_2$ ,  $\text{CHF}_2\text{CONH}_2$  and  $\text{CF}_3\text{CONH}_2$ . The structure of monofluoroacetamide (Hughes & Small, 1962) in which the fluorine atom is almost exactly coplanar with the amide group and in *cis* conformation relative to the  $\text{NH}_2$  group, suggested the possibility of intramolecular hydrogen bonding. It is of interest, therefore, to determine the configuration of the two fluorine atoms relative to the amide group in difluoroacetamide.

### Preparation and unit cell data

Difluoroacetamide was prepared by passing anhydrous ammonia through an alcoholic solution of ethyl difluoroacetate. The excess alcohol was distilled off under vacuum and the product purified by vacuum sublimation. The melting point was 51 °C.

Whether grown by sublimation or recrystallized from solvent, crystals of difluoroacetamide grow as long needles with a marked tendency to twin. For diffraction work single crystals grown from benzene solution were sealed in Lindemann-glass tubes to avoid sublimation, which occurs rapidly at room temperature.

Weissenberg photographs taken with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542$  Å) showed systematic absences consistent with the space group  $P2_1/c$  and were used also for the measurement of approximate cell constants. More accurate values of the cell dimensions were obtained from measurements made on the diffractometer described by Small & Travers (1961) following the method of Bracher & Small (1967) to eliminate zero

errors and any mis-settings of  $\varphi$  and  $\chi$ . The results are:  $a = 5.143 \pm 0.005$ ,  $b = 12.809 \pm 0.002$ ,  $c = 7.037 \pm 0.004$  Å,  $\beta = 128.3 \pm 0.1^\circ$ ,  $D_{\text{obs}} = 1.72$  g.cm<sup>-3</sup>,  $D_{\text{calc}} = 1.735$  g.cm<sup>-3</sup> for  $Z = 4$ .

### Intensity data

Using the diffractometer and  $\text{Cu K}\alpha$  radiation, intensity data were collected out to the limit  $\theta = 82.5^\circ$  accessible with the instrument. Only 554 unique reflexions out of a possible 800 proved to be measurably significant, most of the absent orders were at higher  $\theta$  values. Corrections for absorption and extinction effects were not made. The measured intensities were converted to structure factors with the program *DATRDN* of the *X-RAY* 63 system on the ATLAS computer at Chilton.

### Determination of the structure

Many primary amide crystals are characterized by a lattice translation of approximately 5.0 Å along one of the directions of hydrogen bonding. In difluoroacetamide the  $a$  length of 5.143 Å and the presence of pronounced cleavage parallel to that direction suggested that the molecules were hydrogen bonded in chains parallel to **a**. Support for this model was given by a  $F^2$  Fourier synthesis, computed with  $0kl$  data, which further indicated that most of the atoms were lying in the plane (041). An initial model, involving only carbon, nitrogen and oxygen atoms lying in this plane so as to form additional hydrogen bonds across a centre of symmetry, was used for calculating structure factors. For these and all other calculations the atomic scattering factors listed in the *International Tables for X-ray Crystallography* (1962) were used. An isotropic  $B$  value of 5.7 Å<sup>2</sup> was used for all atoms, obtained by the method of Wilson (1942). An  $F_o - F_c$  Fourier synthesis using  $0kl$  terms gave a single peak which was interpreted as two overlapping fluorine atoms. Partial refinement of this projection was carried out by least-squares calculations.

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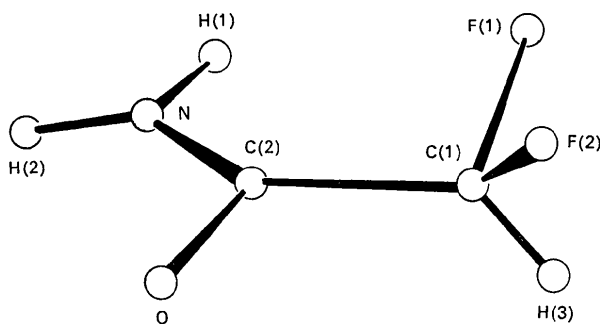


Fig. 1. Atomic numbering scheme.

Using assumed bond distances and angles and the  $y$  and  $z$  coordinates previously refined, a three dimensional model was obtained and refined using, eventually, full-matrix least squares with anisotropic temperature factors. For this purpose, the program *ORFLS* on the *X-RAY* 63 system at the ATLAS computing laboratory, Chilton, was used initially. In later cycles the program *FMLS* of Bracher & Taylor (1967), adapted for the Lancaster University ICL 1909 computer, was used. At an intermediate stage in the refinement, hydrogen atom positions were obtained from peaks on an  $F_o-F_c$  Fourier synthesis; these parameters together with isotropic temperature factors of  $3.5 \text{ \AA}^2$  were included but not refined in subsequent cycles. A weighting factor  $w = \{1 + [(F_o - 10.0)/3.0]^2\}^{-1/2}$  was used in the later stages of refinement and an  $R$  value of 0.089 eventually attained, when the least-squares shifts were less than one tenth of the estimated standard deviations.

In Tables 1 and 2 are given the final position and thermal vibration parameters, and in Table 3 the observed and calculated structure factors are listed.

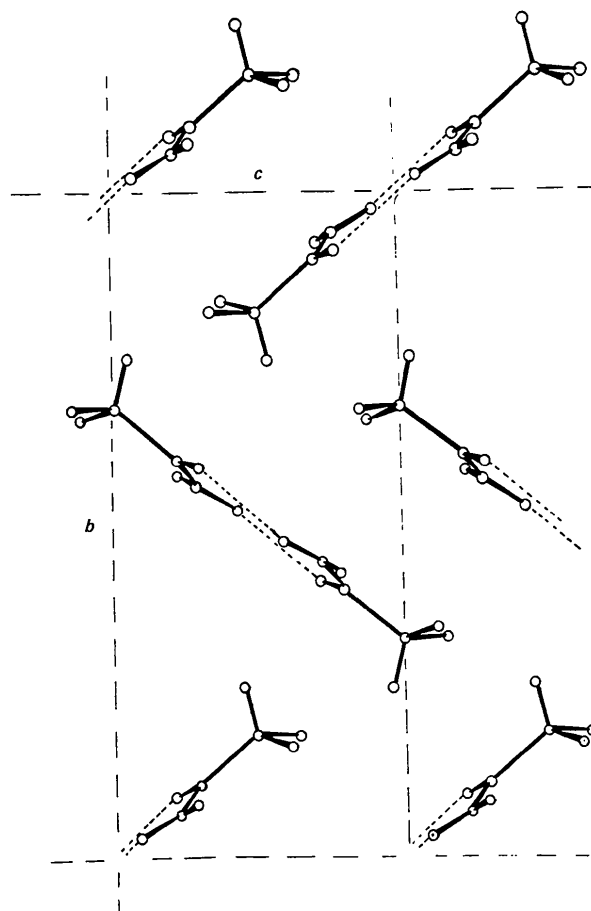
Table 1. Fractional atomic coordinates and their standard deviations (in parentheses)  $\times 10^5$ 

(See Fig. 1 for nomenclature.)

	$x$	$y$	$z$
C(1)	35894 (122)	17780 (37)	50523 (80)
C(2)	21460 (106)	10113 (32)	29345 (75)
N	-7514 (106)	6122 (34)	20490 (76)
O	36986 (89)	8551 (29)	21691 (67)
F(1)	24012 (111)	15598 (32)	62387 (67)
F(2)	68788 (90)	16614 (34)	66476 (69)
H(1)	84500	7200	28100
H(2)	82000	2600	8000
H(3)	31900	25900	46000

## Analysis of thermal vibration parameters

The vibrational motion of rigid-body molecules which do not possess a centre of symmetry may be described in terms of three tensors  $T$ ,  $\omega$  and  $S$ . Schomaker & Trueblood (1968) have introduced the cross tensor  $S$  which accounts for correlation of the translational and librational motions described by the tensors  $T$  and  $\omega$  first used by Cruickshank (1965). The elements of these tensors (and their standard deviations) may be derived from a least-squares fit of the atomic  $b_{ij}$  values obtained from the anisotropic full-matrix structure refinement. The program *MGTL* of Gantzel, Trueblood *et al.* (ACA program No. 1, 1971), was adapted for the ICL 1909 computer and used for these calculations.

Fig. 2. Packing of the structure, viewed along the  $a$  axis.Table 2.  $b_{ij}$  values for C, N, O and F atoms  $\exp \{-10^{-5}(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})\}$ , with standard deviations in parentheses

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
C(1)	4111 (313)	312 (27)	1399 (141)	-335 (150)	2970 (362)	-298 (102)
C(2)	2741 (268)	232 (25)	1266 (136)	-47 (122)	2360 (333)	-43 (87)
N	4051 (291)	496 (30)	2245 (149)	-792 (137)	4688 (362)	-879 (99)
O	4313 (251)	512 (26)	2652 (134)	-812 (117)	5247 (322)	-1049 (90)
F(1)	11350 (376)	895 (33)	3333 (137)	-2932 (169)	10919 (412)	-1872 (102)
F(2)	4799 (258)	940 (34)	3024 (139)	-525 (142)	2186 (319)	-1551 (107)



Table 8. Values of ( $U_{ij} \times 10^4$ ) in  $\text{\AA}^2$ , (a) from  $b_{ij}$  values, (b) from rigid body model

	$U_{11}$		$U_{22}$		$U_{33}$		$U_{12}$		$U_{13}$		$U_{23}$	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
C(1)	348	351	259	311	216	251	-14	-18	43	63	-53	-70
C(2)	221	222	193	154	196	169	-2	19	15	31	-8	36
N	226	230	412	420	347	369	-8	-23	63	48	-157	-163
O	237	220	426	441	410	444	13	10	54	59	-188	-181
F(1)	601	610	744	728	515	499	-224	-227	379	354	-335	-337
F(2)	686	686	781	761	467	419	132	136	-212	-213	-278	-295

of this axis is almost the same as that of the molecular C(1)-C(2) bond (direction cosines 0.109, -0.642, -0.757).

Table 9. Libration corrected atomic coordinates for C, N, O and F atoms  $\times 10^5$  (referred to same origin and axes as Table 2)

	x	y	z
C(1)	35849	17825	50485
C(2)	21393	10136	29238
N	-8091	6117	20349
O	37359	8586	21563
F(1)	23636	15561	62499
F(2)	69368	16587	66658

### Description of the structure

Difluoroacetamide is typical of most primary amide crystals in forming centrosymmetric hydrogen-bonded pairs. These pairs form further hydrogen bonds sideways to similar pairs related by the **a** translation. This arrangement, which involves maximum hydrogen bonding, gives rise to ribbons of two molecules width, extending parallel to **a**. Leiserowitz & Schmidt (1969) have designated this general type amongst amide structures as translation packing. Neighbouring molecular ribbons in difluoroacetamide are related by the screw axis parallel to **b** and perpendicular to the ribbon length, to give the 'staggered' packing illustrated in Fig. 2. The inclination of the mean hydrogen bonding plane to **b** is  $50^\circ$ .

The bond distances and angles within the molecule are given in Table 10. The carboamide group is effectively planar, the equation of the mean plane and the deviations of the carbon, nitrogen and oxygen atoms from it are given in Table 11. The torsion angles involving the fluorine atoms are  $156^\circ$  [F(1)C(2)C(1)O] and  $39^\circ$  [F(2)C(2)C(1)O] respectively. In Table 12 are given distances and angles involved in the hydrogen-bonding system.

Table 10. Bond distances and angles

(a) Intramolecular distances (after libration correction) and their standard deviations, where determined.			
C(1)-C(2)	1.543 (7) $\text{\AA}$	C(1)-H(3)	1.06 $\text{\AA}$
C(1)-F(1)	1.361 (9)	N-H(1)	0.85
C(1)-F(2)	1.364 (9)	N-H(2)	0.82
C(2)-N	1.334 (8)		
C(2)-O	1.247 (8)		

Table 10 (cont.)

(b) Bond angles (after libration correction) and their standard deviations, where determined.

C(2)-C(1)-F(1)	109.5 (5) $^\circ$	C(2)-C(1)-H(3)	116 $^\circ$
C(2)-C(1)-F(2)	109.6 (5)	H(3)-C(1)-F(1)	108
F(1)-C(1)-F(2)	106.7 (5)	H(3)-C(1)-F(2)	106
C(1)-C(2)-N	115.2 (5)	C(2)-N-H(1)	118
C(1)-C(2)-O	118.0 (5)	C(2)-N-H <sub>2</sub>	119
O-C(2)-N	126.7 (4)	H(2)-N-H <sub>1</sub>	123

Table 11. Deviations of atoms from the 'best' plane defined by C(1), C(2), O, N (referred to orthogonal axes),  $\text{\AA}$ 

$$-0.0868x + 0.7638y - 0.6396z = -0.0120$$

C(1)	0.0038	F(1)	-0.5421
C(2)	-0.0139	F(2)	-0.7770
O	0.0053	H(1)	-0.101
N	0.0048	H(2)	0.094
		H(3)	0.953

Table 12. Hydrogen bonded distances and angles and their standard deviations (where obtained). The numerals in parentheses in the angle and distance descriptions refer to molecules related as follows: <sup>(i)</sup>  $x, y, z$  <sup>(ii)</sup>  $\bar{x}, \bar{y}, \bar{z}$  <sup>(iii)</sup>  $1+x, y, z$ 

Distance ( $\text{\AA}$ )			
N <sup>i</sup> ...O <sup>ii</sup>	3.011 (6)	H(2 <sup>i</sup> )...O <sup>ii</sup>	2.20
N <sup>iii</sup> ...O <sup>i</sup>	2.924 (9)	O <sup>i</sup> ...H(1 <sup>iii</sup> )	2.20
Angle ( $^\circ$ )			
N <sup>iii</sup> -H(1 <sup>iii</sup> )-O <sup>i</sup>	141	C(2 <sup>i</sup> )-O <sup>i</sup> -H(2 <sup>ii</sup> )	120
N <sup>i</sup> -H(2 <sup>i</sup> )-O <sup>ii</sup>	169	C(2 <sup>i</sup> )-O <sup>i</sup> -H(1 <sup>iii</sup> )	150

### Discussion of the structure

#### (a) Molecular dimensions and conformation

The length of the carbon-carbon bond (1.543  $\text{\AA}$ ) found in this compound is slightly greater than that found in acetamide (1.530  $\text{\AA}$ : Denne & Small, 1971) or monofluoroacetamide (1.533  $\text{\AA}$ : Hughes & Small, 1962). There are no other reported values of the carbon-carbon bond length linking a -CHF<sub>2</sub> group to an  $sp^2$ -hybridized carbon atom, but the length found in this determination is greater than that (1.51  $\text{\AA}$ ) usually expected between  $sp^3$  and  $sp^2$  hybridized carbon atoms. Similar lengthened carbon-carbon bonds have also been found in the trifluoroacetate ion, 1.542  $\text{\AA}$  in

ammonium trifluoroacetate (Cruickshank, Jones & Walker, 1964) and 1.541 Å in potassium hydrogen bis trifluoroacetate (MacDonald, Speakman & Hadži, 1972).

The C–O and C–N bond lengths are within the range of values previously reported in other primary amide structures. The two C–F bonds, which are equal in length within the limits of error of this work, are significantly shorter than that found in monofluoroacetamide (1.406 Å) but larger than that found in ammonium trifluoroacetate, 1.346 Å (mean), and in potassium hydrogen bis trifluoroacetate, 1.326 Å (mean). A comparable progressive decrease in C–F distance along the series  $-\text{CH}_2\text{F}$ ,  $-\text{CHF}_2$ ,  $-\text{CF}_3$  has previously been noted in simple gas-phase molecules (Bent, 1960).

The conformations of the fluorinated methyl groups relative to the amide group differ considerably between monofluoroacetamide and difluoroacetamide. In the former, the conformation is such that the fluorine atom 'eclipses' the amide  $\text{NH}_2$  group. In difluoroacetamide, the two fluorine atoms are roughly equidistant from the carbo-amide plane and on the same side, as the torsion angles show. This suggests that in difluoroacetamide repulsion between the whole amide group and the  $-\text{CHF}_2$  group is minimized to give the 'staggered' conformation, whereas in monofluoroacetamide repulsion between the oxygen atom of the amide group and the fluorine atom of the  $-\text{CH}_2\text{F}$  group is predominant. The difference may arise from the greater electronegativity of the single fluorine atom in the mono-substituted  $-\text{CH}_2\text{F}$  group compared with the two fluorine atoms in the group  $-\text{CHF}_2$ . It is of interest to note that the shortest intramolecular  $\text{F}\cdots\text{H}$  (amide) distances in these two structures do not differ significantly (2.30 Å in monofluoroacetamide and 2.44 Å in difluoroacetamide). These values may be compared with the sum of the van der Waals radii (Bondi, 1964), 2.60 Å. The shortest intermolecular distance between hydrogen and fluorine atoms in this structure is 2.40 Å.

#### (b) Hydrogen bonding

Hydrogen-bonded distances and angles fall into the general pattern found in primary amide structures which involve translation packing. In particular, the hydrogen bond between centrosymmetrically related molecules is more nearly linear ( $\text{N}-\text{H}\cdots\text{O}$  angle  $169^\circ$ ) than the bond between a-translation-related molecules ( $\text{N}-\text{H}\cdots\text{O}$  angle  $141^\circ$ ). The mean planes of the amide groups of pairs of molecules hydrogen bonded across a centre of symmetry are separated by only 0.024 Å and the mean inclination of each amide group to  $\mathbf{a}$  is  $5^\circ$ .

We are indebted to Dr B. M. Bracher who supplied a copy of the program *FMLS* and to Professor K. N. Trueblood for the program *MGTL*. We are grateful to Dr R. E. Cobbleck who adapted both of these programs to the ICL 1909 computer.

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