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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 CH_3CONH_2, CH_2FCONH_2, CHF_2CONH_2 and CF_3CONH_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 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 Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ 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 φ and χ. The results are: $a = 5{\cdot}143 \pm 0{\cdot}005$, $b = 12{\cdot}809 \pm 0{\cdot}002$, $c = 7{\cdot}037 \pm 0{\cdot}004$ Å, $\beta = 128{\cdot}3 \pm 0{\cdot}1°$, $D_{obs} = 1{\cdot}72$ g.cm^{-3}, $D_{calc} = 1{\cdot}735$ g.cm^{-3} for $Z = 4$.

Intensity data

Using the diffractometer and Cu $K\alpha$ radiation, intensity data were collected out to the limit $\theta = 82{\cdot}5°$ 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 θ 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^2 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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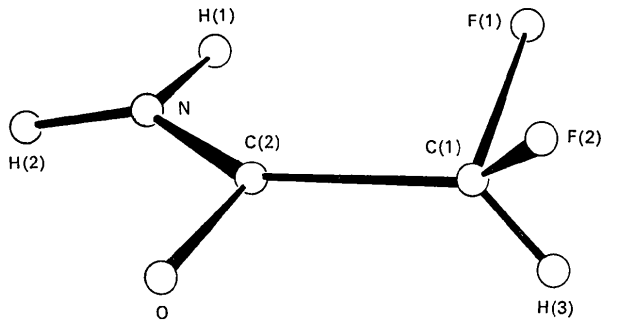

Fig. 1. Atomic numbering scheme.

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 Å^2 were included but not refined in subsequent cycles. A weighting factor $w=\{1+[(F_o-10{\cdot}0)/3{\cdot}0]^2\}^{-1/2}$ 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**, **ω** 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 **ω** 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.

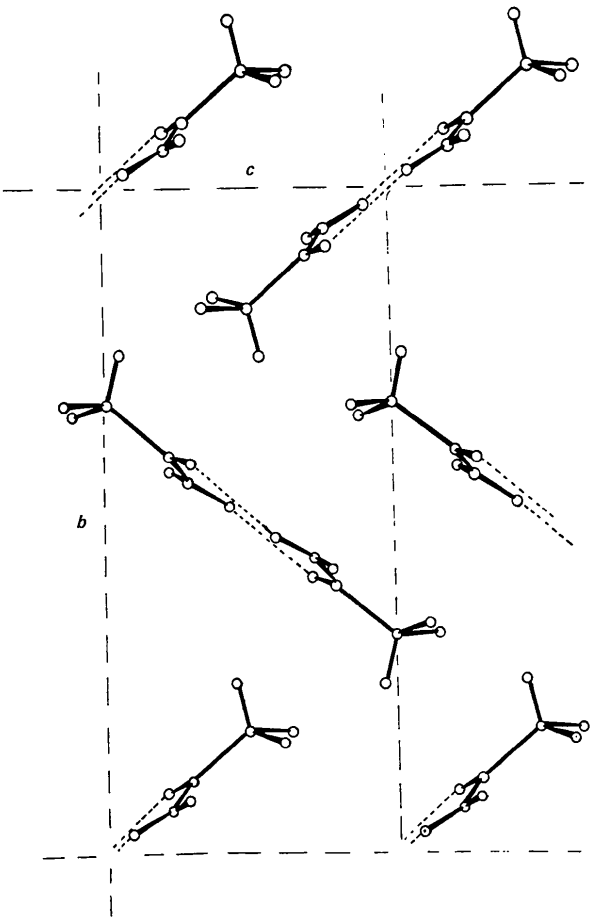

Fig. 2. Packing of the structure, viewed along the a axis.

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 3. *Values of hkl and observed and calculated structure factors* ($\times 10^2$)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	2	4295	4312	0	14	0	335	434	1	6	3	629	603	1	15	-1	487	511	2	7	-7	141	105	3	2	3	173	201	3	9	-6	361	366	4	8	-2	456	444
0	0	4	425	390	0	14	2	296	359	1	6	-1	550	547	2	0	0	3036	3524	2	7	0	251	245	3	2	-1	613	624	3	10	0	204	191	4	8	-3	346	328
0	0	6	632	674	0	15	1	296	387	1	6	-2	173	92	2	0	-4	3492	3340	2	7	1	503	474	3	2	-2	613	576	3	10	1	110	117	4	8	-5	818	813
0	1	1	2399	1997	1	0	0	1352	1365	1	6	-3	597	484	2	0	-6	1997	1935	2	7	2	1130	1095	3	2	-3	755	744	3	10	-1	361	352	4	8	-6	471	479
0	1	2	4527	4234	1	0	2	157	43	1	6	-4	582	573	2	0	-8	267	258	2	7	-1	1693	1608	3	2	-4	377	371	3	10	-2	943	931	4	8	-7	173	111
0	1	3	296	222	1	0	4	1164	1138	1	6	-5	393	277	2	1	0	456	631	2	7	-2	471	389	3	2	-5	1305	1210	3	10	-3	173	199	4	9	-1	251	340
0	1	4	980	850	1	0	-2	975	1128	1	6	-6	723	698	2	1	1	1809	2829	2	7	-3	1478	1428	3	2	-6	1006	1080	3	10	-4	644	700	4	9	-2	692	649
0	1	5	193	202	1	0	-4	1148	1008	1	7	0	1541	1321	2	1	2	1022	1199	2	7	-4	1384	1369	3	2	-7	351	405	3	10	-5	644	666	4	9	-4	314	339
0	1	6	141	199	1	0	-6	1274	1187	1	7	1	676	577	2	1	3	1242	1238	2	7	-5	183	246	3	2	-8	173	210	3	11	-2	173	81	4	9	-5	314	355
0	2	0	219	117	1	1	0	2060	2912	1	7	2	2013	1874	2	1	4	613	588	2	7	-7	424	454	3	3	0	692	653	3	11	-3	770	916	4	9	-6	393	335
0	2	1	1857	1497	1	1	1	802	819	1	7	3	173	182	2	1	-1	1368	1612	2	8	0	409	358	3	3	1	692	616	3	11	-4	471	464	4	10	-1	377	345
0	2	2	3586	3000	1	1	2	125	150	1	7	-1	676	661	2	1	-2	1620	1773	2	8	1	1604	1447	3	3	2	597	553	3	11	-5	314	355	4	10	-2	267	283
0	2	3	2979	3083	1	1	3	849	878	1	7	-2	2291	2061	2	1	-3	928	847	2	8	2	660	635	3	3	-1	644	569	3	12	-3	597	588	4	10	-3	566	518
0	2	4	915	934	1	1	4	723	760	1	7	-3	377	293	2	1	-4	1966	1888	2	8	3	157	149	3	3	-2	330	332	3	12	-4	94	45	4	10	-4	424	416
0	2	5	1070	1075	1	1	-1	2375	2851	1	7	-4	346	335	2	1	-5	440	442	2	9	-1	1463	1365	3	3	-3	755	738	3	13	-2	125	118	4	10	-5	251	257
0	2	6	335	405	1	1	-2	1919	1785	1	7	-5	110	68	2	1	-6	1352	1341	2	9	-2	487	557	3	3	-4	1368	1377	3	13	-3	94	96	4	11	-3	597	609
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0	3	3	1934	1864	1	1	-5	833	672	1	8	2	173	87	2	2	1	409	584	2	8	-6	393	407	3	3	-7	1130	1104	4	1	-1	503	571	5	0	-6	1667	1812
0	3	4	890	830	1	1	-7	346	347	1	8	3	692	656	2	2	2	755	662	2	9	0	723	749	3	4	0	471	506	4	1	-2	755	777	5	0	-8	896	939
0	3	5	567	583	1	2	0	1494	1879	1	8	4	393	389	2	2	3	1667	1730	2	9	1	1242	1236	3	4	1	707	722	4	1	-3	2029	1935	5	1	-1	519	440
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0	4	0	5327	5713	1	2	3	409	415	1	8	-2	1038	995	2	2	-1	2196	2295	2	9	3	456	399	3	4	-1	865	869	4	1	-6	1132	1167	5	1	-4	1402	1271
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0	10	1	348	376	1	5	1	1997	1773	1	12	-2	235	241	2	5	-4	975	929	3	1	1	157	272	3	8	-1	283	283	4	6	-4	125	67	5	7	-3	739	630
0	10	3	748	890	1	5	3	692	655	1	12	-3	519	499	2	5	-5	377	297	3	1	2	755	769	3	8	-2	235	195	4	6	-5	534	538	5	7	-4	519	434
0	10	4	348	432	1	5	4	440	318	1	12	-4	173	137	2	5	-6	566	620	3	1	3	298	416	3	8	-4	975	990	4	6	-6	125	345	5	7	-5	613	594
0	10	5	116	198	1	5	5	692	739	1	13	0	880	847	2	5	-7	503	561	3	1	-1	770	789	3	8	-5	1211	1212	4	6	-7	393	495	5	7	-6	298	260
0	11	1	541	649	1	5	-1	660	765	1	13	2	346	407	2	6	0	1321	1304	3	1	-2	613	753	3	8	-6	157	175	4	7	0	220	187	5	8	-3	283	250
0	11	2	928	1050	1	5	-2	2013	2030	1	13	-1	141	147	2	6	1	440	440	3	1	-4	2611	2577	3	8	-7	802	873	4	7	-1	456	501	5	8	-4	157	144
0	11	3	361	379	1	5	-3	755	764	1	13	-2	125	97	2	6	2	1085	1029	3	1	-5	409	241	3	9	0	173	160	4	7	-2	94	140	5	8	-5	928	844
0	11	4	554	603	1	5	-4	1400	1210	1	13	-3	393	448	2	6	-1	629	505	3	1	-6	393	428	3	9	1	314	352	4	7	-3	487	497	5	8	-6	409	397
0	12	0	1457	1429	1	5	-5	125	169	1	13	-4	125	158	2	6	-2	1368	1703	3	1	-7	1431	1465	3	9	-1	487	443	4	7	-4	1038	1054	5	9	-4	267	244
0	12	1	361	393	1	5	-6	377	369	1	14	0	173	162	2	6	-3	975	1113	3	2	0	487	455	3	9	-2	141	101	4	7	-5	707	762	5	9	-5	188	173
0	12	2	167	195	1	6	0	1022	902	1	14	1	298	329	2	6	-4	503	464	3	2	1	377	404	3	9	-3	409	452	4	7	-6	157	155	6	2	-4	110	117
0	12	4	64	85	1	6	1	566	489	1	14	-1	204	241	2	6	-5	157	149	3	2	2	141	155	3	9	-5	865	834	4	7	-7	377	464	6	2	-5	125	178
0	13	3	116	98	1	6	2	424	425	1	14	-2	456	435	2	6	-6	361	393																					

Values of the tensors **T**, **ω** and **S** (and their standard deviations) are given in Tables 4, 5 and 6; in Table 7 are the magnitudes of the principal axes of **ω** and their direction cosines relative to orthogonal axes *a*, *b*, *c**.

Table 4. *Rigid body translation tensor. Elements* ($T_{ij} \times 10^4$) *of the mean square tensor, in* Å^2, *and their standard deviations*

T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
312 (19)	255 (33)	191 (19)	−4 (17)	39 (14)	−13 (22)

Table 5. *Rigid body librational tensor. Elements* ($\omega_{ij} \times 10^4$) *of the mean square tensor, in rad*^{2}, *and their standard deviations*

ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{13}	ω_{23}
25 (57)	200 (15)	256 (52)	−15 (12)	−26 (11)	186 (25)

Table 6. *The cross tensor* **S**. *Elements* ($S_{ij} \times 10^4$), *in* rad.Å, *and their standard deviations*

13 (16)	−73 (7)	39 (9)
123 (8)	−8 (13)	−2 (7)
74 (13)	7 (9)	−5 (33)

Table 7. *Rigid body librational tensor.* (*a*) *Principal axes* (*root mean square displacement in degrees*). (*b*) *Direction cosines relative to orthogonal axes a, b, c**

(*a*)	(*b*)		
11·73	0·0747	−0·6500	−0·7563
3·69	0·2631	0·7446	−0·6135
2·66	0·9627	−0·1507	0·2245

A useful check of the fit of the rigid-body motion is to compare values of the U_{ij}'s for each atom calculated from the rigid-body tensors **T**, **ω** and **S** with those derived directly from the b_{ij} values of the structure refinement. A comparison of these two sets of U_{ij} is made in Table 8; the differences may be compared with a mean σU_{ij} of 23×10^{-4} Å^2 obtained from b_{ij} e.s.d.'s in Table 2. The agreement indicates that the rigid-body model of the thermal motion is a reasonable approximation. Libration corrections to the position parameters within one molecule have therefore been made and the corrected coordinates are given in Table 9. It will be noted from Table 7 that there is an exceptionally large amplitude of libration (r.m.s. amplitude 11·7°) about the first principal axis of **ω**; the direction

Table 8. *Values of* $(U_{ij} \times 10^4)$ *in* Å^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 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°.

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° [F(1)C(2)C(1)O] and 39° [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) Å	C(1)–H(3)	1·06 Å
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)°	C(2)–C(1)–H(3)	116°
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_2	119
O—C(2)–N	126·7 (4)	H(2)–N—H_1	123

Table 11. *Deviations of atoms from the 'best' plane defined by* C(1), C(2), O, N (*referred to orthogonal axes*), Å

$$-0{\cdot}0868x + 0{\cdot}7638y - 0{\cdot}6396z = -0{\cdot}0120$$

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*: (i) x,y,z (ii) $\bar{x},\bar{y},\bar{z}$ (iii) $1+x,y,z$

Distance (Å)			
$N^i \cdots O^{ii}$	3·011 (6)	$H(2^i) \cdots O^{ii}$	2·20
$N^{iii} \cdots O^i$	2·924 (9)	$O^i \cdots H(1^{iii})$	2·20
Angle (°)			
N^{iii}–$H(1^{iii})$–O^i	141	$C(2^i)$–O^i–$H(2^{ii})$	120
N^i–$H(2^i)$–O^{ii}	169	$C(2^i)$–O^i–$H(1^{iii})$	150

Discussion of the structure

(*a*) *Molecular dimensions and conformation*

The length of the carbon–carbon bond (1·543 Å) found in this compound is slightly greater than that found in acetamide (1·530 Å: Denne & Small, 1971) or monofluoroacetamide (1·533 Å: Hughes & Small, 1962). There are no other reported values of the carbon–carbon bond length linking a $-CHF_2$ group to an sp^2-hybridized carbon atom, but the length found in this determination is greater than that (1·51 Å) 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 Å 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 $-CH_2F$, $-CHF_2$, $-CF_3$ 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 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 $-CHF_2$ 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 $-CH_2F$ group is predominant. The difference may arise from the greater electronegativity of the single fluorine atom in the mono-substituted $-CH_2F$ group compared with the two fluorine atoms in the group $-CHF_2$. Is is of interest to note that the shortest intramolecular F···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 (N–H···O angle 169°) than the bond between **a**-translation-related molecules (N–H···O angle 141°). 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 **a** is 5°.

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