

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 , $\text{CH}_2\text{FCONH}_2$, $\text{CHF}_2\text{CONH}_2$ 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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) 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: $a = 5.143 \pm 0.005$, $b = 12.809 \pm 0.002$, $c = 7.037 \pm 0.004$ Å, $\beta = 128.3 \pm 0.1^\circ$, $D_{\text{obs}} = 1.72 \text{ g.cm}^{-3}$, $D_{\text{calc}} = 1.735 \text{ g.cm}^{-3}$ 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 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 (011). 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 Å² 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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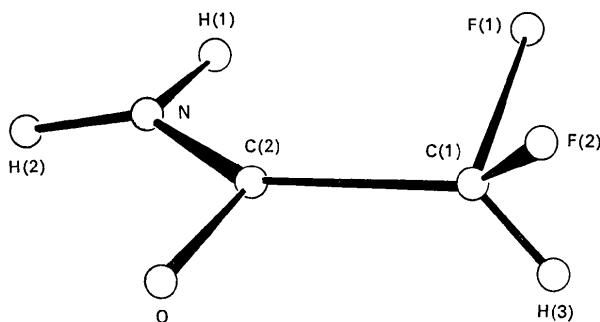


Fig. 1. Atomic numbering scheme.

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 \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.

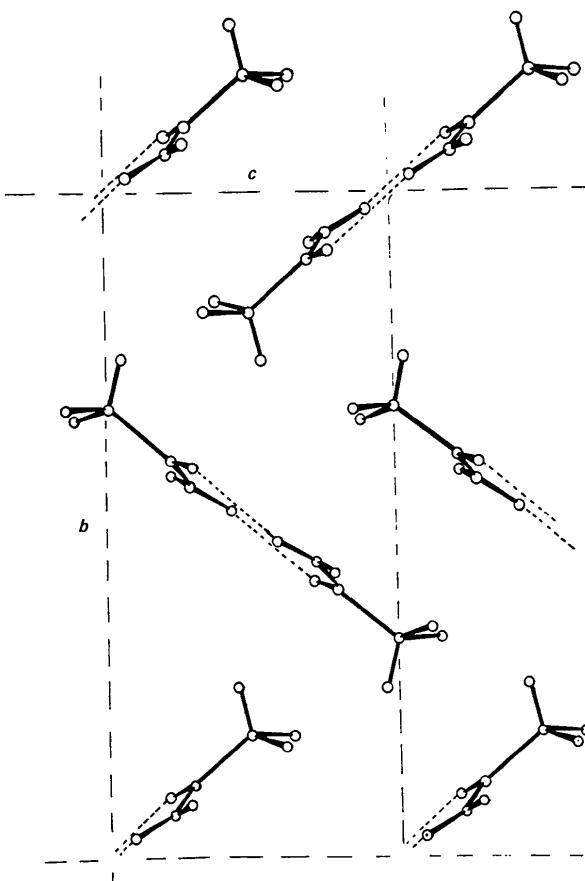
Table 1. Fractional atomic coordinates and their standard deviations (in parentheses) $\times 10^5$

(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 , 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 $\exp \{-10^{-5}(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hkb_{12} + hlb_{13} + kl b_{23})\}$, 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	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	
0	0	2	4295	4312	0	14	0	335	434	1	6	3	629	603	1	15	-1	487	511	1	6	-7	141	105	
0	0	4	425	390	0	14	2	295	359	1	6	-1	550	547	2	0	0	3036	3524	2	7	0	251	245	
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	
0	1	1	2399	1997	1	0	0	1352	1365	1	6	-3	597	484	2	0	-6	1997	1935	2	7	2	113	1095	
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	
0	1	3	292	262	1	0	4	1164	1138	1	6	-5	393	277	2	1	0	456	631	2	7	-2	471	389	
0	1	4	980	850	1	0	-2	975	1128	1	6	-6	723	698	2	1	1	1809	2629	2	7	3	1475	1428	
0	1	5	193	202	1	0	-4	1148	1065	1	7	0	1541	1321	2	1	2	1028	1199	2	7	-4	1384	1369	
0	1	6	141	199	1	0	-5	1274	1187	1	7	1	676	577	2	1	3	1242	1238	2	7	-7	391	405	
0	2	0	219	117	1	0	0	2050	2912	1	7	2	203	1874	2	1	4	613	588	2	7	-7	424	428	
0	2	1	1582	1407	1	1	0	666	519	1	7	3	173	162	2	1	-1	1512	1487	2	8	0	409	358	
0	2	2	2979	2983	1	1	3	849	765	1	7	-2	2891	2621	2	1	-2	1620	1703	2	8	-2	560	847	
0	2	3	915	924	1	1	4	723	760	1	7	-3	377	293	2	1	-1	1966	1888	2	8	-3	157	149	
0	2	4	1070	1075	1	1	-1	2375	2651	1	7	-4	345	335	2	1	-1	440	442	2	8	-9	1463	1365	
0	2	5	335	405	1	1	-2	1919	1785	1	7	-5	110	68	2	1	-6	1352	1341	2	8	-8	497	487	
0	3	0	4953	5258	1	1	-3	2595	2279	1	7	-6	393	424	2	1	-7	157	166	2	9	-1	564	632	
0	3	1	2599	1319	1	1	-4	157	126	1	8	1	251	191	2	2	0	1258	1487	2	9	-5	1132	1168	
0	3	2	1595	1319	1	1	-5	833	672	1	8	2	173	87	2	2	1	409	584	2	9	-6	393	407	
0	3	3	1934	1864	1	1	-7	346	347	1	8	3	692	656	2	2	2	755	662	2	9	0	723	749	
0	3	4	890	830	1	1	-8	1494	1879	1	8	4	393	389	2	3	3	1667	1730	2	9	1	1242	1236	
0	3	5	567	583	1	1	-9	1566	563	1	8	-1	1525	1432	2	2	4	566	493	2	9	2	534	513	
0	4	0	5327	5713	1	1	-8	409	405	1	9	2	1038	995	2	3	-1	2196	2295	2	9	-4	865	864	
0	4	1	7314	7255	1	2	-4	298	315	1	8	-3	110	94	2	2	-2	1966	2128	2	9	-1	377	414	
0	4	2	2605	2202	1	2	-5	314	309	1	8	-4	188	175	2	3	-3	2205	2063	2	9	-4	204	252	
0	4	3	967	747	1	2	-6	2752	3284	1	8	-5	409	384	2	2	-5	361	298	2	9	-3	173	175	
0	4	4	245	179	1	2	-7	325	303	1	8	-6	110	141	2	2	-6	440	379	2	9	-2	293	263	
0	4	5	102	154	1	2	-8	252	233	1	9	-7	176	154	2	2	-7	1221	1189	2	10	0	220	261	
0	4	6	432	412	1	2	-9	110	150	1	9	-8	1307	1207	2	3	-2	0	292	1902	2	10	-1	424	357
0	5	0	2076	2040	1	2	-10	566	566	1	9	-9	351	351	2	3	-3	2076	2057	2	10	-2	487	570	
0	5	1	8205	2057	1	2	-11	566	351	1	9	-3	393	345	2	3	-3	2105	1900	2	10	-1	437	457	
0	5	2	314	141	1	2	-12	456	408	1	9	-4	644	626	2	3	-3	296	268	2	10	-1	503	503	
0	5	3	90	65	1	3	-1	2818	2005	1	9	-5	235	154	2	4	-6	456	418	2	10	-3	928	922	
0	5	4	245	176	1	3	-6	346	355	1	9	-7	440	440	2	4	-7	1541	1420	2	10	-4	298	311	
0	5	5	412	525	1	3	-7	1557	1351	1	9	-8	409	403	2	4	-8	1714	2044	2	10	-5	125	134	
0	6	0	670	701	1	3	-8	1038	1014	1	9	-9	1053	958	2	4	-9	3264	2598	2	10	-6	530	544	
0	6	1	1057	910	1	3	-9	125	141	1	9	-5	534	521	2	4	-3	254	277	2	10	-1	503	494	
0	6	2	2799	2580	1	3	-10	546	346	1	10	0	440	440	2	4	-4	1494	1454	2	10	-2	577	595	
0	6	3	399	330	1	3	-11	2422	2295	1	10	1	377	352	2	4	-5	1204	1094	2	10	-3	231	239	
0	6	4	1251	1198	1	3	-12	2233	2193	1	10	2	456	504	2	4	-6	1195	1108	2	10	-4	393	342	
0	6	5	128	29	1	3	-13	1368	1275	1	10	2	456	422	2	4	-7	2029	2198	2	10	-5	283	272	
0	6	6	386	476	1	3	-14	314	214	1	10	1	298	295	2	4	-8	1384	1340	2	10	-6	519	510	
0	7	1	1418	1353	1	3	-15	770	872	1	10	1	35	959	2	4	-9	865	873	2	10	-7	770	793	
0	7	2	1805	1702	1	3	-16	1269	1178	1	10	1	44	283	2	4	-4	478	484	2	10	-8	1000	954	
0	7	3	3785	1605	1	4	-1	707	629	1	10	-5	235	275	2	4	-1	723	670	2	10	-2	173	190	
0	7	4	257	275	1	4	-2	294	74	1	10	0	267	243	2	4	-2	1057	1094	2	10	-4	204	241	
0	7	5	450	515	1	4	-3	3179	1060	1	11	1	833	821	2	4	-3	896	798	2	10	-5	157	167	
0	8	0	2076	2231	1	4	-4	642	624	1	11	2	739	682	2	4	-4	1195	1108	2	10	-6	361	370	
0	8	1	3392	3112	1	4	-5	141	146	1	11	3	770	762	2	4	-5	2642	2564	2	10	-7	503	441	
0	8	2	1095	103	1	4	-6	1085	953	1	11	4	188	165	2	4	-6	302	294	2	10	-8	597	584	
0	8	3	314	317	1	4	-7	1448	1377	1	11	5	597	577	2	4	-7	198	199	2	10	-9	263	265	
0	8	4	317	178	1	4	-8	1666	1580	1	11	6	57	67	2	5	-1	1625	1691	2	10	-10	1593	1743	
0	8	5	309	293	1	4	-9	487	487	1	11	7	325	307	2	5	-2	2465	2150	2	10	-11	1693	1729	
0	9	1	1212	1235	1	4	-10	503	486	1	12	0	582	547	2	5	-3	665	577	2	10	-12	575	603	
0	9	2	128	62	1	4	-11	739	567	1	12	1	393	350	2	5	-4	566	534	2	10	-13	440	421	
0	9	3	593	333	1	4	-12	314	295	1	12	2	141	144	2	5	-5	288	286	2	10	-14	2092	2272	
0	10	0	219	211	1	5	-1	1069	952	1	12	3	245	211	2	5	-6	188	182	2	10	-1	298	197	
0	10	1	348	376	1	5	-2	1997	1773	1	12	4	235	241	2	5	-7	975	929	2	10	-2	157	272	
0	10	2	348	432	1	5	-3	692	556	1	12	5	319	499	2	5	-8	377	397	2	10	-3	295	416	
0	10	3	5	116	196	1	5	-4	692	739	1	13	0	880	847	2	5	-7	1211	1212	2	10	-4	251	245
0	11	1	541	649	1	5	-5	660	765	1	13	1	246	407	2	5	-8	1381	1304	2	10	-5	575	577	
0	11	2	268	1050	1	5	-6	2013	2030	1	13	1	141	147	2	5	-7	440	440	2	10	-6	261	2577	
0	11	3	361	379	1	5	-7	755	764	1	13	2	125	97	2	6	-8	2085	1029	2	10	-7	357	371	
0	11	4	554	603	1	5	-8	1400	1210																

Table 8. Values of $(U_{ij} \times 10^4)$ in Å², (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°.

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

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

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

Distance (Å)			
N ⁱ —O ⁱⁱ	3.011 (6)	H(2 ⁱ)—O ⁱⁱ	2.20
N ⁱⁱⁱ —O ⁱ	2.924 (9)	O ⁱ —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 $-\text{CHF}_2$ 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 –CH₂F, –CHF₂, –CF₃ 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 NH₂ 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 –CHF₂ 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 –CH₂F group is predominant. The difference may arise from the greater electronegativity of the single fluorine atom in the mono-substituted –CH₂F group compared with the two fluorine atoms in the group –CHF₂. It 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 α -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 \mathbf{a} is 5°.

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