

Neutron Diffraction at 20 K and *ab initio* Molecular-Orbital Studies of the Structure of Monofluoroacetamide

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(Received 12 January 1981; accepted 23 March 1981)

Abstract

The crystal structure of C₂H₄FNO, determined by Hughes & Small [*Acta Cryst.* (1962), **15**, 933–940], has been refined using single-crystal neutron diffraction data measured at 20 K [$a = 5.0974$ (9), $b = 5.1531$ (10), $c = 6.6501$ (11) Å, $\alpha = 102.52$ (2), $\beta = 101.33$ (2), $\gamma = 99.54$ (1)°, $P\bar{1}$]. The final $R(F) = 0.023$, $wR(F) = 0.013$, $S = 1.124$, for 1376 recorded reflections. The molecule is very close to having m (C_s) symmetry with the C–F, C=O bonds *trans*. The non-hydrogen atoms lie in one plane within ± 0.0070 (4) Å. The amide H atoms are $+0.0199$ (8) and -0.0103 (8) Å out of this plane, corresponding to a twist about the C–NH₂ bond of 1°. The torsional oscillation of the NH₂ group about the C–N bond is 8°, as determined by a segmented-body thermal-motion analysis. The observed and thermally corrected bond lengths (Å) are: C–C, 1.5109 (5), 1.513; C–N, 1.3242 (2), 1.326; C=O, 1.2437 (5), 1.246; C–F, 1.3906 (5), 1.393; C–H, 1.0937 (8), 1.0942 (7), 1.113, 1.112; N–H, 1.0227 (8), 1.0138 (7), 1.037, 1.029. *Ab initio* molecular-orbital calculations were carried out at the Hartree–Fock 3-21G level. The conformation of the lowest energy for the isolated molecule is that with m symmetry and C–F, C=O *trans*, as observed in the crystal structure. The theoretical optimized bond lengths (Å) are: C–C, 1.517; C–N, 1.341; C=O, 1.216; C–F, 1.405; C–H, 1.078; N–H, 0.997, 0.994. The mean discrepancy between theory and experiment is reduced to 0.015 Å when the theoretical values are adjusted for higher-order molecular-orbital approximations and for intermolecular hydrogen bonding. The poorest agreement is for the C–H bond lengths, where large thermal motion appears to cause an overestimate of the bond-length corrections.

Introduction

The crystal structure of monofluoroacetamide was studied by X-ray diffraction at room temperature by Hughes & Small (1962). A neutron diffraction refinement at 20 K has been carried out to provide more precise experimental data for comparison with *ab initio* molecular-orbital calculations. Such a comparison of neutron diffraction and theoretical studies has previously been made for acetamide by Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople (1980).

Several questions are addressed in this paper. The first is to determine whether the substitution of an F atom in the methyl group of acetamide produces significant changes in other structural parameters. Theoretically, this can be studied by treating both molecules, in isolation, by the same *ab initio* molecular-orbital technique. Changes predicted by the theory (Hartree–Fock, split-valence 3-21G basis set) are compared with those derived from the neutron diffraction crystal structure refinement. However, a comparison of this type is complicated by perturbations in the molecular structure due to intermolecular interactions, particularly hydrogen bonding, in the crystal environment. Evidence that these are significant for acetamide was presented in our previous paper (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980). To determine, at least approximately, the effects of hydrogen bonding on the molecular structures, theoretical calculations were made for formamide and its hydrogen-bonded dimer. Comparable studies on dimers of larger molecules are impractical at present. These data are used to re-evaluate the theoretical and experimental structure of acetamide and to provide a better basis for comparison of acetamide and monofluoroacetamide. Finally, using simple molecules, we explore further the corrections obtained by extension to

higher levels of theory (polarization basis functions and treatments of electron correlation).

Experimental

The neutron diffraction data collection and structure refinement followed the same methods and procedures as described for acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980) except for the information provided below.

Crystals of monofluoroacetamide were obtained by slow evaporation of an ethanol solution at room temperature. A specimen $4.0 \times 1.5 \times 0.8$ mm, cut from a longer crystal, had six natural faces $\{001\}$, $\{0\bar{1}1\}$, $(0\bar{1}0)$, $(\bar{1}01)$ and one artificial face (100) , and weighed 0.00486 g. It was mounted with the a axis 10° off the ϕ axis of the diffractometer, and was cooled at a rate of 1° min^{-1} to 20.0 ± 0.5 K, which was maintained during data collection. The lattice parameters given in Table 1 were determined from 36 reflections with $48^\circ < 2\theta < 59^\circ$ ($\lambda = 1.0442 \text{ \AA}$). The neutron integrated intensities were measured for $\pm h, -k, \pm l$ using scan widths of $\Delta(2\theta) = 3.6^\circ$ for $\sin \theta/\lambda \leq 0.48 \text{ \AA}^{-1}$, and varied according to the dispersion formula, $\Delta(2\theta) = (3.326 + 1.909 \tan \theta)^\circ$ for 0.48 \AA^{-1}

$< \sin \theta/\lambda < 0.79 \text{ \AA}^{-1}$. The transmission factors in the absorption corrections ranged from 0.77 to 0.88. The data for 55 symmetry-related $h0l$ reflections gave an agreement factor $\sum | \langle F^2 \rangle - F_c^2 | / \sum \langle F^2 \rangle = 0.0094$. Of the 1376 intensities measured, 1321 were symmetry independent. There were 14 intensities with a negative net count, none significantly different from zero.

The initial atomic coordinates for the refinement were from Hughes & Small (1962) with assumed isotropic thermal factors of $U = 0.006 \text{ \AA}^2$ for the non-hydrogen atoms and $U = 0.009 \text{ \AA}^2$ for the H atoms. The function minimized in the least-squares refinement was $\sum w_i | F_o^2 - F_c^2 |^2$, where the observational weight, w_i , was taken to be $[\sigma_{\text{counter}}^2 + (0.01F_o^2)^2 + (9.90/F_o^2)^2]^{-1/2}$.^{*} The scattering lengths used were those given by Koester (1977). After the final cycle of refinement against all 1376 recorded observations, there were no changes in any of the parameters varied greater than 0.01σ . The largest feature on the final difference map was less than $0.01 \sigma(\rho)$, where the error in ρ was estimated from $\sigma(F)$. The final agreement factors were $R(F) = 0.023$, $R(F^2) = 0.023$, $wR(F) = 0.013$, $wR(F^2) = 0.025$, $S = 1.124$. Extinction was severe; 22% of the reflections were significantly attenuated with $F_o/F_c \leq 0.95$; the most affected was $0\bar{1}2$ with $F_o/F_c = 0.63$. The atomic notation and thermal-motion ellipsoids are shown in Fig. 1. The final parameters are given in Table 2.[†]

Table 1. *Crystal data for monofluoroacetamide*

Formula, $\text{C}_2\text{H}_4\text{FNO}$, CAS Reg. No. 640-19-7
Space group $P1$, $Z = 2$, $D_x = 1.568 \text{ Mg m}^{-3}$ at 20 K;
 1.471 Mg m^{-3} at 298 K

	This work	Hughes & Small (1962)
a	5.0974 (9) \AA	5.103 (5) \AA
b	5.1531 (10)	5.343 (5)
c	6.6501 (11)	6.901 (5)
α	102.52 (2) $^\circ$	104.77 (5) $^\circ$
β	101.33 (2)	100.43 (5)
γ	99.54 (1)	100.12 (5)

^{*} The third term in this expression was added to decrease the weight of weak reflections for which $(F_o^2 - F_c^2)/\sigma_{\text{counter}}$ was positive and often as large as 10. The value $9.90 \times 10^4 \text{ fm}^4$ was selected so that $F_o^2 = \sigma(F_o^2)$ for the systematic space-group extinction with the largest F_o^2 value in a data set from a crystal of diformohydrazide of similar size, which showed the same feature.

[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36106 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic parameters for monofluoroacetamide at 20 K*

The fractional coordinates are $\times 10^5$ for non-hydrogen atoms, $\times 10^4$ for H atoms. Anisotropic temperature factors ($\text{\AA}^2 \times 10^5$ for non-hydrogen atoms, $\times 10^4$ for H atoms) are referred to the crystal axes and correspond to the temperature-factor expression, $T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$. Estimated standard deviations given in parentheses refer to the least significant digit. Anisotropic extinction parameters g are in $\text{rad}^2 \times 10^8$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	26693 (6)	66862 (6)	34527 (4)	529 (11)	474 (11)	615 (10)	49 (9)	143 (8)	-44 (8)
C(2)	15555 (5)	38780 (5)	19628 (4)	332 (11)	402 (11)	495 (10)	46 (9)	93 (8)	13 (8)
N	32930 (4)	26310 (4)	11018 (3)	466 (9)	583 (8)	793 (8)	123 (6)	209 (6)	-49 (6)
O	-9368 (6)	28841 (7)	16134 (5)	369 (13)	585 (12)	829 (12)	26 (10)	158 (10)	-72 (10)
F	54800 (7)	74917 (8)	36962 (6)	572 (14)	743 (14)	1088 (13)	-123 (11)	194 (10)	-148 (10)
H(1)	1658 (2)	8141 (2)	2801 (1)	222 (3)	152 (3)	293 (3)	77 (2)	9 (2)	67 (2)
H(2)	2269 (2)	6690 (2)	5010 (1)	231 (3)	260 (3)	138 (2)	9 (3)	82 (2)	12 (2)
H(3)	2550 (1)	741 (2)	76 (1)	181 (3)	141 (3)	219 (3)	25 (2)	45 (2)	-38 (2)
H(4)	5321 (1)	3491 (2)	1459 (1)	101 (3)	210 (3)	257 (3)	-1 (2)	50 (2)	2 (2)
			g_{11}	3.13 (7)	g_{12}	0.47 (7)			
			g_{22}	3.14 (13)	g_{13}	-0.09 (6)			
			g_{33}	3.13 (14)	g_{23}	0.48 (9)			

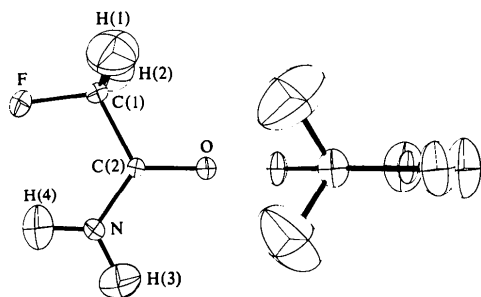


Fig. 1. Atomic notation and thermal ellipsoids (75%) for monofluoroacetamide at 20 K, viewed normal to and in the plane of the molecule.

The thermal-motion analysis

The thermal motion of the molecule was analyzed using the segmented-body method, *ORSBA* (Johnson, 1970). An initial analysis gave estimates of non-torsional internal motion of the H atoms, which were then subtracted before fitting the torsional segmented-body model. The nine atoms were grouped into four segments, FCCON, the amide H atoms and each of the two methyl H atoms, with four flexible joints interconnecting the segments and the stationary lattice. Using an assumed internal N—H r.m.s. 'stretch' correction of 0.076 Å (Cyvin, 1968), the internal NH₂ r.m.s. 'scissor' correction was calculated to be 0.114 Å. The internal motion for the methyl H atoms was calculated to be 0.074 Å for the r.m.s. 'stretch', 0.146 Å for the r.m.s. 'scissor', and 0.119 Å for the 'wag' motion. The directions of these calculated internal motions are within a few degrees of the principal axes of the observed thermal ellipsoids. These corrections for the internal motion of the H atoms were then subtracted from the r.m.s. displacements before fitting the segmented-body model described below.

This model had two torsional degrees of freedom with two flexible joints, one between the segments and one from the center of mass to the stationary lattice. Only torsional motion of the NH₂ segment with the parent CH₂FCON segment was considered. The overall fit was good with $\langle \text{r.m.s. } U_{ij} - U_{i\text{SMB}} \rangle = 0.0002 \text{ \AA}^2$ and $\sigma(U_{ij}) = 0.0003 \text{ \AA}^2$. The r.m.s. torsion of the NH₂ group about the C—N bond was 8°. With internal torsion and H vibration motion subtracted, the rigid-body motion of the segment consisting of the FCCON atoms only, based on the inertial axes, was:

		I_1	I_2	I_3
T	0.075 Å	89.3°	88.7°	1.5°
	0.062	143.6	126.4	88.6
	0.060	53.6	143.6	89.3
ω	3.2°	27.3	63.4	84.2
	2.2	64.7	153.2	84.1
	1.5	82.1	92.7	171.7

The torsional motion of the amine group (8°) is greater than that in acetamide (7°; Jeffrey *et al.*, 1980) and in formamide oxime (5°; Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981). The torsional motion of the CH₂F group could not be deduced, since the 'scissor' and 'wag' motions greatly exceeded any torsional oscillation. The corrections to the bond lengths not involving H atoms were the same as for acetamide (+0.002 Å). The N—H corrections were the same (+0.015 Å), but the C—H corrections were less (+0.018 Å).

Ab initio molecular-orbital calculations

Theoretical calculations of the structure of monofluoroacetamide were carried out at the Hartree-Fock (HF) level using the 3-21G basis set (Binkley, Pople & Hehre, 1980) as incorporated in the *GAUSSIAN-80* computer program (Binkley, Whiteside, Krishnan, Seeger, DeFrees, Schlegel, Topiol, Kahn & Pople, 1980). Minimization of the total energy with respect to all geometrical parameters led to the values listed in Table 3 and a total energy of $-801074.33 \text{ kJ mol}^{-1}$ (-305.13201 hartrees). This structure has *m* (C_s) symmetry with C=O and C—F bonds *trans*. Optimization of the molecular geometry with these linkages *cis* results in an energy of $-801043.09 \text{ kJ mol}^{-1}$ (-305.12011 hartrees), 31.5 kJ mol^{-1} ($7.5 \text{ kcal mol}^{-1}$) higher than the *trans* conformer.

In order to estimate changes in structure due to the hydrogen bonding in the crystal, a formamide dimer structure was calculated at the HF/3-21G level. The structures of formamide and its dimer have been examined theoretically by several groups (Mehler, 1980, and references therein), but without full geometry optimization. The optimum geometrical parameters were therefore calculated at the HF/3-21G level for the formamide monomer with *m* (C_s) symmetry and for the cyclic formamide dimer with $2/m$ (C_{2h}) symmetry. The resulting geometrical parameters are shown in Fig. 3. The optimum total energies of $-441016.96 \text{ kJ mol}^{-1}$ (-167.98490 hartrees) for the monomer and $-882129.09 \text{ kJ mol}^{-1}$ (-336.00605 hartrees) for the dimer give an attractive interaction energy of $95.18 \text{ kJ mol}^{-1}$ ($22.75 \text{ kcal mol}^{-1}$).

In order to estimate errors introduced by the inadequacies of the HF/3-21G theoretical model, calculations were made of smaller molecules containing bonds equivalent to those in monofluoroacetamide, using higher levels of theory. These are HF/6-31G*, Hartree-Fock theory with the polarization 6-31G basis (Hariharan & Pople, 1973), and MP2/6-31G* and MP3/6-31G*, which account for the correlation energy using Møller-Plesset perturbation theory (Møller & Plesset, 1934; Pople, Binkley & Seeger, 1976) to second and third order, respectively. The results for the pertinent bond lengths are displayed in Table 4. Comparison with the microwave results,

Table 3. *Experimental and theoretical dimensions*

(a) Bond lengths (Å) for monofluoroacetamide at 20 K and acetamide at 23 K. The σ values in parentheses refer to the least significant figure.

	FCH ₂ CONH ₂			CH ₃ CONH ₂		
	Experimental at 20 K		Theoretical HF/3-21G	Experimental at 23 K		Theoretical HF/3-21G
	Observed	Corrected		Observed	Corrected	
C–N	1.3242 (4)	1.326	1.341	1.3351 (11)	1.337	1.358
C=O	1.2437 (5)	1.246	1.216	1.2468 (12)	1.250	1.216
C–C	1.5109 (5)	1.513	1.517	1.5094 (10)	1.513	1.516
C–F	1.3906 (5)	1.393	1.405	–	–	–
C–H(1)	1.0937 (8)	1.113	1.078	1.085 (2)	1.125	1.085
C–H(2)	1.0942 (7)	1.112	1.078	1.076 (2)	1.119	1.082
C–H(3)	–	–	–	1.076 (2)	1.119	1.079
N–H(3)	1.0227 (8)	1.037	0.997	1.023 (2)	1.036	0.998
N–H(4)	1.0138 (7)	1.029	0.994	1.023 (2)	1.037	0.994

(b) Bond angles (°) and torsion angles (°) for monofluoroacetamide

	Observed	Theoretical		Observed	Theoretical		Observed	Theoretical
C–C–N	117.93 (2)	113.6	C–C–H(1)	109.06 (5)	109.2	H(1)–C–H(2)	109.39 (6)	109.4
C–C–O	118.04 (2)	120.2	C–C–H(2)	109.83 (5)	109.2	C–N–H(3)	118.40 (5)	119.7
N–C–O	124.03 (3)	126.2	F–C–H(1)	108.76 (5)	109.4	C–N–H(4)	121.60 (5)	120.1
C–C–F	111.05 (2)	110.3	F–C–H(2)	108.73 (5)	109.4	H(3)–N–H(4)	119.99 (6)	120.2
	Observed	Theoretical		Observed	Theoretical		Observed	Theoretical
F–C–C–N	–0.99 (4)	0.0*	H(2)–C–C–O	58.99 (6)	59.8	H(4)–N–C–C	1.98 (7)	0.0*
H(1)–C–C–O	–60.87 (6)	–59.8	H(3)–N–C–O	0.51 (7)	0.0*			

* Fixed values.

Table 4. *Effect of level of approximation on some small-molecule bond lengths (Å)*

Bond	Molecule	HF/3-21G ^(a)	HF/6-31G* ^(b)	MP2/6-31G* ^(b)	MP3/6-31G* ^(c)	Spectroscopic ^(d)
C–H	Methane	1.083	1.084	1.090	1.091	1.094
	Methyl fluoride	1.080	1.082	1.092	1.093	1.100
	Acetaldehyde	1.084	1.085			1.094
N–H	Ammonia	1.002	1.002	1.017	1.017	1.012
	Methylamine	1.004	1.001	1.018	1.018	1.010
C–C	Ethane	1.542	1.528	1.526		1.526
	Acetaldehyde	1.507	1.504			1.504
C–N	Methylamine	1.471	1.453	1.465	1.466	1.471
C=O	Formaldehyde	1.207	1.184	1.221	1.210	1.206
	Acetaldehyde	1.209	1.188			1.217
C–F	Methyl fluoride	1.403	1.365	1.392	1.388	1.383

(a) Binkley, Pople & Hehre (1980). (b) DeFrees, Levi, Pollack, Hehre, Binkley & Pople (1979). (c) DeFrees, Krishnan, Schlegel & Pople (1981). (d) Harmony, Laurie, Kuczkowski, Schwendeman, Ramsay, Lovas, Lafferty & Maki (1979).

shown in the final column, indicates that the MP3/6-31G* model gives excellent agreement between theory and experiment for the isolated molecules.

Discussion of the crystal structural results

The crystal structure and the nonhydrogen geometry agree with that deduced by Hughes & Small (1962), within the accuracy of their room-temperature X-ray analysis. The molecule is very close to having *m* symmetry as shown by the torsion angles in Table 3(b).

The non-hydrogen atoms lie in one plane within ± 0.0070 (4) Å. The amide H atoms, H(3) and H(4), are -0.0103 (8) and $+0.0199$ (8) Å out of the plane, due to the small twist of 1° of the NH₂ group from the exactly planar orientation. The angle between the C(1)–N bond and the normal to the NH₂ plane is 91.0° , compared with 96.5° in acetamide. The C–C and C=O bond lengths are not significantly different in acetamide and fluoroacetamide, but there is a significant difference in the C–N bond lengths of 0.0109 (12) Å, as shown in Table 3(a). The small differences observed between the two C–H bond

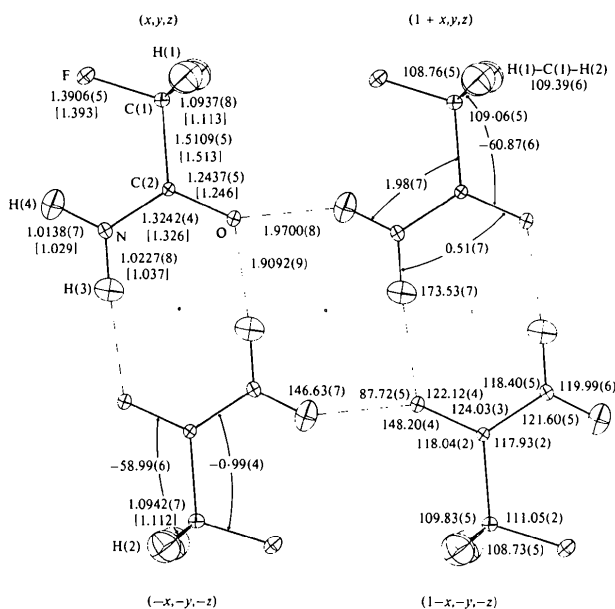


Fig. 2. Hydrogen bonding in the crystal structure of monofluoroacetamide, viewed normal to the molecular plane. The values in square brackets are corrected for thermal motion. (Distances in Å, angles in degrees.)

lengths and between the two N—H bond lengths in monofluoroacetamide are not significant. Although the C—H bonds are observed to be longer than the corresponding bonds in acetamide, they are significantly shorter when corrected for thermal motion. The corrected N—H bonds are not significantly different in the two structures.

The hydrogen bonding is illustrated in Fig. 2 of Hughes & Small (1962) and, from a different view, in Fig. 2 of this paper. It contains classic (H—N—C=O)₂ bonded dimers, with almost linear N—H...O hydrogen bonds. These dimers are cross-linked into a network with longer N—H...O bonds, which are not linear.

Comparison of experimental and theoretical results

The observed conformation for monofluoroacetamide is that of the theoretical minimum energy for the isolated molecule with *m* (C_s) symmetry and the C—F and C=O bonds *trans*. This was not the case for the acetamide molecule in its rhombohedral crystal structure (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980). As shown in Table 3(a) the significant difference of 0.011 (1) Å in the C—N bond lengths in acetamide and monofluoroacetamide is reproduced by theory except that the difference is larger, 0.017 Å.

The differences between the observed and calculated (HF/3-21G) bond lengths are shown in the first column of Table 5. With the exception of the C—C bonds, these

Table 5. Analysis of bond-length discrepancies in acetamide and monofluoroacetamide (Å)

Where there are two entries, the upper is for acetamide.

Bond	3-21G Δ theory — experi- mental	Higher-level theory — 3-21G extrap- olation	H-bonded dimer — monomer extrap- olation	Residual discrepancy
C—C	+0.003 +0.005	—	—	0.000 +0.002
C=O	—0.034 —0.030	+0.003 ^(d)	+0.018 ^(g)	—0.013 —0.009
C—F	+0.011	—0.015 ^(e)	—	—0.004
C—N	+0.021 +0.014	—0.005 ^(f)	—0.023 ^(g)	—0.007 —0.014
N—H ^(a)	—0.038 —0.040	+0.014 ^(f)	+0.018 ^(g)	—0.006 —0.008
C—H ^(b)	—0.037 —0.034	+0.001 ^(c) +0.013 ^(e)	—	—0.036 —0.021

(a) N—H(3). (b) C—H(2). (c) HF/6-31G* acetaldehyde. (d) MP3/6-31G* formaldehyde. (e) MP3/6-31G* methyl fluoride. (f) MP3/6-31G* methylamine. (g) Based on HF/3-21G calculation on the formamide dimer.

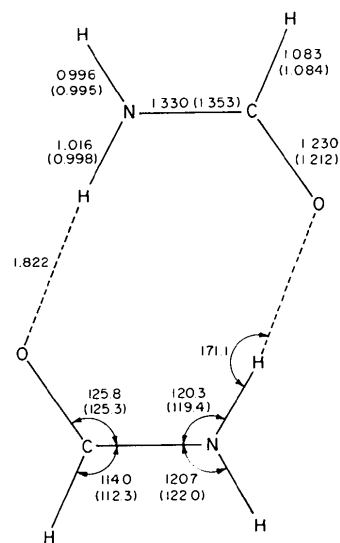


Fig. 3. Theoretical geometry optimization of formamide and the hydrogen-bonded formamide dimer with HF/3-21G using GAUSSIAN 80. The values in parentheses refer to the monomer. (Distances in Å, angles in degrees.)

differences are highly significant in terms of the experimental σ 's. These differences can be accounted for, at least in part, by extrapolation from the results of theoretical calculations given in Tables 4 and 5 and in Fig. 3. The second column of Table 5 gives the corrections for the bonds in the acetamides extrapolated from the difference between HF/3-21G and higher-order calculations given in Table 4 for equivalent bonds in simpler molecules. Fig. 3 shows the effects of hydrogen bonding on the molecular geometry of

formamide by comparing the HF/3-21G optimized geometry of the monomer with that of the hydrogen-bonded dimer.

After adding these extrapolated corrections, the residual differences between the 'best' theoretically predicted values and the experimental bond lengths are shown in the final column of Table 5. The residual differences for the C—C and C—F bonds are not significant in terms of the experimental σ 's. The results for the C—N and C=O bonds indicate that much of the discrepancy between the theoretical and experimental values is due to the hydrogen bonding in the crystalline state. For the C—N bond, the correction from the formamide dimer model appears to give an over-emphasis, whereas for the C=O bond it gives an under-emphasis. The N—H bond agreement is as good as can be expected in view of the fact that the NH₂ groups are undergoing significant thermal oscillations (r.m.s. values of 7 and 8° respectively), and the riding-motion bond-length corrections have uncertainties comparable with the residual differences.

Significant discrepancies remain in the C—H bond lengths associated with the —CH₃ and CH₂F groups. Both these groups were undergoing large oscillatory motion. The r.m.s. oscillation of 15° in acetamide and the r.m.s. 'scissors' motion of 8° in monofluoroacetamide correspond to r.m.s. displacements of the H atoms of 0.26 and 0.15 Å respectively. The assumption of harmonicity made in the treatment for thermal-motion foreshortening of the bond lengths is therefore likely to lead to an over-estimation of the thermal corrections. For C—H bonds, the thermal motion leads to short observed bond lengths compared to the molecule *at rest*, but anharmonicity will give rise to long bond lengths. If the displacements are large enough, these two corrections can be mutually compensatory.

The largest discrepancies in bond angles are in those around C(2). The closure of the C(1)—C(2)—N valence angle to 113.6° in the isolated molecule is a consequence of the strong interaction between the F atom and H(4) of the NH₂ group, which stabilizes the C=O, C—F *trans* conformation relative to the *cis* alternative.

In the crystal structure, this distortion effect is presumably offset by the intermolecular forces, particularly the hydrogen bonds.

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