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ON THE MOLECULAR STRUCTURE OF DIFLUOROACETIC ACID AS INVESTIGATED BY MEANS OF GAS ELECTRON DIFFRACTION

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ABSTRACT

Two conformations were found by means of an analysis of the electron diffraction patterns of gaseous difluoroacetic acid at 140 °C: 74% of a conformation with the CHF_2 group rotated 82.5° from a position with the hydrogen atom eclipsed with respect to the C=O bond, the remainder in a conformation with the CHF_2 group rotated 18° from this eclipsed position.

The important bond lengths in Å, $r_g(l)$, and bond angles with, in parentheses, their standard deviations are: C—F: 1.354 (0.007), C—C: 1.517 (0.006), C=O: 1.212 (0.004), C—O: 1.345 (0.009), O—H: 0.96 (0.02) Å, C—C=O: 123.9 (1.0), C—C—O: 110.6 (1.0), C—C—F: 108.7 (0.7), F—C—F: 108.6 (0.6)°.

INTRODUCTION

The research in our section aims at the prediction of the stacking of molecules in crystals and, naturally, the investigation of free molecules is one part of the program. We restrict ourselves to compounds that exhibit intermolecular hydrogen bonding in the solid and within this class of compounds to simple carboxylic acids and their derivatives.

The present report on difluoroacetic acid is an extension of the work on acetic acid (monomer and dimer) [1], propionic acid (monomer and dimer) [2], monofluoroacetic acid [3] and monochloroacetic acid [4, 5], that has been done in our laboratory. Accordingly this paper includes data inferred from an infrared study of the conformations of halogenated acetic acids in carbon tetrachloride solution and in the vapour state that was recently completed [6].

In cooperative work additional information was obtained by means of some CNDO/2 calculations on difluoroacetic acid. De With [8] has predicted one conformation in the CNDO/2 approximation in good agreement with the dominating conformation found in this investigation.

The interpretation of the complex microwave spectrum of difluoroacetic acid is in progress.

EXPERIMENTAL AND DATA PROCESSING

The electron diffraction experiments were carried out on the Balzers KDG 2 electron diffraction unit under the supervision of G. Renes. The electron wavelength was calibrated with TlCl powder diffraction data and a $3^{\circ}/_{oo}$ correction was applied to yield the correct $r_g(l)$ values [9] for CO_2. The nozzle temperature was kept at 140 °C in order to prevent the presence of dimer molecules. Diffraction patterns were collected with a sample of difluoroacetic acid from Aldrich (99%) at camera heights of 100 cm for 40 kV electrons, and of 50 and 25 cm for 60 kV electrons.

We followed the usual data reduction procedure [10, 11], and used the coherent scattering factors of Cox and Bonham [12] and the incoherent scattering factors of the tables of Tavard et al. [13]. After subtracting a theoretical background only a small empirical background correction was necessary. For the atoms k and l in the modification factors $s/(f(k) = f(l))$ O and F were chosen. In Table 1 the modified intensities ranging from s = 1.50 to 34.50 $Å^{-1}$ are listed. The unlevelled, undamped radial distribution function calculated from these data is shown in Fig. 1.

STRUCTURE ANALYSIS

In the region of the bond lengths, up to 2 Å, the interpretation of the radial distribution function (RDF) was rather simple owing to the analogy with monofluoroacetic acid. The first tentative models with the hydrogen atom of the CHF_2 group in the plane of the oxygen and carbon atoms did not result in a good agreement of the observed and calculated RDF's.

A much better agreement was found with a conformation with $\alpha \simeq 80°$, see Fig. 2, where α indicates the internal rotation angle in relation to the eclipsed position of C—H and C=O bonds. The O · · · F distances, which give the main information about the CHF_2 group position, for this rotational isomer correspond to peaks in the observed RDF at 2.5, 2.8 and 3.5 Å (see Figs. 1 and 5).

At the same time De With [8] predicted this conformation in the CNDO/2 approximation. Dependent on the position of the O—H hydrogen atom he found a minimum in the rotational barrier function at 90 or at 75°.

However, to arrive at a good fit of the theoretical and observed RDF's the contribution of a second conformation was needed. Calculations and refinements with a mixture of rotational isomers with $\alpha \simeq 80°$ and $\alpha \simeq 15°$ (see Fig. 3) yielded good agreement between observed and calculated molecular intensities. All bond distances, bond angles and vibrational amplitudes of the two conformations were assumed to be the same. The strong correlation between these parameters did not permit any reliable conclusion about small differences that were expected. The bond distances, bond angles and rotational angles involving hydrogen atoms, except the O—H bond distance, were given fixed values; the low scattering power of the hydrogen atoms inhibited the determination of their position.

TABLE 1

Modified molecular intensities

A												
1791	−89	−1121	−1481	−1160	−940	−770	−632	−963	−1192	−1667	−1976	−2081
−1582	−754	406	1952	2955	3232	2943	2092	663	−680			
B												
152	674	1042	1172	1045	666	185	−264	−521	−625	−580	−463	−336
−201	−84	7	86	110	64	−2	−7	41	160	341	472	453
237	15	−215	−418	−527	−530	−417	−209	−5	141	275	339	304
239	147											
C												
−207	−441	−490	−513	−474	−381	−222	−63	82	138	96	42	3
12	85	209	344	396	358	186	−33	−261	−422	−494	−475	−376
−217	−47	113	238	302	274	206	125	83	61	41	66	85
61	−32	−132	−214	−244	−218	−172	−110	−30	31	89	130	146
159	157	136	84	18	−35	−69	−96	−125	−140	−139	−97	−77
−7	22	65	117	143	151	98	65	29	0	−48	−99	−130
−141	−129	−115	−80	−5	24	35	85	124	136	155	137	108
75	33	−32	−84	−128	−147	−161	−146	−114	−61	−15	22	60
114	158	149	151	127	111	42						

A data for the 100 cm camera height, 40 kV: s = 1.50 (0.25) 7.00 Å^{-1};
B for the 50 cm distance, 60 kV: s = 5.25 (0.25) 15.25 Å^{-1};
C for the 25 cm distance, 60 kV: s = 7.00 (0.25) 34.50 Å^{-1}.

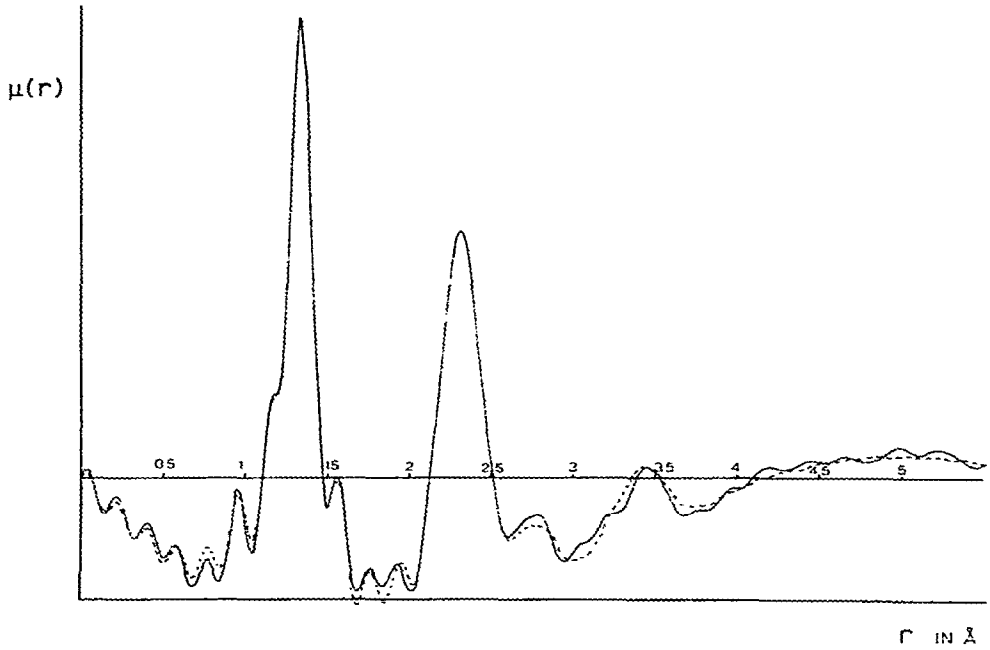

Fig. 1. Unlevelled, undamped radial distribution curve: (———) observed, (-------) calculated.

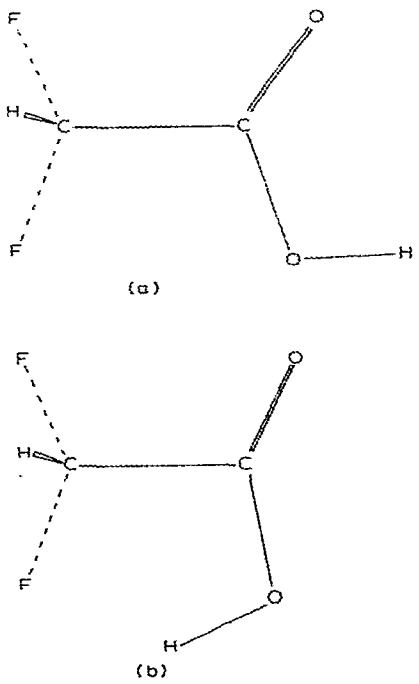

Fig. 2. Rotational isomers of difluoroacetic acid, $\alpha = 82.5°$.

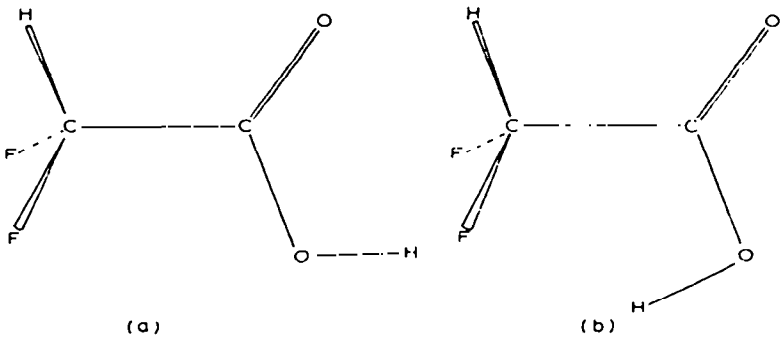

Fig. 3. Rotational isomers of difluoroacetic acid, α = 18°.

TABLE 2

Molecular parameters for difluoroacetic acid obtained by the least squares method

Bond lengths (Å)		Bond angles (degrees)	
C—C	1.517 ± 0.006	C—C=O	123.9 ± 1.0
C=O	1.212 ± 0.004	C—C—O	110.6 ± 1.0
C—O	1.345 ± 0.009	C—C—F	108.7 ± 0.7
C—F	1.354 ± 0.007	F—C—F	108.6 ± 0.6
C—H	1.102 (ass.[a])	C—C—H	109.5 (ass.)
O—H	0.96 ± 0.02	C—O—H	107 (ass.)
		Conf. 1	Conf. 2
Rotational angle α (degrees)		82.5 ± 3.0	18 ± 4
Quantities (mol.%)		74 ± 1	26 ± 1

R.m.s. amplitudes of vibration for bonds (Å)

C—C	0.053 ± 0.005
C=O	0.045 ± 0.004
C—O	0.052 ± 0.005
C—F	0.043 ± 0.005
C—H	0.078 (ass.)
O—H	0.070 (ass.)
Scale 50 cm 60 kV	285 ± 7
Scale 25 cm 60 kV	261 ± 9
Scale 100 cm 40 kV	803 ± 20
R[b]	0.0836
$\Sigma \lvert I_{obs} \rvert$	42433
$\Sigma w.\Delta^2$	0.121×10^6

[a]"ass." means that this value was assumed and kept constant during the refinements.
[b]R is defined as $\Sigma(\lvert I_{obs} - I_{calc} \rvert)/\Sigma \lvert I_{obs} \rvert$.

The important parameters resulting from the least squares refinement procedures are presented in Table 2. To remove roughly the effect of correlation between the intensity data the standard deviations from the normal equations were multiplied by a factor of 2.

DISCUSSION OF THE STRUCTURE

Calculations with a mixture of two conformations of difluoroacetic acid show a good agreement between its calculated and observed molecular intensities. The occurrence of the conformation at $\alpha = 82.5°$ agrees well with the CNDO/2 calculations. The other conformation at $\alpha = 18°$ however, is not predicted by this method.

Our study of the infrared carbonyl stretching frequencies of the halogenated derivatives of acetic acid in very dilute CCl_4 solution and in the vapour phase [6] shows two bands for difluoroacetic acid monomer (ν_1 and ν_2 are respectively 1798 and 1771 cm^{-1} for the solution, and 1819 and 1805 cm^{-1} for the vapour). These distinct bands confirm the existence of two conformations. The infrared results are supported by a related study on the corresponding ethyl acetates [7] ($\nu_1 = 1780$ cm^{-1}, $\nu_2 = 1766$ cm^{-1}), which were also assigned to two conformations.

Most of the structural parameters found have the expected values. The C—C=O bond angle of 123.9° is small in relation to that in acetic acid monomer (126.6°) [1]. Moreover CNDO/2 calculations (using a computer program of QCPE [14]) of the total molecular energy as a function of this bond angle show a rather broad minimum in the region of 124°. The electron diffraction investigation of (in this respect) a related molecule trifluoroacetone [15] shows a similar effect; its C—C=O bond angle at the trifluoro-side is found to be 116.8°, whereas at the methyl-side it is 122.0°. The F—C—F bond angle (108.6°) is smaller than a tetrahedral one, but this has also been found in studies of other difluoro compounds such as difluoromethane [16, 17] (108.5°) and 1:1 difluoroethane [18] (109.1°). In the CNDO/2 approximation an energy minimum was found at 106° for this angle.

It must be noted, that the values of the rotational angles of both conformations we found are average values with respect to torsional movements, and that the vibrational amplitudes involved contain a contribution due to these torsions [19]. However, the $\alpha = 18°$ angle is not likely to be an average value of a very large torsional movement around the $\alpha = 0°$ position. As Fig. 5 shows, the function of the O · · · F distance against the rotational angle α is steep for all distances in this region.

The position of the hydroxyl hydrogen atom is open to dicussion. In the CNDO/2 approximation the potential function for rotation of the O—H bond around the adjacent C—O axes was calculated for $\alpha = 82.5°$ (see Fig. 4). Minima were calculated at $\theta = 0$ and at $\theta = 190°$ (we define $\theta = 0$ in the position shown in Fig. 2 (a), and rotate clockwise looking from the carbon to the oxygen atom).

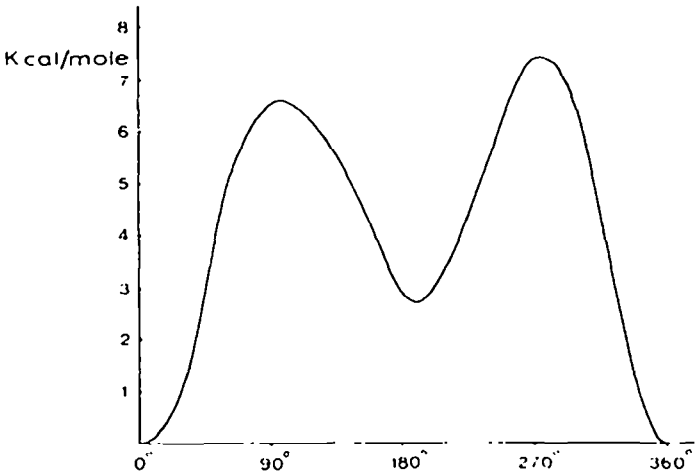

Fig. 4. Rotational barrier of difluoroacetic acid (α = 82.5°) calculated with the CNDO/2 method.

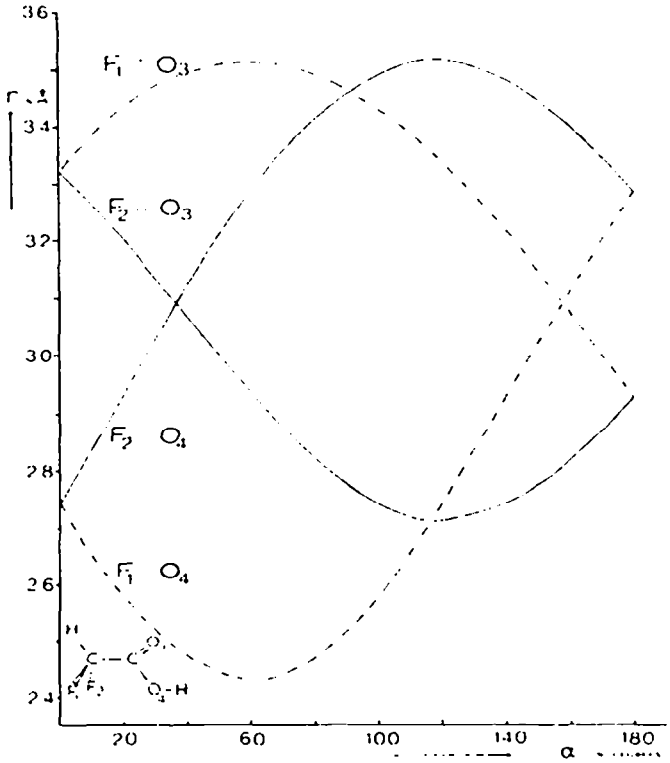

Fig. 5. O · · · F distances as a function of the rotational angle α.

The vapour infrared investigation shows no splitting and/or shift of the O—H stretching frequency [6] (3587 cm^{-1}) in relation to acetic acid monomer (3586 cm^{-1}). Other halogenated acetic acids also did not show any

splitting in the vapour phase nor in CCl_4 solution; this is in contrast with the related 2-haloethanols [20—22] where the two sub-bands were assigned to a gauche and a trans conformation. The discussion whether or not the gauche conformation has an internal hydrogen bond has not yet ended. The absence of any splitting of the O—H stretching frequency and the normal value of the O—H bond length (0.96 Å), although rather uncertain, does not suggest an internal hydrogen bond interaction in either conformation of difluoroacetic acid.

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