A STUDY OF THE MOLECULAR STRUCTURE OF MONOCHLOROACETIC ACID BY MEANS OF GAS ELECTRON DIFFRACTION

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ABSTRACT

The results of an interpretation of the gas electron diffraction pattern of monochloroacetic acid at 170 °C and a microwave investigation by Van Eijck et al. from this laboratory were combined. Three conformations with respect to internal rotation around the C—C bond were found, viz. 56% of a conformation with C_s molecular symmetry and the C—Cl bond eclipsed with the C=O bond, 30% of a conformation with the CH₂Cl group rotated 131° from the former position and the remaining 14% of a conformation with 79° rotation of the CH₂Cl group. The bond lengths and the bond angles determined by means of this procedure are (standard deviations in parentheses): C—Cl: 1.778(0.005), C—C: 1.508 (0.006), C=O: 1.223(0.004), C—O: 1.352(0.005), C—H: 1.09(0.02), O—H: 0.97 (0.015) Å; C—C=O: 126.1(0.5), C—C—O: 110.6(0.4), C—C—Cl: 112.5(0.4), C—O—H: 105.8(1.1)°. A conformational distribution obtained by means of CNDO/2 calculations is not in agreement with our experimental radial distribution.

INTRODUCTION

In our research program on internal rotation around C—C bonds in carboxylic acids [1-3], the molecular structure of chloroacetic acid is now being studied. At the present stage an interpretation of the microwave spectrum by van Eijck et al. [4] has revealed the presence of a planar *trans* conformation, with the chlorine atom lying in the carboxylic plane eclipsed with the carbonyl group. However, the microwave spectrum allows the presence of one or more other conformations, which could not yet be identified. It was hoped to obtain additional information on these conformations by means of gas electron diffraction experiments at a temperature sufficiently high to avoid intermolecular hydrogen bonded species.

EXPERIMENTAL AND DATA PROCESSING

60 kV electron diffraction experiments with a sample of chloroacetic acid from Analar (> 99.0%) were done at 170 °C nozzle temperature on the Balzers Eldigraph KDG2 electron diffraction unit [5] at the Rijksuniversiteit

of Leiden. The electron wavelength was calibrated with TiCl powder diffraction data and a 3‰ correction was applied to yield the correct $r_g(1)$ values for CO_2 [6].

Diffraction photographs were taken at camera heights of 1000, 500, 250 and 110 mm. Owing to the extreme corrosiveness of the compound the nozzle system was affected severely and became clogged repeatedly, causing an irregular gas stream. Also an unusually large background scattering was observed. In spite of many efforts, the molecular intensities obtained for the compound were less accurate than usual.

The data reduction procedure described in ref. 7 was followed. We used the scattering factors of Cox and Bonham [8] and we applied empirical background corrections. The molecular intensities, modified with the function $s/(f_C f_{Cl})$, ranging from $s = 1.625$ to $31.0 \text{ \AA}^{-1}$, are listed in Table 1. The unlevelled radial distribution function calculated from these data is shown in Fig. 1.

TABLE 1

Observed molecular intensities for monochloroacetic acid

100 mm camera height, $s = 1.625 (0.125) 7.125 \text{ \AA}^{-1}$, scale = 808.1

-73	-124	-311	-447	-529	-520	-512	-500	-428	-376
-344	-328	-333	-374	-380	-453	-531	-596	-653	-728
-788	-823	-798	-719	-555	-351	-97	157	355	496
625	729	753	717	671	660	634	608	552	486
434	367	285	137	5					

500 mm camera height, $s = 3.75 (0.25) 15.25 \text{ \AA}^{-1}$, scale = 351

-290	-360	-351	-266	-154	52	249	328	321	280
236	211	169	84	-76	-197	-200	-129	8	85
100	19	-104	-207	-250	-222	-168	-116	11	196
350	392	374	220	0	-200	-290	-351	-275	-137
-60	21	100	177	148	125	18			

250 mm camera height, $s = 9.00 (0.25) 25.00 \text{ \AA}^{-1}$, scale = 213

16	-49	-113	-160	-155	-134	-63	23	140	225
265	213	106	-26	-125	-181	-176	-132	-89	-56
5	72	112	100	62	18	-39	-41	-40	-13
34	54	19	5	-34	-36	-33	-6	26	33
22	27	-13	-48	-64	-48	-34	-24	-14	22
52	86	77	81	47	23	7	-27	-62	-76
-75	-79	-44	-24	-9					

110 mm camera height, $s = 25.00 (0.25) 31.00 \text{ \AA}^{-1}$, scale = 806

-7	82	169	180	208	184	142	34	-17	-100
-140	-94	-85	-46	111	156	112	66	-53	-88
-74	-117	-120	-141	-60

Fig. 1. Unlevelled radial distribution for monochloroacetic acid. Damping factor $e^{-0.0015^2}$; (—) observed, (---) calculated. The difference curve was multiplied by a factor 2.37.

STRUCTURE ANALYSIS

Analogy of bond lengths, bond angles and vibrational amplitudes with those in monofluoroacetic acid [1], acetic acid [2] and propionic acid [2] made the interpretation of the experimental radial distribution function (RDF) up to 2.7 Å relatively easy.

To get an insight in the conformations with respect to internal rotation of the CH_2Cl group around the C—C bond, the $\text{O} \cdots \text{Cl}$ distances were calculated as function of this rotation (see Fig. 2), and these distances were compared with the RDF from 2.7 to 4.0 Å. It could be concluded that at least two conformations are present in large fractions, viz. conformations with $\alpha \approx 0^\circ$ and $\alpha \approx 130^\circ$ (we define the internal rotational angle $\alpha = 0^\circ$ when the C—Cl bond is eclipsed with the C=O bond and call this the *trans* position [1]). However, calculated RDF's showed that the peak at 3.45 Å remained to be accounted for and that the calculated peaks at 3.0 and 3.85 Å were too high. Therefore a third conformation had to be introduced, with $\alpha \approx 80^\circ$. A conformation with $\alpha \approx 90^\circ$ has a nearly identical set of $\text{O} \cdots \text{C}$ distances but was ruled out by the subsequent least-squares refinements.

In contrast to the findings in monofluoroacetic acid [1] the occurrence of a conformation with $\alpha \approx 180^\circ$ is not in agreement with the RDF. The presence of hydrogen bonded dimers could also be excluded: from the peak heights in the RDF it is seen that there is no contribution of the $\text{O} \cdots \text{O}$

Fig. 2. Variation of O $\cdots$ Cl distances with conformational angle α , and Newman projections of the three conformations described in the text.

distances of 2.65, 3.2 and 3.7 Å expected for these dimers. The bond lengths, the bond angles and the vibrational amplitudes for all distances except Cl $\cdots$ O were assumed not to vary with the conformational angles. The hydrogen atom parameters were assumed to have fixed values, the low contribution of the hydrogen atoms to the molecular intensity inhibited the determination of their positions. The results of least-squares refinements of the parameters describing the molecular model with the above three conformations are presented in Tables 2 and 3. In order to correct for the effect of correlation between the intensity data [9], the standard deviations resulting from the normal equations were multiplied by a factor of 2. In addition a 1% uncertainty in the wavelength has been included.

After completion of this refinement the results of the microwave analysis of van Eijck et al. [4] became available. The inertia moments and substitution coordinates of the Cl and the hydroxyl H atoms for the planar *trans* conformation are given in Table 4. The problem of the difference of r_s and $r_g(1)$ structures obtained by microwave spectroscopy and electron diffraction respectively was realized. A thorough treatment [10], however, is in this case impossible with the limited amount of data available. Therefore a least-squares

TABLE 2

Results from least-squares refinements of model parameters for monochloroacetic acid, using only electron diffraction data and for combined electron diffraction data and microwave spectroscopy data

Parameter	Electron diffraction		Electron diffraction + Microwave spectroscopy	
	Value	Standard deviation	Value	Standard deviation
C—Cl	1.778 Å	0.005 Å	1.778 Å	0.005 Å
C—C	1.509	0.006	1.508	0.006
C=O	1.224	0.004	1.223	0.004
C—O	1.354	0.005	1.352	0.005
C—H	1.09	0.02	1.09	0.02
O—H	0.983	^a	0.97	0.015
C—C=O	126.2°	0.5°	126.1°	0.5°
C—C—O	110.7	0.4	110.6	0.4
C—C—Cl	112.8	0.6	112.5	0.4
C—O—H	106	^a	105.8	1.1
C—C—H	109.5	^a	109.5	^a
H—C—H	109.5	^a	109.5	^a
α(I)	10°	10°	10°	^a
α(II)	132	4	131	4
α(III)	78	6	79	4
%(I)	51%	9	56%	6
%(II)	33	9	30	6
%(III)	16		14	
scale 100 cm	0.0813	0.00274	0.08118	0.00280
scale 50 cm	0.00352	0.00014	0.00353	0.00014
scale 25 cm	0.00213	0.00012	0.00214	0.00012
scale 11 cm	0.00848	0.000208	0.00908	0.000252
$\Sigma w\Delta^2$	110.5		109.5 (electron diffraction alone)	
R^b	0.094		0.096 (electron diffraction alone)	

^aThis parameter was assumed and fixed in the refinements.

^b R is defined as $\Sigma |I_{\text{obs}} - I_{\text{calc}}| / \Sigma I_{\text{obs}}$.

refinement was done in which the microwave data were assigned weights according to expected difference of 0.005 and 0.003 Å between r_s and r_g (1) values of C—H and C—Cl bonds respectively, and the electron diffraction intensities were given their usual weights, based upon experimental errors. The results of this procedure, now including refined values for the O—H bond length and the C—O—H bond angle, are shown in Tables 2 and 4. It was realized that a continuous distribution of conformations gives an even better agreement between calculated and observed molecular intensities. Attempts to determine it soon showed that the parameters describing the distribution were very ill determined and that they showed a large correlation with the vibrational amplitudes.

TABLE 3

Root mean square amplitudes of vibration from electron diffraction data refinement of monochloroacetic acid

Distance	Value	Standard deviation
C—Cl	0.062 Å	0.004 Å
C—C	0.054	0.007
C—O	0.051	0.007
C=O	0.043	0.007
C—H	0.078	^a
O—H	0.070	^a
C --- O	0.054	0.010
O --- O	0.051	0.010
O --- Cl	0.093	0.009
Cl --- O short	0.128	0.015
Cl --- O medium	0.100	^a
Cl --- O long	0.096	0.024
all other	0.12	^a

^aThis means that this parameter was assumed and kept constant during the refinements.

TABLE 4

Microwave data used in the least-squares refinements

Experimental Microwave data	Calculated Microwave data	Assigned Standard deviation
$I_a = 48.0630 \text{ amu Å}^2$	48.13 amu Å ²	0.24 amu Å ²
$I_b = 214.9294$	216.48	1.08
$b_H^2 = -0.0003 \text{ Å}^2$	0.0011 Å ²	0.001 Å ²
$a_H^2 = 8.1100$	8.087	0.03
$b_{Cl}^2 = 0.0016$	0.0011	0.0005
$a_{Cl}^2 = 3.0443$	3.0632	0.01

DISCUSSION

The structural parameters of monochloroacetic acid, derived from the electron diffraction data alone, and those from the combined refinement of the electron diffraction data and the microwave data for the planar *trans* conformation, show a difference no greater than one standard deviation. The bond lengths and bond angles all have expected values in relation to those in acetic and propionic acid monomer [2], and those in monofluoroacetic acid [1].

The electron diffraction molecular intensity could well be described with a molecular model with three conformations due to hindered internal rotation of the CH₂Cl group around the C—C bond. The *trans* conformation ($\alpha \approx 10^\circ$)

present in an amount of 56%, was already found in the microwave investigation of van Eijck et al. [4]. The value of 10° found for the conformational angle in our refinements may be interpreted as an average angle of displacements from the $\alpha \approx 0^\circ$ position due to oscillatory movements. It has a large standard deviation particularly due to the relatively weak dependence of the $\text{Cl} \cdots \text{O}$ distances on internal rotation when $\alpha \approx 0^\circ$ (see Fig. 2). The 30% of a *gauche* conformation with $\alpha = 131^\circ$ and the remaining 14% of a conformation with $\alpha = 79^\circ$ may account for unassigned lines in the microwave spectrum [4]. The presence of at least two conformations is also indicated in an infrared spectroscopic study [11] of the $\text{C}=\text{O}$ stretch frequency in very diluted CCl_4 solution, where two separated bands were found at 1794 and 1676 cm^{-1} . In order to understand the conformations found in our experiments, we performed some CNDO/2 calculations [12]. The molecular energy computed as function of the internal rotational angle α , with all other geometry parameters kept constant at our experimental values, is shown in Fig. 3. Also shown in this figure is the conformational distribution calculated from this energy curve using Boltzmann statistics, viz. the curve

$$P(\alpha) = \exp[-V(\alpha)/RT] / \int_0^{2\pi} \exp[-V(\alpha)/RT] d\alpha$$

Fig. 3. (—) Molecular energy of monochloroacetic acid as function of the internal rotation angle α , calculated by CNDO/2 (----); $P(\alpha)$, distribution curve of the conformations, calculated by means of Boltzmann statistics from this energy.

Fig. 4. Part of radial distribution curve for monochloroacetic acid (—) observed, (---) calculated for CNDO/2 — distribution.

It is seen that according to CNDO/2 theory, the conformation with $\alpha=180^\circ$ should occur in the largest proportion.

A calculated radial distribution curve, assuming this distribution, shows a bad agreement (see Fig. 4) with the experimental RDF. We attribute this to failure of the CNDO/2 approximation for second row elements when repulsion plays an important part.

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REFERENCES

- 1 B. P. van Eijck, G. van der Plaats and P. H. van Roon, *J. Mol. Struct.*, 11 (1972) 67.
- 2 J. L. Derissen, *J. Mol. Struct.*, 7 (1971) 67, 81.
- 3 J. M. J. M. Bijen and J. L. Derissen, *J. Mol. Struct.*, 27 (1975) 233.
- 4 B. P. van Eijck, A. A. J. Maagdenberg and J. Wanrooy, *J. Mol. Struct.*, 22 (1974) 61.
- 5 W. Zeil, J. Haase and L. Wegmann, *Z. Instrumentenk.*, 74 (1966) 84.
- 6 J. Murata, K. Kuchitsu and M. Kimura, *Jap. J. Appl. Phys.*, 9 (1970) 591.

- 7 B. Andersen, H. M. Seip, T. G. Strand and R. Stölevik, *Acta Chem. Scand.*, 23 (1969) 3224.
- 8 H. L. Cox and R. A. Bonham, *J. Chem. Phys.*, 47 (1967) 2599.
- 9 H. M. Seip, T. G. Strand and R. Stölevik, *Chem. Phys. Lett.*, 3 (1969) 617.
- 10 K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Struct.*, 1 (1967-8) 463.
- 11 J. M. J. M. Bijen, Thesis, Conformation and internal hydrogen bonding. Investigation of derivatives of formic acid and acetic acid in the vapour, Rijksuniversiteit Utrecht, 1974.
- 12 P. A. Dobosch, *CNDO and INDO Molecular Orbital Programme*, QCPE 142, Indiana University, Bloomington, 1974.