Investigation on the Molecular Structure of Monochloroacetamide by Gas Electron Diffraction and Dipole Moment

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In the previous investigation, the molecular structures of acetamide and N-methylacetamide were determined by electron diffraction[1]. It was pointed out that the bond length of the peptide bond in gaseous acetamide is longer than that in the crystalline proteins determined by Corey et al.[2] and that the difference is due mainly to the hydrogen bond present in a crystal.

The present investigation deals with the structure of monochloroacetamide. Since the molecule has a carbon-carbon bond as a rotational axis, it is of interest to determine the rotational structure and the bond length of a peptide bond.

Experimental Method and Results

[I] **Electron Diffraction.** — Since monochloroacetamide is in the crystalline state at room temperature, it was vaporized through a high temperature nozzle[1]. The feature, and the positions of the maxima and the minima were estimated by a visual method and are shown in Fig. 2V and in Table I respectively. Here $q=10\,s/\pi$ and $s=4\pi\sin(\theta/2)/\lambda$. Since the observed q values

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[1] M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).

[2] R. B. Corey and J. Donohue, *J. Am. Chem. Soc.*, **72**, 2899 (1950).

TABLE I

OBSERVED q VALUES FOR MONOCHLOROACETAMIDE

Max.	Min.	q	Max.	Min.	q
1		10.6	7		42.7
	2	13.7		8	44.7
2		16.6	8		46.6
	3	19.3		9	49.7
3		21.5	9		52.6
	4	24.4	10		58.5
4		27.3	11		63.2
	5	30.0	12		68.2
5		32.5	13		73.8
	6	34.1	14		79.3
6		37.0	15		83.1
	7	39.7	(16)		91.4
			(17)		96.8

were inaccurate for the minima beyond $q=50$, they were omitted from Table I and were not used for the quantitative comparison with the theoretical values. In Fig. 2V, the features of the 16th and 17th maxima are drawn by a dotted line since they are not very accurate and the first maximum was estimated by use of the theoretical intensity curves to be mentioned later.

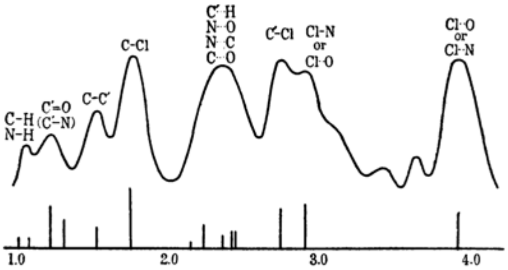

Fig. 1. The radial distribution curve for monochloroacetamide. The vertical bars under the curve show the interatomic distances r_{ij} and z_iz_j/r_{ij} for the structure determined by the present investigation.

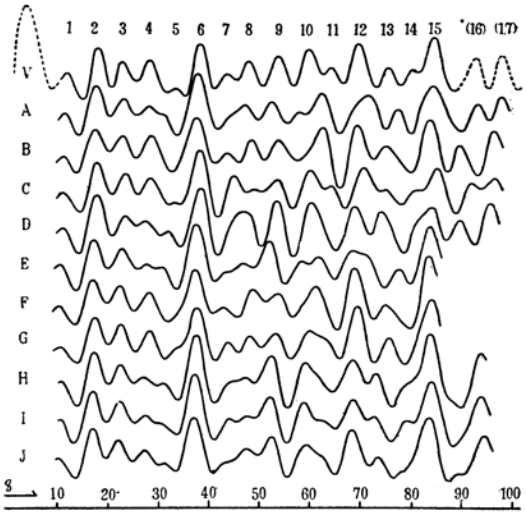

Fig. 2. The visual and theoretical curves for monochloroacetamide.

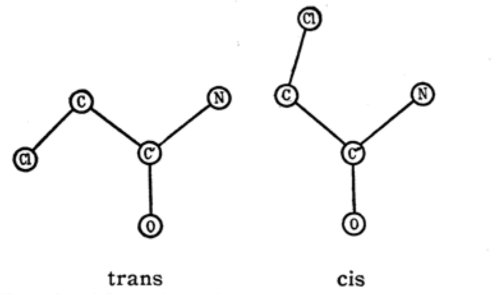

Fig. 3. Monochloroacetamide.

The radial distribution curve,

$$rD(r)=\sum_{q=1}^{q_m} I(q)\exp(-aq^2)\sin(\pi qr/10),$$

calculated by use of the visual curve (Fig. 2V) is shown in Fig. 1, where a was chosen as $\exp(-aq^2_{\max})=0.1$. The pair of atoms corresponding to each peak is also indicated in Fig. 1. The peak corresponding to C-Cl bond is very sharp and its bond length was determined to be 1.75 Å. C-C′ and C′-Cl interatomic distances could also be determined to be 1.53 Å (the same value as those determined for C-C bond in acetamide, N-methylacetamide[1], glycyl-glycine, etc.[2]) and 2.73 Å respectively, although less accurate than that of a C-Cl bond. The other interatomic distances could not be determined owing to overlapping with the contributions from various interatomic distances (cf. Fig. 3). From the values obtained above, ∠C′CCl can be obtained to be about 113°. The peaks at 2.89 Å and 3.89 Å correspond to Cl···N and Cl···O interatomic distances. From these results alone, we cannot determine the form of the molecule. However, since two peaks are very distinct and are separated from each other by about 1 Å, it is reasonable to consider that the molecule is in the trans or cis configuration, at least approximately.

The theoretical intensity curves were calcutated with the simplified equation,

$$I(q)=\sum\sum_{i\neq j} z_iz_j\exp(-b_{ij}q^2)\sin(\pi r_{ij}q/10)/r_{ij}.$$

Here z_i and z_j are atomic numbers for the ith and jth atoms respectively, and r_{ij} is the interatomic distance between the ith and jth atoms. A factor $\exp(-b_{ij}q^2)$ is related to intramolecular vibrations. The intramolecular vibrations did not affect the features of the theoretical intensity curves, except the rotational vibration about a C-C′ bond. Therefore the theoretical curves were mostly calculated for fixed models. When the rotational vibration was taken into account, b_{ij} was taken as 0.0004 for both Cl-O and Cl-N. Some of the intensity curves are reproduced in Fig. 2.

Since there are many parameters involved, we had to be satisfied with an analysis with some assumptions. We used C-Cl=1.75 Å and ∠C′CCl

=113°, which were determined from the radial distribution curve, and also assumed the structure of gaseous acetamide determined by electron diffraction1) (A form) or the structure of crystalline acetamide suggested by Corey et al. from a probable dimension of polypeptid chain (B form). These assumptions do not contradict with the result obtained from the radial distribution curve and appear to be reasonable since the molecule may be considered to take the structure nearly equal to that of acetamide in the gaseous as well as in the crystalline state (cf. Table II). These assumptions seem to be sufficient at least to estimate the position of C—Cl bond and a probable structure of monochloroacetamide. Thus the only parameter to be adjusted is the rotational angle about a C′—C bond.

TABLE II

THE STRUCTURE OF ACETAMIDE

	A form	B form
Authors	Kimura and Aoki	Corey and Donohue
C=O	1.21	1.23
C−N	1.36	1.32
C−C′	1.53	1.53
State	gas	crystal
method	electron diffraction	X-ray diffraction

In the case of A form, the theoretical intensity curves are shown in Fig. 2 for the models having 180° (the trans configuration, Fig. 2 A), 150° (Fig. 2 B), 30° (Fig. 2 C) and 0° (the cis configuration, Fig. 2D) as rotational angles (cf. Fig. 3). When rotational angles were given values ranging from 60° to 120° the theoretical intensity curves did not agree with the visual one, as expected from the radial distribution curve, and hence are not reproduced in Fig. 2. Curves E, F, G and H are the theoretical curves for the model with B form and the same rotational angle as in curves A, B, C and D respectively. These curves are in agreement to some extent with the visual curve for the maxima in the region $q<37$. But in both A and B form, the theoretical curves (A, B, E and F) for the models having the trans configuration exactly or approximately are not in agreement with the visual one, especially in regard to the 10th and 11th maxima. Moreover in the case of A form the theoretical curve for model C is in fair agreement with the visual one. But the calculated values for the maxima beyond $q=58$ shifted to q values larger than the observed values and the features of the 7th, 8th and 9th maxima were not in agreement with the visual curue. These curves were not in agreement with the visual one, even if we took into account the rotational vibration. In the case of B form, the curves G and H did not agree with the visual one in regard to the 13th and 14th maxima. For the model with the rotational angle of 15° (curve I), however, the theoretical curve was obtained in good agreement with the visual one. When we took into account the rotational vibration for this model, we obtained curve J. In this curve, the features of the 5th maximum, the 7th, 8th and 9th maxima and minima were improved, while the features of the 10th, 11th, 14th and 15th maxima became worse. These results are due entirely to the rather large value of b_{ij}, 0.0004, which was used in the case of taking into account the rotational vibration in N-methylacetamide. Thus the theoretical curve was obtained in good agreement with the visual one by taking into account the rotational vibration with an amplitude smaller than that in N-methylacetamide. The curve is not reproduced in Fig. 2.

Thus the structure of monochloroacetamide was determined as follows: C−Cl=1.75Å, ∠C′CCl =113°, N···Cl=2.89 Å and the twisted angle from the *cis* configuration is about 15°. For the structure of the part corresponding to acetamide the following structure was assumed. : C=O=1.23 Å, C−C=1.53Å, C−N=1.32Å, C−H=1.09Å, N−H=1.02Å, ∠C′CH=109°28′, ∠CC′O=121°, ∠OC′N=122°, ∠CC′N=117°, ∠C′NH=107°. The interatomic distances r_{ij} and $z_i z_j/r_{ij}$ for the structure obtained above are shown in Fig. 1 by means of vertical bars.

[II] Dipole Moment.—The measurement was made in benzene solution at 30°C. The apparatus and the method of measurements have already been reported3). The results are shown in Table III.

TABLE III

DIELECTRIC CONSTANT AND DENSITY INCREMENTS OF BENZENE SOLUTIONS AT 30°C

$\epsilon_B=2.2625$, $d_B=0.86629$

$w\times10^5$	$\Delta\epsilon\times10^4$	$\Delta d\times10^5$
30.3	25	—
64.6	60	31
85.5	58	30
88.1	72	—
130.1	76	39

The measurements of dielectric constants of monochloroacetamide could not be made on solutions of concentrations exceeding 0.1 weight percent, because the solubility in benzene is rather small*. Therefore it was difficult to determine the dipole moment of monochloroacetamide very accurately. From the results shown in Table III, the dipole moment of monochloroacetamide can be estimated to be 2.2D∼2.8D. The value thus obtained may be considered to be that in an unassociated state since it was obtained from the measurement on very dilute solutions, although it is known that the molecules of acetamide and its derivatives associate in benzene solutions4).

The moment of monochloroacetamide was calculated by the use of the valence angles determined by electron diffraction and by assuming the three valence bonds of nitrogen directed in a plane with three valence angles equal to 120°. The bond moments used are:

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3) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**, 10 (1951).

4) W. W. Bates and M. E, Hobbs, *J. Am. Chem. Soc.*, **73**, 2151 (1952); M. E. Hobbs and W. W. Bates, *J. Am. Chem. Soc.*, **74**, 746 (1952).

* The solubility in carbon tetrachloride is smaller than that in benzene.

C—Cl=1.5 D, C—N=0.45 D, C—H=0.4 D, C=O =2.5 D and N—H=1.3 D. The results are 1.4 D, 1.7 D, 2.6 D, 3.5 D and 4.7 D for the configuration with the rotational angles of 0° (the *cis* configuration), 30°, 60°, 90° and 180° respectively. The calculated moment of acetamide is 3.2 D with the assumptions similar to those used for monochloroacetamide. The observed value is 3.44 D[4] in benzene solution. The difference between the calculated and the observed values of acetamide will be due to the values of bond moments used, resonance effect, induction effect and solvent effect. Since monochloroacetamide may be considered to have the same degree of these effects as in acetamide, the calculated value of monochloroacetamide to be compared with the observed one is about 0.2 D larger than those mentioned above. Therefore the configuration of monochloroacetamide may be concluded to take the rotational angle of 60~30° from a comparison of the calculated values with the observed one. Even if the crudeness of the observed and the calculated values is taken into account, the configuration of monochloroacetamide is definitely far from the *trans* configuration*. The discussion on this point will be given later in some detail.

Discussion

According to the results obtained by electron diffraction, C—Cl bond takes the *cis* position to C—N bond. This is due to an electrostatic interaction between C—Cl bond and C=O bond and to a hydrogen bond across Cl···N.

The part corresponding to acetamide does not take the structure of a gaseous acetamide molecule already determined[1], but that similar to a crystalline acetamide with intermolecular hydrogen bonds. This is likely to show a larger contribution of a polar resonance form to the structure of monochloroacetamide than to gaseous acetamide. The effects of an intermolecular hydrogen bond on bond lengths were already pointed out by us in the case of acetamide[1] and hydroquinone[5] by comparing the structure in the crystalline state with that in the gaseous state and by Vaughan and Donohue in carboxylic acids, a peptide and its related compounds from the change of bond lengths owing to the change of the number and the state of hydrogen bonds in crystal[6]. The present investigation shows that an intramolecular hydrogen bond also affects the bond lengths in the molecule.

The result obtained from the measurement of dipole moment is in fairly good agreement with the result obtained by electron diffraction regarding the position of C—Cl bond. As pointed out by Kumler[7], one must take into consideration the state, in which measurements are made, in comparing observed values with calculated ones. So far the effect of a hydrogen bond has not been taken into account by us. But according to the result by electron diffraction, an intramolecular hydrogen bond is present in a gaseous monochloroacetamide molecule. The displacement of charges due to such a hydrogen bond causes mainly the increase of polarity of C=O bond and the shift of a lone pair of an oxygen atom to a hydrogen atom*. As a result, the total moment of monochloroacetamide will increase. Therefore the theoretical moment of monochloroacetamide will possibly be greater than that calculated above. If such is the case, the twisted angle of C—Cl bond from the *cis* configuration becomes smaller and agrees with the result obtained by electron diffraction better than the result mentioned in the experimental part.

Vaughan and Donohue[6] estimated the double bond characters of C=O and C—N bonds to be 70 and 30% respectively in crystalline acetamide, yielding the bond lengths of C=O and C—N equal to 1.23 Å and 1.35 Å respectively**. These values are nearly equal to those obtained in monochloroacetamide. Therefore it is highly probable that an acetamide molecule in crystal has such a structure. Moreover, the contribution of a polar resonance form will probably be smaller in gaseous acetamide than that estimated by Vaughan and Donohue in crystalline acetamide, since the bond lengths are 1.21 Å for C=O and 1.36 Å for C—N in gaseous acetamide.

Summary

1) The structure of monochloroacetamide was determined by gas electron diffraction as follows: C—Cl=1.75 Å, ∠C′CCl=113°, N···Cl=2.89Å, and the twisted angle from the *cis* configuration is about 15°. The structure of the part corresponding to acetamide is nearly equal to that of acetamide with an intermolecular hydrogen bond. This suggests that a monochlorocetamide molecule has an intra molecular hydrogen bond.

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* This conclusion is not altered even in the case of the three valence bonds of nitrogen taking a pyramidal form.

5) M. Kimura and S. Shibata, presented at the 4th annual meeting of the Chem. Soc. Japan held on April 7, 1951.

6) P. Vaughan and J. D. Donohue, *Acta Cryst.*, **5**, 530 (1952).

7) W. D. Kumler, *J. Am. Chem. Soc.*, **74**, 261 (1952).

* That the dipole moment of acetamide is 3.90 D in dioxane solution, may be considered to be due to an intermolecular hydrogen bond.

** This values are definitely different from the values obtained by F. Senti and D. Harker. *J. Am. Chem. Soc.*, **62**, 2008 (1940).

2) The dipole moment of monochloroacetamide was estimated to be 2.2 D~2.8 D from the measurement in benzene solution. The observed value was compared with the calculated one. The result agrees with that obtained by electron diffraction in regard to the position of C—Cl bond. The agreement becomes better if the effect of an intramolecular hydrogen bond is taken into account.

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