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Molecular Structure of Acetamide as Studied by Gas Electron Diffraction

Mitsuo KITANO and Kozo KUCHITSU

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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The bond distances (r_g) and angles (r_α) in acetamide CH_3CONH_2 have been determined by gas electron diffraction as follows: C–C=1.519±0.006 Å, C–N=1.380±0.004 Å, C=O=1.220±0.003 Å, C–H (average)=1.124±0.010 Å, N–H (average)=1.022±0.011 Å, ∠N–C=O=122.0±0.6°, ∠C–C–H (average)=109.8±2°, and ∠C–C–N=115.1±1.6° (or 112.2±1.6°). In comparison with the molecular structure in the crystal, the C–N bond is about 0.05 Å longer, whereas the C=O bond is about 0.04 Å shorter. The C–N and C=O bonds appear to be slightly shorter than the corresponding bonds in *N*-methylacetamide.

The present paper is a part of the systematic analyses of simple amide structures by gas electron diffraction, following the study of *N*-methylacetamide reported in a previous paper.[1] The gas-phase structure of acetamide was first determined by Kimura and Aoki[2] by the visual method of electron diffraction, and the molecular structures in the trigonal and orthorhombic crystals were studied by Senti and Harker[3] and by Hamilton,[4] respectively. The purpose of the present study is to improve the accuracy by an order of magnitude by the sector-microphotometer method of elec-

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4) W. C. Hamilton, *Acta Crystallogr.*, **18**, 866 (1965).

tron diffraction.

Experimental

A commercial sample was heated to about 160 °C by a high-temperature nozzle,[5] and diffraction photographs were taken with 40 kV electrons at camera distances of 112.30 mm (short) and 246.86 mm (long). The scale factors of the diffraction patterns were calibrated to within 0.10% with reference to the r_a(C=O) distance of carbon dioxide (1.1646 Å).[6] The densities of four plates taken at each camera distance were measured by a digital microphotometer.[7] Other experimental conditions are described elsewhere.[6,8]

Molecular intensities in the ranges $s=2.2$—15.7 and 9.4—37.7 Å^{-1} were obtained from the long and short distance data, respectively.[9] Since they agreed with each other in the overlapping region within experimental error (about 0.03 in the absolute $sM(s)$ scale), they were joined at $s=11.6$ Å^{-1} (Fig. 1). Most of the calculations were carried out on a HITAC-5020E in the Computer Centre of the University of Tokyo.

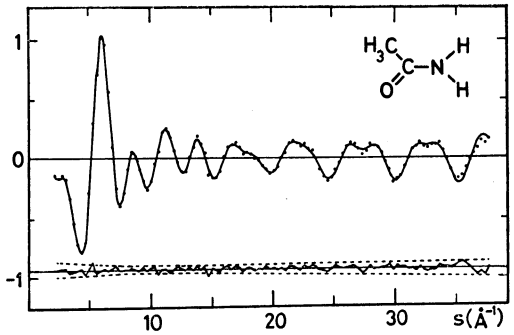

Fig. 1. Experimental and theoretical molecular intensities for acetamide. Typical observed $sM(s)$ values are shown in dots, and the best-fit theoretical is shown in the solid curve. The indices of resolution for long and short camera distances are 0.935 and 0.985, respectively. The lower solid and broken curves represent the residuals and the error limits in the $sM(s)$ to a fractional error of 1×10^{-3} of the original photocurrent,[7] respectively.

Analysis

The molecular intensity was analyzed under the following assumptions:

1) All the atoms except for the two hydrogen atoms of the methyl group are coplanar.

2) One of the hydrogen atoms of the methyl group eclipses the C=O bond.[10] The threefold potential barrier of the methyl torsion is 1 kcal/mol.[10]

3) The methyl group has local C_{3v} symmetry with the tilt angle equal to zero.

4) Two N–H distances (r_g) are equal to each other.

5) The C–N–H_1 and C–N–H_2 angles (r_α), which are *trans* and *cis* to the C=O bond, are equal to the corresponding r_s angles in formamide,[11] 120.0° and 118.5°, respectively.

The mean amplitudes of vibration and the vibrational corrections for the shrinkage effect (r_a-r_α)[12,13] were calculated from a set of modified Urey-Bradley force constants reported by Suzuki[1] and a number of force constants for out-of-plane displacements reported by Itoh[15] for *N*-methylacetamide, both determined from frequencies observed in the liquid phase. The results are given in Table 1. The contributions to the vibrational corrections from the methyl and C–N torsions were estimated in the way described in a previous paper.[1] The asymmetry parameters κ for the bonded C–H and N–H distances were assumed to be 1.8×10^{-5} Å^3, and the rest of the κ parameters were ignored.[16]

The r_g distances and r_α angles derived from least-squares analyses[17] are listed in Table 2 with limits of error estimated from the internal consistency and reproducibility of the parameters, with additional account for systematic errors.[17–19] The mean amplitudes for the C=O, C–N, and C–C bonds were varied and were

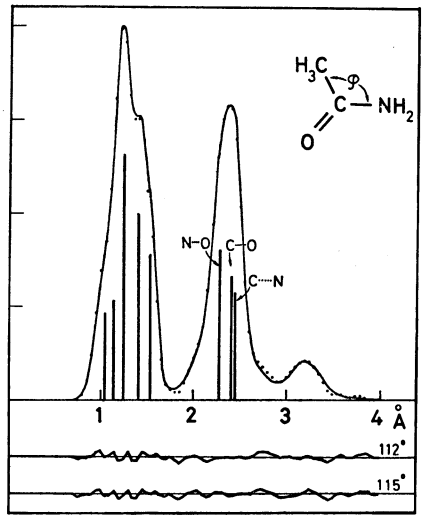

Fig. 2. Experimental (dots) and theoretical radial distribution curves. The lower curves represent residuals based on the models with the C-C-N angle (φ) assumed to be 112° and 115°. Vertical bars represent principal atom pairs based on the 115° model. A damping factor, exp $(-0.0016s^2)$, is used.

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TABLE 1. MEAN AMPLITUDES AND VIBRATIONAL CORRECTIONS FOR ACETAMIDE[a] (in 10^{-4} Å)

	l	$r_a - r_\alpha$		l	$r_a - r_\alpha$
C′=O	399	18	N···H_3	1016	−369
C′-N	431	13	N···H_4	1792	88
C-C′	522	5	O···H_1	904	41
N-H	736	57	O···H_2	1266	11
C-H	787	68	O···H_3	1410	−232
N···O	533	−1	O···H_4	1376	−190
C···O	628	−9	H_1···H_2	1172	21
C···N	676	−12	H_3···H_4	1283	30
C′···H_1	947	41	H_1···H_3	1539	82
C′···H_3	1068	13	H_1···H_4	2804	−130
C···H_1	1408	−9	H_2···H_3	1314	92
C···H_2	960	31	H_2···H_4	1856	71

a) Calculated at 160 °C. The carbonyl carbon atom is denoted as C′. The amide hydrogen atoms which are *trans* and *cis* to the C=O bond are denoted as H_1 and H_2, respectively, and H_3 and H_4 are the inplane and out-of-plane hydrogen atoms, respectively, in the methyl group.

TABLE 2. STRUCTURAL PARAMETERS FOR ACETAMIDE AND *N*-METHYLACETAMIDE[a]
(Distances in Å and angles in degrees)

	Gas AA[b]	Gas AA[c]	Cryst. AA[d]	Cryst. AA[e]	Gas NMAA[f]
C-C	1.519(6)	1.53(3)	1.51	1.505(13)	1.520(5)
C-N	1.380(4)	1.36(2)	1.38	1.334(17)	1.386(4)
C=O	1.220(3)	1.21(2)	1.28	1.260(11)	1.225(3)
C-H (av)	1.124(10)	1.09 (as)[g]	—	—	—
N-H (av)	1.022(11)	1.02 (as)[g]	—	—	—
∠C-C-N	115.1(16)	113	109	117.2(15)	114.1(15)
	or 112.2(16)				
∠O=C-N	122.0(6)	125(3)	122	123.1(5)	121.8(4)
∠C-C=O	123.0	122(4)	129	119.7	124.1
	or 125.9				
∠C-C-H (av)	109.8(20)	109.5 (as)[g]	—	—	—

a) Numbers in parentheses represent uncertainties attached to the last significant figures. b) Present study for acetamide (AA): the parameters determined in the least-squares analyses (r_g distances and r_α angles) with estimated limits of error. c) Ref. 2. d) Ref. 3. e) Ref. 4. f) The r_g distances and r_α angles for *N*-methylacetamide (NMAA) with estimated limits of error.[1] g) Assumed.

TABLE 3. ERROR MATRIX FOR ACETAMIDE

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	l_1	l_2	l_3	k_1	k_2
X_1	14	7	−6	−4	5	8	12	−5	3	5	3	17	−6
X_2		13	−6	4	13	−13	−7	13	3	−4	−6	11	−36
X_3			44	12	−13	12	4	11	−4	−12	−6	−40	58
X_4				9	5	16	−8	10	6	−7	3	−9	38
X_5					41	−21	−8	−19	11	1	−4	−31	−43
X_6						139	−27	−65	35	25	36	68	192
X_7							23	−22	−10	−2	−8	−15	−47
X_8								153	−23	−22	−26	−56	−114
l_1									18	14	18	20	82
l_2										19	19	21	57
l_3											26	22	84
k_1												100	95
k_2													446

X_1=C-C′, X_2=C′-N, X_3=N-H (average), X_4=C′=O, X_5=C-H (average), X_6=∠C-C′-N, X_7=∠N-C′=O, X_8=∠C′-C-H (average), $l_1=l$(C′=O), $l_2=l$(C-N), $l_3=l$(C-C′), k_1=index for long and k_2=index for short. Units ($\times 10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless.

found to be 0.043±0.005, 0.049±0.005, and 0.055± 0.007 Å, respectively. In comparison with the corresponding calculated values in Table 1 (0.040, 0.043, and 0.052 Å), a slight discrepancy is observed in the C–N amplitude. This difference is possibly due to that in the C–N stretching force constants in the gas and liquid phases (See Discussion for the C-N bond lengths in the gas and condensed phases). The rest of the mean amplitudes were fixed to the calculated values listed in Table 2. The error matrix is given in Table 3. The theoretical molecular intensity and radial distribution curves based on this structure are compared in Figs. 1 and 2, respectively, with the corresponding observed curves.

The least-squares analyses resulted in two alternative choices for the C–C–N and C–C=O angles. The C–C–N angle converged to about 115° and 112° when its initial estimates were larger and smaller, respectively, than 114°. The double minimum character of the weighted sum of squared residuals arises from the alternative assignments of the nonbonded C–O and C–N distances to 2.40 and 2.44 Å. All the rest of the parameters, including the O=C–N angle, are not essentially influenced by this ambiguity. As illustrated in Fig. 2, the radial distribution curves based on these alternative sets are almost equally acceptable, and therefore, no definite conclusion can be reached by electron diffraction alone. Since the 115° model is closer to the structure of *N*-methylacetamide,[1] it seems to be more plausible than the 112° model.

As for the torsional motion of the methyl group, the present experimental data are insensitive to the minimum position and the barrier of the potential. A least-squares analysis based on the model that the methyl group is staggered with the C=O bond gave a set of structural parameters essentially equal to those given in Table 3.

Discussion

The structure of acetamide determined in the present study is compared in Table 2 with those in the gas and crystal phases reported in the past and with the structure of *N*-methylacetamide. The most remarkable differences in the gas and crystal structures are found in the C–N and C=O bond distances, which are about 0.05 Å longer and 0.04 Å shorter, respectively, in the gas phase than in the crystal phase. This trend, which is also observed in *N*-methylacetamide, may be interpreted as due to the effect of intermolecular hydrogen bonds in the crystal.[1] Acetamide and *N*-methylacetamide have nearly equal C–C bond distance and O=C–N angles, whereas the former molecule has slightly shorter C–N and C=O bonds than the latter.