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Molecular Structure of *N*-Methylacetamide as Studied by Gas Electron Diffraction

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The bond distances (r_g) and angles (r_α) in *N*-methylacetamide have been determined by gas electron diffraction as follows: C–C$=1.520\pm0.005$ Å, N–C (methyl)$=1.469\pm0.006$ Å, N–C (carbonyl)$=1.386\pm0.004$ Å, C=O$=1.225\pm0.003$ Å, C–H (average)$=1.107\pm0.005$ Å, ∠N–C=O$=121.8\pm0.4°$, ∠C–N–C$=119.7\pm0.8°$, ∠C–C–N$=114.1\pm1.5°$, ∠H–C–H(average)$=110.4\pm2°$ and ∠H–N–C(carbonyl)$=110\pm5°$. In comparison with the molecular structure in the crystal, the N–C(carbonyl) bond is about 0.10 Å longer, whereas the C–C and C=O bonds are about 0.02 and 0.01 Å shorter, respectively. The two methyl groups are in the *trans* conformation about the N–C (carbonyl) bond, no other conformer being observed.

N-Methylacetamide (Fig. 1) has frequently been taken as one of the simplest models of a polypeptide chain.[1] Previous studies of infrared, Raman and ultraviolet spectra,[2,3] the dipole moment,[2] and X-ray diffraction data[4] revealed the existence of the *trans* conformer in regard to the methyl groups about the C_2–N bond in all phases, whereas an infrared band (*ca.* 3429 cm^{-1}) observed by Russell and Thompson[5] in a dilute solution of carbon tetrachloride was tentatively assigned to the N–H stretching vibration of a *cis* conformer with an estimated abundance ratio of about 5%. The structure of this molecule in the gas phase was first investigated by the visual method of electron diffraction by Kimura and Aoki,[6] who estimated the N–C_3 distance and the C–N–C angle and also favored the *trans* conformation. The rest of the structural parameters were transferred from those of acetamide determined by the same authors. In view of the importance of this molecule in chemistry and biochemistry, the present study was undertaken to determine its structure in the gas phase with higher accuracy.

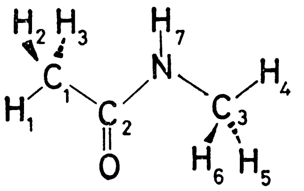

Fig. 1. *N*-methylacetamide.

Experimental

A commercial sample purified by vacuum distillation was heated to about 160°C by a high-temperature nozzle,[7] and diffraction photographs were taken with 40 kV electrons at camera distances of 111.80 mm (short) and 248.47 mm (long).[8] The scale factors of the diffraction patterns were

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[1] S. Mizushima, "Structure of Molecules and Internal Rotation," ed. by E. Hutchinson, Academic Press, New York (1954), p. 118.

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[3] T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **19**, 1479 (1951).

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[7] A. Yokozeki and K. Kuchitsu, *ibid.*, **44**, 72 (1971).

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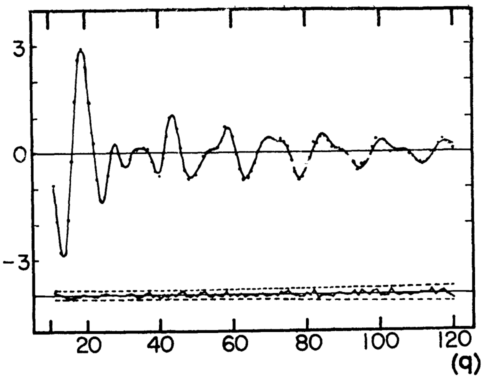

Fig. 2. Experimental and theoretical molecular intensities for *N*-methylacetamide. Typical observed $qM(q)$ values are shown in dots, and the best-fit theoretical is shown in the solid curve. The indices of resolution for long and short intensities are 0.950 and 0.763, respectively. The lower solid and broken curves represent the residuals and the error limits in the $qM(q)$ to a fractional error of 1×10^{-3} of the original photocurrent, respectively.

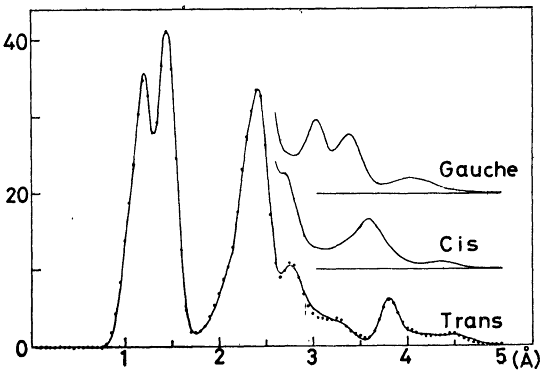

Fig. 3. Experimental (dots) and theoretical radial distribution curves. A damping factor, $\exp(1.599 \times 10^{-4} q^2)$, is used.

calibrated to within 0.10% with reference to the r_a(C–O) distance of carbon dioxide (1.1646 Å)[8] for the short camera distance and to the r_a(N–N) distance of nitrogen (1.1007 Å)[9] for the long camera distance. The densities of four plates taken at each camera distance were measured by a digital microphotometer.[10]

Molecular intensities in the ranges q=7—50 and 30—120 Å^{-1} were obtained from the long and short distance data, respectively.[11] Since they agreed with each other in the overlapping region within experimental error (about 0.1 in the absolute $qM(q)$ scale), they were joined at 41 Å^{-1} (Fig. 2). The corresponding radial distribution curve shown in Fig. 3 has confirmed that the dominant conformer has *trans* methyl groups. Most of the calculations were carried out on a HITAC-5020E in the Computer Center of the University of Tokyo.

Analysis

TABLE 1. MEAN AMPLITUDES AND VIBRATIONAL CORRECTIONS FOR N-METHYLACETAMIDE (IN 10^{-4}Å)

	l	r_a-r_α		l	r_a-r_α
C_1–C_2	519	30	N$\cdots$$H_2$	2165	187[b]
N–C_3	472	60	N$\cdots$$H_4$	1007	83
C_2–N	439	16	$C_3$$\cdots$$H_1$	1158	−264[b]
C_2=O	399	18	$C_3$$\cdots$$H_2$	1867	112[b]
C_1–H_1	780	73	$C_3$$\cdots$$H_7$	962	83
N–H_7	740	128	O$\cdots$$H_1$	1395	376[b]
$C_1$$\cdots$N	687	18	O$\cdots$$H_2$	1755	−137[b]
$C_1$$\cdots$$C_3$	697	−49[a]	O$\cdots$$H_4$	1218	−249[b]
$C_1$$\cdots$O	637	9	O$\cdots$$H_5$	4404	339[b]
$C_2$$\cdots$$C_3$	635	15	O$\cdots$$H_7$	912	32
N$\cdots$O	571	3	$H_1$$\cdots$$H_2$	1262	30
$C_3$$\cdots$O	1045	28[a]	$H_1$$\cdots$$H_4$	1371	3
$C_1$$\cdots$$H_4$	1201	−130[b]	$H_1$$\cdots$$H_5$	2928	−31
$C_1$$\cdots$$H_5$	1870	32[b]	$H_1$$\cdots$$H_7$	1541	30
$C_1$$\cdots$$H_7$	1426	5	$H_2$$\cdots$$H_4$	2924	−33
$C_2$$\cdots$$H_1$	1039	47	$H_2$$\cdots$$H_5$	2194	−15
$C_2$$\cdots$$H_4$	991	−156[b]	$H_2$$\cdots$$H_6$	2070	−61
$C_2$$\cdots$$H_5$	2432	86[b]	$H_2$$\cdots$$H_7$	3707	−17
$C_2$$\cdots$$H_7$	930	59	$H_4$$\cdots$$H_7$	1579	60
N$\cdots$$H_1$	1022	−349[b]	$H_5$$\cdots$$H_7$	1541	92

a) The shrinkages due to the torsional motion around the C_2–N axis are included as mentioned in the text.

b) The shrinkage effects due to the two menthyl torsions are included.

The molecular intensity was analyzed under the following assumptions:

1) The molecule has a symmetry plane.
2) The two methyl carbon atoms are in the *trans* conformation about the C_2–N axis.
3) The *N*-methyl group is in the staggered conformation with the C_2–N bond.
4) One of the hydrogen atoms in the *C*-methyl group is in the eclipsed position with the C=O bond.
5) The methyl groups have local C_{3v} symmetry.
6) All the C–H distances are equal.
7) The r_α(N–H) distance is equal to the corresponding r_s(N–H) distance in formamide,[12] 1.002 Å.

The mean amplitudes of vibration and the vibrational corrections for the shrinkage effect[13] (r_a-r_α listed in Table 1) were calculated from a set of modified Urey-Bradley force constants determined by Itoh[14,15] from frequencies observed in the liquid phase. In the calculation of the vibrational corrections, contributions from the skeletal and methyl torsions, for which a conventional approximation of infinitesimal amplitudes breaks down,[16] were estimated by a high barrier

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11) Numerical experimental data of the leveled total intensity and the background have been deposited with the Chemical Society of Japan (Document No. 7302).

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approximation.[17—20] The skeletal torsion around the C_2–N axis was assumed to obey the potential function, $V=(1/2)V_2(1-\cos 2\phi)$, where V_2 is 20 kcal/mol as estimated by Warshel *et al.*[21] The contributions from this motion to the r_a-r_α for the skeletal atom pairs were −0.0040 Å for C_1–C_3 and 0.0053 Å for O–C_3. The contributions from the skeletal torsion to the corrections for other atom pairs involving hydrogen were ignored, since they are obscured by much larger contributions from the methyl torsions. The effects of the methyl torsions on the nonbonded pairs indicated as b) in Table 1 were estimated from threefold potential barriers of 1 and 2 kcal/mol for the *C*-methyl and *N*-methyl torsions,[22] respectively, whereas those on the bonded and next-to-bonded pairs were assumed to be independent of the torsional motion. Uncertainties equal to 100% of the values calculated above were included in the limits of error of the structural parameters. The uncertainties from this origin are practically negligible except for the H–C–H angle.

The asymmetry parameters κ for the bonded C–H and N–H distances were assumed to be[23] 1.8×10^{-5} Å^3, and the rest of the κ parameters were ignored.

The r_g distances and r_α angles[13,24] derived from least-squares analyses[25] are listed in Table 2 with their limits of error estimated from the internal consistency and reproducibility of the parameters with additional account of systematic errors.[25—27] The error matrix is given in Table 3. The theoretical molecular intensity and radial distribution curves based on this structure are compared in Figs. 2 and 3, respectively, with the corresponding observed curves.

The experimental radial distribution and molecular intensity curves were further examined in detail in order to corroborate the above-mentioned assumptions 2—4) concerning the skeletal and methyl conformations. As for the skeletal conformation, the observed molecular intensity curves ($q=11$ to 40) were analyzed by the least-squares method on the assumption that the system is composed of *trans* (with a dihedral angle of 180°), *cis* (0°) and *gauche* (60°) conformers. Their frame structures were assumed to be identical, and the abundance ratios were the only variable parameters. The analysis gave 98±5, 0±5, and 2±4%, respectively. Analyses of the radial distribution curve and the background functions[28—30] were

Table 2. Structural parameters for *N*-methylacetamide in the gas and crystal phases (in Å and degrees)

	Present study[a)] Gas	K. A.[b)] Gas	K. P.[c)] Crystal
C_1-C_2	1.520_3 (5)	1.53	1.536 (16)
N-C_3	1.468_5 (6)	1.44 (40)	1.465
C_2-N	1.386_2 (4)	1.36	1.290 (13)
C_2=O	1.224_6 (3)	1.21	1.236 (12)
C-H (av)	1.106_7 (5)	1.09	—
∠N-C_2=O	121.8_3 (0.4)	125	123
∠C_2-N-C_3	119.6_7 (0.8)	117 (5)	120.5
∠C_1-C_2-N	114.1_2 (1.5)	113	116.5
∠H-C-H (av)	110.4 (2)	109.6	—
∠C_2-N-H	$110._4$ (5)	107	—

a) The r_g distances and r_α angles derived from the present analysis with estimated limits of error in parentheses. The limits of error of bond distances are in 10^{-3}Å units. b) Parameters estimated by visual method of gas electron diffraction by Kimura and Aoki.[6] c) Crystal structure determined by X-ray diffraction by Katz and Post[4] and estimated standard deviations.

Table 3. Error matrix for *N*-methylacetamide[a)]

	X_1	X_2	X_2	X_3	X_4	X_5	X_6	X_7	X_9	X_{10}	k_1	k_2
X_1	19	−4	−13	3	5	−8	−8	20	16	28	−9	35
X_2		15	8	8	−2	−28	−12	−8	−7	−32	13	−43
X_3			16	3	−5	−23	−8	−22	−11	−33	19	−35
X_4				19	7	−14	−9	−4	4	21	−23	−19
X_5					9	10	−4	14	1	19	−15	23
X_6						127	−42	36	−19	83	−46	93
X_7							44	4	14	39	19	31
X_8								71	22	87	−50	63
X_9									26	64	−21	33
X_{10}										315	−99	122
k_1											85	−57
k_2												184

a) $X_1=C_1$-C_2, $X_2=C_2$-N, X_3=N-C_3 X_4=C-H (average), $X_5=C_2$=O, X_6=∠C_1-C_2-N, X_7=∠C_2-N-C_3, X_8=∠H-C-H (average), X_9=∠N-C_2=O, X_{10}=∠C_2-N-H_7, k_1=index for long and k_2=index for short. Units ($\times10^{-4}$) for the distances are Å, those for the angles are rad., and those for the indices are dimensionless.

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Table 4. Comparison of skeletal structures[a)]

	NMAA[b)]	Related compounds		Ref.
C-C	1.520 (5)	1.520 (3)	acetone	32, 33
N-C_{Me}	1.469 (6)	1.467 (2)	methylamine	31
		1.469 (4)	ethylenediamine	30
		1.455 (2)	dimethylamine[c)]	34
		1.466 (8)	dimethylamine[d)]	35
C=O	1.225 (3)	1.213 (4)	acetone	32, 33
∠C-C=O	124.1 (1.5)	122.0 (1)	acetone	32, 33
∠C-N-C	119.7 (0.8)	111.8 (0.6)	dimethylamine[c)]	34
		111.6 (0.6)	dimethylamine[d)]	35
∠C-C-N	114.1 (1.5)	110.2 (0.7)	ethylenediamine	30

a) The r_g distances in Å and r_α angles in degrees. The limits of error of bond distances are in 10^{-3} Å units. b) *N*-methylacetamide determined in the present study. c) r_a structure. d) r_s structure.

not more sensitive than the least-squares analysis and also limited the concentration of conformers other than *trans* to less than 5%. The staggered conformation of the *N*-methyl group with respect to the C_2–N bond resulted in significantly better agreement with experiment than the eclipsed conformation. On the other hand, the conformation about the *C*-methyl group is less definitive, because both the eclipsed and staggered models gave acceptable radial distribution curves within experimental error. The most probable parameters derived from a least-squares analysis based on the staggered model are essentially equal to those given in Table 2, except that the N–C_2=O angle is 121.5°.

Discussion

The present structure is compared in Table 2 with those determined in previous studies[4,6)] and in Table 4 with those for related molecules. The most remarkable difference in the structural parameters in the gas and solid phases is seen in the C_2–N bond distance (*ca.* 0.10 Å). The C_2=O and C_1–C_2 bonds are found to be slightly shorter in the gas phase (*ca.* 0.01 and 0.02 Å, respectively) than in the solid phase. The presence of intermolecular hydrogen bonds (N–H···O) in the crystal[4)] seems to be the principal origin of these differences. The C_3–N distance, on the other hand, is nearly equal to that in the crystal and is about 0.08 Å longer than the C_2–N distance. Since the C_3–N distance is also nearly equal to those in methylamine[31)] and ethylenediamine,[30)] this bond can be regarded as a normal C–N single bond.

In comparison with the structure of acetone,[32,33)] *N*-methylacetamide has a very similar C–C bond distance but a slightly (*ca.* 0.01 Å) longer C=O bond and a slightly (*ca.* 2°) larger C–C=O angle. The C–N–C angle in *N*-methylacetamide is larger than that in dimethylamine[34,35)] by more than 7°, and the C–C–N angle is larger than that in ethylenediamine[30)] by more than 3°.

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