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

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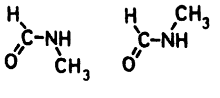
The bond distances (r_g) and angles (r_α) in *N*-methylformamide $HCONHCH_3$ have been determined by gas electron diffraction as follows: N–C(methyl) = 1.459 ± 0.006 Å, C(carbonyl)–N = 1.366 ± 0.008 Å, C=O = 1.219 ± 0.005 Å, C–H(methyl) = 1.114 ± 0.025 Å, $\angle$N–C=O = $124.6 \pm 0.5°$ and $\angle$C–N–C = $121.4 \pm 0.9°$, where uncertainties represent estimated limits of experimental error. Systematic trends are observed among the skeletal structures of formamide, acetamide, *N*-methylformamide and *N*-methylacetamide. A conformer with the C(carbonyl)–H and N–C(methyl) bonds *trans* to each other is found to be dominant in the gas phase. The presence of a small fraction of the *cis* conformer is suggested, but the experimental evidence is not conclusive.

The present work is a part of our systematic study of simple amide structures by gas electron diffraction. In the preceding studies of formamide,[1] acetamide,[2] and *N*-methylacetamide,[3] significant differences in the C′–N[4] and C′=O distances and in the N–C′=O angles were observed. The question was then raised whether the skeletal structure of *N*-methylformamide (Fig. 1), which has never been reported,[5] conforms to these trends.



trans *cis*

Fig. 1. *N*-methylformamide.

As for the possibility of rotational isomerism about the C′–N bonds, Phillips[6] observed a single methyl-proton NMR spectrum and reported that only one of the two possible conformers (*trans* and *cis* relative to the C′–H and N–C bonds) was present. Jones[7] remarked that the general character of the infrared spectrum in the vapor phase was more consistent with the *cis* model and that the rotation about the C′–N bond was severely hindered. However, his assignment was questioned by Miyazawa[8] and Suzuki,[9] who interpreted the spectrum as that of the *trans* conformer, though a small fraction of the *cis* conformer could exist. The abundance ratio of the *cis* form in a dilute solution of carbon tetrachloride was estimated from the N–H stretching bands to be about 5% by Russell and Thompson.[10]

Experimental

A commercial sample was heated to about 130 °C by a high-temperature nozzle,[11] and diffraction photographs were taken with 40 kV electrons[12] 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).[12] The densities of four plates taken at each camera distance ($D = 0.82 - 0.25$) were measured by a digital microphotometer.[13] Other experimental conditions are described elsewhere.[11-14]

Molecular intensities in the ranges $s = 2.2 - 15.7$ and $9.4 - 37.7$ Å^{-1} were obtained[15] from the long and short distance data, respectively, by use of hand-drawn backgrounds.

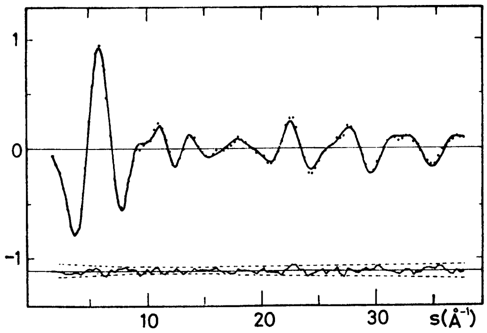


Fig. 2. Experimental and theoretical molecular intensities for *N*-methylformamide. Typical observed $sM(s)$ values are shown in dots, and the best-fit theoretical intensity based on a mixture model of 83% *trans* and 17% *cis* conformers is shown in the solid curve. The lower solid and broken curves represent the residual and the error limits in the $sM(s)$ to a fractional error of 1×10^{-3} of the original photocurrent, respectively. A 100% *trans* model gives residuals of nearly equal magnitude.

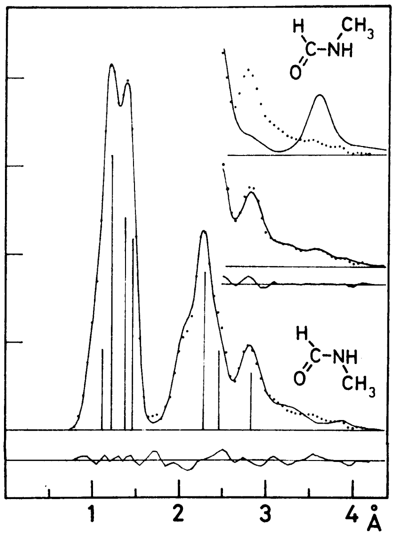


Fig. 3. Experimental (dots) and theoretical radial distribution curves for 100% *cis* (top), 83% *trans* and 17% *cis* (middle), and 100% *trans* (bottom) models. Vertical bars represent principal atom pairs. A damping factor, $\exp(-0.0016\,s^2)$ is used. Residuals are shown below.

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 $s=12.7$ Å^{-1} (Fig. 2). The corresponding radial distribution curve, shown in Fig. 3, confirmed that the dominant conformer has the C′–H and N–C bonds *trans* to each other. Most of the calculations were carried out on a HITAC-5020E and a HITAC-8800 in the Computer Centre of the University of Tokyo.

Analysis

Skeletal Structure. The skeletal parameters were determined by a least-squares analysis of molecular intensities with conventional diagonal weights[16] under the following assumptions:

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

2) The C′–H and N–C bonds are *trans* to each other.

3) The *N*-methyl group is in the staggered conformation with the C′–N bond.[17]

4) The methyl group has local C_{3v} symmetry and has no tilt.

5) The H–C–H angle (r_α defined in Ref. 18) is equal to that in dimethylamine,[19] 108.6°.

6) The r_g(C′–H) and r_g(N–H) distances are equal to the corresponding distances in formamide,[1] 1.125 and 1.027 Å, respectively.

7) The C′–N–H and N–C′–H angles (r_α) are equal to the corresponding angles in formamide,[1,20] 118.7 and 112.7°, respectively.

8) The barriers hindering the skeletal and methyl torsions, V_2 and V_3, are 20 kcal/mol[21] and 1 kcal/mol, respectively.

9) The asymmetry parameters κ for the bonded C–H and N–H distances are 1.8×10^{-5} Å^3, and the rest of the κ parameters are zero.[22]

Mean vibrational amplitudes and vibrational corrections for shrinkage effects (r_a-r_α)[18,23] were calculated by use of the modified Urey-Bradley force constants reported by Suzuki[9] with a number of additional force constants for out-of-plane displacements for *N*-methylacetamide reported by Itoh,[24,25] both determined from frequencies observed in the liquid phase. The results are given in Table 1. Contributions to the vibrational corrections from the skeletal and methyl torsions were estimated in the way described in a previous paper[3] by use of assumption 8. All the mean amplitudes except for those of the C′=O and C′–N bonds were fixed to the values listed in Table 1.

TABLE 1. MEAN AMPLITUDES AND VIBRATIONAL CORRECTIONS FOR *N*-METHYLFORMAMIDE (in 10^{-4} Å)

	l	r_a-r_α		l	r_a-r_α
C′=O	394	31	O···H_t	901	35
C′–N	426	27	O···H_1	1268	−609
N–C	498	22	O···H_2	4293	−335
N–H_t	718	44	N···H_a	960	−12
C′–H_a	799	0	N···H_1	1032	33
C–H_1	800	70	C···H_a	1011	27
N···O	531	5	C···H_t	1017	46
C′···C	719	−11	H_a···H_t	1549	35
C···O	1128	12	H_a···H_1	1349	88
C′···H_t	949	−9	H_a···H_2	2120	44
C′···H_1	1027	−591	H_t···H_1	1670	103
C′···H_2	2493	−14	H_t···H_2	2035	120
O···H_a	906	4	H_1···H_2	1298	35

a) Calculated at 130 °C. The carbonyl carbon atom is denoted as C′. The amide hydrogen and carbonyl hydrogen atoms are denoted as H_t and H_a, respectively; H_1 and H_2 are the in-plane and out-of-plane hydrogen atoms of the *N*-methyl group, respectively. The shrinkage effects due to the skeletal and methyl torsions are included as described in Ref. 3.

TABLE 2. STRUCTURAL PARAMETERS FOR *N*-METHYLFORMAMIDE AND RELATED MOLECULES[a]

	$HCONH(CH_3)$[b]	$HCONH_2$[c]	CH_3CONH_2[d]	$CH_3CONH(CH_3)$[e]
C–H (methyl)[f]	1.114 (25)	—	1.124 (10)	1.107 (5)
C′=O	1.219 (5)	1.212 (3)	1.220 (3)	1.225 (3)
C′–N	1.366 (8)	1.368 (3)	1.380 (4)	1.386 (4)
N–C	1.459 (6)	—	—	1.469 (6)
∠N–C′=O	124.6 (5)	125.0 (4)	122.0 (6)	121.8 (4)
∠C–N–C′	121.4 (9)	—	—	119.7 (8)
l(C′=O)	0.043 (4)	0.043 (3)	0.043 (5)	—
l(C′–N)	0.044 (5)	0.050 (4)	0.049 (5)	—

a) Distances r_g and mean vibrational amplitudes l in Å, and angles r_α in degrees.[18] Estimated limits of experimental error attached to the last significant decimal places are enclosed in parentheses. The carbonyl carbon atom is denoted as C′. b) Structure of *N*-methylformamide determined in the present least-squares analysis.

c) Formamide, Ref. 1. d) Acetamide, Ref. 2. e) *N*-Methylacetamide, Ref. 3. f) Average r_g(C–H) distances for the *N*-methyl group in *N*-methylformamide, for the *C*-methyl group in acetamide, and the mean value for the *N*-methyl and *C*-methyl groups in *N*-methylacetamide.

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

	X_1	X_2	X_3	X_4	X_5	X_6	l_1	l_2	k_1	k_2
X_1	17	8	8	12	−10	−20	−6	−7	18	−66
X_2		20	9	8	−16	−9	−4	−16	22	52
X_3			11	15	−6	−14	5	−9	−13	40
X_4				45	−5	−17	13	−9	−48	54
X_5					45	12	6	13	−11	−20
X_6						35	5	10	−11	65
l_1							12	9	−12	52
l_2								18	−10	−42
k_1									110	−77
k_2										458

a) X_1=C′–N, X_2=N–C, X_3=C′=O, X_4=C–H, X_5=∠C–N–C′, X_6=∠N–C′=O, l_1=l(C′=O), l_2=l(C′–N), k_1, k_2= indices of resolution for long and short distance data (0.98 and 0.97), respectively. 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.

The r_g distances and the r_α angles derived from the least-squares analysis are listed in Table 2 with limits of error estimated from random and systematic errors.[16,26,27] The skeletal parameters are not sensitive to any of the above assumptions 1—9, and systematic errors caused by uncertainties in the assumptions are included in the quoted error limits. The error matrix[28] is given in Table 3.

Skeletal Torsion. The observed radial distribution curve shown in Fig. 3 seems to have a small hump around 3.6 Å, which can be assigned to the O···C (methyl) distance in a *cis* conformer. Though the hump is almost comparable with the noise level of the observed radial distribution curve, the peak is reproducible, and a fraction of about 17% is suggested. Accordingly, the molecular intensity was further examined by a least-squares analysis. The system was assumed to be a mixture of *trans* and *cis* conformers with identical frame structures, and their fractions were taken as an additional variable. The analysis gave identical structural parameters and 17±10% for the *cis* fraction, corresponding to a free energy difference ΔG of about 1.3 kcal/mol. This estimate is compatible with the spectroscopic prediction by Miyazawa.[8] This model was also acceptable according to a further analysis of background functions[29,30] based on a criterion of their smoothness. However, a 100% *trans* model was equally acceptable in this criterion within experimental error. Furthermore, the *cis* fraction derived from the least-squares analysis mentioned above was found to have strong correlation with the assumptions about the methyl conformation and the methyl torsional barrier. The *cis* fraction decreased to 11±10% when the methyl torsion was assumed to be essentially free. In further consideration of the uncertainties in the experimental molecular intensity and in the above-mentioned assumptions made in the analysis, it was im possible to unambiguously demonstrate the presence of the *cis* conformer. Further precise spectroscopic or diffraction experiments are necessary for a definite confirmation of the rotational isomerism.

Methyl Torsion. Theoretical radial distribution curves were calculated with different conformations of the methyl hydrogens and with different barrier heights for the methyl torsion. When the V_3 value was assumed to be less than 1 kcal/mol, theoretical curves based on any equilibrium position agreed with the observed curve within the range of experimental error. The agreement became worse when the barrier height was increased, and for $V_3 \simeq 3.8$ kcal/mol, which corresponds to a methyl torsional frequency of about 242 cm^{-1} assigned by DeGraaf and Sutherland,[31] only a model with a dihedral angle of about 30° between the C′–N and one of the C–H bonds remained acceptable. Consequently, it seems to be the case that either the barrier is lower than those in methylamine,[32] 2.0 kcal/mol, and in dimethylamine,[33] 3.2 kcal/mol, or the equilibrium dihedral angle is about 30°.

The theoretical molecular intensity and radial distribution curves based on the most probable structure are compared with the corresponding observed curves in Figs. 2 and 3, respectively.

Discussion

In comparison with the skeletal structures of formamide, acetamide, and *N*-methylacetamide listed in Table 2, the following trends are observed:

1) The C(carbonyl)–N bond lengths in formamide and *N*-methylformamide are essentially equal to each other and are about 0.01 Å shorter than those in acetamide and *N*-methylacetamide.

2) The N–C=O angles in formamide and *N*-methylformamide are nearly equal to each other and are about 3° larger than those in acetamide and *N*-methylacetamide. As remarked in Ref. 1, this trend conforms to the similar trends observed in other systems, where X–CH=Y angles are consistently larger than the corresponding X–C(CH$_3$)=Y angles by about 3°.

3) On the other hand, the C=O bond lengths in *N*-methylformamide and acetamide are nearly equal to each other and are slightly longer than that in formamide and slightly shorter than that in *N*-methylacetamide.

4) The N–C(methyl) bond length in *N*-methylformamide appears to be shorter than that in *N*-methylacetamide.

5) The C–N–C angle in *N*-methylformamide is larger than that in *N*-methylacetamide.

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References

1) M. Kitano and K. Kuchitsu, This Bulletin, **47**, 67 (1974).

2) M. Kitano and K. Kuchitsu, *ibid.*, **46**, 3048 (1973).

3) M. Kitano, T. Fukuyama, and K. Kuchitsu, *ibid.*, **46**, 384 (1973).

4) The carbonyl carbon atom is denoted as C′.

5) The structure of *N*-methylformamide is now being studied by microwave spectroscopy. R. A. Elzaro and R. H. Schwendeman, Symposium on Molecular Structure and Spectroscopy, CC6, Columbus, Ohio, June, 1973.

6) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955).

7) R. L. Jones, *J. Mol. Spectrosc.*, **2**, 581 (1958).

8) T. Miyazawa, *ibid.*, **4**, 155 (1960).

9) I. Suzuki, This Bulletin, **35**, 540 (1962).

10) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

11) A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 72 (1971).

12) Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **7**, 591 (1970).

13) Y. Morino, K. Kuchitsu, and T. Fukuyama, This Bulletin, **40**, 423 (1967).

14) M. Tanimoto, K. Kuchitsu, and Y. Morino, *ibid.*, **43**, 2776 (1970).

15) Numerical experimental data of the leveled total intensity and the background have been deposited with the Chemical Society of Japan (Document No. 7404).

16) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

17) Note, however, that Yan *et al.* favored the eclipsed conformation of the C′–N bond and one of the C(methyl)–H bonds from their CNDO/2 and extended Hückel calculations. J. F. Yan, F. A. Momany, R. Hoffman, and H. A. Scheraga, *J. Phys. Chem.*, **74**, 420 (1970).

18) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Chapter 12, Elsevier, Amsterdam (1972).

19) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968).

20) E. Hirota, R. Sugisaki, C. J. Nielsen, and G. O. Sørensen, *J. Mol. Spectrosc.*, in press.

21) A. Warshel, M. Levitt, and S. Lifson, *ibid.*, **33**, 84 (1970).

22) K. Kuchitsu, This Bulletin, **40**, 505 (1967).

23) K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).

24) K. Itoh, Ph. D. Thesis, The University of Tokyo (1969).

25) K. Itoh and T. Shimanouchi, *Biopolymers*, **9**, 383 (1970).

26) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Structure*, **1**, 463 (1958).

27) K. Kuchitsu, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Chapter 10, Elsevier, Amsterdam (1972).

28) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

29) Y. Morino and K. Kuchitsu, *ibid.*, **28**, 175 (1958).

30) M. M. Abe, K. Kuchitsu, and T. Shimanouchi, *J. Mol. Structure*, **4**, 245 (1969).

31) D. E. DeGraaf and G. B. B. M. Sutherland, *J. Chem. Phys.*, **26**, 716 (1957).

32) K. Takagi and T. Kojima, *J. Phys. Soc. Jap.*, **30**, 1145 (1971).

33) J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **54**, 532 (1971).