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The Structure of Liquid *N*-Methylformamide by Means of X-Ray Diffraction and Ab Initio LCGO-MO-SCF Calculations

Hitoshi OHTAKI,* Sumiko ITOH, and Bernd M. RODE†
Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta,
4259 Nagatsuta-cho, Midori-ku, Yokohama 227
† Institute of Inorganic and Analytical Chemistry, The University of Innsbruck,
Innrain 52a, Innsbruck A-6020, Austria
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The liquid structure of *N*-methylformamide (NMF) has been investigated by the X-ray diffraction method and the ab initio MO-SCF method. The structure parameters within a molecule were obtained as follows: C=O: 122(1) pm, C(methyl)–N: 145(2) pm, C(carbonyl)–N: 134(2) pm, N···O: 222(4) pm, C(methyl)···O: 278(6) pm. The intermolecular hydrogen-bonded N···O distance was estimated to be 298(11) pm. A linear and flexible chain structure was proposed for the liquid structure of NMF on the basis of scattered intensity data by the X-ray diffraction method and of interaction energies and geometries of hydrogen-bonded NMF molecules calculated by the ab initio MO calculations.

N-Methylformamide (NMF) is a methyl-substituted derivative of formamide (FA), and many physicochemical properties of NMF show intermediate values between those of formamide and *N,N*-dimethylformamide (DMF). Some properties of FA, NMF, and DMF are compared in Table 1. In spite of the increasing order of the molecular weight from FA to DMF, the boiling points, melting points and viscosities of the compounds decrease in the order FA>NMF>DMF. The trend indicates that intermolecular interaction energies may decrease in the same order. However, it must be noted that the relative dielectric constant of NMF is extremely large, 64% larger than that of FA, although the dipole moment of NMF is only 15% larger.

In previous papers we studied the liquid structures of FA¹⁾ and DMF²⁾ by the X-ray diffraction method in combination with MO-SCF calculations for interaction energies between molecules and concluded that the former liquid has a relatively strong hydrogen-bonded structure through $-CHO\cdots H_2N-$ interactions, while the latter has an almost random structure due to weak intermolecular interactions.

In the present study we aim at determining the liquid structure of NMF in order to compare the structures of FA and DMF and to explain physicochemical properties of the amides on the basis of structural information of the liquids.

The structural investigation of NMF is also an interesting subject for biochemists, because the molecule has the -OC-NH- moiety which is found in peptides. Thus the definition of the cis- and trans-forms of an NMF molecule is given on the basis of the -CO-NH- bond in peptides (Fig. 1).

Infrared spectroscopic studies in the liquid phase3,4) and in carbon tetrachloride solutions5) revealed that the trans-isomer was predominant in the liquid and in the solution phase. The result agreed with that found in the gas phase by using infrared6) and microwave7) spectroscopies and the electron diffraction method.8) NMR spectra obtained in the liquid phase9) and measurements for the dipole moment of NMF in dioxane solutions10) indicated that 90—92% of NMF molecules were present in the trans-form. Theoretical calculations11) supported the more stable conformation of the trans-form than the cis-form of

Table 1. Some Physicochemical Properties of Formamide (FA), *N*-Methylformamide (NMF) and *N,N*-Dimethylformamide (DMF)a)

	$HCONH_2$	$HCONH(CH_3)$	$HCON(CH_3)_2$
Molecular weight	45.041	59.068	73.095
Boiling point (θ_b/°C)	210.5	180—185	153.0
Melting point (θ_m/°C)	2.55	−3.8	−60.43
Viscosity/cP (25 °C)b)	3.302	1.65	0.802
Relative dielectric constant	111.0 (20 °C)	182.4 (25 °C)	36.71 (25 °C)
Dipole moment (10^{-30} C m)	11.2 (30 °C)	12.9 (25 °C)	12.9 (25 °C)
Donor number	24	—	26.6
Acceptor number	39.8	—	16.0

a) Data are taken from "Techniques of Chemistry, II, Organic Solvents," J. A. Riddick and W. B. Bunger, Ed., Wiley-Interscience, New York (1970), except for the donor and acceptor numbers, which are quoted from "The Donor-Acceptor Approach to Molecular Interactions" V. Gutmann, Plenum Press, New York (1978). b) 1 cP = 10^{-3} N s m^{-2}.

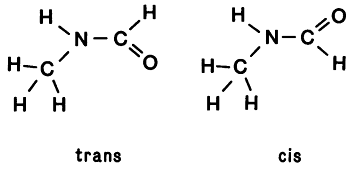


Fig. 1. *N*-Methylformamide: Definition of trans- and cis-forms.

NMF molecules. Therefore, it seems to be generally accepted that most NMF molecules exist in the trans-form in the gas and liquid phases. However, since no diffraction study has so far been examined for NMF in the condensed phase, we try to confirm the molecular conformation of NMF in the liquid state by using the X-ray diffraction method.

The energy for the hydrogen-bonds between NMF molecules was estimated by the ab initio LCGO-MO-SCF method in order to compare the strength of the intermolecular interactions in NMF with those in FA and DMF.

Experimental

Reagents. Commercially available NMF of analytical grade was dehydrated with molecular sieves and distilled in a dry nitrogen atmosphere under a reduced pressure.

X-Ray Scattering Measurements. X-Ray scattering measurements were carried out with a JEOL θ—θ diffractometer by using LiF monochromatized Mo*Kα* radiation (λ=71.07 pm) at (25±2) °C. The range of the scattering angle (2θ) was from 4 to 127°. Times spent to accumulate 80000 counts were recorded over the whole angle range. The methods of data corrections and treatments were essentially the same as those described previously.[12,13] The scattering and correction factors were quoted from the literature.[14]

The reduced intensities $i(s)$ were obtained from the following equation:

$$i(s)_{\text{obsd}} = K \cdot I_{\text{corr}}(s) - \sum \mathrm{n}_i[\{f_i(s)+\Delta f_i'\}^2+(\Delta f_i'')^2], \tag{1}$$

where n_i is the number of atom i in a stoichiometric volume V, and $f_i(s)$ denotes the atomic scattering factor at angle s. $\Delta f_i'$ and $\Delta f_i''$ are the real and imaginary parts of the anomalous dispersion of atom i, respectively. I_{corr} denotes the measured scattering intensity corrected for the back ground, absorption, polarization, multiple scattering and incoherent scattering. K is a factor for converting measured intensities to the absolute ones and was obtained by the high angle method and the Krogh-Moe-Norman method.[15,16] The radial distribution function $D(r)$ was then obtained by Eq. 2

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_{s_{\min}}^{s_{\max}} s \cdot i(s) \cdot M(s) \cdot \sin(sr)\mathrm{d}s \tag{2}$$

where ρ_0 is the average electronic density of sample solution. $s_{\max}$ and $s_{\min}$ correspond to the maximum and minimum values of s for the Fourier transform, which are 15.7×10^{-2} and 0.6×10^{-2} pm^{-1}, respectively. $M(s)$ is a modification function and is given as follows:

$$M(s) = [\sum \mathrm{n}_i\{(f_i(0)+\Delta f_i')^2+(\Delta f_i'')^2\}/ \\ \sum \mathrm{n}_i\{(f_i(s)+\Delta f_i')^2+(\Delta f_i'')^2\}] \cdot \exp(ks^2), \tag{3}$$

and the damping factor k is set to be 100 pm^2.

Theoretical reduced intensities were calculated according to Eq. 4:

$$\begin{aligned} i(s)_{\text{calcd}} = {} & \sum \mathrm{n}_j[\sum\sum n_{pq}\{(f_p(s)+\Delta f_p')(f_q(s)+\Delta f_q') \\ & +\Delta f_p''\Delta f_q''\} \cdot \sin(sr_{pq})/(sr_{pq}) \cdot \exp(-b_{pq}s^2)] \\ & -[4\pi R_j^3/(3V)] \cdot [3\{\sin(sR_j)-sR_j\cos(sR_j)\}/ \\ & (sR_j)^3] \cdot \exp(-B_js^2) \cdot \{\sum \mathrm{n}_i(f_i(s)+\Delta f_i') \cdot \\ & \sum \mathrm{n}_j(f_j(s)+\Delta f_j')+\sum \mathrm{n}_i\Delta f_i''\sum \mathrm{n}_j\Delta f_j''\}, \end{aligned} \tag{4}$$

where r_{pq}, b_{pq}, and n_{pq} stand for the distance, the temperature factor and the frequency factor of the p–q atom pair, respectively. R_j denotes the distance from an atom j beyond which a continuous electron distribution is assumed. A parameter B_j is introduced to avoid a sudden emergence of a continuous electron distribution at R_j. The program *KURVLR*[17] was employed for the intensity calculations. Structural parameters of each atom-pair in the system were determined by employing the least-squares method to measured intensities. The error-square sum $U=\sum w(s)\{i(s)_{\text{obsd}}-i(s)_{\text{calcd}}\}^2$ was minimized by using the program *NLPLSQ*[18], where the weighting function $w(s)$ is given to proportional to $\cos\theta/I(s)_{\text{obsd}}^2$.

Data Analysis

The procedure for determining the structural parameters of each atom-pair in the system was performed on the following assumptions:

(1) The initial structural parameters within an NMF molecule, which will be refined by the least-squares method, are assumed to be the same as those found in a DMF molecule; C=O: 122 pm, C(carbonyl)–N: 134 pm, C(methyl)–N: 145 pm. The temperature factors for these three bonds are first assumed to be 0.3×10^2 pm^2.

(2) The N–H and C(methyl)–H and C(carbonyl)–H bond distances are assumed to be 103, 109, and 109 pm, respectively, and these temperature factors are 0.1×10^2 pm^2.

(3) The methyl group has a tetrahedral form. Nonbonding interactions of H atoms are neglected except for the 3N···H and 3H···H interactions.

After corrections for spurious peaks, the experimental $s \cdot i(s)$ curve was compared with theoretical curves of the cis- and trans-isomers of NMF by using the first term of Eq. 4. The theoretical curve calculated for the trans-form showed a better agreement than that obtained from the cis-form (see Fig. 2). Intermolecular interactions were then taken into account for the least-squares fitting of the experimental data to the theoretical ones. Each molecule was assumed to link with other molecules through the –NH···OCH– hydrogen-bond. The least-squares refinement of the data was performed for the trans- and cis-conformations of NMF molecules. In the course of the calculations a continuous electron distribution was assumed. The results are depicted in Fig. 3 for the trans- and cis-forms of NMF molecules. It is obvious from the figure that the curve calculated on the basis of the trans-conformation of NMF molecules gave a much better agreement with the experimental curve than that of the cis-conformation.

The radial distribution curve $D(r)$-$4\pi r^2\rho_0$ of NMF is shown in Fig. 4. The first peak at 120 pm corresponds to the C–N and C=O bonds within an NMF molecule, and the second peak around 230 pm is ascribed to the N···O and C···C nonbonding interactions within a molecule. The difference of the contribution of the isomeric conformations is expected to appear at about 280 pm for the trans-

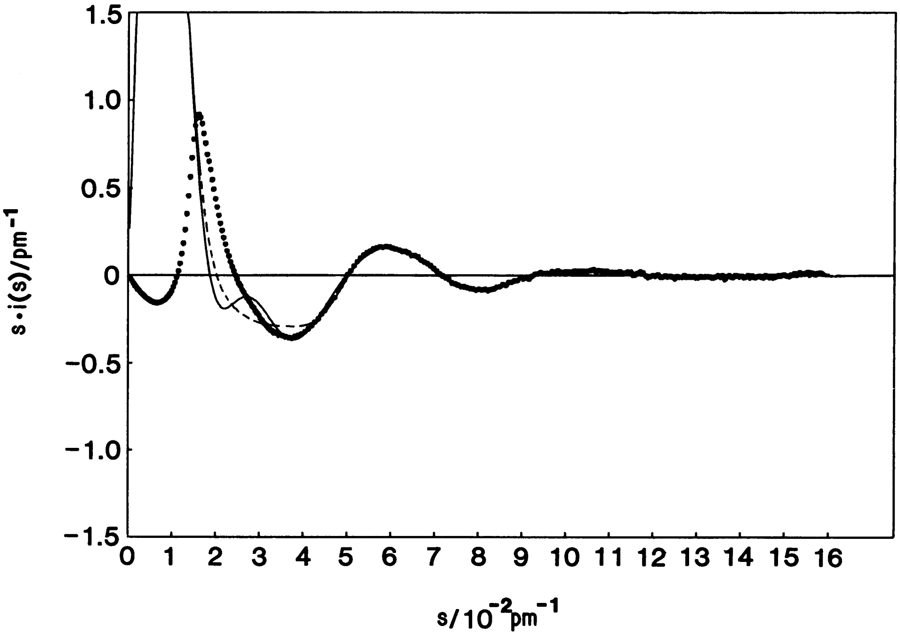


Fig. 2. Comparison between observed (circles) and the calculated $s \cdot i(s)$ corresponding to cis-(broken line) and trans-(solid line) forms. The contributions of the intermolecular N···O interaction are included.

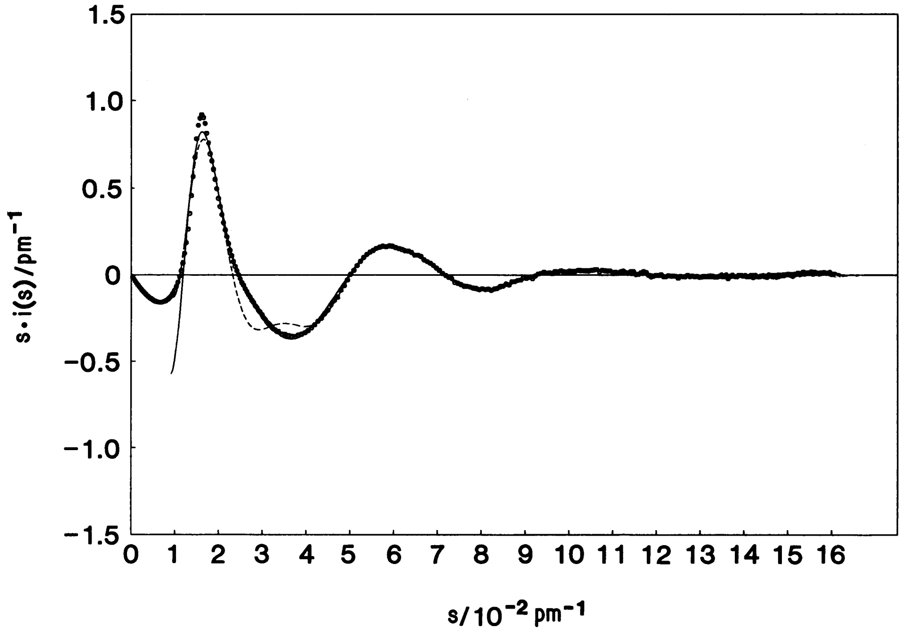


Fig. 3. Experimental (circles) and the theoretical $s \cdot i(s)$ curves for the chain structures consisting of the trans-isomer (solid line) and the cis-isomer (dashed line).

isomer and 350 pm for the cis-isomer due to the nonbonding interaction of C(methyl)···O within a molecule. On the supposition that the cis-isomer was predominant, the peak at 300 pm should be attributed only to the intermolecular N···O interaction and it was required to increase in the number of the hydrogen bonds per molecule to be 3. But even at that time, the theoretical $s\cdot i(s)$ curve showed the manifest discrepancy with the experimental one at about 4×10^{-2} pm^{-1} of s.

Therefore, we concluded that most NMF molecules in the liquid have the trans-conformation, as have been found in previous works.[4–11] The final results thus obtained for the structure parameters of NMF are listed in Table 2, together with those of FA and DMF.

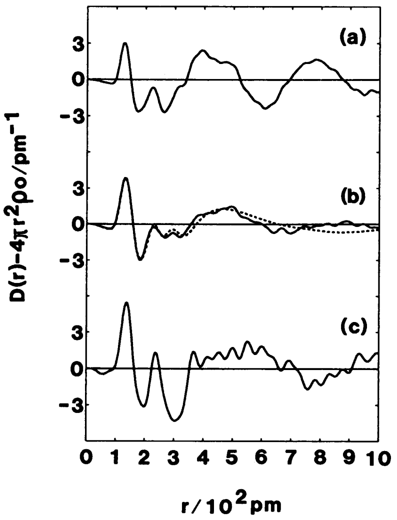


Fig. 4. Experimentally obtained $D(r)$-$4\pi r^2\rho_0$ curve of three amides. (a) Formamide, (b) *N*-Methylformamide. The dashed line represents calculated curve from the linear chain model structure of the trans-form molecules and the continuous electron distribution by using parameters in Table 2. (c) *N,N*-Dimethylformamide.

Theoretical Treatment

Stabilities of the cis- and trans-conformations of an NMF molecule, as well as the interaction energies between molecules through the -NH···OCH- hydrogen bond, were investigated by the ab initio LCGO-MO-SCF method with the minimal basis sets. The bond lengths within an NMF molecule were kept at the values experimentally obtained by the present X-ray diffraction study as shown in Table 2. Total energies for the cis- and trans-conformations, both being examined for the staggered and eclipsed orientations, are shown in Table 3. The stabilities were in the order, trans(staggered)>trans(eclipsed)> cis(eclipsed)>cis (staggered), which agreed well with the result found by Sugawara, et al., using the STO-41-G basis set.[11] The energy differences between the trans- and cis- forms were about 11 kJ mol^{-1} (0.00431 hartrees), which may be compared with the energy difference calculated by Sugawara et al. (5.7 kJ mol^{-1}).[11]

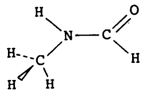
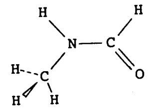
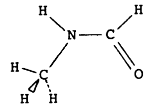
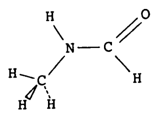
Interaction energies between NMF molecules were calculated by assuming some plausible geometries of NMF dimers which consisted of molecules of trans(staggered)-form, except for the cyclic dimer which must be constructed from molecules of the cis-form. The results are summarized in Table 4. For the calculation the counterpoise correction[19] had been performed. The energy of the hydrogen bond was the largest in the type D3 in Table 4. The cyclic dimer (D5) has the smallest interaction energy per hydrogen bond among the models examined.

Table 2. The Structure Parameters of Liquid FA, NMF and DMF. r and b Denote the Distance and the Temperature Factor, Respectively. The Values in Parentheses are Their Standard Deviations

	FA[1]	NMF		DMF[2]
	r/pm	r/pm	b/10² pm²	r/pm
C=O	124(1)	122 (1)	0.2 (1)	124 (2)
N-C(CO)	133(1)	134 (2)	0.4 (2)	135 (3)
N-C(CH$_3$)	—	145 (2)	0.2 (1)	145 (2)
N···O	225(2)	222 (4)	0.7 (3)	225 (6)
C(CH$_3$)···C(CO)	—	248 (4)	0.7 (3)	238(10)
C(CH$_3$)···C(CH$_3$)	—	—	—	257(15)
C···O	—	278 (6)	1.5 (7)	274(12) 364(16)
N···O(inter)	305(5) 292[a] 310[b]	298(11)	3.6(20)	—

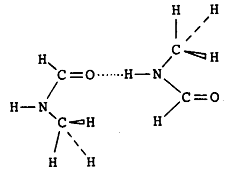
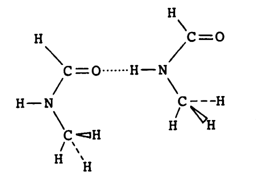
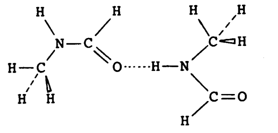
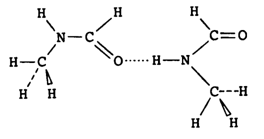
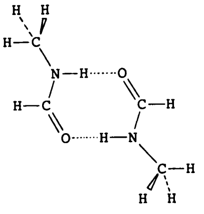
a) Ref. 20. b) Ref. 21.

Table 3. Energies of Monomers of NMF

Number	Model		Energy/hartree
M1		(cis eclipsed)	−176.47569
M2		(trans eclipsed)	−176.47679
M3		(trans staggered)	−176.48000
M4		(cis staggered)	−176.47523

1 hartree = 2625.34 kJ mol^{-1}.

Table 4. Energies of Hydrogen-bonds E_h for Various Dimers of NMF

Number	Model	E_h/kJ (per H-bond)
D1		−22.16
D2		−22.16
D3		−26.76
D4		−26.35
D5		−18.40

Furthermore, the interaction energy was additive when another NMF molecule was combined with a linear dimer to form a trimer with elongation of the same conformation of the type from D1 to D4.

Intensities $s \cdot i(s)$ calculated from the models D1 to D4 gave very similar curves and all fitted well the experimental curve. Figure 3 shows the $s \cdot i(s)$ curve for the chain structure consisting of the D3 units and the continuous electron distribution are also included.

Discussion

The radial distribution curve $D(r)$-$4\pi r^2 \rho_0$ of NMF is shown in Fig. 4, together with the curves of FA and DMF for comparison. The calculated radial distribution curve (broken line) for the chain structure using the structural parameters given in Table 2 for NMF and a continuous electron distribution satisfactory agreed with the experimental curve. In the case of NMF, the peak due to the hydrogen bonded N-(H)···O interaction appears at about 300 pm at almost the same position of that of FA, but no significant corresponding peak was observed in the case of DMF. The obtained N-(H)···O distance for NMF is compared with the value for FA[1,20,21] in Table 2. The hydrogen-bond distances are not appreciably changed between NMF and FA.

The radial distribution curve of NMF indicates a practically random distribution of molecules at a long distance r>500 pm, which is similar to the curve of DMF, in spite of the existence of relatively strong

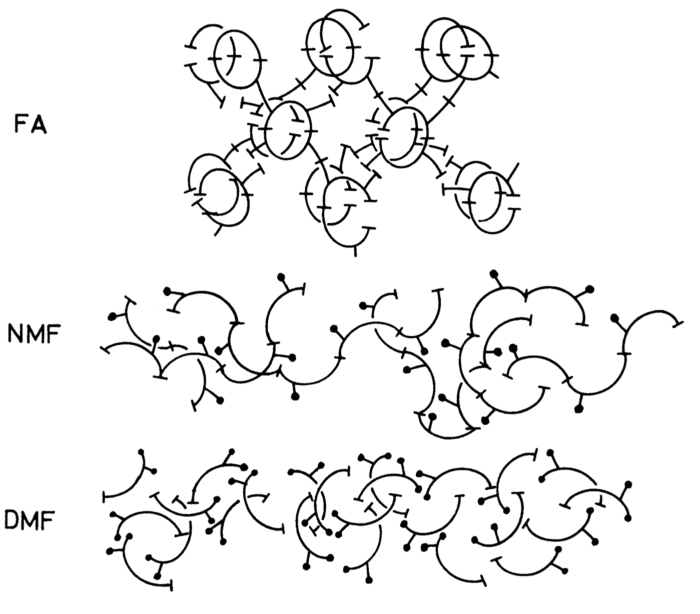


Fig. 5. Models for the liquid structures of formamide, *N*-methylformamide and *N*,*N*-dimethylformamide. —• indicates $-CH_3$,  and  represent $-\mathrm{N}\langle^{\mathrm{H}}_{\mathrm{H}}$ and $-\mathrm{N}\langle^{\mathrm{H}}_{\mathrm{CH_3}}$, respectively.  shows a hydrogen-bond between molecules.

hydrogen bonds in the system. On the contrary, FA has a three-dimensional hydrogen-bonded structure consisting of ring-dimer and chain moieties,[22] which has long-range order correlations over the ranges 350—500 pm and 700—850 pm. The energies of the hydrogen bonds in FA and NMF were estimated to be similar (E_h=—68.8[1] and −59.8 kJ mol^{-1} without the counterpoise corrections).

From the experimental results obtained by the X-ray diffraction studies and theoretical estimations for energies of hydrogen-bonds in FA,[1,22] NMF, and DMF,[2] we propose the liquid structure of these compounds as follows:

(1) Formamide has a three-dimensional structure containing the ring and chain moieties. The energy for the hydrogen-bond may be the largest among the three systems. Therefore, FA has a high boiling point and a high melting point and a large viscosity. According to most investigations from vibrational spectroscopies, however, the liquid FA has been proposed to have a chain structure.[23] This suggests that FA has a chain-like structure as the V-structure, but the time and space averaged structure (D-structure) shows a more or less crystal-like three-dimensional arrangement of molecules. So the life time of the chain moieties is suggested to be longer than that of the ring ones. A relatively high dielectric constant of FA is explained in terms of the relatively large dipole moment and the ordered structure. The ratio of the dielectric constants of FA to NMF was smaller than that expected from their dipole moments, which should be ascribed to the formation of ring-dimers in the liquid formamide in which the dipole moment is cancelled each other.

(2) *N*-Methylformamide has a hydrogen-bonded chain structure without the formation of a net-work structure. The chain may be so flexible that long-range ordered structure could not be seen from the diffraction method. Ring-dimer units hardly form in the system. The lower viscosity of NMF than FA may be explained by a slightly smaller value of the energy of the hydrogen-bond between NMF molecules, flexibility of the chain structure, and probably also by the absence of a net-work structure. The donor number and acceptor number of NMF have not been determined, but they may be similar to the corresponding values of FA.

(3) *N,N*-Dimethylformamide has a practically random structure, although DMF molecules interact each other through weak -HCO···HCO- hydrogen bonds. Therefore, the boiling and melting points of DMF are lower than those of FA and NMF. In spite of a larger molecular volume of DMF than those of the other two liquids, viscosity of DMF is smaller because of weaker intermolecular interactions. The relative dielectric constant is also much smaller than those of the other two solvents because of the random structure of DMF in the liquid state.

Models for the structures of FA, NMF, and DMF are depicted in Fig. 5.

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