^{13}C Nuclear Magnetic Resonance Studies of the Hindered Internal Rotation and the Molecular Association of *N,N*-Dimethylacetamide

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The concentration and temperature dependences of the ^{13}C chemical shifts of *N,N*-dimethylacetamide (DMA) in CCl_4, H_2O, and H_2SO_4 solutions were measured by means of a ^{13}C FT-NMR spectrometer at 25.15 MHz. From the temperature dependence of the chemical-shift difference between the *cis*- and *trans*-NCH_3 carbons, the activation energy, E_a, for the hindered internal rotation about the C–N bond was obtained to be 10—17.5 kcal/mol; it was also found to be *ca.* 10 kcal/mol at an infinite dilution in a CCl_4 solution. The chemical shift of each carbon in the DMA molecule was calculated using Pople's expression under the average excitation-energy approximation by means of the CNDO/2 method. The calculated finding that each carbon in DMA appears in the order of carbonyl, *trans*-NCH_3, *cis*-NCH_3, and acetyl carbons from the low field agrees with the order assigned by McFarlane. Further, as for the molecular association in neat liquid, various models are discussed on the basis of quantum-chemical calculations, and a model is proposed which has antiparallel oriented carbonyl groups in associated states of the molecules of more than two. The observed differences between the chemical shifts of the carbonyl carbons at dilutions in CCl_4 and H_2O solutions, and between those in CCl_4 and H_2SO_4 solutions, are found to agree well with the results calculated using the model in which the DMA molecules at dilutions in CCl_4, H_2O, and H_2SO_4 exist as monomer, hydrogen-bonded DMA with H_2O, and protonated DMA respectively.

Since the first NMR study of the hindered internal rotation of the C–N bond in amide compounds was carried out by Gutowsky *et al.*,[1] many studies have been concerned with the activation energy, E_a, for the hindered internal rotation and the molecular association[2] of amide compounds through the proton chemical shift, the line shape, and the spin-lattice relaxation time. Recently a quantum-chemical study of the hindered internal rotation has been done,[3] and some interesting results have been obtained. However, the mechanisms of the molecular association have scarcely been studied at all theoretically from the viewpoint of the chemical shift, even though this approach is very interesting. From the viewpoint of the chemical shift, the proton-decoupled carbon-13 (^{13}C) NMR spectra have greater advantages than ^1H NMR because of their simplicity. In addition, the ^{13}C chemical shift can be treated theoretically by the molecular orbital method, and the observed and calculated ^{13}C chemical shifts can be compared quantitatively with each other. Therefore, these results may be of use in obtaining information on the molecular association mechanism. In this paper, we will seek to compare the observed and calculated chemical shifts of the *N,N*-dimethylacetamide (DMA) molecule, which does not form a hydrogen bond itself and which may be a much-favored dipolar model. We will be concerned with the amide-amide associate, the hydrogen-bonded amide, and the protonated amide, which correspond to the behavior in neat liquid, H_2O, and H_2SO_4 solutions respectively, and with the monomer amide, which corresponds to the behavior at an infinite dilution in CCl_4.

Experimental

Materials. The DMA, CCl_4, and H_2SO_4 were obtained from the Tokyo Kasei Co., while the H_2O was distilled.

Measurements. High-resolution natural-abundance pulsed ^{13}C FT-NMR spectra were obtained at 25.15 MHz using a Japan Electron Optics Laboratory JNM PS-100 spectrometer equipped with the PFT-100 Fourier transform system, a JEC-6 spectrum computer, a ^2D field-frequency lock, and a noise-modulated proton-decoupling system. The core memory of the computer is 12K words, and the memory of the magnetic drum used is 8K words. The length of each word is 16 bits. The observed free induction decay (FID) was sampled in 8192 points. The pulse-recycle time was chosen as 60 s, considering the *N*-methyl carbon spin-lattice relaxation time, T_1, of 14 s. However, when only the measurement of the chemical shift was required, the recycle time of 30 s was used. The FID signal was observed after a 90° pulse with a width of 20 μs.

The activation energy for the hindered internal rotation was estimated for the N–CH_3 carbon signals by the peak-separation method.[1] The temperature range of the measurements was 22.5—100 °C. The concentration range of the solution measured was 2—100%. An accumulation of 20 or 500 scans was necessary for a 100 or 2% solution respectively, but when the NCH_3 carbon signals become broad at 60 °C, the accumulations were about 2—3 times greater.

Theoretical Calculation

The magnetic shielding constant, σ_A, of any specified carbon atom, A, in a molecule can be approximately estimated by means of the sum of the following diamagnetic and paramagnetic terms:[4]

$$\sigma_A = \sigma_A^{dia} + \sigma_A^{para} \quad (1)$$

where σ_A^{dia} and σ_A^{para} are the diamagnetic and paramagnetic contributions respectively.

The approximate value of σ_A^{dia} is given as:[6]

$$\sigma_A^{dia} = 4.45\, Z^* q \quad (2)$$

where:

$$Z^* = 3.25 - 0.35\ (q-4) \quad (3)$$

in which q is the total electron density around the carbon atom, and Z^*, the "effective nuclear charge" estimated according to Slater's rule.

The paramagnetic term is estimated according to Pople's theory,[4] with the average excitation-energy (ΔE) approximation as follows:

$$\sigma_A^{para} = -(e^2\hbar^2/2m^2c^2\Delta E)\ \langle r^{-3}\rangle_{2p} \sum_{B(=A)} Q_{AB} \quad (4)$$

where:

$$Q_{AB} = \frac{4}{3}\delta_{AB}(P_{x_Ax_B}+P_{y_Ay_B}+P_{z_Az_B}) - \frac{2}{3}(P_{y_Ay_B}P_{z_Az_B}+P_{z_Az_B}P_{x_Ax_B}+P_{x_Ax_B}P_{y_Ay_B}) + \frac{2}{3}(P_{y_Az_B}P_{z_Ay_B}+P_{z_Ax_B}P_{x_Az_B}+P_{x_Ay_B}P_{y_Ax_B})$$

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24a_0^3}(3.25-0.35(q-4))^3 \quad (6)$$

In these formulae, $\sum_{B(=A)}$ is a summation over all the atoms; $\langle r^{-3}\rangle_{2p}$; δ_{AB}, the Kronecker symbol; a_0, the Bohr radius, and $P_{x_Ax_B}$, the element of the bond-order matrix for the $2p_x$ atomic orbitals on the A and B atoms.

σ_A^{dia} and σ_A^{para} were estimated by the CNDO/2 method.[5] The bond lengths and bond angles used in a DMA molecule are shown in Table 1.

Table 1. The used bond lengths and bond angles of *N,N*-dimethylacetamide[a]

Bond lengths (Å)		Bond angles (°)	
C-C	1.54	C-C-H	109.5
C-N	1.32	N-C-H	109.5
C=O	1.24	C-C=O	120
C-H	1.09	N-C=O	120
		C-N-C	127

a) All the data were taken from standard bond lengths and bond angles in Ref. 5 except that the bond angles of C-C=O, N-C=O and C-N-C were taken from Ref. 7.

Results and Discussion

CCl_4 Solution. Concentration Dependence: Each carbon signal in the ^{13}C NMR spectrum of DMA in the CCl_4 solution appears in the order of carbonyl, *trans*-NCH_3, *cis*-NCH_3, and acetyl carbons from the low field, based on the assignment by McFarlane[8], where their positions appear at −73.90, 59.58, 62.67 and 66.26 ppm respectively (relative to CCl_4) in a 20% v/v CCl_4 solution at 30 °C. His assignment agrees with the calculated results for each carbon in the molecule, as will be described below.

Next, let us discuss the concentration dependence of the chemical shift for each carbon. The concentration dependences of the carbonyl carbon at 30, 60, and 80 °C are shown in Fig. 1. This carbon shows a considerable concentration dependence and shifts to a low field with an increase in the concentration of DMA. The chemical-shift change from an infinite dilution to an 80% solution is about 1.5 ppm. On the other hand, the concentration dependences of the chemical shifts for the other carbons are small, as is shown in Fig. 2. These concentration dependences do not show any large change upon a variation in the temperature except for the $COCH_3$ carbon. Further, the chemical-shift difference between the *trans*- and *cis*-NCH_3 carbons is found to increase by

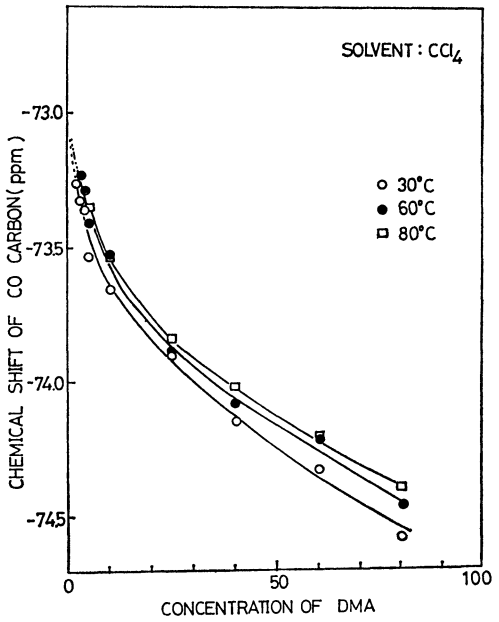

Fig. 1. Concentration dependence of the ^{13}C chemical shift of carbonyl carbon in CCl_4 solution.

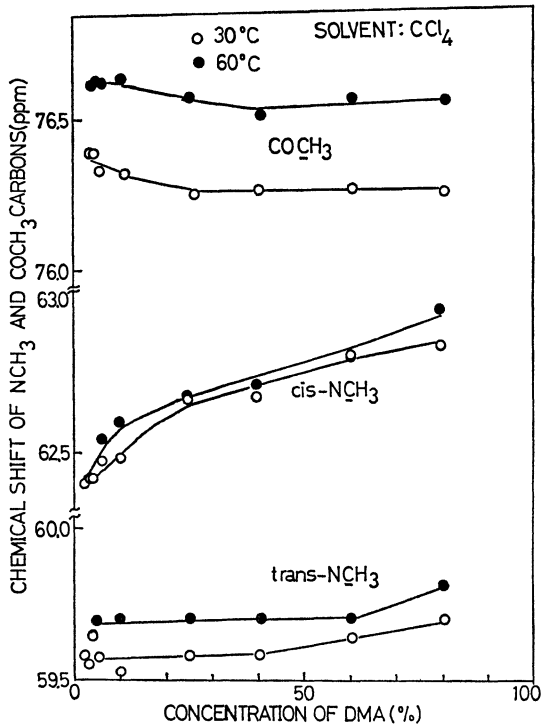

Fig. 2. Concentration dependence of the ^{13}C chemical shifts of *trans*-NCH_3 and acetyl carbons in CCl_4 solution.

about 0.3 ppm with the variation in the concentration from a 2% solution to neat liquid with an increase in the concentration, as is shown in Fig. 3. This indicates that the value of E_a increases with an increase in the concentration of DMA. A rapid increase within the range from zero to 20% corresponds well to the rapid decrease in the carbonyl carbon's shift, which suggests that the solution structure changes rapidly in this concentration range and that it may be

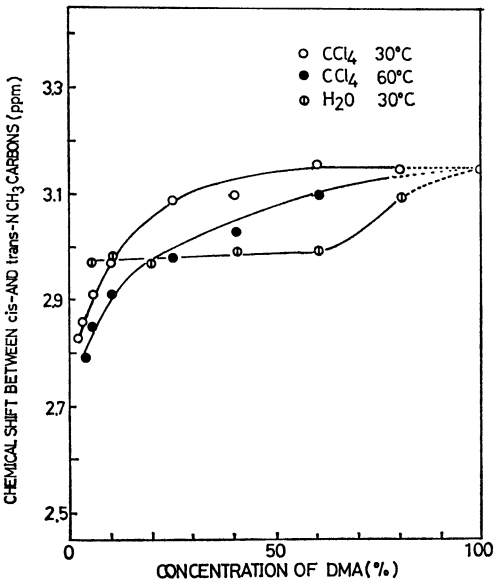

Fig. 3. Concentration dependence of the ^{13}C chemical shifts of *cis*-NCH_3 and *trans*-NCH_3 carbons in CCl_4 and H_2O solution.

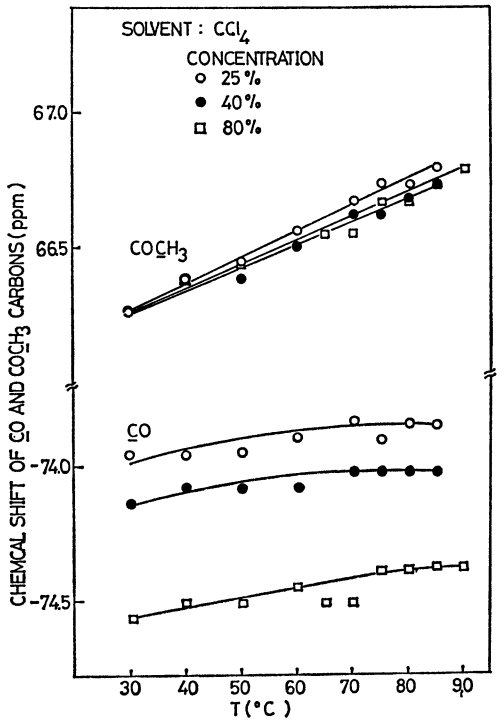

Fig. 4. Temperature dependence of the ^{13}C chemical shifts of carbonyl and acetyl carbons in CCl_4 solution.

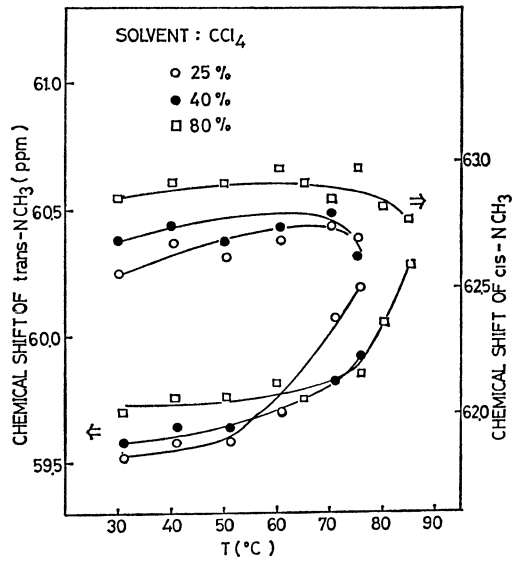

Fig. 5. Temperature dependence of the ^{13}C chemical shifts of *cis*-NCH_3 and *trans*-NCH_3 carbons in CCl_4 solution.

qualitatively interpreted in terms of an association model as well as the results of a similar study by means of ^1H NMR.[2h] Also, Sato *et al.*[21] have reported that the slopes of linear plots of the ^1H relaxation rate, $1/T_1$, against the concentration differ considerably from each other on both sides of concentration of about 3 mol/l, which corresponds to the above-mentioned concentration; these slopes have been qualitatively interpreted in terms of association.

Rabinovitz *et al.*[2h] have reported regarding the change in the ^1H chemical shift observed with the concentration of *N,N*-dimethylformamide in CCl_4 that a more satisfactory explanation lies in the contribution of the direct dimer shielding described in a monomer-dimer equilibrium. Therefore, it is considered that, in the monomer-dimer equilibrium, the monomer state increases with a decrease in the concentration. It is likely that the behavior of DMA in the CCl_4 solution may be described as in a monomer-dimer equilibrium. Thus, the value extrapolated using the data of low concentrations (we define this the value at an infinite dilution) may correspond to the value in a monomer state. The chemical-shift difference between the *trans*- and *cis*-NCH_3 carbons at an infinite dilution is obtained to be about 2.75 ppm, but it may possibly give a somewhat larger value than the true value at an infinite dilution because the present experiment was not done below the concentration of 2%. This value is used to compare with the calculated value.

Temperature Dependence: Next, the temperature dependences of each group in DMA at various concentrations are discussed in the temperature range from 30 to 90 °C. First, the results of the carbonyl and acetyl carbons are shown in Fig. 4. The carbonyl carbon shifts slightly by *ca.* 0.1 ppm at a high field with an increase in the temperature from 30 to 90 °C, whereas the acetyl carbon shifts linearly by *ca.* 0.5 ppm at a high field with an increase in the temperature. The former changes are smaller than those caused by the concentration. Thus, it may be predicted that the influence of the association caused by the variation in the concentration is larger than that caused by the variation in the temperature. As is shown in Fig. 5, the temperature dependence of the *cis*-NCH_3 carbon is slight, but that of the *trans*-NCH_3 carbon shifts greatly at a high field above 50 °C. Therefore, the chemical-shift difference between the two carbons decreases considerably at high temperatures. This is due to the internal rotation about the C–N bond in DMA.

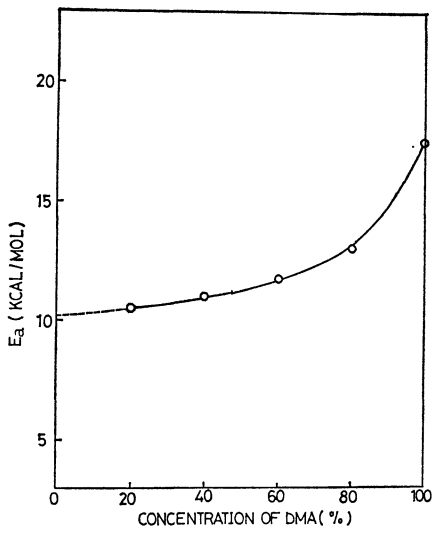

Fig. 6. Concentration dependence of activation energy E_a for the hindered internal rotation about the C–N bond in CCl_4 solution.

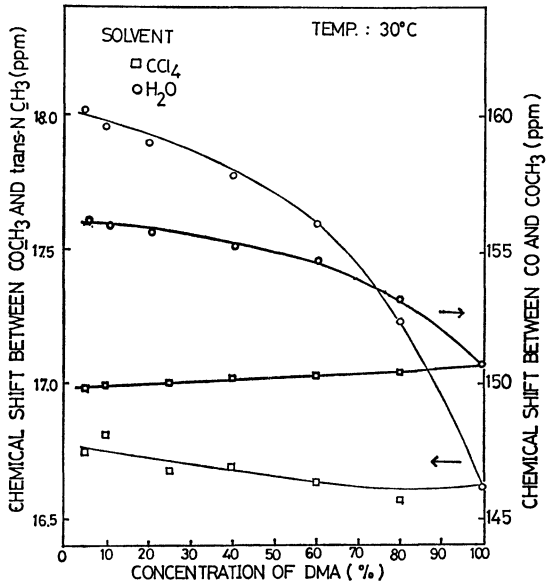

Fig. 7. Concentration dependence of the ^{13}C chemical-shift differences between carbonyl and acetyl carbons, and between *trans*-NCH_3 and acetyl carbons in CCl_4 and H_2O solutions.

From these data, the activation energies of the hindered internal rotation about the C–N bond at various contributions were obtained; they are shown in Fig. 6. The value in a neat liquid was obtained 17.5 kcal/mol, which agrees well with the value of 18.1 kcal/mol obtained from the study of ^1H NMR by Newman *et al.*[2d] Further, the value at an infinite dilution in CCl_4 is given as about 10 kcal/mol. The larger value of E_a in a neat liquid than in the CCl_4 solution may be qualitatively interpreted in terms of the association.

H_2O Solution. Concentration Dependence: The concentration dependence of the chemical-shift difference between the carbonyl and acetyl carbons in H_2O solution was found to be larger than in the CCl_4 solution, as is shown in Fig. 7. This may mainly be due to the existence of the hydrogen bond in the case of the former, while the latter case has no such bond. At an infinite dilution the difference between the two cases is about 6 ppm. On the other hand, the chemical-shift difference between the acetyl and *trans*-NCH_3 carbons in the H_2O solution was found to decrease rapidly, contrary to the case in the CCl_4 solution, as is shown in Fig. 7. Remembering that the chemical shift of the NCH_3 carbon depends hardly at all upon the concentration, this tendency shows that the acetyl carbon shifts to a low field through the formation of a hydrogen bond in an aqueous solution. At an infinite dilution in CCl_4 and H_2O solutions, the difference between the two values becomes about 1.2 ppm; this may be due to an indirect interaction through the formation of a hydrogen bond between the carbonyl group and H_2O. It is well-known that the carbonyl carbon shifts to a low field as a result of the formation of a hydrogen bond; the results shown in Fig. 7 are consistent with this.

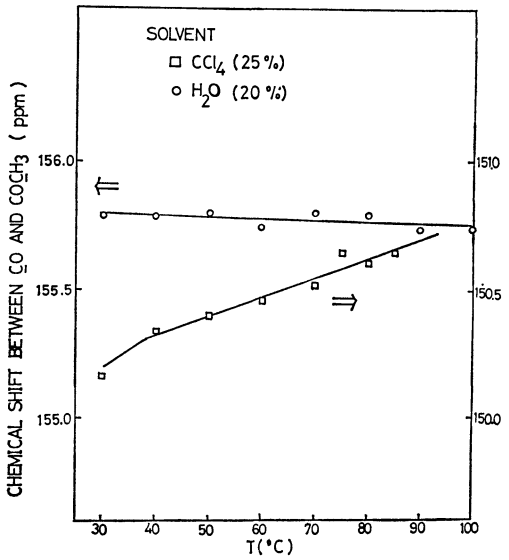

Fig. 8. Temperature dependence of the ^{13}C chemical-shift difference between carbonyl and acetyl carbons in CCl_4 and H_2O solution.

Temperature Dependence: The results of the temperature dependence of each carbon in this system are shown in Figs. 8 and 9. As may be seen from Fig. 8, the chemical-shift difference between the acetyl and carbonyl carbons in an aqueous solution is almost constant from 30 to 100°C, contrary to the case of the CCl_4 solution. This shows that probably the hydrogen bond with the H_2O molecule is stronger than the interaction between the DMA molecules and is more stable in this range of temperatures. Figure 9 shows the temperature dependence of the chemical-shift difference between the *trans*- and *cis*-NCH_3 carbons at various concentrations in an aqueous solution. These chemical-shift differences decrease with a decrease in the concentration below 60 °C. The hydrogen bonds between DMA and H_2O molecules are formed at low concentrations with the internal rotation about the C–N bond, being somewhat hindered, but at higher

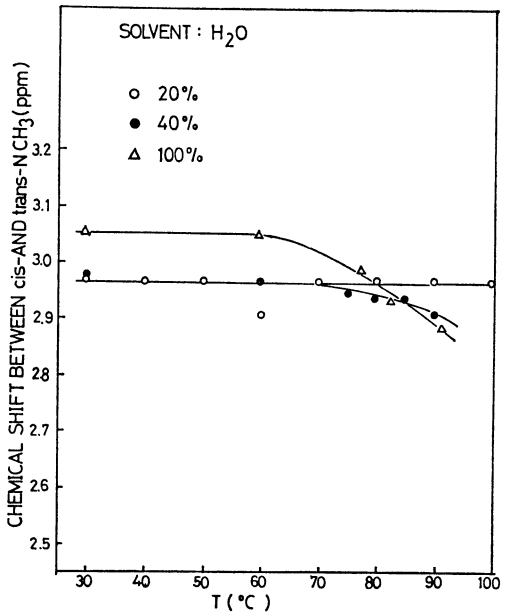

Fig. 9. Temperature dependence of the ^{13}C chemical-shift difference between *cis*-NCH_3 and *trans*-NCH_3 carbons in H_2O solution.

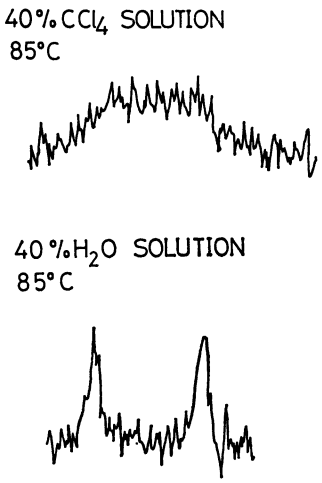

Fig. 10. ^{13}C NMR signals of NCH_3 carbons in CCl_4 and H_2O solution.

concentrations the interaction among DMA molecules becomes effective and, therefore, the rotation about the C–N bond becomes more hindered than in aqueous solutions of low concentrations. Generally, the hydrogen bond may be stronger than the interaction among the DMA molecules. The N–CH_3 carbon signals at 85 °C in 40% CCl_4 and H_2O solutions are shown in Fig. 10. From this it is clear that the rotation about the C–N bond in the H_2O solution is more hindered than in the case of the CCl_4 solution at the same concentration.

H_2SO_4 Solution. Concentration Dependence: The concentration dependence of the chemical shifts of each carbon in DMA is shown in Fig. 11. It is found particularly that the dependence of the carbonyl carbon is somewhat larger than that of the other carbons and that the carbonyl carbon shifts to a low field with a decrease in the concentration. This

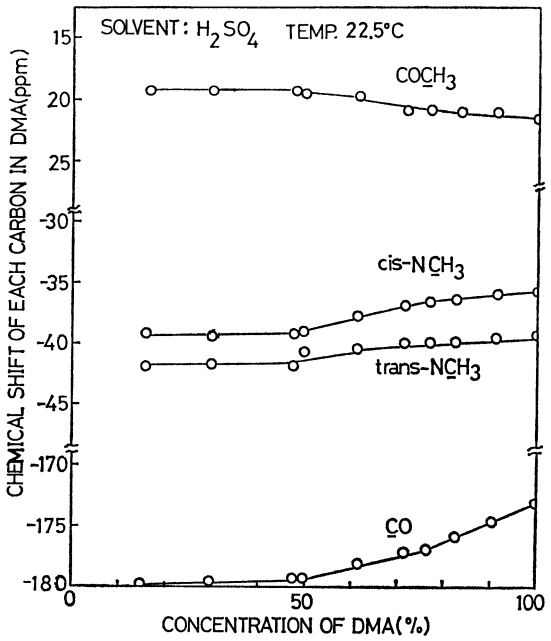

Fig. 11. Concentration dependence of the ^{13}C chemical-shifts of each carbon of *N,N*-dimethylacetamide in H_2SO_4 solution (relative to TMS).

may be due to the formation of protonated DMA molecules at the site of the carbonyl group in the H_2SO_4 solution. Further, the dependence of the *cis*-NCH_3 carbon slightly greater than that of the *trans*-NCH_3 carbon, and these carbons shift to a low field with a decrease in the concentration, contrary to the behavior of the acetyl carbon. These tendencies differ considerably from those of the aqueous solution. Therefore, it may be suggested that the influence of the protonation on the electronic state of DMA differs from that in the case of the hydrogen bond. (This tendency appears in the calculated electron-density distribution, as will be described below.)

Next, the concentration dependence of the nuclear Overhauser enhancement (NOE)[9] of the intensity of

Table 2. Concentration dependence of the enhancement of the carbonyl carbon due to ^1H decoupling in H_2SO_4 solution at 25 °C

Concentration of H_2SO_4 (% v/v)	Ratio of intensity of carbonyl carbon to TMS[a)]
0	1.85
9	1.74
16.7	1.76
23	1.70
28.5	1.83
37.5	1.99
50	3.17
58	3.21
70	3.16
85	3.02

a) Tetramethylsilane is contained as the standard signal (as external reference) to obtain the magnitude of the enhancement due to ^1H decoupling.

Table 3. Chemical shift of monomer *N,N*-dimethylacetamide by average excitation energy method using CNDO/2 method (ppm)

	σ_{dia}	σ_{para}	σ_t
$CO_3\underline{C}H_3$	58.68	−376.80	−318.12
cis-$N\underline{C}H_3$	56.54	−404.43	−347.89
trans-$N\underline{C}H_3$	56.26	−408.47	−352.21
$\underline{C}O$	54.77	−537.73	−480.96

The used value of average excitation energy is 5.69 eV.

the carbonyl carbon signal by the ^1H decoupling is shown in Table 2 to facilitate further study of the nature of the protonation. The enhancement increases rapidly in a 50% solution and the enhancement becomes constant. It may be considered that, when the ratio of the number of DMA's to that of protons is 1 : 1, the enhancement is at its maximum, and that even in high concentrations of H_2SO_4 the full protonation is maintained.

The observed behavior of DMA molecules in various solutions has been described above. We will now discuss this behavior theoretically.

Theoretical Considerations. We have described in a section that the DMA molecule at an infinite dilution in the CCl_4 solution can be considered as in a monomeric state. First, let us discuss this. The results of the calculated chemical shifts as a monomer DMA molecule are shown in Table 3, where, as the average excitation energy, ΔE, the value of 5.69 eV (maximum absorption of amide[10]; 208 nm) obtained by ultraviolet absorption spectroscopy, is adopted. The chemical shift of each carbon is found to be dominated mainly by the paramagnetic term. Each carbon appears in the order of acetyl, *cis*-NCH_3, *trans*-NCH_3, and carbonyl carbons; this order coincides with that of the experimental results. Also, the quantitative agreement between the two sets of results is good. Thus, the present results support McFarlane's statement that the ^{13}C resonance of the methyl group *cis* to the carbonyl group is at a higher field than that which is *trans*. As for these carbons, the observed and calculated chemical-shift differences between the two carbons are 3.09 ppm and 5.32 ppm respectively. Although the latter gives a somewhat larger value than the former, it seems natural to consider the chemical-shift difference between *trans*- and *cis*-NCH_3 carbons as being due to the contribution of the paramagnetic term; this is contrary to McFarlane's suggestion[8] that the principal contribution to this difference arises from an intramolecular electric field due to the carbonyl group.

In the neat liquid the DMA molecule has been suggested, on the basis of experimental results, to exist as the self-association state. We will now proceed to discuss its association based on the quantum-chemical calculation of the conformational energy and the ^{13}C chemical shift, and the experimental data. As has been described in the introduction, several models for the self-association of DMA molecules are possible. In Fig. 12 some models are shown, where (a) is the model of the cyclic structure proposed by Woodbrey

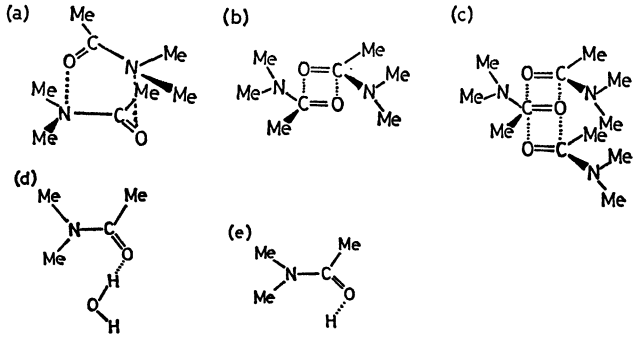

Fig. 12. Some association models (a), (b), (c), and Hydrogen-bonded (d) and protonated (e) DMA models.

et al.[2c] and Newman *et al.*,[2d] and where (b) and (c) are the dimer and trimer of an antiparallel orientation respectively, extending Saito's[12] model proposed for the acetone molecule, *etc.* to the case of the DMA molecule. For these models, the total energies were calculated by the CNDO/2 method; the results are shown in Table 4. The dimerization model (a) becomes unstable, but the (b) and (c) models become stable. The (a) model is unstable by 1.8 kcal/mol (the distance between the N and O atoms is 3 Å). The stabilization energies for the (b) and (c) models are 2.8 and 5.11 kcal/mol respectively (the distance between the C and O atoms is 3 Å). Thus, as the form of the association the (b) and (c) models may be suggested to be more appropriate than the (a) model. The total electron-density distributions of the monomer, dimer, and trimer models are shown in Table 5. As is shown in the (a) model, both N and O atoms have negative charges; therefore, this model may become unstable as a result of the electrostatic repulsion between these atoms. In the (b) and (c) models, however, the C and O atoms have positive and negative charges respectively; therefore, these models become stable as a result of electrostatic attraction between the atoms. As for the (b) model, the dependences of the total energy and the stabilization energy on the distance between the C and O atoms were calculated; the results are shown in Table 6, where the distances of 2.5,3 and 3.5 Å were used. In all of these distances, the formation of dimerization is stable; the stabilization energy at 3 Å is the largest, 2.8 kcal/mol.

Table 4. Total energies of various models in *N,N*-dimethylacetamide calculated by CNDO/2 method

Model	Total energy (eV)	Stabilization energy (eV)	Stabilization energy (kcal/mol)
Monomer	−1776.31104		
Dimer[a]			
(a) Model[b]	−3552.55607	0.06601	1.80
(b) Model[c]	−3552.72559	−0.10351	−2.82

a) These models correspond to those shown in Fig. 15. b) The distance between N and O atoms is 3 Å. c) The distance between C and O atoms is 3 Å.

Table 5. Electron density distributions of various models in *N,N*-dimethylacetamide calculated by CNDO/2 method

Atom		Monomer	(a)[a]	(b)[b]	(c) model[c]		DMA···H_2O	DMA···H
					Central	External		
O_1		6.351	6.370	6.372	6.374	6.374	6.374	6.161
N_2		5.152	5.140	5.142	5.143	5.139	5.134	5.032
C_3	CO	3.649	3.642	3.637	3.633	3.634	3.624	3.585
C_4	*trans*-NCH_3	3.813	3.815	3.814	3.815	3.813	3.818	3.871
C_5	$COCH_3$	4.103	4.105	4.105	4.108	4.104	4.107	4.118
C_6	*cis*-NCH_3	3.846	3.853	3.847	3.848	3.848	3.851	3.903
H_7	*trans*-NCH_3	1.042	1.041	1.044	1.044	1.045	1.036	0.969
H_8		1.045	1.035	1.036	1.039	1.038	1.041	0.996
H_9		1.045	1.049	1.048	1.039	1.038	1.041	0.996
H_{10}	*cis*-NCH_3	1.031	1.029	1.031	1.031	1.032	1.025	0.960
H_{11}		1.017	1.021	1.018	1.020	1.017	1.014	0.975
H_{12}		1.017	1.015	1.021	1.020	1.021	1.014	0.975
H_{13}	$COCH_3$	0.958	0.955	0.957	0.955	0.958	0.953	0.904
H_{14}		0.966	0.964	0.959	0.962	0.958	0.956	0.906
H_{15}		0.966	0.969	0.970	0.962	0.958	0.956	0.906

These models correspond to those shown in Fig. 12. The terms "Central" and "External" correspond to the central and external *N,N*-dimethylacetamides in trimer.
a) The distance between N and O atoms is 3 Å. b), c) The distance between C and O atoms is 3 Å. d) H_7, H_{10}, and H_{13} are *trans* position relative to OC-N bond respectively.

Table 6. Dependence of total energy of dimer (b) and trimer (c) models in *N,N*-dimethylacetamide on distance between C and O atoms calculated by CNDO/2 method

	Distance (Å)		
	2.5	3.0	3.5
Dimer			
Total energy (eV)	−3552.6799	−3552.7256	−3552.6402
Stabilization energy (kcal/mol)	−1.57	−2.82	−0.49
Trimer			
Total energy (eV)	−5329.0162	−5329.1213	−5328.9616
Stabilization energy (kcal/mol)	−2.26	−5.11	−0.53

Next, let us consider the trimer model. The dependences of the total energies and stabilization energies upon the distance between the DMA molecules at trimeric state are shown in Table 6. Just as in the case of the dimer model, the formation of the trimer is stable, and the stabilization energy at 3 Å becomes the largest value, 5.11 kcal/mol, twice the value in the dimer model. It may be suggested that the DMA molecules in a neat liquid are preferable polymerized in the antiparallel oriented form.

In order to obtain more detailed information about the associated form, let us consider the dipole moment briefly. The dipole moments calculated for various models are shown in Table 7, together with the observed results. The calculated values of the monomer and the (c) model agree well with the observed value. The (a) and (b) models have no dipole moment. Thus, in the odd *n*-mer model it is clear that the *n*-mer has a definite dipole moment. The experimental results cannot be interpreted by the dimer model; therefore, an equilibrium among the various *n*-mers, including the monomer, must exist in the neat liquid or the CCl_4 solution at high concentrations.

Next, let us discuss the value of n in terms of the stabilization energy. The results in Fig. 6 show that the energy difference between the hindered rotational energies at an infinite dilution in the CCl_4 solution and in the neat liquid is about 7.5 kcal/mol; this difference may be considered to be the energy due to the change from monomer to *n*-mer. As is shown in Table 6, the stacking between the DMA molecules corresponds to a stabilization energy of about 2—2.5 kcal/mol, one third of the value of 7.5 kcal/mol obtained above. Therefore, the value of n is about 4. Accordingly, the DMA molecule may be supposed roughly to exist in a tetramer in the neat liquid, though this is not conclusive.

Further, let us discuss the chemical shift as a continuation of the above description of the chemical shift of the monomer DMA molecule. First, we will treat the concentration dependence of the chemical shift in the CCl_4 solution on the basis of the theoretical results. As is shown in Fig. 1, the chemical shift of the carbonyl carbon shifts to a lower field with an increase in the concentration and shifts about 1.5 ppm in the range from an infinite dilution to a neat liquid. The calculated chemical shift, σ_t, of the carbonyl carbon of the monomer, which corresponds to the molecular structure at an infinite dilution, is −480.36 ppm (Table 3); the σ_t's of the dimer and the trimer, which have been suggested to exist at the neat liquid, are −483.14 ppm and −483.87 ppm for the central DMA and −483.38 ppm for the outside DMA in the trimer, as is shown in Tables 8 and 9 (in this case,

Table 7. Dipole moment of *N,N*-dimethylacetamide calculaed by CNDO/2 methoed and observed (D.U.)

Monomer	(a)model	(b)model	(c)model	DMA···H_2O	DMA···H	Obsd[a]
3.22	0.0	0.0	3.39	5.44	6.99	3.79

In (b) and (c) models the distance between C and O atoms is 3 Å.
a) Observed at 30 °C in benzene (Ref. 11).

Table 8. Dependence of chemical shift of dimer (b)model in *N,N*-dimethylacetamide on distance between C and O atoms by average excitation energy method using CNDO/2 method. σ_t (ppm)

	Distance (Å)		
	2.5	3.0	3.5
$CO\underline{C}H_3$	−317.62	−318.02	−318.13
cis-$N\underline{C}H_3$	−347.49	−348.01	−348.54
trans-$N\underline{C}H_3$	−351.99	−352.05	−352.10
$\underline{C}O$	−484.68	−483.14	−482.05

The used value of average excitation energy is 5.69 eV.

Table 9. Chemical shift of trimer (c)model in *N,N*-dimethylacetamide calculated by average excitation energy using CNDO/2 method. σ_t (ppm)

	Central[a]	External[a]
$CO\underline{C}H_3$	−317.75	−318.10
cis-$N\underline{C}H_3$	−348.07	−347.97
trans-$N\underline{C}H_3$	−351.73	−352.19
$\underline{C}O$	−483.87	−483.38

a) The terms "Central" and External" correspond to the central and external *N,N*-dimethylacetamide in trimer model.
The used value of average excitation energy is 5.69 eV.
The distance between C and O atoms is 3 Å.

the distance between the DMA molecules is 3 Å). From this, the carbonyl carbon is found to shift about 2 ppm to a lower field upon the formation of the dimer and the trimer. Therefore, this result agrees well with the observed one. The observed chemical shifts of the acetyl, *cis*-NCH_3, and *trans*-NCH_3 carbons did not depend as greatly on the concentration as in the case of the carbonyl carbon. On the other hand, the calculated chemical shifts of these carbons in the monomer, dimer, and trimer differ almost not at all from each other; this agrees with the observed results.

Next, let us concern ourselves with the behavior of DMA in the H_2O and H_2SO_4 solutions in terms of the chemical-shift calculation in addition to the above observed results. de Jeu[13] has suggested a reasonable model for the molecular structure of the acetone molecule in the corresponding solution based on his study of ^1H, ^{13}C, and ^{17}O NMR. We have adopted his model for the molecular structure of DMA which have a carbonyl group like the acetone molecule in their solutions. These corresponding models are shown in Fig. 12. The hydrogen-bonded $>C=O\cdots H-O-H$ amide–solvent associate (d) and protonated $>C=O\cdots H$ associate (e) are formed in the H_2O and H_2SO_4

Table 10. Chemical shift of model hydrogen-bonded and protonated model in *N,N*-dimethylacet amide calculated by average excitation energy method using CNDO/2 method. σ_t (ppm)

	DMA···H_2O	DMA···H
$CO\underline{C}H_3$	−317.93	−319.07
cis-$N\underline{C}H_3$	−347.19	−340.23
trans-$N\underline{C}H_3$	−351.42	−344.06
$\underline{C}O$	−487.18	−497.05

The used value of average excitation energy is 5.69 eV.

solutions respectively. Here, the $\angle >C=O\cdots H$ and $\angle H-O-H$ bond angles are set at 120° and 105° respectively, while the O–H bond length is set at 1.05 Å. The distances between the oxygen of the carbonyl group and the hydrogen atom for the cases of $>C=O\cdots H-O-H$ and $>C=O\cdots H$ are 1.34 Å and 0.985 Å respectively.[13] The electron-density distributions of these models are shown in Table 5. The protonated DMA shows a very high charge separation, as a whole, compared with the other structures. Correspondingly, as is shown in Table 7, the dipole moment is larger than that of the other structure. However, in the DMA···H_2O structure, although the charge separation does not change compared with the monomer, the dipole moment is relatively large because of the association with H_2O. If these results are confirmed experimentally, it will give important information about the DMA association in solution. Further, let us discuss the chemical shifts of these models. The carbonyl carbon is sensitively influenced by the formation of a hydrogen bond and by protonation. The difference between the carbonyl carbons at infinite dilutions in the CCl_4 and H_2O solutions is found to be about 6 ppm, as is shown in Fig. 7. These structures correspond to the monomer and the structure (d) shown in Fig. 12. From Tables 3 and 10, the corresponding calculated chemical-shift difference is found to be about 6 ppm (=487.18—480.96 ppm). This agrees well with the observed results. Also, as for the NCH_3 carbons, the observed results agree with the calculated result that the *trans*- and *cis*-NCH_3 carbons in the H_2O solution shift at a higher fileld than in the CCl_4 solution. These results suggest that the association model described above for the structure of the DMA molecule in the H_2O solution is a plausible model.

Next, let us concern ourselves with the chemical shift of DMA in the H_2SO_4 solution. As expected for the electron-density distribution of this model, the calculated chemical shift of the carbonyl carbon occurs at a lower field than that of the hydrogen-bonded model and appears at a field lower by about 16 ppm

than that of the monomer model. However, the observed chemical shift of the carbonyl carbon at an infinite dilution in the H_2SO_4 solution appears at a field lower by only about 5 ppm than that at an infinite dilution in the CCl_4 solution; this value is smaller than the value obtained in the case of the hydrogen-bonded DMA with H_2O. Further, the calculated chemical shifts of the other carbons do not agree with the observed results. As the causes of these disagreements, the following reasons may be noted. i) the present model is not always appropriate, ii) the ΔE approximation for this case is gross, and so on. It will be necessary to study this problem in more detail in order to obtain exact information about the protonated DMA molecule.

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