arising from rotational orientation of the alkoxy groups. The measurements on solutions of decyl alcohol in carbon tetrachloride give critical wave length values much shorter than the high frequency region value tabulated by Brot, Magat and Reinisch.[18] It is reasonable to suppose that the single molecules existing in the solutions are responsible for the short critical wave length, and the viscosities of the moderately dilute solutions in carbon tetrachloride are so much lower than that of the pure alcohol that the critical wave lengths should be much lower. The critical wave lengths in the highly viscous Nujol solution are much higher than those in carbon tetrachloride, although the increase in critical wave length from one solvent to the other is much less than the increase in viscosity. The general behavior of the high frequency critical wave length of decyl alcohol in the pure state and in solution seems to parallel that of the alkyl bromide critical wave lengths,[17] in particular, that of tetradecyl bromide, which has been investigated in the same solvents[18] as well as in the pure state.[17] However, the apparent critical wave length values for decyl alcohol are somewhat shorter than would be expected for a molecule of this size and the values of the distribution coefficient α are very large, probably as a result of the persistence of molecular association in the solutions.[19]

The seemingly curious absence of any considerable distribution of relaxation times for the low frequency dispersion region of the pure alcohols is possibly explicable if the rate controlling process is the destruction of quasi-crystalline complexes by the breaking of hydrogen bonds. In the calculation of the critical wave lengths of dodecyl and tetradecyl alcohol in Table IV the distribution of relaxation times was arbitrarily neglected because of the uncertainty introduced by the probable contributions of two different dispersion regions. The effect of two dispersion regions may possibly account for the large values of the distribution parameters α (Table IV) given by the Cole and Cole arc plots for cetyl and octadecyl alcohols.

The dielectric constant and loss values for *t*-butyl, octyl and decyl alcohols in Table II appear to be fairly accurate, but they are too far from the low frequency dispersion region to give information concerning the critical wave lengths corresponding to this region and contain contributions from this region which make calculation of the high frequency critical wave lengths too uncertain for inclusion in Table IV. The values for pure octyl and decyl alcohols have been analyzed in detail elsewhere.[20]

As previously stated, the apparent critical wave lengths calculated for long chain alcohols from the measurements of dielectric constant and loss in the microwave region reported in this paper must be regarded as approximate because of the absence of measurements at somewhat lower frequencies. However, the results are consistent with the explanation of measurements on shorter chain alcohols by other investigators as involving a low frequency dispersion region arising from hydrogen bonds and a high-frequency region arising from rotational orientation of the alkoxy groups.

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[17] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, This Journal, **70**, 4102 (1948).

[18] A. J. Curtis, P. L. McGeer, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 644 (1952).

[19] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 80–84.

[20] G. B. Rathmann, Ph.D. Thesis, Princeton University, 1951.

[Contribution from the Chemical Laboratory, Faculty of Science, Tokyo University]

Internal Rotation in N-Methylchloroacetamide

By San-ichiro Mizushima, Takehiko Shimanouchi, Isao Ichishima, Tatsuo Miyazawa, Ichiro Nakagawa and Tsuneo Araki

Received April 18, 1955

Infrared and Raman spectra and dipole moments of N-methylchloroacetamide have been observed. From the experimental results it has been concluded that in the liquid state the molecules are in both the *trans* and *gauche* forms, of which only the *gauche* form persists in the solid state. In solutions the *trans* molecules become less in number with decreasing dielectric constant of the solvent until they become hardly detectable spectroscopically in non-polar solutions and in the gaseous state. Based on these experimental data, as well as those previously obtained for halogenoacetyl halides and chloroacetone, the nature of the hindering potential to internal rotation about the CH_2–CO axis is discussed.

In a series of investigations we have been interested in the determination of the configuration of the polypeptide chain in relation to the internal rotation about single bonds as axes.[1] The present experiment has been made with the object of determining the molecular structure of N-methylchloroacetamide in order to obtain more information on the internal rotation about the CH_2–CO axis, which is one of the three internal rotation axes contained in the main chain of polypeptides.

Experimental

N-Methylchloroacetamide was prepared by adding aqueous sodium hydroxide solution and chloroacetyl chloride to the aqueous solution of methylamine.[2] The reaction product was extracted with chloroform and the pure sample was obtained by vacuum distillation, m.p. 46°.

The Raman spectra were measured in the solid state at room temperature and in the liquid state at 60°. The result is shown in Table I. Saturated aqueous solution of sodium nitrite and carbon tetrachloride solution of iodine were used as filters in the measurement in the solid state.

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[1] For the summary see S. Mizushima, "Advances in Protein Chemistry," Vol. IX, Academic Press, New York, N. Y., 1954.

[2] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **21**, 145 (1915).

TABLE I

RAMAN AND INFRARED SPECTRA OF $ClCH_2CONHCH_3$

Raman spectra		Infrared spectra[a]			Assignment[b]	
Liquid	Solid	Vapor	Liquid	Solid		
188(3b)	190(3b)				L	
252(2)						M
308(3)	313(3)				L	M
395(3)						M
416(5)	420(4)				L	
580(4b)	583(1)				L	
627(2)	634(2)				L	
700(5)						M
763(8)	763(8)	758(m)	763(s)	762(s)	L	
786(7)			786(m)			M
891(6)	895(4)		895(vw)	896(w)	L	
925(3)			922(w)	926(m)	L	M
1062(3)			1057(w)			M
	1082(2)		1074(w)	1084(w)	L	
				1127(sh)	L	
1154(7b)	1157(2)		1157(s)	1156(s)	L	M
			1241(m)			M
1256(6b)	1267(3)	1250(s)	1258(s)	1265(s)	L	
1289(4b)	1290(4)			1290(m)	L	
1331(6b)			1328(w)	1316(vw)	L	
				1342(vw)	L	
1411(6)	1415(4)	1420(s)	1413(s)	1412(s)	L	
1451(3b)	1457(1)		1441(sh)	1449(w)	L	M
			1530(sh)			
1550(1b)	1560(1b)	1515(s)	1550(vs)	1565(vs)	L	M
			1570(sh)			
1654(9b)	1644(5)	1710(vs)	1660(vs)	1643(vs)	L	M
2795(2)			2800(vw)	2810(vw)		
2948(10b)	2953(10)	2920(m)	2940(m)	2950(m)		
3012(4)	3017(3)		3080(w)	3100(w)		
3300(1b)			3300(vs)	3300(vs)		
		3470(w)				

[a] vs, very strong; s, strong; m, medium strong; w, weak; vw, very weak. [b] L, the less polar form; M, the more polar form.

The infrared spectra were recorded in the region 2 to 14 μ, by the Baird spectrometer in the gaseous state at 180° (path length 4 cm., vapor pressure about 20 mm.), in the liquid state at 60° (very thin film) and in the solid state at room temperature (see Table I). The change of relative intensity with solvent (carbon disulfide, carbon tetrachloride acetone, nitromethane and acetonitrile) was observed for some absorption bands in a cell of the thickness of 0.1 mm. The concentration in each case was so chosen that the absorption of the stronger band amounted to about 50%.

The dipole measurement was made at 25° in carbon tetrachloride solutions. The apparent moments calculated by the use of Debye's equation from the experimental results at different concentrations are shown in Table II.

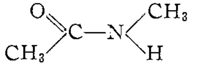
TABLE II

APPARENT MOMENTS OF $ClCH_2CONHCH_3$ IN CCl_4[a]

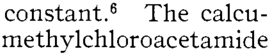
Wt. fraction	Dielectric constant	Density	Orientation polarization (cc.)	Dipole moment (*D*)
0.01422	2.5223	1.5793	190	2.84
.00891	2.3673	1.5811	141	2.38
.00507	2.2949	1.5822	127	2.25
.00205	2.2559	1.5835	127	2.25

[a] The sum of the electronic and atomic polarizations was assumed to be equal to the sum of atomic refractions (25 cc.).

Discussion

The molecule of N-methylchloroacetamide has two axes of internal rotation, CO–NH and CH_2–CO. The rotation about the former axis can be expected to be similar to that of N-methylacetamide, which was shown to be in the planar *trans* form  $\overset{O}{\underset{CH_3}{>}}C{-}N\overset{CH_3}{\underset{H}{<}}$ by the measurement of the Raman, infrared, ultraviolet spectra and dielectric constant.[3] Actually N-methylchloroacetamide shows absorption peaks at 3300, 3100, 1650 and 1550 cm.$^{-1}$ characteristic of the *trans* peptide bond. If this were in the alternative form or the *cis* form,[4] the substance would show peaks at 3200, 3100 and 1650 cm.$^{-1}$, just as in the case of δ-valerolactam. Since there is only one configuration (*i.e.*, the *trans* form) for the peptide bond, the rotational isomerism of N-methylchloroacetamide should be explained with regard to the internal rotation about the CH_2–CO bond as axis.

As to the internal rotation about this axis, we have studied that of $ClCH_2$–COCl, $BrCH_2$–COCl, $BrCH_2$–COBr and $ClCH_2$–$COCH_3$.[5] In all these molecules the X–CH_2 stretching frequency of one isomer (X = Cl or Br) was found to have a different value from that of the other, both appearing in the frequency region predicted by the normal vibration calculation. From the comparison of the spectra of these compounds with that of N-methylchloroacetamide, the two peaks observed at 763 and 786 cm.$^{-1}$ can be assigned to the Cl–C stretching frequencies. The fact that these two peaks have almost the same intensity in the liquid state and that one of them disappears completely in the solid state shows that there are two rotational isomers in the liquid state and only one of them persists in the solid state, since only one Cl–C stretching frequency is expected for one rotational isomer.

This conclusion is confirmed by the experimental result that in the frequency region below 800 cm.$^{-1}$ we observed ten Raman lines in the liquid state and only six lines in the solid state; we can expect six Raman frequencies in this region for one isomer: *i.e.*, one Cl–C stretching, one out-of-plane  $O{=}C\overset{CH_2}{\underset{NH}{<}}$ and four skeletal deformation frequencies. The solvent effect to be described below provides further experimental evidence for the view stated above.

The relative intensities of the bands at 763, 786, 1241 and 1258 cm.$^{-1}$ have been measured in various solvents. According to the result of our previous measurement the more polar form becomes more stable than the other (or the less polar form) in a solvent of higher dielectric constant.[6] The calculated dipole moment of N-methylchloroacetamide depends considerably on the azimuthal angle of internal rotation: 4.3 *D* at 0° and 30°, 4.0 *D* at 60°, 3.5 *D* at 90°, 2.8 *D* at 120°, 2.2 *D* at 150° and 2.0 *D* at 180°. Therefore, the two rotational isomers differ considerably in polarity from each other and we can expect the apparent solvent effect for this substance. In fact the intensities of the bands at 786 and 1241 cm.$^{-1}$ become weaker with decreasing dielectric constant of the solvent until these bands

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(3) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, THIS JOURNAL, **72**, 3490 (1950).

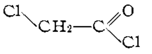
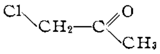
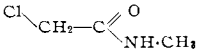
(4) From the partial double bond character of the C–N bond only the *trans* and the *cis* forms are conceivable as the rotational isomers of this molecule. See reference 3.

(5) (a) I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **20**, 1720 (1952); (b) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa and N. Shido, *ibid.*, **21**, 815 (1953).

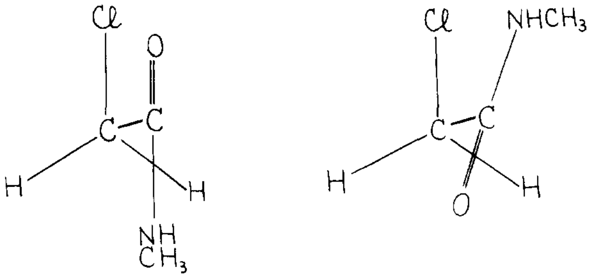
(6) I. Watanabe, S. Mizushima and Y. Masiko *Sci. Pap. Inst. Phys. Res. Tokyo*, **40**, 425 (1943); Y. Morino, S. Mizushima, K. Kuratani and M. Katayama, *ibid.*, **18**, 754 (1950).

Table III

Comparison of the Molecules of the Type $ClCH_2COR$

Molecule	 $ClCH_2COCl$	 $ClCH_2COCH_3$	 $ClCH_2CONH{\cdot}CH_3$
Van der Waals radius of R, Å.	1.8	2.0	1.5
$\mu_{\perp}$(COR), D	0.5	2.0	3.0
Stability in the gaseous state	*trans* > *gauche*	*trans* ≪ *gauche*	*trans* ≪ *gauche*
Stability in the liq. state	*trans* ≈ *gauche*	*trans* ≈ *gauche*	*trans* ≈ *gauche*
$\mu_{trans} - \mu_{gauche}$, D	1	2	2
Dielectric constant of the liq.		30	>100

become hardly detectable in non-polar solvents such as carbon disulfide and carbon tetrachloride and in the gaseous state. Therefore, these two bands at 786 and 1241 cm.$^{-1}$, which disappear in the solid state at room temperature, can be assigned to the more polar form. The two other bands at 763 and 1258 cm.$^{-1}$, which become stronger in a less polar solvent and persist in the solid state, can be assigned to the less polar form. As the calculated dipole moment decreases with the azimuthal angle of internal rotation,[7] the chlorine and nitrogen atoms will be at or near the *trans* position in the more polar form (Fig. 1), and they are in the *gauche* position not far from the *cis* in the less polar form. Taking into account this solvent effect for other bands as well as the behavior of the bands in the liquid and solid state, we can assign the observed bands as shown in Table I.



trans (θ = 0°)   *gauche* (θ = 150°)

Fig. 1.—Stable molecular forms of N-methylchloroacetamide.

In order to obtain more information about the molecular configurations of the two rotational isomers the moment values observed by us will be discussed. As shown in Table II these values increase with increasing concentration, just as in the case of N-methylacetamide, for which we have concluded the presence of linear chain polymers.[3] This type of polymerization for N-methylchloroacetamide is compatible with the planar *trans* form of the peptide bond concluded from the experimental result in the 3 μ region.

It is to be noted that at lower concentrations at which the dipole measurement was made, the non-bonded NH absorption at 3470 cm.$^{-1}$ becomes stronger and the bonded NH absorption at 3300 cm.$^{-1}$ becomes weaker; the latter disappears at the concentration of 0.2%. This means that at this concentration the molecule can be considered to be practically non-associated and is compatible with the fact that the dipole moment becomes almost independent of concentration. (The same value of moment was obtained at the two concentrations, 0.5 and 0.2%). Furthermore, the absorption intensity of the band at 786 cm.$^{-1}$ of the more polar form amounts only to about 4% of the corresponding band at 763 cm.$^{-1}$ of the less polar form. Therefore, the moment value 2.25 D observed at the concentration of 0.2% can be considered to be the value of the single molecule in the less polar form.

The dipole moment of different azimuthal angles has been calculated as the vector sum of the moments of $CH_3CONHCH_3$ and C–Cl, taking into account the induction effect.[8] By comparing the computed values with the observed, we can conclude that the azimuthal angle of the less polar form (or the *gauche* form) differs from the *trans* form by about 150° (see Fig. 1). This angle is almost equal to that of the *gauche* form of halogenoacetyl halides and chloroacetone reported in our previous papers.[5]

In conclusion the molecule of N-methylchloroacetamide is in the *trans* and the *gauche* forms in the liquid state and of these only the *gauche* form persists in the solid state at ordinary temperature. In solutions the *trans* molecules become less in number with decreasing dielectric constant of the solvent until they become hardly detectable spectroscopically in non-polar solutions and in the gaseous state. From the value of dipole moment the difference of the azimuthal angle between the *trans* and *gauche* molecules is estimated to be about 150°.

Nature of the Hindering Potential to Internal Rotation about the CH_2–CO Axis.—In Table III are summarized the data so far obtained in our laboratory for molecules with the CH_2–CO bond. Based on these let us discuss the nature of the hindering potential to internal rotation about this bond as axis.

As shown in a previous paper,[9] the most important element in determining the hindering potential is the steric repulsion, and therefore the stable molecular forms should correspond approximately to the minima of the steric repulsive potential. In these minima the repulsive force may become of the same order of magnitude as the electrostatic force; in other words, in the energy difference between the two potential minima the electrostatic potential may play significant role.

In the case of $ClCH_2COCl$ and $ClCH_2COCH_3$ the

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[7] The origin of this angle has been taken at the *trans* position.

[8] The moment of $CH_3CONHCH_3$ was found to be 4.12 D in dioxane (see reference 3). However, as Bates and Hobbs, This Journal, **73**, 2151 (1951), found the moment value of $RCONH_2$ in dioxane to be larger by 0.4 D than that in benzene, we have considered 4.12–0.4 = 3.7 D to be the moment value of $CH_3CONHCH_3$ in the free state.

[9] S. Mizushima, Y. Morino and T. Shimanouchi, *J. Phys. Chem.*, **56**, 324 (1952).

oxygen atom was found not to contribute much to the steric repulsive potential.[5] We can, therefore, consider that in general the stable configuration of a molecule of the type $\mathrm{ClCH_2COR}$ ($\mathrm{R = Cl, CH_3}$ or $\mathrm{NHCH_3}$) is mainly determined by the steric repulsion between Cl and R, and consequently that the *trans* form is more stable than the *gauche* form from the steric point of view (Fig. 1).

As to the electrostatic potential, this is determined mainly by the interaction between the component of the $-\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{R}}$ moment perpendicular to C–C axis, $\mu_\perp(\mathrm{COR})$, and that of C–Cl moment, $\mu_\perp(\mathrm{CCl})$. The former is in the same sense as the perpendicular component of the C=O moment, which is in the same direction as $\mu_\perp(\mathrm{CCl})$ in the *trans* form and is in the opposite direction in the *gauche* form. Therefore, so far as the electrostatic potential is concerned, the *gauche* form is more stable than the *trans* form.

For R = Cl, $\mu_\perp(\mathrm{COCl})$ is calculated as 0.5 *D*, which is considerably smaller than $\mu_\perp(\mathrm{COCH})_3$ = 2.0 *D* for R = $\mathrm{CH_3}$. For R = $\mathrm{NHCH_3}$ the contribution of the resonance structure $-\underset{\substack{|\\ \mathrm{O^-}}}{\mathrm{C}}=\mathrm{N^+HCH_3}$ gives rise to a larger value of $\mu_\perp(\mathrm{CONHCH_3})$, calculated to be 3.0 *D*. As a consequence the contribution of the electrostatic potential to the energy difference between the two rotational isomers can be concluded to be small for $\mathrm{ClCH_2COCl}$ and considerable for $\mathrm{ClCH_2COCH_3}$ and $\mathrm{ClCH_2CONHCH_3}$. Therefore, the energy difference in $\mathrm{ClCH_2COCl}$ is mainly due to the steric repulsive potential. This potential, which makes the *trans* form more stable, should play a more significant role in $\mathrm{ClCH_2COCH_3}$, since the van der Waals radius of $\mathrm{CH_3}$ is greater than Cl. However, from the infrared intensity measurement in the gaseous state, the *gauche* form is concluded to be much more stable than the *trans* form. This fact can only be understood by consideration of the fact that for the energy difference between the two potential minima of $\mathrm{ClCH_2COCH_3}$, the electrostatic potential is more significant than the steric potential. (This should not be confused with the problem of the potential barrier of the hindering potential which is mainly determined by the steric potential.)

As the van der Waals radius of the N atom is smaller than that of the $\mathrm{CH_3}$ group, the contribution of the steric repulsion in the energy difference of $\mathrm{ClCH_2CONHCH_3}$ is smaller than that of $\mathrm{ClCH_2COCH_3}$. However, as referred to above, the electrostatic potential of $\mathrm{ClCH_2CONHCH_3}$ plays a more significant role than in the case of $\mathrm{ClCH_2COCH_3}$ and consequently the energy difference between the rotational isomers of $\mathrm{ClCH_2CONHCH_3}$ is expected to be larger than that of $\mathrm{ClCH_2COCH_3}$. This has been shown to be the case from the absorption measurement, in which the *trans* band in the gaseous state was found to be so weak as to escape detection.

From what has been described above, we can conclude that in the internal rotation of a molecule of the type $\mathrm{ClCH_2\text{-}COR}$, the C=O group makes an important contribution to the electrostatic potential and no large effect to the steric potential.

This conclusion naturally refers to the gaseous state. In the liquid state, where there is considerable interaction between molecules, the situation is different and the *trans* bands of $\mathrm{ClCH_2COCH_3}$ and $\mathrm{ClCH_2CONHCH_3}$ which are very weak or almost escape detection in the gaseous state become almost as strong as the *gauche* band in the liquid state. Such is not the case for $\mathrm{ClCH_2COCl}$, for which the two isomers are not much different from each other in polarity. In other words in $\mathrm{ClCH_2COCl}$ the equilibrium ratio of the *trans* and the *gauche* molecules in the liquid state is not much different from that in the gaseous state.

In addition to the results of our studies concerning the internal rotation about the $\mathrm{CH_2\text{–}CH_2}$ axis,[10] we now have experimental data from which we could derive a conclusion on the essential feature of the internal rotation about the $\mathrm{CH_2\text{–}CO}$ axis. These data constitute a factual basis for conjectures regarding the stable configurations of a polypeptide chain and provide us with another evidence for the polypeptide model presented from our laboratory.[11]

We would like to add a few lines on the molecular form in the second solid phase of N-methylchloroacetamide. In addition to the solid phase at room temperatures, there is another one which is stable at higher temperatures. It is very interesting that the molecules are found to be in the *trans* form in contrast to the first solid phase where, as concluded above, the molecules are in the *gauche* form. We are studying by the infrared absorption this phase transition accompanied by the isomeric change of internal rotation.

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[10] For the summary of this work see S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

[11] T. Shimanouchi and S. Mizushima, *Kagaku*, **17**, 24, 52 (1947). See also reference 1.