*The Resonance Effect of Amide Group on the Polymerizability of Lactam Derivatives. I. The Infrared Spectrum of N-Methyl Lactams**

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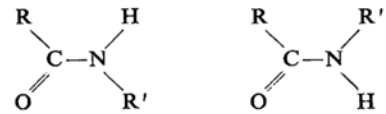
The amide linkage of chain amide molecule tends to take a planar structure owing to the resonance in the molecule[1]. The two configurations of cis and trans forms shown below are possible:



trans form cis form

It it known that the trans form of an amide group is more stable than the cis form and monosubstituted acid amide RCONHR′ takes the trans[1,2] form, while lactams of less than 9 membered rings take the cis form owing to the steric hindrance[3].

It has been reported on the polymerizability of ε-caprolactam that the configuration of the amide group relates to its reactivity[4] and *N*-alkyl-substituted derivatives of the cis amide such as *N*-methyl-ε-caprolactam are too stable to polymerize[5].

The great stability of *N*-alkyl-substituted lactams can not be explained from the difference in the ring strain or in the thermodynamical character[6] caused by the intramolecular rotational isomerism, but it is supposed to be due to the increase of resonance in the amide group[7]. Therefore, the infrared spectra of several chain and cyclic amide compounds have been measured with special interest in the range of 1600~1800 cm^{-1}, and the effect of the resonance on the characteristic band of the amide group has been investigated.

Experimental

The infrared spectra of several amide compounds were measured with a Hitachi model EPI-2 spectrophotometer in the range of 2~15 μ, with a rock salt prism. The cell thickness was 0.01 mm.

The infrared spectra of chloroform solution of *N*-alkyl-substituted chain or cyclic amides were measured in the range of 5.5~6.5 μ at various concentrations and temperatures. The cell thickness was selected suitably so that the transmittance at the absorption maximum is within the range of 20 ~80%. Although it is desirable to use a nonpolar solvent such as carbon tetrachloride, *N*-methyl lactams do not dissolve in carbon tetrachloride.

Results

The infrared spectra of several amide compounds are shown in Figs. 1—5. The frequencies of the carbonyl absorption (amide I band) of these compounds are shown in Table I, in which values in parentheses mean the frequencies of shoulders in the amide I band. The absorptions of the chloroform solution of *N*-methyl lactams are shown in Fig. 6. *N, N*-Disubstituted chain amide shows a sharp absorption at 1626 cm^{-1} (Fig. 7), while the amide I band of *N*-methyl lactams splits into

Table I. The frequencies of the carbonyl absorption

Kind of amide	Frequency, cm^{-1}	State
N-Hexylacetamide	1653	Liquid
N, N-Dibutylacetamide	1650	〃
ε-Caprolactam	1645	KBr disk
N-Methyl-ε-caprolactam	(1739), 1634	Liquid
α-Piperidone	1664	〃
N-Methyl-α-piperidone	(1739), 1672, 1631	〃
α-Pyrrolidone	1680	〃
N-Methyl-α-pyrrolidone	1681, (1629)	〃

Table II. The molar extinction coefficient of *N*-methyl-ε-caprolactam in chloroform solution

Concn. mol./l.	1733 cm^{-1}			1634 cm^{-1}		
	20°C	40°C	60°C	20°C	40°C	60°C
0.02	26.8	26.8	28.8	554	506	483
0.05	24.4	25.9	27.4	484	406	379
0.1	—	29.7	—	545	552	484
0.2	—	31.2	29.2	467	520	456
0.3	—	21.6	27.5	—	—	—
0.5	—	21.0	26.3	—	—	—
1.0	—	26.0	24.4	—	—	—
Mean	25.6	26.0	27.3	512	496	451

* Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) M. Tsuboi, This Bulletin, 22, 215 (1949).
2) S. Mizushima et al., *J. Am. Chem. Soc.*, 72, 3490 (1950).
3) R. Huisgen and H. Walz, *Chem. Ber.*, 89, 2616 (1956).
4) N. Ogata, *Makromol. Chem.*, 30, 212 (1959).
5) J. Procházka, *Chem. Listy*, 37, 158 (1943).
6) H. Yumoto, *J. Chem. Phys.*, 29, 1234 (1958).
7) N. Ogata, This Bulletin, 32, 813 (1959).

TABLE III. THE MOLAR EXTINCTION COEFFICIENT OF *N*-METHYL-α-PIPERIDONE IN CHLOROFORM SOLUTION

Concn. mol./l.	1736 cm^{-1}			1669 cm^{-1}			1631 cm^{-1}		
	20°C	40°C	60°C	20°C	40°C	60°C	20°C	40°C	60°C
0.02	22.8	—	—	167	—	150	83	87	118
0.05	25.5	30.2	—	182	145	150	93	100	142
0.1	23.3	27.9	18.5	182	139	113	88	130	163
0.2	24.9	28.6	19.5	176	186	—	103	119	—
0.3	—	—	19.2	166	174	112	99	114	150
0.5	—	—	18.7	167	164	—	99	101	—
1.0	—	—	18.0	168	149	—	109	88	—
Mean	24.1	28.9	18.8	173	159	131	96	106	143

TABLE IV. THE MOLAR EXTINCTION COEFFICIENT OF *N*-METHYL-α-PYRROLIDONE IN CHLOROFORM SOLUTION

Concn. mol./l.	1675 cm^{-1}			1630 cm^{-1}		
	20°C	40°C	60°C	20°C	40°C	60°C
0.01	—	—	538	—	—	—
0.02	583	562	538	—	—	—
0.05	464	438	—	42.1	37.0	35.8
0.1	634	636	473	45.5	41.3	36.4
0.2	512	644	425	46.2	40.6	36.0
0.3	—	582	441	—	—	—
0.5	—	497	426	—	—	—
1.0	—	—	—	—	—	—
Mean	548	560	474	44.6	39.6	36.1

TABLE V. THE MOLAR EXTINCTION COEFFICIENT OF CHAIN AMIDE IN CHLOROFORM SOLUTION

Concn. mol./l.	*N*-Hexylacetamide 1653 cm^{-1}		*N*,*N*-Dibutylacetamide 1626 cm^{-1}		
	20°C	40°C	20°C	40°C	60°C
0.1	478	462	568	642	557
0.2	442	433	528	582	—
0.3	443	397	512	563	—
0.5	350	—	453	—	—
1.0	—	—	413	—	—
Mean	428	431	515	596	557

TABLE VI. THE FREQUENCIES OF THE AMIDE I BAND OF *N*-METHYL LACTAM

Lactam	Ring member	I-a	I-b	I-c
N-Methyl-α-pyrrolidone	5	—	1675*	1630
N-Methyl-α-piperidone	6	1736	1669*	1631
N-Methyl-ε-caprolactam	7	1733	—	1634*

* Maximum absorption

two or three absorptions. The molar extinction coefficients at the absorption maximum of the amide I band for these *N*-methyl lactams are almost constant regardless of concentrations, but change with temperature, as shown in Tables II—V.

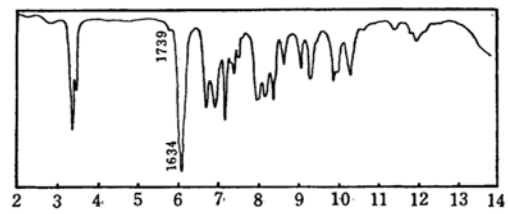


Fig. 1. The infrared spectrum of *N*-methyl-ε-caprolactam (Liquid).

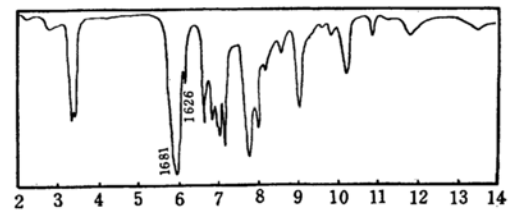


Fig. 2. The infrared spectrum of *N*-methyl-α-pyrrolidone (Liquid).

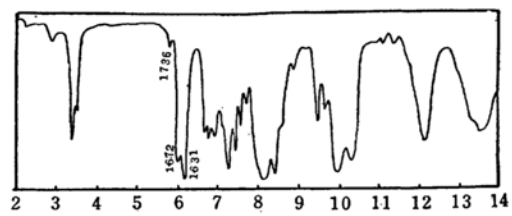


Fig. 3. The Infrared spectrum of *N*-methyl-α-piperidone (Liquid).

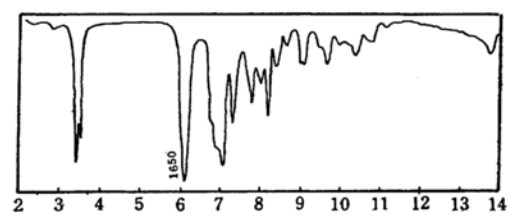


Fig. 4. The infrared spectrum of *N*, *N*-dibutyl-acetamide (Liquid).

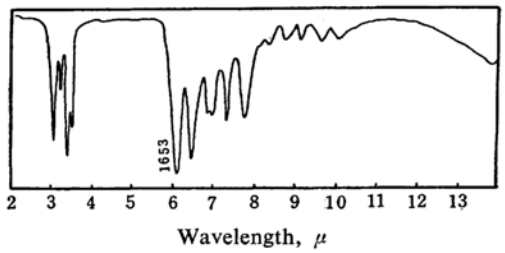
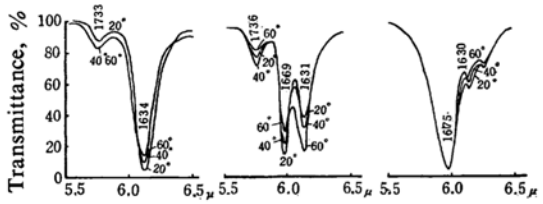


Fig. 5. The infrared spectrum of *N*-hexylacetamide (Liquid).



N-Methyl-ε-caprolactam *N*-Methyl-α-piperidone *N*-Methyl-α-pyrrolidone

Fig. 6. The carbonyl absorption of *N*-methyl lactams in chloroform solution at the concentration of 0.1 mol./l.

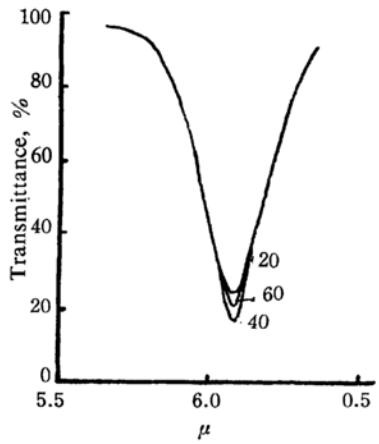


Fig. 7. The carbonyl absorption of *N*, *N*-dibutylacetamide in chloroform solution at the concentration of 0.1 mol./l.

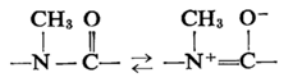
TABLE VII. THE INTEGRATED ABSORPTION INTENSITY OF THE AMIDE I BAND (5.5~6.5 μ) OF *N*-METHYL LACTAM

Lactam	Temp. °C	Intensity, $mol^{-1}\,l.\,cm^{-2}$
N-Methyl-α-pyrrolidone	20	2.5×10^4
	40	2.5 〃
	60	2.0 〃
N-Methyl-α-piperidone	20	1.8×10^4
	40	1.7 〃
	60	1.8 〃
ε-Caprolactam	20	2.5×10^4
	40	2.5 〃
	60	2.4 〃

Discussion

N-Methyl-ε-caprolactam is too stable to polymerize at a temperature over 200°C and *N*-methyl-ε-aminocaproic acid transforms easily into *N*-methyl-ε-caprolactam by heating[8].

The rate of hydrolysis[7] of *N*-methyl-ε-caprolactam into *N*-methyl-ε-aminocaproic acid is much slower than that of ε-caprolactam. Since the cyclic structure of *N*-methyl-ε-caprolactam is the same as that of ε-caprolactam, it is supposed that this stability of *N*-methyl-ε-caprolactam is not due to the change in the ring strain, but to the increase of the resonance in the amide group as shown below by the −I effect of the methyl group:



All *N*-monosubstituted acid amides show a strong absorption band usually near 1640 cm^{-1} in the solid state[8,9]. The lower frequencies of the carbonyl absorption of these amides are considered to be due to the resonance with the ionic form. The shifts of the carbonyl absorption towards lower frequencies by the *N*-alkyl substitution, therefore, seem to suggest the increase of the resonance in the amide group.

As stated before, the infrared spectra of *N*-methyl lactams with less than 7 membered rings exhibit a doublet or triplet in the region of the amide I band, and this is not caused by the interaction among molecules or by the solvent effect, since the molar extinction coefficients of these amide I bands in the chloroform solution are hardly influenced by the change of the amide compounds. The changes with temperature of the molar extinction coefficients of these absorption peaks are different from each other, as can be seen from Fig. 6. The elucidation of the cause of this interesting fact requires further investigation. The frequency of the maximum intensity among these doublets or triplets shifts towards lower frequencies with the enlargement of the ring. These bands are now named amide I-a, I-b and I-c in the order of the increasing frequency, respectively. These are shown in Table VI.

The integrated intensity of these split amide I bands was measured as follows: a point by point measurement of $\log(I_0/I)$ was made at intervals of 0.02 μ in the range of 5.5~6.5 μ and these data were plotted against the wavelength and the area under the curve was

8) H. Yumoto, K. Ida and N. Ogata, ibid., **31**, 249 (1958).
9) H. K. Hall, Jr. and R. Zbinden, *J. Am. Chem. Soc.*, **80**, 6428 (1958).

graphically determined. The true integrated absorption intensities were obtained by the method proposed by Ramsey[10]. The integrated absorption of the amide I band is almost unaltered with the ring size, as shown in Table VII. Therefore, these split absorptions are estimated to be due to the amide group.

Summary

The infrared spectra of several *N*-methyl lactams and acid amides have been measured in chloroform solution in order to investigate the correlation between the polymerizability of lactams and the frequencies of the carbonyl absorption of the amide group. The observed frequency lowering of the amide I band by *N*-methyl substitution can be related to the increasing contribution of the ionic structure to the resonance in the amide group, and to the low polymerizability. The infrared spectra of *N*-methyl lactams exhibit doublets or triplets in the carbonyl stretching region.

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10) D. A. Ramsey, ibid., 74, 72 (1952).