The Resonance Effect of Amide Group on the Polymerizability of Lactam Derivatives. II. The Basicity of Amide Group of Lactams***

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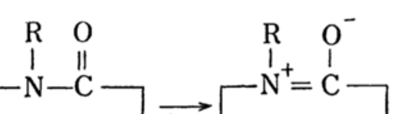
Th polymerizability of lactams becomes very small by *N*-alkyl substitution[1,2]. *N*-Methyl-ε-caprolactam, for instance, is too stable to polymerize at a temperature above 200°C and *N*-methyl-ε-aminocaproic acid converts easily into *N*-methyl-ε-caprolactam by heating. The increase in the stability of the ring structure by the *N*-alkyl substitution of lactams is explained[3] from the increase of resonance in the amide group as shown below:



If the resonance effect of the amide group increases by *N*-alkyl substitution, it is expected that the basicity of the amide group will decrease. In this connection, an addition reaction of hydrogen chloride with several cyclic or chain amides has been investigated by the measurement of the infrared spectrum.

Experimental

Measurement ot the Infrared Spectrum of Addition Products of Hydrogen Chloride and Amide Compounds.—A chloroform solution of hydrogen chloride of 0.15 mol./l. was prepared by introducing dry hydrogen chloride gas into chloroform. This hydrogen chloride solution was diluted with chloroform to the concentrations of 0.08, 0.04, 0.02 and 0.01 mol./l. and 3.5 cc. of each of the solutions was mixed with 3.5 cc of a chloroform solution of several amide compounds of 0.04 mol./l.

The infrared spectra of the mixtures and the amide solutions were measured by a Hitachi model EPI-2 spectrophotometer with a rock salts prism, using hydrogen chloride-chloroform solution or pure chloroform as reference, respectively.

Determination of Equilibrium Constant of the Addition Reaction between the Amide Group and Hydrogen Chloride.—The equilibrium constants of the addition reaction between the amide group and hydrogen chloride were determined for several cyclic or chain amides by the intensity measurement of the carbonyl absorption in the infrared spectra.

The calibration curves for several amide compounds in chloroform were determined by measuring absorbances of the amide I band at 20°C which are shown in Figs. 1 and 2. The calibration curves at

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* I, This Bulletin, 34, 245 (1961).

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

1) J. Procházka, *Chem. Listy*, 37, 202 (1943), *Chem. Abstr.*, 40, 2113 (1946).

2) H. Yumoto, K. Ida and N. Ogata, This Bulletin, 31, 249 (1948).

3) N. Ogata, ibid., 32, 813 (1959).

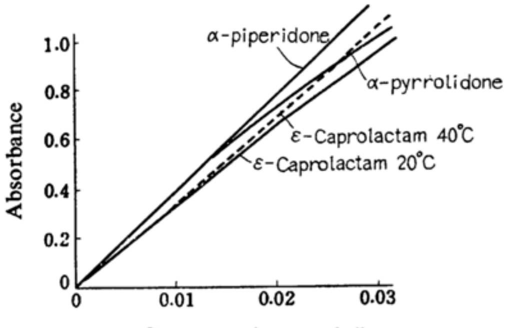


Fig. 1. The calibration curves for several lactams in chloroform solutions.

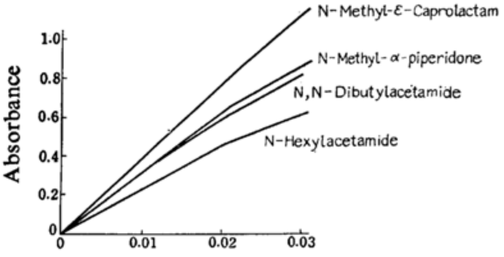


Fig. 2. The calibration curves for several amides in chloroform solutions.

40 and 55°C were almost the same as those at 20°C.

The concentrations of amide [-NHCO-] in chloroform solutions in the presence of hydrogen chloride were determined by these calibration curves. As hydrogen chloride has a tendency to be volatilized with rise of temperature, infrared spectra were measured for the narrow range of 1400~1800 cm^{-1} to avoid the change of concentration. The concentration of hydrogen chloride in chloroform was determined by titrating with N/100 sodium hydroxide.

The equilibrium constant K of the addition reaction between the amide group and hydrogen chloride can be calculated as follows:

$$[\text{-NH}_2^+\text{CO-}] = [\text{-NHCO-}]_0 - [\text{-NHCO-}]_{\text{HCl}}$$

$$[\text{H}^+] = [\text{HCl}] - [\text{-N}^+\text{H}_2\text{CO-}]$$

$[\text{-NHCO-}]_0$: Initial concentration of amide

$[\text{-NHCO-}]_{\text{HCl}}$: Concentration of amide in the presence of HCl

$$K = \frac{[\text{-N}^+\text{H}_2\text{CO-}]}{[\text{-NHCO-}][\text{H}^+]}$$

Results

Figs. 3—9 show the spectra, where a solid line represents the spectrum of the chloroform solution of the amide compound in the presence of hydrogen chloride and a dotted line the spectrum of the amide compound only.

In the presence of equal moles of hydrogen chloride and amide, the N—H absorption of cyclic or chain amides in the 3400~3500 cm^{-1} region is replaced by a broad absorption in the 2000~2400 cm^{-1} region and the intensity of the C=O absorption near 1650 cm^{-1} becomes weaker, accompanied by the appearance of a weak absorption in the 1750~1800 cm^{-1} region as shown in Table I.

The whole infrared spectrum of secondary or tertiary chain amide is not much altered in the presence of hydrogen chloride, while that of cyclic amide is altered considerably, accompanying a new absorption in the 1560~1640 cm^{-1} region.

The broad absorption in the 2000~2400 cm^{-1} region which appears in the chloroform solution of the amides in the presence of hydrogen chloride is supposed to be due to the $\rangle\text{N}^+\text{H}_2$ stretching motion.

The values of K at various concentrations of hydrogen chloride at 20, 40 and 55°C are shown in Table II. Table III shows the mean values of K for several amide compounds. The value of K decreases with the rise of temperature. K for chain amides is considerably smaller than that for cyclic amides. The values of K for cyclic amides increase with the enlargement of the lactam ring and those for tertiary amides are smaller than those for the corresponding secondary amides, especially for lactams.

From the slope of the linear relationship between the logarithm of K and reciprocals of absolute temperatures as shown in Fig. 10, heats of the addition reaction of the amide with hydrogen chloride are obtained. These are shown in Table IV. The heats of the addition reaction for cyclic amides become lower

TABLE I. THE CARBONYL ABSORPTION OF SEVERAL AMIDES IN THE PRESENCE OF HCl

Kind of lactam	Ring member	The C=O absorption band, cm^{-1}				
		Lactam alone	In the presence of HCl			
α-Pyrrolidone	5	1689	1800	1689*	1639	
α-Piperidone	6	1658	1800	1658*	1577	1565
ε-Caprolactam	7	1658	1800	1659*	1575	

* Maximum absorption

TABLE II. THE VALUES OF K

Sample	Temp. °C	Concn. of HCl mol./l.	Absorbance of C=O	Concn. of [-NHCO-] mol./l.	Concn. of [H$^+$] mol./l.	Concn. of [-N$^+$H$_2$CO-] mol./l.	K
α-Pyrrolidone	20	0.0030	0.654	0.0174	0.0009	0.0021	134
		0.0058	0.586	0.0157	0.0020	0.0038	121
		0.0112	0.456	0.0117	0.0034	0.0078	196
		0.0224	0.275	0.0069	0.0098	0.0126	186
	40	0.0030	0.552	0.0148	0.0018	0.0012	45
		0.0058	0.514	0.0135	0.0033	0.0025	56
		0.0114	0.421	0.0108	0.0062	0.0052	78
		0.0220	0.283	0.0072	0.0132	0.0088	93
α-Piperidone	20	0.0048	0.686	0.0175	0.0013	0.0035	154
		0.0094	0.564	0.0143	0.0027	0.0067	174
	40	0.0054	0.632	0.0161	0.0025	0.0029	72
		0.0084	0.548	0.0140	0.0041	0.0043	75
		0.0106	0.495	0.0125	0.0041	0.0065	51
		0.0168	0.376	0.0095	0.0080	0.0088	116
		0.0330	0.266	0.0068	0.0215	0.0115	79
ε-Caprolactam	20	0.0098	0.721	0.0218	0.0016	0.0082	235
		0.0132	0.697	0.0212	0.0035	0.0097	131
		0.0264	0.419	0.0118	0.0073	0.0191	222
		0.0375	0.353	0.0098	0.0173	0.0202	119
	40	0.0054	0.580	0.0173	0.0024	0.0030	72
		0.0104	0.485	0.0140	0.0041	0.0063	110
		0.0204	0.291	0.0080	0.0081	0.0123	190
	55	0.0040	0.586	0.0175	0.0017	0.0023	77
		0.0076	0.529	0.0155	0.0033	0.0043	84
		0.0280	0.269	0.0073	0.0155	0.0125	111
N-Methyl-*α*-piperidone	20	0.0022	0.737	0.0192	0.0014	0.0008	30
		0.0046	0.695	0.0182	0.0028	0.0018	35
		0.0092	0.604	0.0158	0.0050	0.0042	53
		0.0190	0.433	0.0112	0.0102	0.0088	77
	40	0.0036	0.609	0.0160	0.0023	0.0013	35
		0.0071	0.577	0.0150	0.0048	0.0023	32
		0.0144	0.479	0.0125	0.0096	0.0048	40
		0.0286	0.355	0.0092	0.0205	0.0081	43
N-Methyl-*ε*-caprolactam	20	0.0060	0.616	0.0195	0.0043	0.0017	20
		0.0124	0.530	0.0165	0.0077	0.0047	37
		0.0246	0.395	0.0122	0.0156	0.0090	47
	40	0.0037	0.593	0.0188	0.0030	0.0007	12
		0.0074	0.559	0.0175	0.0054	0.0020	21
		0.0146	0.486	0.0151	0.0102	0.0044	29
		0.0288	0.393	0.0141	0.0234	0.0054	16
	55	0.0060	0.569	0.0178	0.0050	0.0010	11
		0.0114	0.548	0.0172	0.0098	0.0016	10
		0.0200	0.492	0.0153	0.0165	0.0035	14
		0.0374	0.423	0.0131	0.0317	0.0057	14
N,*N*-Dibutyl-acetamide	20	0.0028	0.627	0.0213	0.0016	0.0012	35
		0.0054	0.602	0.0203	0.0032	0.0022	34
		0.0106	0.548	0.0182	0.0063	0.0043	38
		0.0222	0.467	0.0150	0.0147	0.0075	34
	40	0.0042	0.570	0.0190	0.0032	0.0010	17
		0.0076	0.539	0.0178	0.0054	0.0022	23
		0.0148	0.482	0.0155	0.0103	0.0045	28
		0.0288	0.420	0.0135	0.0223	0.0065	22
N-Hexyl-acetamide	20	0.0034	0.422	0.0183	0.0017	0.0017	55
		0.0067	0.382	0.0166	0.0033	0.0034	62
		0.0130	0.329	0.0142	0.0072	0.0058	57
	40	0.0044	0.413	0.0180	0.0024	0.0020	46
		0.0078	0.381	0.0165	0.0043	0.0035	49
		0.0154	0.329	0.0143	0.0097	0.0057	41

TABLE III. THE EQUILIBRIUM CONSTANT OF THE ADDITION REACTION OF SEVERAL AMIDES AND HCl

Sample	Configuration of amide	*K* 20°C	*K* 40°C	*K* 60°C
α-Pyrrolidone	5 membered cyclic cis amide	159	68	—
α-Piperidone	6 membered cyclic cis amide	164	79	—
ε-Caprolactam	7 membered cyclic cis amide	177	124	91
N-Methyl-α-piperidone	6 membered cyclic tertiary amide	49	38	—
N-Methyl-ε-caprolactam	7 membered cyclic tertiary amide	35	20	12
N,*N*-Dibutylacetamide	tertiary chain amide	35	22	—
N-Hexylacetamide	secondary trans amide	58	48	—

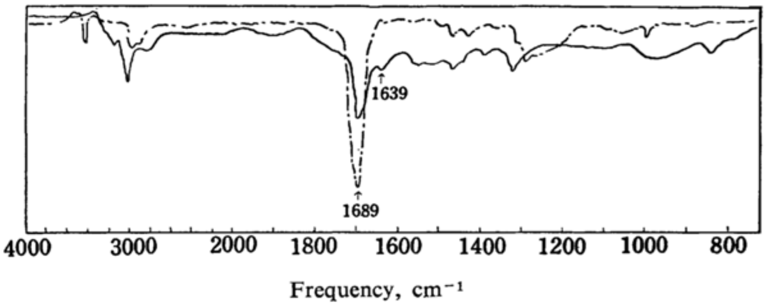


Fig. 3. The infrared spectrum of α-pyrrolidone in the presence of HCl (Chloroform solution).

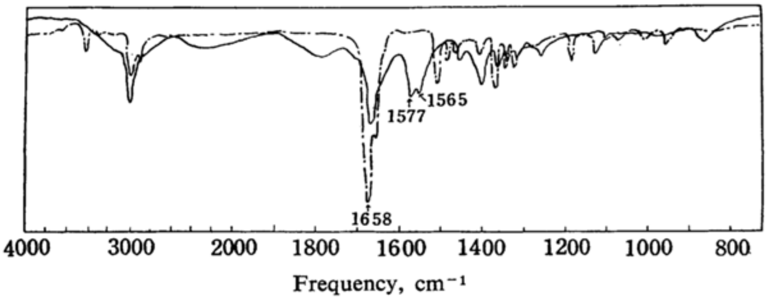


Fig. 4. The infrared spectrum of α-piperidone in the presence of HCl (Chloroform solution).

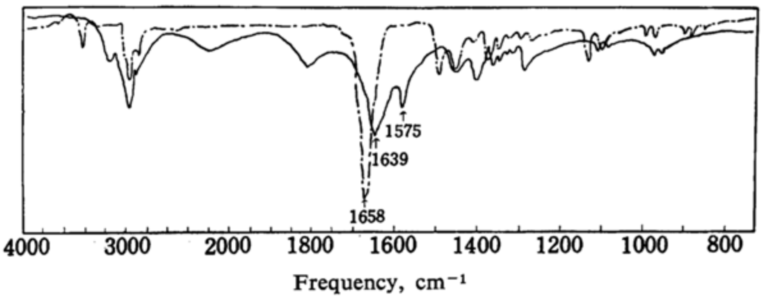


Fig. 5. The infrared spectrum of ε-caprolactam in the presence of HCl (Chloroform solution).

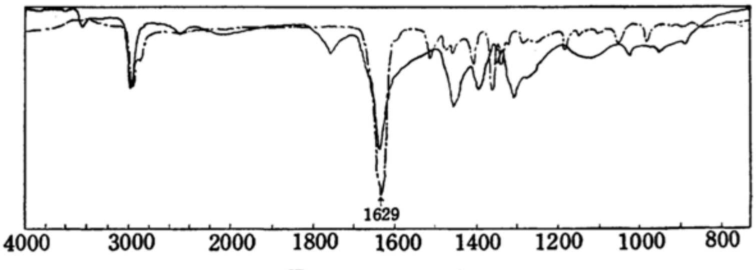


Fig. 6. The infrared spectrum of *N*-methyl-α-piperidone in the presence of HCl (Chloroform solution).

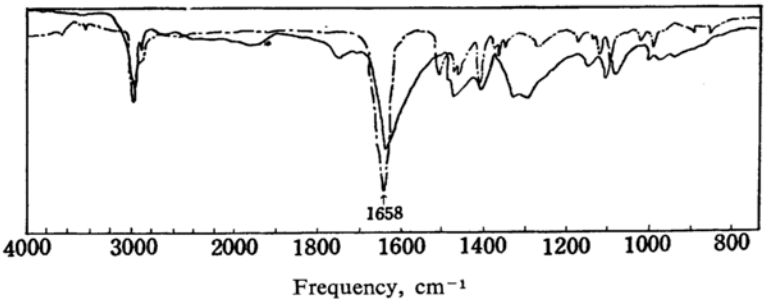


Fig. 7. The infrared spectrum of *N*-methyl-ε-caprolactam in the presence of HCl (Chloroform solution).

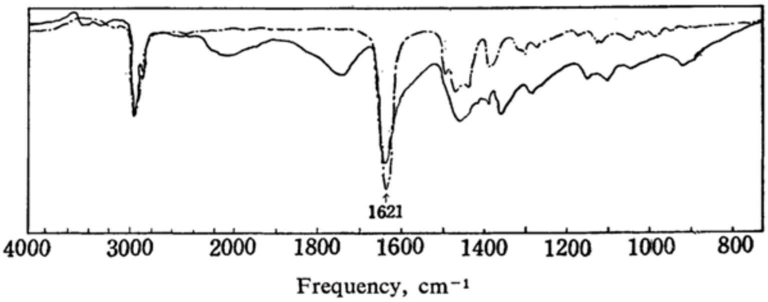


Fig. 8. The infrared spectrum of *N*, *N*-dibutylacetamide (Chloroform solution).

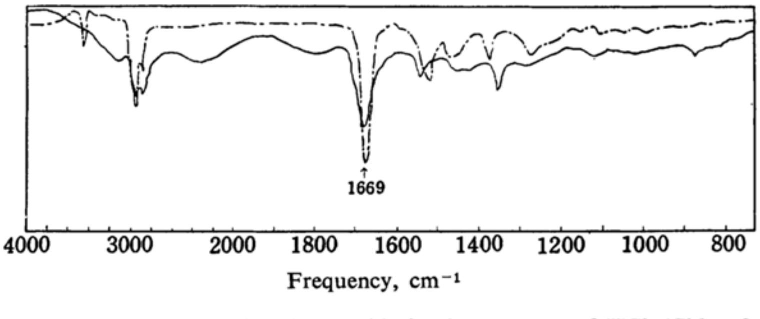


Fig. 9. The infrared spectrum of *N*-hexylacetamide in the presence of HCl (Chloroform solution).

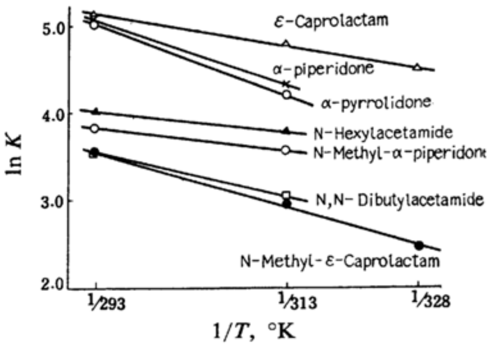


Fig. 10. The relationship between ln K and $1/T$.

TABLE IV. THE HEAT OF ADDITION REACTION OF SEVERAL AMIDES AND HCl

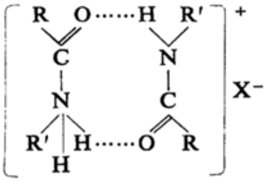
Sample	$-\Delta H$, kcal./mol.
α-Pyrrolidone	7.6
α-Piperidone	6.6
ε-Caprolactam	3.2
N-Methyl-α-piperidone	2.3
N-Methyl-ε-caprolactam	5.1
N, *N*-Dibutylacetamide	4.1
N-Hexylacetamide	2.2

with the enlargement of the ring and those for chain amides are generally lower than those for cyclic amides.

Discussion

The configuration of the amide group takes a planar structure owing to the resonance and two configurations of trans and cis forms are possible. It is known[4-7] that chain amides take the trans form, while cyclic amides of less than 9 membered rings take the cis form.

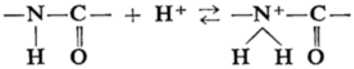
Although the basicity of the nitrogen atom of the amide becomes very weak by the +E effect of the carbonyl group, the amide group acts as a base, adding a proton[8]. It has been reported[9] that chain amide reacts with hydrogen chloride forming an addition product with 1/2 or 1 mol. of hydrogen chloride to 1 mol. of amide. The structure of the 1/2 mol. salt is proposed[9] as follows:



The intensity of the absorption which appears in lactams near 1800 cm^{-1} in the presence of hydrogen chloride becomes stronger with the enlargement of the lactam ring. This absorption shifts towards 1759 cm^{-1} in the case of *N*-methyl lactams or tertiary amide.

It has been presumed[10] that the higher frequencies of the carbonyl absorption of acid halide, which appears near 1800 cm^{-1}, is due to the strong +I effect of the halogen atom. Therefore, it is expected that the absorption near 1800 cm^{-1} in the amide-hydrogen chloride addition product may be the free carbonyl absorption which shifts towards higher frequencies by the increase in the electron affinity of the nitrogen atom of the amide.

It is supposed that a proton adds to the nitrogen atom of the amide group as shown in the following equation, since the N—H absorption disappears and new absorption due to the $>N^+H_2$ and the free C=O stretching motion (near 1800 cm^{-1}) appear in the infrared spectrum of the amide hydrogen chloride addition product.



$$-\underset{\substack{|\\ H}}{N}-\underset{\substack{\|\\ O}}{C}- + H^+ \rightleftarrows -\underset{H\ \ H}{N^+}-\underset{\substack{\|\\ O}}{C}-$$

Primary and secondary amides show a strong absorption in the 1600~1500 cm^{-1} region, which is absent from those of cyclic lactams, and this band is refered to generally as the amide II band. The origin of the amid II band is generally supposed to be due to a mixed vibration which can be described as an out-of-phase combination of OCN and NH vibrations. The frequency of the amide II band of secondary amide shifts from 1530 cm^{-1} to 1550 cm^{-1} in the presence of hydrogen chloride, as shown in Fig. 9. This is explained from the increase in the ionic character of the N—H linkage by the addition of a proton.

The addition products of lactams and hydrogen chloride show a sharp absorption in the region of 1570~1640 cm^{-1}. This absorption does not appear in *N*-methyl lactams or tertiary chain amides in the presence of hydrogen chloride. It is supposed that this band may be assigned to the N—H deformation vibration. The assignment of this band to the C—N stretching motion is not accepted, since no absorption in the 1570~1640 cm^{-1} region appears in tertiary cyclic or chain amides in the presence of hydrogen chloride.

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[4] M. Tsuboi, ibid., 22, 215 (1949).

[5] R. Huisgen and H. Walz, *Chem. Ber.*, 89, 2616 (1956).

[6] H. K. Hall, Jr., *J. Am. Chem. Soc.*, 80, 6404 (1958).

[7] N. Ogata, *Makromol. Chem.*, 30, 212 (1959).

[8] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry", Oxford University Press, London (1949), p. 96.

[9] E. H. White, *J. Am. Chem. Soc.*, 77, 6215 (1955).

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley & Sons, Inc., New York (1958), p. 125.

The equilibrium constants K of the addition reaction of hydrogen chloride and cyclic amide (cis form) are considerably greater than those of chain amide (trans amide). It is supposed that the basicity of the nitrogen atom of the cis amide may increase owing to the decrease of resonance in the amide group. The addition of hydrogen chloride to cyclic amide becomes easier with the enlargement of the ring, as shown by the greater value of K and the lower heat of addition reaction.

The values of K for *N*-methyl lactams are considerably smaller than those for the corresponding lactams and they are almost the same as those for tertiary chain amide. The heat of the addition reaction of hydrogen chloride with amide becomes higher with the *N*-methyl substitution of an amide hydrogen in lactams. This is expected to be due to the fact that the amide group is stabilized by hyperconjugation of methyl group as well as the increase in resonance by the $-I$ effect of methyl group. It is presumed that the small polymerizability of *N*-methyl-substituted lactams is due to the increase of resonance in the amide group.

Summary

The addition reaction of hydrogen chloride with several cyclic or chain amides has been investigated by the infrared absorption measurement in order to study the correlation between the polymerizability of lactams and the resonance in the amide group. The equilibrium constant K for the addition reaction with cyclic amide (cis form) is $150\sim180$ and it becomes greater with enlargement of the ring size, while K for *N*-methyl lactams is about $30\sim40$. The K value for secondary chain amide (trans form) is 60. The heat of the addition reaction of hydrogen chloride with lactams becomes lower with the enlargement of the lactam ring and also with the *N*-methyl substitution of the amide hydrogen.

The stronger basicity of the cis amide compared with the trans amide may be due to the decrease of resonance in the amide group, and the stabilization of the lactam ring by the *N*-methyl substituion may be ascribed to the increase in resonance by hyperconjugation of the methyl group.

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