Nuclear Magnetic Resonance Studies on Small-, Medium-, and Large-Sized N-Methyl Lactams. Solvent Effects[1]

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The 11- and 13-membered N-methyl lactams, N-methyl caprilactam (VII), and N-methyl lauryllactam (VIII) display doublet N-methyl absorption in the nmr. The doublet pattern is due to the existence of *s-cis* and *s-trans* torsional isomers arising from hindered internal rotation about the carbonyl carbon–nitrogen bond of the amido group. Assignment of the chemical shifts for the *s-cis* and *s-trans* resonances in each compound was made on the basis of dilution studies using various aromatic solvents. The general pattern of solvent-induced chemical shifts observed upon dilution with benzene, substituted benzenes, and pyridine is a progressive shift upfield for both components of the N-methyl doublet. The low-field peak of the pure sample is shifted by a greater amount than the high-field peak and crossover with change in sign of the relative chemical shifts occurs. The direction and relative magnitude of the solvent-induced chemical shifts for the CH_2CO, CH_2N, and CH_3N resonances are discussed in terms of a weakly associated solvent–solute collision complex which possesses a nonrandom stereochemical structure. On the basis of the assumed structure for the complex the low-field N-methyl resonance is identified with the *s-trans* position and the high-field resonance is identified with the alternative *s-cis* orientation. The conformer ratio in dilute carbon tetrachloride solution for the 11-membered ring is *s-cis*:*s-trans* ~55:45; and for the 13-membered ring the ratio is reversed, *s-cis*:*s-trans* ~40:60. The barrier height for exchange, E_a, for N-methyl lauryllactam (VIII) in carbon tetrachloride is 26.5 ± 1 kcal/mole, log A = 17. The *cis* N-methyl lactams, N-methyl butyrolactam (II), N-methyl valerolactam (III), N-methyl caprolactam (IV), N-methyl enantholactam (V), and methyl caprylactam (VI), also exhibit behavior upon dilution with aromatic solvents which is explicable on the basis of a solvent–solute complex. The 4-membered N-methyl lactam, N-methyl propiolactam (I), behaves in a manner completely analogous to the other N-methyl lactams upon dilution with benzene. This observation contrasts with the nontypical chemical and physical properties usually associated with this member of the series. Furthermore the C-13 H coupling constants for all the *cis* N-methyl groups are of similar magnitude of about 138 cps. This may indicate a similarity in the electronegativity of the nitrogen atom of the amido group.

Hindered internal rotation about the carbonyl carbon–nitrogen bond of the amido group in N-methyl amides causes the existence of planar, dipolar, interconverting *s-cis* and *s-trans* torsional isomers.[2] In temperature ranges where the rate of exchange between the *s-cis* and *s-trans* conformations is slow, $\tau_a >> \sqrt{2}/2\pi(\delta_a - \delta_b)$, two N-methyl resonances are observed: one for the N-methyl group at site A and one for the N-methyl at site B. As the temperature is increased to a point where the rate of rotation becomes comparable with the angular frequency separation, coalescence to a singlet absorption peak occurs. This characteristic spectroscopic behavior has been used extensively in qualitative and quantitative studies of torsional isomerism in N-methyl amides.[2,3]

We have observed the related phenomenon in a cyclic analog of an N-methyl amide, namely, in the case of the 13-membered N-methyl lauryllactam[4] (Scheme I).

In the present investigation we sought to determine whether *s-cis* and *s-trans* conformers might be observed by means of nmr in cyclic N-methyl lactams of ring sizes smaller than 13. Furthermore, in cases where coexisting *s-cis* and *s-trans* isomers might occur, it appeared to be of interest to determine the relation of ring size to conformer ratio. Elucidation of this aspect of the problem requires the assignment of the two peaks of the N-methyl doublet to the *s-cis* and *s-trans* N-methyl orientations. The relative positions of the two peaks have been assigned by Hatton and Richards for N,N-dimethylacetamide on the basis of dilution studies using aromatic solvents.[5] Others have used this procedure for the assignment of resonances in *s-cis* and *s-trans* conformational isomers of amides[6] as well as several other molecular systems which exhibit torsional isomerism.[7,8] As a preliminary step in this study, the effect of dilution with aromatic solvents upon the chemical shifts of the CH_2N, CH_3N, and CH_2CO protons for a series of *cis* N-methyl lactams from ring size four to nine was carried out. These compounds are designated as *cis* configurational isomers because the methyl group is sterically constrained to a *cis* orientation with respect to the carbonyl oxygen. The *s-cis* and *s-trans* designations indicate conformational isomerism about the amido cabon–nitrogen bond. The operational difference between the terms *cis* and *s-cis* is that, in the nmr, the former shows a singlet absorption even at low temperatures while the latter appears as one component of a doublet absorption band.

Results

The chemical shifts for the CH_2CO, CH_2N, and CH_3N protons for the *cis* N-methyl lactams are collected in Table I. The pattern of chemical shift variation caused by dilution of N-methyl butyrolactam (II) with benzene or pyridine, either as a neat liquid or

(1) (a) Presented in part at the 8th European Congress on Molecular Spectroscopy, Copenhagen, Denmark, Aug 14–20, 1965. (b) Preliminary communication: R. M. Mariarty and J. M. Kliegman, *Tetrahedron Letters*, **No. 9**, 891 (1966).

(2) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 218–225, 365–377.

(3) (a) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958). (b) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963). (c) For an excellent discussion of possible errors in the use of present and past day nmr instruments for the determination of barrier heights for amides, see C. W. Fryer, F. Conti and C. Franconi, *Chim.*, **8**, 1 (1965).

(4) R. M. Moriarty, *J. Org. Chem.*, **29**, 2748 (1964).

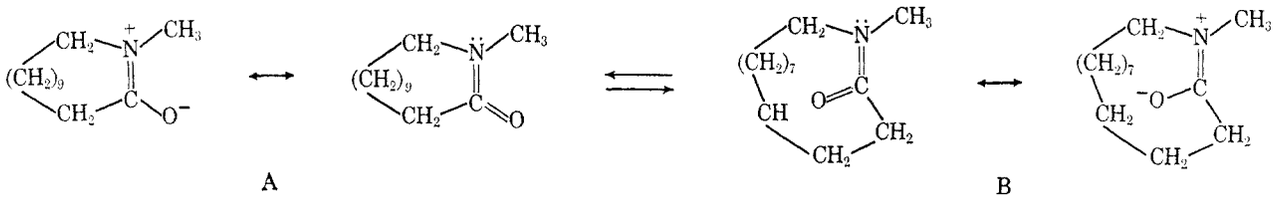
(5) (a) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960); (b) J. V. Hatton and R. E. Richards, *ibid.*, **5**, 139 (1960).

(6) L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 337 (1964).

(7) (a) J. V. Hatton and R. E. Richards, *Mol. Phys.*, **5**, 153 (1962); (b) G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, **86**, 4373 (1964).

(8) For an excellent discussion of the use of solvent-induced chemical shifts as a means for structure elucidation, see N. A. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 7.

SCHEME I



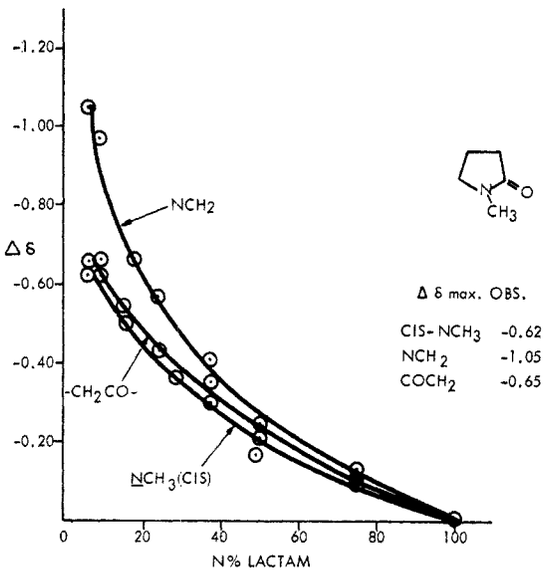


Figure 1.—Dilution of a carbon tetrachloride solution of N-methyl butyrolactam (II) with benzene.

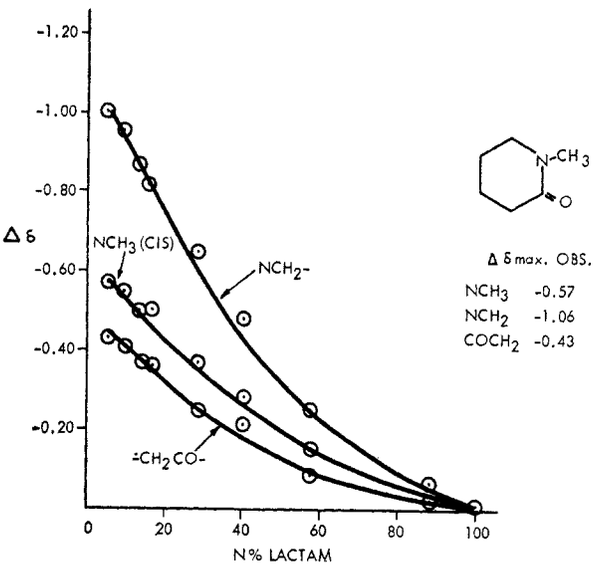


Figure 2.—Dilution of N-methyl valerolactam (III) with benzene.

as a solution in carbon tetrachloride, was a consistent diamagnetic displacement of the absorption bands. As shown in Table II and Figure 1, dilution of a carbon tetrachloride solution of II with benzene caused the CH_2CO, CH_2N, and CH_3N resonances to shift upfield but by relatively different amounts. The CH_2N protons experienced the largest diamagnetic shift

TABLE I

CHEMICAL SHIFTS FOR N-METHYL LACTAMS IN CARBON TETRACHLORIDE SOLUTION[a]

N-Methyl lactam	CH_2N[b]	CH_2CO[b]	CH_3N
Propiolactam (I)	3.20	2.82	2.75
Butyrolactam (II)	3.38	2.23	2.80
Valerolactam (III)	3.32	2.27	2.88
Caprolactam (IV)	3.45	2.47	2.97
Enantholactam (V)	3.49	2.39	2.81
Capryllactam (VI)	3.50	2.30	2.75
Caprilactam (VII)	3.27	2.43	2.87 (*s-cis*)
			3.13 (*s-trans*)
Lauryllactam (VIII)	3.37	2.33	2.88 (*s-cis*)
			3.03 (*s-trans*)

[a] Chemical shifts are from tetramethylsilane at $\delta = 0$ ppm at 60 Mc. Solutions are about 5% (w/w) with respect to lactam in CCl_4. [b] Chemical shift for center of multiplet.

while the CH_2CO and CH_3N were displaced in the same direction by about equal increments. Dilution of N-methyl butyrolactam (II) with carbon tetrachloride caused a downfield shift of the N-methyl peak (2.62–2.80 ppm). This is probably due to reversal of bimolecular association and resulting deshielding of the N-methyl group. Dilution leads to dissociation and formation of the solvated monomeric lactam with net deshielding of the N-methyl group.

As the ring size of the N-methyl lactam increases the solvent shift for the N-methyl resonance upon dilution with carbon tetrachloride decreases from a maximum value of $\Delta\delta = -0.18$ for N-methyl butyrolactam (II) to $\Delta\delta = -0.03$ ppm for N-methyl lauryllactam (VII). This variation may be due to steric hindrance to self association in the larger membered rings.

Figure 2 shows the pattern of high-field shifts observed upon dilution of N-methyl valerolactam (III) with benzene. The CH_3N and $COCH_2$ are shifted upfield equally with respect to each other and by about one-half as much as the CH_2N protons. Dilution of pure III with pyridine or dilution of a carbon tetrachloride solution of III with either pyridine or benzene resulted in similar high-field shifts (Table II). Consistently similar behavior was observed for dilution of N-methyl caprolactam (IV), N-methyl enantholactam (V), and N-methyl capryllactam (VI) with benzene and pyridine starting with either the pure lactam or with a dilute carbon tetrachloride solution. Figures 3 and 4 depict the dilution of lactams IV and VI with benzene, respectively. The CH_2N protons are shifted by approximately twice the amount of the CH_2CO and CH_3N protons while the latter resonances are shifted upfield by almost equal amounts.

In the dilution of N-methyl caprilactam (VII) with benzene (Figure 5) both N-methyl absorption bands are shifted upfield; however, the low-field peak is shifted by $\Delta\delta = 1.10$ ppm while the high-field component of the doublet is shifted by only $\Delta\delta = 0.62$ ppm. The *s-cis* and *s-trans* CH_2CO and CH_2N protons appear as unresolved multiplets. The net diamagnetic displacement of the CH_2N multiplet is invariably greater than that of the CH_2CO resonance (Table II).

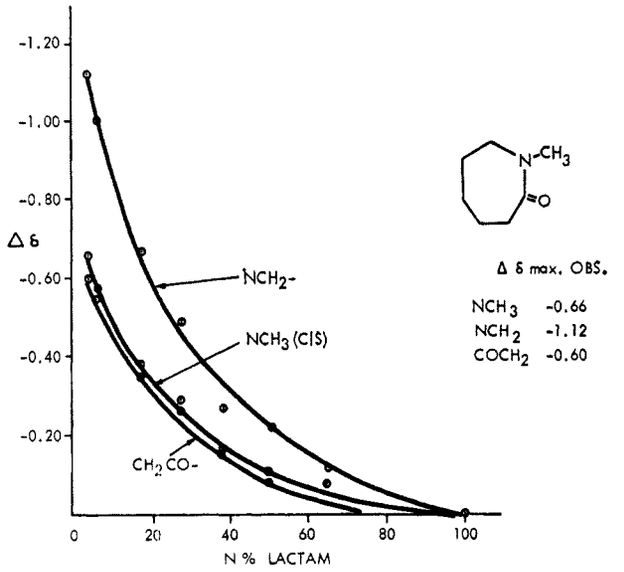


Figure 3.—Dilution of N-methyl caprolactam (IV) with benzene in CCl_4.

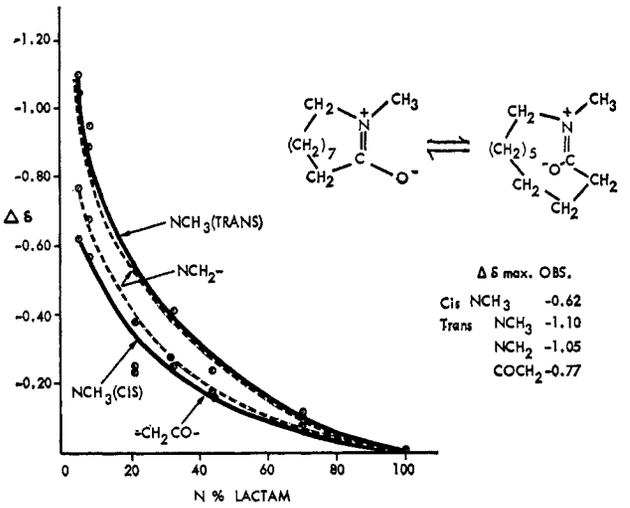


Figure 5.—Dilution of N-methyl caprilactam (VII) with benzene in CCl_4.

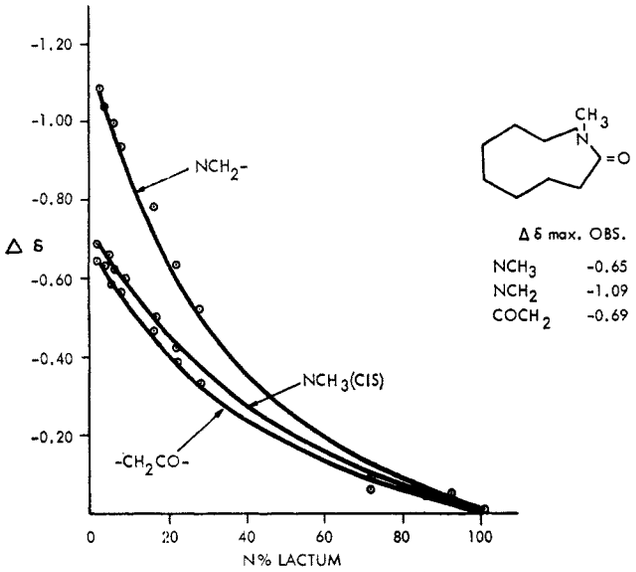


Figure 4.—Dilution of N-methyl capryllactam (VI) with benzene.

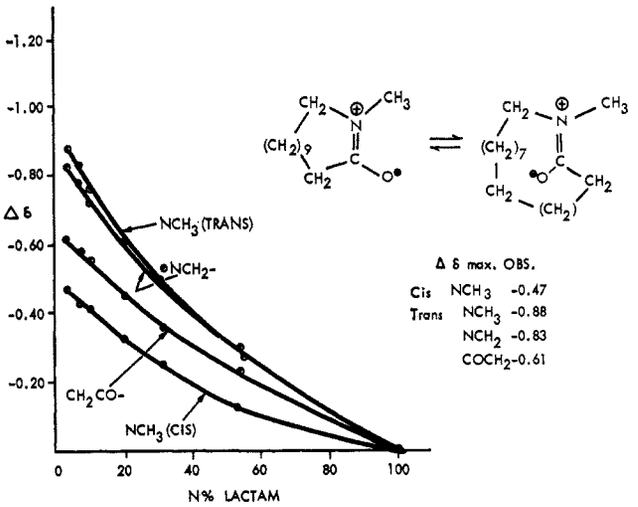


Figure 6.—Dilution of N-methyl lauryllactam (VIII) with anisole.

The same general pattern of highfield shifts obtains for the N-methyl doublet of N-methyl lauryllactam (VIII) upon dilution with various aromatic solvents. Figure 6 presents the typical variation in shifts for dilution with anisole. The low-field N-methyl peak is shifted by twice as much as the high-field N-methyl peak. Again only unresolved triplets attributable to the *s-cis* and *s-trans* CH_2CO and CH_2N protons were observed. These unresolved multiplets also moved to new upfield positions upon dilution with aromatic solvents with the net diamagnetic displacements of the CH_2N resonance exceeding that of the CH_2CO proton resonance. Upfield dilution shifts for the CH_3N and CH_2N protons of N-methyl propiolactam (I) were also observed (Table II).

Discussion

In summary, the general behavior upon dilution with aromatic solvents for the various *cis* N-methyl lactams is quite constant. The CH_2N protons experience the largest upfield shift while the magnitude of the upfield shift of both the CH_2CO and CH_3N protons is about equal, and smaller by one-half compared to the CH_2N shift. The observed changes may be discussed in terms of an equilibrium involving a weakly associated solvent–solute collisional complex. The stoiochiometry of the complex cannot be deduced from the present data. As far as the structure of the complex is concerned, it is clear, that an edgewise collision of the planar benzene molecule with the amido group of the lactam is less probable than a parallel plane configuration for collision. For "complex" in the present context, time-averaged environment of solute with respect to solvent might be taken as an equivalent expression. Assuming a 1:1 composition for the complex and also a model in which the solvent and the solute occupy parallel planes, one can proceed to a discussion of the relative magnitudes of the diamagnetic shifts. As has been pointed out for amides by Richards and Hatton,[5] it is reasonable to assume that the electron-rich benzene ring would be attracted to partial

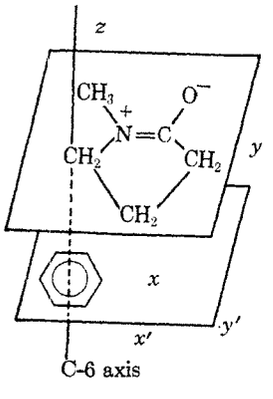
TABLE II
SOLVENT SHIFTS FOR N-METHYL LACTAMS I–VIII[a]

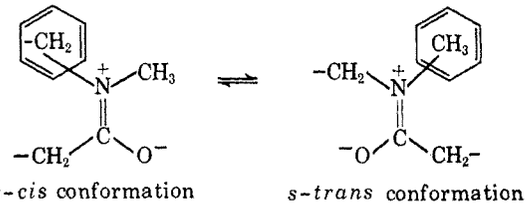
N-Methyl lactam	Solvent	Δδ, ppm CH_2N	CH_2CO	CH_3N
Propiolactam (I)	CCl_4	−0.10	−0.12	−0.12
	Benzene–CCl_4	0.40		0.20
	Benzene	0.57		0.33
	Pyridine	0.30		0.25
Butyrolactam (II)	CCl_4	−0.12	−0.16	−0.18
	Benzene–CCl_4	1.05	0.65	0.62
	Pyridine–CCl_4	0.85	0.49	0.62
	Benzene	1.18	0.84	0.67
	Pyridine	0.83	0.54	0.56
Valerolactam (III)	CCl_4	−0.13	−0.16	−0.14
	Benzene–CCl_4	1.08	0.52	0.62
	Pyridine–CCl_4	0.80	0.60	0.56
	Benzene	1.06	0.43	0.57
	Pyridine	0.85	0.44	0.52
Caprolactam (IV)	CCl_4	−0.10	−0.11	−0.10
	Benzene–CCl_4	1.12	0.60	0.66
	Pyridine–CCl_4	0.78	0.52	0.35
	Benzene	1.22	0.57	0.61
	Pyridine	0.90	0.55	0.58
Enantholactam (V)	CCl_4	−0.05	−0.04	−0.03
	Benzene–CCl_4	0.70	0.20	0.20
	Benzene	0.72	0.14	0.14
Capryllactam (VI)	CCl_4	−0.05	−0.04	−0.02
	Benzene–CCl_4	0.85	0.41	0.47
	Pyridine–CCl_4	0.84	0.55	0.62
	Benzene	1.09	0.69	0.65
	Pyridine	0.87	0.65	0.60
Caprilactam (VII)	CCl_4	−0.05	−0.03	−0.03
	Benzene–CCl_4	1.05	0.77	0.62 (*s-cis*), 1.10 (*s-trans*)
	Pyridine–CCl_4	0.82	0.63	0.60 (*s-cis*), 1.10 (*s-trans*)
	Benzene	0.76	0.80	0.61 (*s-cis*), 0.90 (*s-trans*)
	Pyridine	0.81	0.63	0.46 (*s-cis*), 1.11 (*s-trans*)
Lauryllactam (VIII)	CCl_4			
	Benzene–CCl_4	0.90	0.45	0.47 (*s-cis*), 0.80 (*s-trans*)
	Pyridine–CCl_4	0.83	0.70	0.63 (*s-cis*), 0.88 (*s-trans*)
	Benzene	0.80	0.85	0.65 (*s-cis*), 1.21 (*s-trans*)
	Pyridine	0.86	0.68	0.57 (*s-cis*), 1.12 (*s-trans*)

[a] The quantity Δδ (ppm) represents the maximum observable shift for dilution of the lactam with a given solvent. The final concentration was in the range N% ~1–5. Positive and negative signs refer to upfield and downfield shifts, respectively.

positive charge on nitrogen and repelled by the negative charge on oxygen. The relative orientation of the benzene ring with respect to the N-methyl lactam as drawn below takes into consideration the fact that the point of greatest diamagnetic shielding is at the center of the benzene. Were it not for the repulsion involving the oxygen atom, the nitrogen of the lactam would be on the C-6 principal axis (Chart I) of the benzene molecule at some equilibrium distance along the axis. The dipolar repulsion between the benzene and oxygen atom causes the benzene ring to be displaced in the $x'y'$ plane as shown. Thus the most shielded protons are the CH_2N while CH_3N and CH_2CO, which are about equidistant from the C_6 principal axis, are equally shielded. This geometry correlates well with the observed relative chemical shift changes upon dilution. The same steric considerations apply to the other *cis* N-methyl lactams. Also it should be noted that the size of the shifts for the relatively bulky lactams are similar to those observed for the dilution of N,N-dimethylacetamide with benzene.[5a] Since the diamagnetic effect decreases with the inverse cube of the distance, one may conclude that apparently no important steric effects operate against solvation in these cases. Now turning to the 11- and 13-membered lactams, the corresponding solvent–solute complexes for this *s-cis* and *s-trans* conformation are speculatively represented as follows.

CHART I



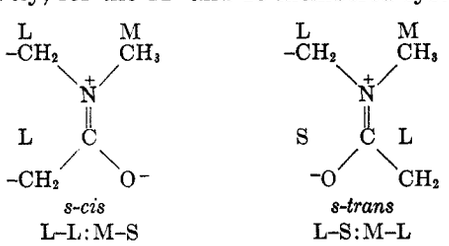


s-cis conformation *s-trans* conformation

These models lead to the prediction that the *s-trans* N-methyl group should experience the largest upfield shift. Since the low-field peak of the N-methyl doublet is shifted by the largest amount it is concluded that the low-field resonance corresponds to the *s-trans* conformation of the N-methyl group and the high-field peak is consequently identified with the *s-cis* conformation. Also based upon these models for the solvent–solute complexes one would predict the CH_2N proton multiplet to be shifted by a greater amount relative to the CH_2CO protons and this is found to be the case.

The nature of the substituent on the aromatic ring does not exert any large effect upon the magnitude of the upfield shift. The shifts for nitrobenzene are smaller than those observed for benzene; however, the solvent shifts observed with anisole as solvent are also smaller than those observed with benzene even though anisole possesses the electron-donating methoxy group.

As the ring size is increased from 11 to 13 members, the relative intensities of the high- and low-field N-methyl peaks indicate that the *s-trans* conformation becomes the more stable. The methylene groups attached to nitrogen and the carbonyl group are large relative to the smaller N-methyl (medium) and small oxygen atom. The two conformations depicting these steric effects are shown below. The integrated intensities correspond to *s-cis*:*s-trans* ~55:45 and 40:~60, respectively, for the 11- and 13-membered systems.



The preference for the *s-trans* conformation is in agreement with expectation in that eclipsing of groups of similar size leads to greater steric destabilization. Presumably if the ring size were increased further the *s-cis*:*s-trans* ratio would approach that of a comparably substituted straight chain N-methyl amide. Huisgen[9] has studied the parent (unmethylated) lactams from 5 to 16 members and finds that a transition from *s-cis* to *s-trans* occurs between the 9- and 10-membered examples. The *s-trans* form predominates in the larger ring examples. It is reasonable that the replacement of hydrogen by the methyl group on nitrogen would shift the transition point to a higher ring size.

Exchange between the *s-cis* to oxygen and *s-trans* position of the N-methyl group is a typical first-order rate process. The conformations P_a and P_b are unequal and do not change appreciably over the temperature range studied.

$$\textit{s-trans}\text{ N-methyl lactam} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \textit{s-cis}\text{ N-methyl lactam}$$

The mean lifetime of the *s-cis* is τ_a and the mean lifetime of the *s-trans* is τ_b.

$$\tau_a = \frac{\tau}{P_b},\ \tau_b = \frac{\tau}{P_a},\ k_f = \frac{1}{\tau_a},\ k_r = \frac{1}{\tau_b}$$

(9) R. Huisgen and H. Walz, *Chem. Ber.*, **89**, 2616 (1965).

In order to determine the first-order rate constant for exchange for N-methyl lauryllactam (VIII) at various temperatures, line shapes for several values of τ were calculated using a computer program based upon the density matrix method proposed by Alexander.[10] The input data are the peak separation in the absence of exchange, the peak width at half-height and conformation population. The activation energy, E_a, obtained from an Arrhenius plot is given in Table III along with

TABLE III
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR N-METHYL AMIDES

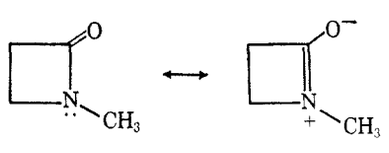
N-Methyl amide	$\Delta\epsilon$, kcal/mole	Log γ_0	T_c[a]
N-Methyl lauryllactam (VIII)	26	17	347
N,N-Dimethylacetamide[b]	24	16	346
N,N-Dimethylpropionamide[b]	21	15	327
N,N-Dimethylbutyramide[b]	17	13	330

[a] T_c, coalescence temperature in °K. [b] These values are taken from ref 3.

values found for other N-methyl amides. The value of 26.5 ± 1 kcal/mole found for N-methyl lauryllactam (VIII) is quite close to the barrier height of 24 kcal/mole determined for N,N-dimethylacetamide. The experimental frequency factor A is larger than kT/h indicating that a relatively high entropy of activation exists for rotation in this system. The close similarity of the values of the transmission coefficient for N,N-dimethylacetamide and N-methyl lauryllactam (VIII), log γ_0 = 16 and log γ_0 = 17, respectively, may be taken as an indication of the basic similarity between the two rotational processes.

The 4-membered N-methyl propiolactam (I) may be discussed separately because of the conspicuously different chemical and physical properties which it possesses compared to the other members of the homologous series. For example, the carbonyl stretching frequency is abnormally high, occurring at 1760 compared to 1653 cm^{-1} for N-methyl caprolactam (IV). N-methyl propiolactam undergoes hydrolysis with alkali about 10^3 times faster than N,N-dimethylpropionamide.[11]

The concept of steric inhibition of resonance as applied to the amido group of the β-lactam unit of the penicillins has been discussed by Woodward.[12] This effect is due to a twisting of the carbonyl group out of the plane of the nitrogen ring by 55° with resultant loss of the $p\pi - p\pi$ overlap. In the case of N-methyl propiolactam (I) such overlap, as implied by the resonance structure A, might be considered unimportant owing to the strain associated with the partial double



A

(10) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962). We wish to thank Dr. Martin Saunders, Yale University, for supplying us with a copy of his program.

(11) R. W. Holley and A. D. Holley, *J. Am. Chem. Soc.*, **71**, 2129 (1949).

(12) R. B. Woodward, in "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p 443.

bond.[13] The increased reactivity of the lactam toward hydrolytic cleavage could be explained by viewing the carbonyl group as being ketonic in nature and attached to the electronegative nitrogen.

In fact, however, the 4-membered lactam behaves perfectly normally toward dilution with benzene. The CH_3N group is shifted upfield by 0.32 and the CH_2N is shifted by 0.57 ppm. If one accepts that the solvent–solute association for the amide–benzene system is due to an electrostatic attraction between the electron-rich aromatic ring and the partial positive charge on nitrogen, then the observed solvent shifts imply the contribution of resonance structure A.

In an effort to gain further information about the percentage of positive charge on nitrogen in the various *cis* N-methyl lactams, the C-13H coupling constants for the methyl groups were determined.

The presence of a partial positive charge on nitrogen, as implied by the dipolar resonance form, should increase the electronegativity of the nitrogen atom. A consequence of the increased electronegativity is greater p character in the carbon atomic orbitals of the C–N bonds with concomitantly more s character in the C–H bonds of the carbon attached to nitrogen. To a first approximation, increased s character should lead to a larger C-13 H coupling constant.[14,15] Other factors such as effective nuclear charge also contribute to the magnitude of J, however, comparison of variations within the series is of interest.

Reference to Table IV indicates that very little variation exists for the measured C-13H coupling constants. Significantly the value for the 4-membered lactam I is very close to the higher homologs. The average value of about 138 cps is the same as that observed for N,N-dimethylacetamide. This corresponds to about 40% double-bond character for the C–N bond of the amido group. This estimate is based on information given.[15]

TABLE IV

C-13 H COUPLING CONSTANTS FOR N-METHYL LACTAMS[a]

Compd	J
N-Methyl propiolactam (I)	138
N-Methyl butyrolactam (II)	137
N-Methyl valerolactam (III)	138
N-Methyl caprolactam (IV)	138
N-Methyl enantholactam (V)	138
N-Methyl capryllactam (VI)	137
Trimethylamine	134
N,N-Dimethylacetamide	138

[a] All samples were measured neat. Coupling constants were determined on an A-60 spectrometer at 100-cps sweep width. Several compounds were measured using a frequency counter and acceptable internal agreement was attained. Values are considered to be within +0.20 cps.

Experimental Section

A Varian Associates high-resolution nmr spectrometer operating at ν_0 = 60 Mc/sec was used. For qualitative work the temperature of the probe was approximately 32°. Chemical shifts were measured from tetramethylsilane as internal standard, and the precison is about ±0.6 cps.

In quantitative work the temperature at the sample was controlled to within ±0.3° over the range of interest. Spectra were determined at various temperatures. The spectrum at a given temperature was repeated at least 10 times, and the field homogeniety was checked frequently. Theoretical line shapes for unequal population at various τ (mean lifetimes) were fitted with observed curves. Rate constants $1/\tau$ at various temperatures were used in an Arrhenius plot for the determination of E_a and ν_0.

For the dilution studies solutions were made up by weight using a precalibrated syringe technique. All solvents were distilled prior to use.

C-13 H coupling constants were measured at a sweep width of 100 cps using a frequency counter. Infrared curves were measured on a Perkin-Elmer 137B recording instrument.

N-Methyl propiolactam (I) was prepared according to the method of Holley and Holley.[11] It had bp 63° (18 mm) and was purified by vapor phase chromatography. A polyester cross-linked diethylene glycol adipate column was used: column temperature, 125°; injection point temperature, 235°; retention time, 49 min and 12 sec. The carbonyl stretching frequency occurred at 5.68 μ (CCl_4).

N-Methyl butyrolactam (II), **N-methyl valerolactam** (III), and **N-methyl caprolactam** (IV) are available commercially from the Fisher Chemical Co.

N-Methyl enantholactam (V), **N-methyl capryllactam** (VI), **N-methyl caprilactam** (VII), and **N-methyl lauryllactam** (VIII), were obtained by means of methylation of the parent lactam using the sodium hydride–methyl iodide procedure described previously.[4] N-Methyl enantholactam (V) had bp 110° (7 mm), λ_{max} CCl_4 6.07 μ (C=O); N-methyl caprilactam (VII) had bp 87° (0.15 mm).

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(13) Electron diffraction studies are in progress on the molecular structure of N-methyl propiolactam (I). Dr. J. Karle and I. Karle, Naval Research Laboratory, Washington, D. C., are carrying out these studies.

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