

INFRARED SPECTROSCOPY  
OF 4-AZATRICYCLO[4,4,0,0<sup>3,8</sup>]DECAN-5-ONE — A LACTAM WITH  
A NON-PLANAR *cis*-AMIDE GROUP\*

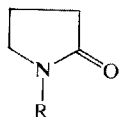
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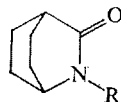
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The IR-spectrum of 4-azatricyclo[4,4,0,0<sup>3,8</sup>]decan-5-one (VII) was measured and compared with the spectra of 4-azatricyclo[4,3,1,0<sup>3,7</sup>]decan-5-one (V), 2-azabicyclo[2,2,2]octan-3-one (III) and 2-pyrrolidone (I). The absorption bands to which the amide-group vibrations contribute have been identified on the basis of deuteration and dilution experiments. Bands with the contribution of the  $\nu(\text{C}'\text{—N})$  mode, particularly in nonassociated molecules, have been found to be potentially suitable for the detection of a non-planar secondary *cis*-amide group. A non-planarity of the amide group causes a shift of the bands to lower wavenumbers. The lesser double bond character of the C'—N bond in a non-planar amide group affects in the predicted sense also N—H stretching vibrations (shift to lower wavenumbers) and C=O stretching vibrations (shift to higher wavenumbers).

Knowledge of infrared spectral parameters of amides with defined geometric arrangement is a necessary condition for determination of the geometry of amides (and peptides) in solution. This concerns not only the distinction between *cis*- and *trans*-conformation of the C'—N bond and the changes in bond angles at the C' and N atoms, but also deviations from planarity of the Pauling's resonance hybrid which have been shown to be rather common (see refs<sup>2-4</sup>). Most of the data hitherto available are based on the results of diffraction methods and therefore they relate to molecules in the crystal or gaseous state<sup>5</sup>.



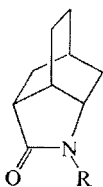
I, R = H  
II, R = <sup>2</sup>H



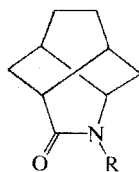
III, R = H  
IV, R = <sup>2</sup>H

\* For preliminary communication see ref.<sup>1</sup>.

We are recently interested in the study of compounds, containing non-planar amide groups, in solutions<sup>6-9</sup>. For this reason we prepared several types of model compounds of polycyclic structure which holds the amide group in a non-planar arrangement. Thanks to the conformational rigidity of these compounds, the geometry of their molecules remains similar in crystals as well as in solutions. For evaluation of the spectral measurements on such compounds we can therefore use the geometric parameters found by the diffraction analysis. Suitable models were found mainly in the lactam series, see<sup>10-12</sup>.



V, R = H  
VI, R = <sup>2</sup>H



VII, R = H  
VIII, R = <sup>2</sup>H  
IX, R = CH<sub>3</sub>

In the present study we investigate vibrations of secondary *cis*-amide groups in conformationally rigid lactams containing five-membered (compounds V and VI) and six-membered (compounds III, IV, VII and VIII) rings with planar (compounds III–VI) as well as non-planar (compounds VII and VIII) amide groups. The exact geometry of the non-planar amide group in the crystalline lactam VII was already known<sup>13</sup> from its three-dimensional analysis. We included into the present series of compounds also the N-methyl derivative IX with a non-planar amide group in order to compare the present results with the previously analysed spectra of tertiary *cis*-lactams<sup>6</sup>. We studied further, under identical conditions, 2-pyrrolidone (I) which contains a planar *cis*-amide group in the five-membered, to a certain extent flexible, ring. For this compound both the experimental interpretation of its spectrum<sup>14</sup> and the computer analysis<sup>15</sup> are known. The spectra were investigated in the region 1500–1200 cm<sup>-1</sup> (amide-II and amide-III bands, see<sup>16</sup>), in the carbonyl stretching vibration region (1800–1600 cm<sup>-1</sup>, amide-I band) and in the N–H stretching vibration region (3500–3000 cm<sup>-1</sup>). In the case of 2-pyrrolidone (I) the range 800–450 cm<sup>-1</sup> was also studied in order to clarify the character of some bands at about 1300 cm<sup>-1</sup>.

## EXPERIMENTAL

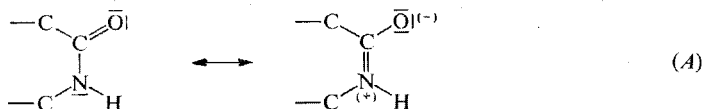
Spectra were measured mainly on a Perkin-Elmer model 621 spectrophotometer with precision  $\pm 1$  cm<sup>-1</sup>. Some of the measurements were performed on a UR-20 (Zeiss, Jena, GDR) instrument;

these cases are mentioned in the Tables. Pertinent concentrations are given in Tables I—VII. The band intensities are described as follows: vs very strong, s strong, m medium, w weak, vw very weak and sh shoulder. Concentrations, at which the concentration dependence measurements were taken, are specified in the Tables. In some cases (mentioned in the text and in the footnotes to the Tables) the temperature dependence was determined in the range 35—95°C. Tetrachloroethylene and bromoform were used as non-polar and polar solvent, respectively.

The compounds were deuterated by the addition of <sup>2</sup>H<sub>2</sub>O followed by azeotropic distillation with the solvent, used in the measurement; this procedure was repeated three times. In all cases it was possible to measure the spectra of the deuterated compounds at various temperatures without any reverse exchange N—<sup>2</sup>H → N—H.

## RESULTS AND DISCUSSION

Our assignment of bands in the spectrum is based on the Pauling's resonance hybrid concept (A) in which the relative contribution of two canonical structures depends on the environment. We turned our attention particularly to the assignment of the amide C'—N stretching vibration which, besides  $\nu(\text{C}'=\text{O})$ , represents the most suitable parameter for the detection of a non-planar amide group by infrared spectroscopy.



Analogously to the identification of the  $\nu(\text{C}'\text{---N})$  band in tertiary amides, we made use of the changes observed when the spectra are taken in two solvents which differ in their polarity and which thus affect differently the weight of the canonical forms of the resonance hybrid<sup>6</sup>.

In order to eliminate the N—H deformation vibrations which appear in the same spectral region, we studied concentration and/or temperature dependences in tetrachloroethylene and bromoform and performed the measurements also on deuterated compounds. This enabled us to separate the bands which are insensitive to these influences and which belong to the carbon skeleton from the sensitive bands which are ascribed to the amide group vibrations.

### *The Region of Wavenumbers 1500—1200 cm<sup>-1</sup>*

We have classified the bands into five types according to their behaviour to solvents, association changes and deuteration.

*Bands of the type 1:* Their position is sensitive neither to the change of solvent nor to the change in association. Neither a great concentration change nor deutera-

TABLE I

Wavenumbers of Absorption Bands (in  $\text{cm}^{-1}$ ) in 2-Pyrrolidone (*I*) Spectra in the Region 850 to  $460 \text{ cm}^{-1}$  (Measured on a Perkin-Elmer model 621 instrument with a precision  $\pm 1 \text{ cm}^{-1}$ )

1 <sup>a</sup>	2	3	4	5	6	7	Assignment <sup>b</sup>
473.0 s	472.2 s	471.4 s	470.5 s	473.4 s	472.6 s	472.5 s	$\delta(\text{C}'\text{O})$ out-of-plane
478.6 s	—	—	—	—	—	—	—
490.6 s	492.0 s	492.0 s	492.0 s	492.0 s	490.6 s	491.3 s	$\delta(\text{C}'\text{O})$ out-of-plane
—	—	—	—	—	506.2 sh	503.0 sh	—
540.0 m	537.5 w	538.0 w	538.0 w	537.0 w	538.5 vw	—	skeletal
—	562.0 w	560.0 m	560.0 m <sup>c</sup>	575.0 m <sup>d</sup>	576.0 m <sup>e</sup>	574.5 s	—
684.7 m	683.5 m	682.5 m	682.0 m	685.0 m	<i>f,g</i>	<i>f,h</i>	$\delta(\text{C}'\text{O})$ in-plane
—	800 s	800 s	790 s	<i>f</i>	<i>f</i>	<i>f,i</i>	$\delta(\text{NH})$ out-of-plane

<sup>a</sup> Experimental conditions (concentration, solvent, cell length): 1 film, neat; 2 saturated,  $\text{CS}_2$ , 0.050 mm; 3 0.1M,  $\text{CS}_2$ , 0.522 mm; 4 0.05M,  $\text{CS}_2$ , 1.0 mm; 5 2.0M,  $\text{CHCl}_3$ , 0.018 mm; 6 0.7M,  $\text{CH}_2\text{Cl}_2$ , 0.107 mm; 7 0.07M;  $\text{CH}_2\text{Cl}_2$ , 1.0 mm. <sup>b</sup> Bands assigned according to ref.<sup>14</sup>, as far as in the cited paper the bands were detected and assigned. <sup>c</sup>  $\epsilon_{\text{max}}^a = 23.65$ . <sup>d</sup>  $\epsilon_{\text{max}}^a = 38.10$ . <sup>e</sup>  $\epsilon_{\text{max}}^a = 65.26$ . <sup>f</sup> Not measured, absorption by solvent. <sup>g</sup> Measurement on a UR 20 (C. Zeiss, Jena) instrument revealed an additional band at  $634.5 \text{ cm}^{-1}$ . <sup>h</sup> 30–40% association. <sup>i</sup> Association below 5%.

tion eliminates these bands from the spectra. They can obviously be attributed to bending vibrations of the C—H bonds in methine or methylene (or, in the case of the tertiary lactam IX, also methyl) groups, and also to stretching vibrations of C—C bonds and non-amide C—N bonds. We denote the bending vibrations of all C—H bond types as  $\delta(\text{C—H})$  and the stretching vibrations of C—C bonds and non-amide C—N bonds as skeletal vibrations, since the procedure adopted by us is not capable of distinction between them.

*Bands of the type 2* can be detected exclusively in the spectra of associated molecules. The intensity of these bands decreases with decreasing association and finally they disappear completely. They are also absent in the spectra of the deuterated compounds. These bands are either completely insensitive to solvent change or they are shifted only slightly to lower wavenumbers on transfer from a non-polar to a polar solvent. This behaviour is in complete accord with the concept of weakening hydrogen bonds by polar solvents. Since the amide group has *cis*-conformation we can assume that the studied compounds associate as cyclic dimers.

According to Rey-Lafon and collaborators<sup>14</sup>, 2-pyrrolidone (*I*) in solution associates mainly in cyclic dimers whereas in the liquid state there is also association in linear oligomers. We measured the spectrum of 2-pyrrolidone and found a band of the type 2 at  $1438.0 \text{ cm}^{-1}$  in the pure

liquid and at 1448.0  $\text{cm}^{-1}$  in solution. The observed shift of the band maximum is in accord with the oligomeric association.

Bands of the type 2, observed in solutions, thus belong to the vibrations of dimers. In the studied region, these vibrations can be: in-plane bending vibrations of the N—H bonds engaged in these dimers, overtones of out-of-plane vibrations of these bonds, and possibly also combination vibrations of N—H out-of-plane vibrations with *e.g.* the both carbonyl bending vibrations.

*Bands of the type 3* belong to nonassociated molecules. Their intensity increases with the decreasing association of molecules and they are not present in the spectra of deuterated or fully associated molecules. Their position is not sensitive to solvent changes. The assignment of bands of the type 3 is analogous to that of the bands of the type 2, only it concerns nonassociated molecules. Their intensity should be —

TABLE II  
Wavenumbers of Absorption Bands in 2-Pyrrolidone(*I*) Spectra in the Region 1500—1200  $\text{cm}^{-1}$  (tetrachloroethylene)

Concentration of the compound *I*: in tetrachloroethylene 0.5M (temperature dependence), 0.1M and 0.02M; in bromoform 1.8M, 1.2M, 0.8M, 0.5M (temperature dependence) and 0.03M; in deuteriochloroform 0.025M; the compound was measured also neat (film). Concentration of the compound *II*: in tetrachloroethylene 1.8M, 0.5M and 0.025M, in bromoform 0.5M and 0.05M.

Wavenumber <sup>a</sup> $\text{cm}^{-1}$	Band type	Solvent shift <sup>b</sup> $\text{cm}^{-1}$	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
Nondeuterated compound <i>I</i>					
1 492.2	1	— 2.1	m	—	$\delta(\text{CH})$
1 464.9	1	— 3.0	m	—	$\delta(\text{CH})$
1 448.0	2	— 5	(w)	disappearance	$\delta(\text{NH})$ assoc. dimer
1425.0	4 and 1	+ 3.5	(m)	disappearance <sup>f</sup>	$\nu(\text{C}'\text{N}), \delta(\text{NH})$ assoc., $\delta(\text{CH})$ next to CO
1 418.3	5	+ 3.7	s	increase	$\nu(\text{C}'\text{N}), \delta(\text{NH})$ free
1 378.0	2	+ 2.0	(m)	disappearance	$\delta(\text{NH})$
1 339.0	g	+ 8.0	vw	increase	$\nu(\text{C}'\text{N}), \delta(\text{NH})$ free
1 307.5	6	+ 0.2	w	increase	$\delta(\text{CH}),$ skeletal $\delta(\text{NH})$ free
1 285.2	6	+ 1.9	s	decrease	$\delta(\text{CH}),$ skeletal $\delta(\text{NH})$ assoc.
1 265.0	2	—	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 253.6	5 <sup>h</sup>	+ 10.8	s	—	$\nu(\text{C}'\text{N}), \delta(\text{NH})$ free
1 224.4	6	+ 2.8	vw	—	$\delta(\text{CH}),$ skeletal, $\delta(\text{NH})$

TABLE II  
(Continued)

Wavenumber <sup>a</sup> cm <sup>-1</sup>	Band type	Solvent shift <sup>b</sup> cm <sup>-1</sup>	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
N-Deuterated compound II					
1 492.4	1	- 1.4	m	—	$\delta(\text{CH})$
1 459.5	1	- 0.5	m	—	$\delta(\text{CH})$
1 426.4	1	—	vw	—	$\delta(\text{CH})$ next to CO
1 413.0		+ 3.0		disappearance	$\nu(\text{C}'\text{N})$ , $\delta(\text{ND})$
1 393.0		+ 14.5		increase	$\nu(\text{C}'\text{N})$
1 315.6	1	2.0	w	—	$\delta(\text{CH})$ , skeletal
1 291.8	1	—	s	—	$\delta(\text{CH})$ , skeletal
1 208.6	1	—		—	$\delta(\text{CH})$ , skeletal

<sup>a</sup> Measured on a Perkin-Elmer model 621 instrument with precision  $\pm 1 \text{ cm}^{-1}$ . <sup>b</sup> Transfer from tetrachloroethylene to bromoform. <sup>c</sup> Only an approximate estimation because band intensities vary with concentration. The intensity of bands, which disappear with decreasing association, was estimated from the spectra of solution of the greatest measured concentration (about 75% association) and the data are given in parentheses. The intensity of the bands, which increase with decreasing concentration, was estimated from the spectra of nonassociated compounds; this was possible to achieve only in bromoform solutions. <sup>d</sup> The change with decrease in association was derived from measurements in which parameters, known to affect the degree of association (concentration, solvent, temperature as specified above), were varied. <sup>e</sup> For details see text; <sup>f</sup> this band disappears but even in the completely nonassociated compound a shoulder remains which is due to the vibration  $\delta(\text{CH}_2)$  in the  $\alpha$ -position relative to CO; <sup>g</sup> see the text; <sup>h</sup> this is obviously the second branch of the  $\nu(\text{C}'\text{—N})$  vibration band, the first branch is at  $1418.3 \text{ cm}^{-1}$ , on deuteration both branches give a single band at  $1393.0 \text{ cm}^{-1}$ .

and actually is — lower than the intensity of the bands of the type 2, as is the common feature of the free N—H bands.

*Bands of the types 4 and 5:* The spectra of the studied lactams display bands which in a non-polar solvent are situated at lower wavenumbers than in a polar solvent. We assume that these bands are due to a contribution of stretching vibration of the C'—N bond which, according to the Pauling's model, should have a more double-bond character (shorter bond length), and therefore also higher wavenumber, in a polar solvent than in a non-polar solvent. The bands do not disappear on deuteration and their wavenumber is only shifted for at most  $30 \text{ cm}^{-1}$ . In the case of the secondary lactams studied in this work, these bands are always concentration-dependent and we divided them into two groups:

TABLE III

Wavenumbers of Absorption Bands in 2-Azabicyclo[2,2,2]octan-3-one (*III*) Spectra in the Region 1200–1500 cm<sup>-1</sup> in Tetrachloroethylene

Concentration of the compound *III*: in tetrachloroethylene and in bromoform is 0.5M; concentration of the compound *IV*: in tetrachloroethylene 0.05M, in bromoform 0.07M. The same concentration were used also in the temperature dependence measurements.

Wavenumber <sup>d</sup> cm <sup>-1</sup>	Band type	Solvent shift <sup>b</sup> cm <sup>-1</sup>	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
Nondeuterated compound <i>III</i>					
1 477.5	2	-0.1	sh	disappearance	$\delta(\text{NH})$ assoc.
1 472.9 <sup>f</sup>	1	—	s	—	$\delta(\text{CH})$
1 455.8	1	-1.3	m	—	$\delta(\text{CH})$
1 449.5	1	-0.5	s	—	$\delta(\text{CH})$
1 425.0	5	+9	s	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{NH})$ free
1 394.1	2	+1.3	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 344.1	1	+1	s	—	$\delta(\text{CH})$
1 336.5	6	-1.5	w	decrease	$\delta(\text{CH})$ , skeletal
1 324.5	2	-1.1	(w)	disappearance	$\delta(\text{NH})$ assoc.
1 287.0	2	—	(w)	disappearance	$\delta(\text{NH})$ assoc.
1 280.5	1	—	vw	—	$\delta(\text{CH})$ , skeletal
1 274.1	1	-2.4	s	—	$\delta(\text{CH})$ , skeletal
1 226.6	6	-0.5	m	—	$\delta(\text{CH})$ , skeletal
N-Deuterated compound <i>IV</i>					
1 471.0	1	+0.9	s	—	$\delta(\text{CH})$
1 455.8	1	-1.8	m	—	$\delta(\text{CH})$
1 451.2	1	-1.2	m	—	$\delta(\text{CH})$
1 429.5		—	m	decrease	
1 411.2		+10.8	s	increase	$\nu(\text{C}'\text{N})$ free
1 404.4		+5.6	sh	increase	$\nu(\text{C}'\text{N})$ free
1 344.0	1	+1.0	s	—	$\delta(\text{CH})$
1 330.6	1	+0.8	m	—	$\delta(\text{CH})$ , skeletal
1 282.0	1	0	sh	—	$\delta(\text{CH})$ , skeletal
1 276.2	1	-0.2	s	—	$\delta(\text{CH})$ , skeletal
1 235.2	6	+0.8	m	—	$\delta(\text{CH})$ , skeletal

<sup>a-e</sup> See Table II. <sup>f</sup> In bromoform because of band overlap in tetrachloroethylene.

Bands of the type 4 can be attributed to associated molecules, since with decreasing association of the lactam molecules their intensity decreases and finally they disappear completely. They are usually slightly shifted to higher wavenumbers

on transfer from a non-polar to a polar solvent. We assume therefore, that the  $\nu(\text{C}'\text{—N})$  vibration mode of the associated molecule contributes only little (when compared with type 5) to the character of the given band. Bending vibrations of the

TABLE IV

Wavenumbers of Absorption Bands in 4-Azatricyclo[4,3,1,0<sup>3,7</sup>]decan-5-one (*V*) Spectra in the Region 1500—1200  $\text{cm}^{-1}$  in Tetrachloroethylene

Concentration of the compound *V*: in tetrachloroethylene 0.25M and 0.05M (temperature dependence), in tetrachloromethane 0.006M, in bromoform 0.7M and 0.5M (temperature dependence); concentration of the compound *VI*: in tetrachloroethylene saturated solution (temperature dependence), in bromoform 0.4M (temperature dependence) and 0.05M.

Wavenumber <sup>a</sup> $\text{cm}^{-1}$	Band type	Solvent shift <sup>b</sup> $\text{cm}^{-1}$	Intensity <sup>c</sup>	Change with decrease in in association <sup>d</sup>	Approximate assignment <sup>e</sup>
Nondeuterated compound <i>V</i>					
1 483.2 <sup>f</sup>	3	—	vw	increase	$\delta(\text{NH})$ free
1 472.1	1	— 2.0	m	—	$\delta(\text{CH})$
1 456.2	1	— 2.0	s	—	$\delta(\text{CH})$
1 446.9	1	— 2.0	m	—	$\delta(\text{CH})$
1 430.0	2	— 4.0	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 397.0	5	+ 9.5	s	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{NH})$ free
1 368.0	2	+ 1.0	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 359.0	1	+ 0.6	m	—	$\delta(\text{CH})$
1 345.0	1	+ 1.0	m	—	$\delta(\text{CH})$
1 339.5	2	— 0.9	(w)	disappearance	$\delta(\text{NH})$ assoc.
1 332.2	3	+ 1.1	w	increase	$\delta(\text{NH})$ free
1 315.0	1	+ 1.0	sh	—	$\delta(\text{CH})$
1 310.3	1	— 0.6	m	—	$\delta(\text{CH})$
1 302.0	2	— 1.0	(s)	disappearance	$\delta(\text{NH})$ assoc.
1 299.0	1	— 1.0	s	—	$\delta(\text{CH})$ , skeletal
1 279.5	1	— 1.0	vw	—	$\delta(\text{CH})$ , skeletal
1 259.0	2	— 0.2	m	disappearance	$\delta(\text{NH})$ assoc.
1 251.0	5	+ 4.6	m	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$
1 224.7	2	— 2.1	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 216.3	5	+ 4.3	s	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$
1 205.0	1	—	sh	—	$\delta(\text{CH})$ , skeletal
N-Deuterated compound <i>VI</i>					
1 470.2	1	— 0.2	m	—	$\delta(\text{CH})$
1 455.0	1	— 0.6	s	—	$\delta(\text{CH})$
1 446.0	1	— 0.9	m	—	$\delta(\text{CH})$



TABLE IV  
(Continued)

Wavenumber <sup>a</sup> cm <sup>-1</sup>	Band type	Solvent shift <sup>b</sup> cm <sup>-1</sup>	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
1 441.2	1	+ 0.1	vw	—	$\delta(\text{CH})$
1 393.0		+ 8.2	(m)	disappearance	$\nu(\text{C}'\text{N})$ assoc.
1 375.2		+ 12.6	s	increase	$\nu(\text{C}'\text{N})$ free
1 360.0		—	m	—	$\delta(\text{CH})$
1 347.4	1	—		—	$\delta(\text{CH})$
1 342.0	1	—	sh	—	$\delta(\text{CH})$
1 315.2	1	+ 0.7	sh	—	$\delta(\text{CH})$
1 309.2	1	+ 0.4	m	—	$\delta(\text{CH})$
1 297.0	1	+ 0.2	w	—	$\delta(\text{CH})$ , skeletal
1 281.2	1	+ 1.1	vw	—	
1 266.0		—	sh	decrease	<sup>g</sup>
1 260.6		+ 4.1	w	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$
1 217.0		+ 8.2	s	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$
1 205.5	1	—	w	—	$\delta(\text{CH})$ , skeletal

<sup>a-e</sup> See Table II. <sup>f</sup> Measurable only in bromoform where a weak association exists. <sup>g</sup> Belongs to a not identified vibration of an associated molecule.

N—H bonds, engaged in cyclic dimers, contribute also a little, as inferred from the small shift of these bands to lower wavenumbers on deuteration. Finally, another vibrations evidently also contribute, but these cannot be identified by the method employed. The number of these bands in the spectra was smaller than the number of the bands of the type 5.

Bands of the type 5 are due to nonassociated molecules. Their intensity increases with decreasing association and in the spectra of completely associated lactams they are not detected at all. Since on deuteration these bands behave similarly to the bands of the type 4, we assume also a small contribution of the free N—H group vibration to the character of these bands. On transfer to a polar solvent, the shift of the bands of the type 5 is usually much greater than that observed for the bands of the type 4. The C'—N stretching vibration contributes thus much more to the bands of the type 5.

Finally, the spectra of the studied lactams contain bands which exhibit small intensity changes with change in association and at the same time small shifts on deuteration. We rank with them also bands which display a solvent shift smaller than 3 cm<sup>-1</sup>. We assume that vibration modes of the carbon skeleton and of the amide

group contribute to an equal extent to these bands. These bands are observed below  $1300\text{ cm}^{-1}$  in the spectra of 2-pyrrolidone (I) as well as other studied lactams.

TABLE V

Wavenumbers of Absorption Bands in the Spectra of 4-Azatricyclo[4,4,0,0<sup>3,8</sup>]decan-5-one (VII) and Its Derivatives VIII and IX

Concentration of VII: in tetrachloroethylene saturated solution (temperature dependence), in bromoform 0.8M, 0.5M (temperature dependence) and 0.05M (temperature dependence), in tetrachloromethane 0.006M. Concentration of VIII: in tetrachloroethylene 0.05M (temperature dependence), in bromoform 0.05M (temperature dependence), in deuteriochloroform 0.5M. Concentration of IX: in tetrachloromethane and in chloroform 0.2M.

Wavenumber <sup>a</sup> cm <sup>-1</sup>	Band type	Solvent shift <sup>b</sup> cm <sup>-1</sup>	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
Nondeuterated compound VII					
1 484.6	1	- 0.6	m	—	$\delta(\text{CH})$
1 469.6	1	- 0.2	m	—	$\delta(\text{CH})$
1 456.3	1	- 1.3	vw	—	$\delta(\text{CH})$
1 450.8	1	- 0.7	m	—	$\delta(\text{CH})$
1 441.5	2	- 1.7	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 404.6	5	+13.2	s	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{NH})$
1 381.8	2	+ 3.0	(m)	disappearance	$\delta(\text{NH})$ assoc.
1 372.7	2	+ 0.5	(w)	disappearance	$\delta(\text{NH})$ assoc.
1 346.0	f	+11.0	vw	slight increase	combination
1 337.6	3	- 0.2	w	increase	$\delta(\text{NH})$ free
1 334.4	1	- 1.6	m	—	$\delta(\text{CH})$ , skeletal
1 323.3	1	- 1.3	m	—	$\delta(\text{CH})$ , skeletal
1 305.9	1	0	m	—	$\delta(\text{CH})$ , skeletal
1 300.0	g	- 1.0	vw	disappearance	
1 290.0	1	+ 1.2	m	—	$\delta(\text{CH})$ , skeletal
1 287.0	1	0	m	—	$\delta(\text{CH})$ , skeletal
1 265.0	1	- 3.0	vw	—	$\delta(\text{CH})$ , skeletal
1 256.2	2	—	(w)	disappearance	$\delta(\text{NH})$ assoc.
1 250.8	5	+ 6.0	m	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$ , skeletal
1 227.0	1	- 4.0	m	—	$\delta(\text{CH})$ , skeletal
1 207.8	1	- 1.3	vw	—	$\delta(\text{CH})$ , skeletal
N-Deuterated compound VIII					
1 484.9	1	1.0	m	—	$\delta(\text{CH})$
1 467.5	1	1.2	m	—	$\delta(\text{CH})$
1 454.4	1	- 1.4	vw	—	$\delta(\text{CH})$
1 450.7	1	- 0.9	m	—	$\delta(\text{CH})$

TABLE V  
(Continued)

Wavenumber <sup>a</sup> cm <sup>-1</sup>	Band type	Solvent shift <sup>b</sup> c <sup>-1</sup>	Intensity <sup>c</sup>	Change with decrease in association <sup>d</sup>	Approximate assignment <sup>e</sup>
1 404.4		+ 8.3	s	decrease	$\nu(\text{C}'\text{N})$ assoc.
1 381.0		+ 14.0	s	increase	$\nu(\text{C}'\text{N})$ free
1 334.4	1	- 1.3	m	—	$\delta(\text{CH})$ , skeletal
1 326.5	1	- 0.9	m	—	$\delta(\text{CH})$ , skeletal
1 306.1	1	—	m	—	$\delta(\text{CH})$ , skeletal
1 299.0	<sup>g</sup>	- 1.0	vw	disappearance	
1 291.1	1	- 0.9	m	—	$\delta(\text{CH})$ , skeletal
1 286.3	1	- 2.1	m	—	$\delta(\text{CH})$ , skeletal
1 262.0	1	—	vw	—	$\delta(\text{CH})$ , skeletal
1 257.5		+ 3.6	m	increase	$\nu(\text{C}'\text{N})$ , $\delta(\text{CH})$ , skeletal
1 227.5	1	0.1	m	—	$\delta(\text{CH})$ , skeletal
1 211.1	1	—	w	—	$\delta(\text{CH})$ , skeletal

## N-Methyl derivative IX

1 483.8		+ 1.8	m		$\delta(\text{CH})$
1 468.0		+ 1.2	m		$\delta(\text{CH})$
1 454.2		+ 1.0	w		$\delta(\text{CH})$
1 450.1		+ 0.3	w		$\delta(\text{CH})$
1 428.0		+ 8.6	s		$\nu(\text{C}'\text{N})$
1 391.9		+ 5.7	s		$\delta(\text{CH}_3)$ , $\nu(\text{C}'\text{N})$
1 337.5		+ 1.6	vw		—
1 334.4		+ 0.2	w		—
1 328.0		0	w		—
1 306.4		0	w		—
1 299.0		+ 0.4	vw		—
1 288.1		+ 1.4	m		—
1 265.9		- 0.9	w		—
1 227.0		—	m		—
1 208.0		—	w		—

<sup>a-e</sup> See Table II. <sup>f</sup> Probably the same band type as described in Table II, note <sup>g</sup> for 2-pyrrolidone (the band was detected in 0.05M tetrachloromethane solution in a 1 cm cell). <sup>g</sup> The band can be due to an overtone of some of the bending vibrations of the associated carbonyl group.

Spectra of 2-Pyrrolidone (I) in the Region 820–460 cm<sup>-1</sup>

The spectrum of 2-pyrrolidone (I) exhibits also a very weak band at 1339.0 cm<sup>-1</sup> (Table II) the intensity of which increases with decreasing molecular association. This band was not detected in the spectrum of strongly associated molecules<sup>14</sup> and it disappears completely on deuteration. In order to clarify its character we measured the spectra of 2-pyrrolidone (I) in the region 820–460 cm<sup>-1</sup> in various solvents which are sufficiently transparent in this region (Table I).

The bands ascribed by Rey-Lafon and coworkers<sup>14</sup> to the C=O bending vibrations were not solvent-sensitive. The spectrum of the liquid compound exhibited a medium band at 540 cm<sup>-1</sup>. Intensity of this band was strongly reduced in a saturated solution and its maximum was shifted by 2.5 cm<sup>-1</sup> to lower wavenumbers. Rey-Lafon<sup>14</sup> assigned this band to a skeletal vibration R<sub>7</sub> with a small contribution of the N—H bending vibration. Also the out-of-plane vibration of the N—H bond engaged in an oligomeric associate, assumed to exist in the liquid state<sup>14</sup>, contributes

TABLE VI

Wavenumbers of Carbonyl Bands (in cm<sup>-1</sup>) in the Spectra of Lactams I–IX

Concentration of the secondary lactams in tetrachloromethane was 4–6 · 10<sup>-4</sup> M, in chloroform 5 · 10<sup>-3</sup> M; in both cases the measured lactams were nonassociated. The concentration of the lactam IX in both solvents was 0.06 M.

Lactam	Solvent	$\nu(\text{CO})$ non-deuterated	$\nu(\text{CO})$ deuterated	$\Delta\nu^{a,b}$
I	CCl <sub>4</sub>	1 717.3, 1 713.0 sh	1 715.8	-1.6
	CHCl <sub>3</sub>	1 701.2, 1 693.6 <sup>c</sup>	1 691.1 <sup>c</sup>	-2.5
III	CCl <sub>4</sub>	1 698.2, 1 685.0 sh	1 696.1, 1 673.0 <sup>e</sup>	+1.3, -1.2
	CHCl <sub>3</sub>	1 682.5 <sup>f</sup> , 1 669.2	1 681.2 <sup>d</sup> , 1 667.6 <sup>f</sup>	-1.3, -1.6
V	CCl <sub>4</sub>	1 720.8, 1 736.3 sh 1 703.2 sh	1 721.5, 1 735.0 sh 1 697.0 sh	+0.7, -1.3
	CHCl <sub>3</sub>	1 700.0, 1 716.0 sh	1 696.8, 1 716.7 <sup>d</sup>	-3.2, +0.7
VII	CCl <sub>4</sub>	1 702.0, 1 716.8 <sup>c</sup>	1 702.5, 1 716.8 <sup>c</sup>	+0.5, 0
	CHCl <sub>3</sub>	1 687.0, 1 675.5 <sup>g</sup>	1 686.1 <sup>d</sup> , 1 678.1 <sup>g</sup>	-0.9, +2.6
IX	CCl <sub>4</sub>	1 682.5	—	—
	CHCl <sub>3</sub>	1 661.1	—	—

<sup>a</sup> See Table II. <sup>b</sup>  $\Delta\nu$  is the difference between wavenumbers of the bands of nondeuterated and deuterated compounds (in cm<sup>-1</sup>). <sup>c</sup> Two strongly overlapping maxima of the same intensity. <sup>d</sup> In deuteriochloroform. <sup>e</sup> Side-band maximum. <sup>f</sup> More intensive. <sup>g</sup> Separated bands of the same intensity.

obviously to the character of this band (the same holds probably for the band at  $478.6\text{ cm}^{-1}$  which was found in the spectrum of the liquid compound; this band disappears on transfer to a concentrated solution where dimeric associates predominate). With a further concentration decrease, the intensity of the band at  $538\text{ cm}^{-1}$  remains very low, whereas the intensity of the previously not detected<sup>14</sup> neighbouring band at  $562\text{ cm}^{-1}$  (in carbon disulphide) increases. Replacement of carbon disulphide by a polar solvent results in a shift  $13\text{--}16\text{ cm}^{-1}$  to higher wavenumbers. Our measurements suggest that this band can be attributed to nonassociated molecules and we assume that it belongs to a vibration, to which the torsional motion about the C—N amide bond predominantly contributes.

Combination vibration of this and the out-of-plane bending vibration of the N—H bond could manifest itself in the above-mentioned band at  $1339.0\text{ cm}^{-1}$ . A band of the same properties was found also in the spectrum of the compound *VII* in tetrachloromethane (Table V); it can be interpreted analogously.

#### *The Region of Wavenumbers 1800—1500 cm<sup>-1</sup>*

The C=O stretching vibration bands in this region are usually accompanied by shoulders or side-bands. Since all the compounds were measured at concentrations excluding any intermolecular association, all the bands must be due to nonassociated carbonyl groups. The only likely explanation of the band multiplicity in this structural type is Fermi resonance which more or less deforms the shape of the band by bringing apart the bands of the interacting vibrations. If we consider from this point of view the values given in Table VI, we see that the  $\nu(\text{C}=\text{O})$  maximum in the compound *I* is shifted to higher wavenumbers as compared with the compound *V*. This may be caused by a different internal bond angle of the carbonyl group and probably also by a small non-planarity of the amide group (*cf.* the behaviour of the  $\nu(\text{N—H})$  band).

In comparison with the compounds *I* and *V*, the compounds *III* and *VII*, in which the amide group is part of a six-membered ring, exhibit the  $\nu(\text{C}=\text{O})$  bands at lower wavenumbers, mainly as the result of a different bond angle of the carbonyl group. In the compound with the non-planar amide group the wavenumber of the carbonyl band is higher (*cf.* the lactam *III vs VII*). The unperturbed wavenumber lies between the values given in the Table. The same situation is found in the case of the deuterated lactams *IV* and *VII*; deuteration of the N—H bond is not accompanied by a shift of the band  $\nu(\text{C}=\text{O})$ . As common for tertiary amides, the  $\nu(\text{C}=\text{O})$  band in the spectrum of *IX* lies at lower wavenumbers than the corresponding bands in secondary amides.

### Region of N—H Stretching Vibrations

The wavenumbers of stretching vibrations of the free and associated N—H groups are given in Table VII. The wavenumber of  $\nu(\text{N—H})$  in the polycyclic compound *V* is lower than that in the compound *I*. If we compare the value of  $\nu(\text{N—H})$  in the nonassociated compound *III* with the value of  $\nu(\text{N—H})$  in the compound *VII* under the same conditions, we see that the latter compound absorbs at  $18\text{ cm}^{-1}$  lower. This fact is in agreement with the considerable non-planarity of the amide group in the compound *VII*, proved by X-ray diffraction.

TABLE VII

Wavenumbers (in  $\text{cm}^{-1}$ ) of the N—H Stretching Vibrations in the Lactams *I*, *III*, *V* and *VII* in Tetrachloromethane

Lactam	$\nu(\text{N—H})$ free <sup>a</sup>		$\nu(\text{N—H})$ assoc.			
<i>I</i> <sup>b</sup>	3 455	3 360 sh	3 210 s	3 130 vw	3 110 m	—
<i>III</i> <sup>c</sup>	3 440.0	3 310 sh	3 190 s	3 120 w	3 090 m	3 040 w
<i>V</i> <sup>c</sup>	3 440.6	3 330 sh	3 225 s	—	3 100 sh	3 080 m
<i>VII</i> <sup>b</sup>	3 421.8	3 330 sh	3 210 s	—	3 085 m	—

<sup>a</sup> Measured on a Perkin-Elmer model 621 instrument with a precision  $\pm 1\text{ cm}^{-1}$ . <sup>b</sup> The region of  $\nu(\text{N—H})$  assoc. was measured in tetrachloromethane on a Perkin-Elmer 621 instrument with a precision  $\pm 5\text{ cm}^{-1}$ . <sup>c</sup> The region of  $\nu(\text{N—H})$  assoc. was measured in chloroform on a UR-10 Zeiss Jena instrument, accuracy  $\pm 5\text{ cm}^{-1}$ .

### Structural Aspects

Inspection of the data in Tables II—V, particularly of the magnitude of the solvent shifts, reveals that a change from associated to nonassociated state is accompanied by a change in the band character. In associated compounds,  $\nu(\text{C'—N})$  evidently contributes to a far greater number of bands than in nonassociated compounds. Contribution of the N—H bending vibration to the particular band in associated or nonassociated molecule is in the first approximation expressed by magnitude of the shift caused by deuteration. Deuteration also alters the character of the bands discussed. From the point of view of the contribution of  $\nu(\text{C'—N})$ , this change is most profound in 2-pyrrolidone (*I* vs *II*, Table II) where the bands with a greater contribution of  $\nu(\text{C'—N})$  can be detected only in the deuterated compound. In conformationally rigid compounds the difference in solvent shifts between nondeuterated and deuterated specimen is small and only in this case we may therefore speak about the band shift, resulting from deuteration.

In the spectrum of the tertiary amide *IX* the  $\nu(\text{C}'\text{—N})$  vibration contributes to two bands (Table V), this contribution being smaller to the band at  $1391.9\text{ cm}^{-1}$  which is usually interpreted as symmetrical bending vibration of the N-methyl group.

The study of deuterated compounds represents thus the most suitable approach for the comparison of the  $\nu(\text{C}'\text{—N})$  vibrations in secondary *cis*-amides. Since the wavenumbers of these bands are conformation-dependent, the conclusions about the properties of the  $\text{C}'\text{—N}$  bond must be based on models which are as similar as possible to the studied type. In such series the wavenumber of the  $\nu(\text{C}'\text{—N})$  band decreases<sup>6</sup> with increasing non-planarity of the amide group.

All the important spectroscopic parameters, *i.e.*  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{N—H})$  and  $\nu(\text{C}'\text{—N})$ , observed in the spectrum of the lactam *VII* with a non-planar amide group, differ from the values for a planar amide group in a six-membered ring. These differences are in the direction which can be expected as the result of a non-planar arrangement of the Pauling's resonance hybrid. However, it is necessary to consider also other geometric parameters. The exact geometry of the molecule is known as yet only for the lactam *VII* (ref.<sup>13</sup>). The observed values (Table VIII) differ substantially

TABLE VIII

Comparison of Geometric Parameters of *cis*-Amide Group in the Lactam *VII* with the Corresponding Parameters in Lactams Containing Virtually Planar Amide Groups in Five-membered and Six-membered Ring

Parameter <sup>a</sup>	Lactam <i>VII</i> (ref. <sup>13</sup> )	Five-membered <sup>b</sup>	"Standard" <sup>c</sup>
$\text{C}_{(5)}\text{—N}_{(4)}$ <sup>d</sup>	1.341 Å	1.35 Å	1.329 Å
$\text{C}_{(5)}\text{—O}$ <sup>d</sup>	1.237 Å	1.24 Å	1.244 Å
$\text{C}_{(6)}\text{—C}_{(5)}\text{—N}_{(4)}$ <sup>e</sup>	110.4°	110°	118°
$\text{C}_{(5)}\text{—N}_{(4)}\text{—C}_{(3)}$ <sup>e</sup>	115.2°	114°	126°
$\text{C}_{(6)}\text{—C}_{(5)}\cdots\text{N}_{(4)}\text{—C}_{(3)}$ <sup>f</sup>	14.49° (0.33)	3° <sup>g</sup>	—
$\text{C}_{(6)}\text{—C}_{(5)}\cdots\text{N}_{(4)}\text{—H}$ <sup>f</sup>	— 179.4° (2.47)	—	—
$\text{O—C}_{(5)}\cdots\text{N}_{(4)}\text{—H}$ <sup>f</sup>	— 4.43° (2.50)	—	—
$\text{O—C}_{(5)}\cdots\text{N}_{(4)}\text{—C}_{(3)}$ <sup>f</sup>	— 170.53° (2.27)	—	—

<sup>a</sup> Numbering of atoms according to the formula 4-azatricyclo[4,4,0,0<sup>3,8</sup>]decan-5-one (*VII*), in other lactams the data relate to the analogous atoms of the amide groups. <sup>b</sup> For 5-iodomethyl-2-pyrrolidone<sup>17</sup>. <sup>c</sup> "Standard" values<sup>18</sup>. <sup>d</sup> Bond length; <sup>e</sup> Bond angle in degrees. <sup>f</sup> Torsion angle about the central bond in degrees (in parentheses experimental error). <sup>g</sup> Estimated graphically using data from ref.<sup>17</sup>.

from the data given by Ramachandran and Sasisekharan<sup>18</sup> for a "standard" amide group and also from the parameters of a lactam group in a six-membered (3-chloro-2-piperidone<sup>19</sup>) or seven-membered (7-heptanelactam<sup>20</sup>) ring with presumably non-deformed *cis*-amide group in an unstrained system. On the other hand, the bond angles and bond lengths in the lactam *VII* are surprisingly similar to the values for the five-membered lactam ring in 5-iodomethyl-2-pyrrolidone<sup>17</sup>. The spectroscopic parameters are undoubtedly affected also by these changes. From the comparison, however, it follows that this cannot be the only influence and that this influence probably is not the decisive one. The values of internal bond angles correspond neither to the wavenumbers of  $\nu(\text{C}=\text{O})$  bands, which vary only slightly, nor to the wavenumbers of  $\nu(\text{N}-\text{H})$  free bands where significant changes are observed. In the latter case, it is possible on the basis of our previous studies<sup>7,12</sup> to exclude also a decisive influence of the partial conformation about the  $\text{NH}-\text{CH}$  bond. We are of the opinion that non-planarity remains the only decisive factor. This is particularly marked in the case of the  $\nu(\text{C}'-\text{N})$  vibration in deuterated compounds. We can justifiably assume that in the model compounds *II*, *IV* and *VI* the amide group is virtually planar. The difference between the wavenumbers of  $\nu(\text{C}'-\text{N})$  vibrations in the compounds *II* ( $1393.0\text{ cm}^{-1}$ ) and *VI* ( $1375.2\text{ cm}^{-1}$ ) is only slightly greater than half of the analogous difference between the values for *IV* ( $1411.2\text{ cm}^{-1}$ ) and *VIII* ( $1381.0\text{ cm}^{-1}$ ). This substantially greater difference in the latter pair of compounds should therefore be ascribed to the non-planarity of the amide group. The contribution of particular factors can of course be discussed in more detail only after the exact geometry of the compounds *III* and *V* will be known.

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