AMINO ACIDS AND PEPTIDES. CXI.*

CONFORMATIONAL DEPENDENCE OF THE STRETCHING VIBRATION OF THE N—H BOND IN *trans*-AMIDES

J.SMOLÍKOVÁ, A.VÍTEK and K.BLÁHA

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 6

Received April 21st, 1972

The infrared spectra of 17 secondary amides (mostly derived from acetic acid) with various primary, secondary, and tertiary alkyls on the nitrogen atom were measured. In the nonassociated state there were at least two absorption bands $\nu(N—H)_{trans}$ for each substance. They were assigned to various conformations in terms of rotation about the N—C bond. For individual partial conformations, ranges of wavenumbers which are characteristic in the infrared spectra are presented.

For the stretching vibrations of N—H bonds of lactams in the nonassociated state several infrared spectral bands were found, both in *cis* and *trans* amide groups. These bands are attributed to stretching vibrations of N—H bonds in various lactam conformations. Luck[1], who investigated stretching vibrations of nonassociated N—H bonds in the region of the second harmonic frequency in lactams with various ring sizes, assigned the observed bands to two conformations, one with N—H bond oriented to the inside of the ring and the second oriented out. He did not state, however, which band belonged to which conformation. This concept was taken over by other authors[2]. On the other hand, in acyclic aliphatic secondary amides $R^1—CONH—R^2$, where one could assume several conformations, there is no reference in the literature to the presence of several bands $\nu(N—H)_{free}$ for the same amide — this despite the fact that attention was given to the effect of the structure of the substituents attached to the amide group[3–7].

From this data it would appear that the wavenumbers of stretching vibrations of N—H in amides basically do not depend on the structure of the alkyl bound to the carbonyl carbon atom, provided the molecule does not involve a highly bulky tertiary alkyl. On the other hand the wavenumber of $\nu(N—H)_{free}$ is very sensitive to a change of substituent in close proximity to the N—H bond, *i.e.* to the structure of the alkyl bound in the secondary amide on the nitrogen atom. The wavenumber of stretching vibration of N—H bond remains practically the same in a number of homologous N-n-alkylamides[5], but decreases with increasing effective steric volume of the alkyl, *i.e.* with branching at C_α. This shift to lower wavenumbers can result from a mass effect, from a bond extension due to proximity of sterically highly branched alkyls[3],

* Part CX: This Journal *38*, 532 (1973).

from electronic effects of alkyls (improbable) and finally from a changed spatial orientation of bonds on C_α in relation to N—H. The latter possibility has already been discussed in the literature[8], but in terms of a single conformation per substance. Since there can co-exist several energetically similar conformations, differing in the dihedral angle at C_α—N as known in peptides[9,10], one should expect for each secondary amide an equilibrium between several conformers. These conformers should be manifest in the infrared spectrum by individual bands for the stretching vibrations of nonassociated N—H bonds. If no other steric effect comes to bear, the wavenumber should have a more or less constant relation to the given local conformation for all substances with the same partial conformation. This would offer a new possibility of utilising infrared spectroscopy for the study of spatial arrangements of substances containing an amide (peptide) bond. This approach could be also used to obtain data for more detailed studies of the relationships of PMR coupling constants between protons on the N atom and on the C_α atom, a problem which requires further examination[11–13]. We therefore studied the infrared spectra of a number of secondary amides. An attempt was made to correlate wavenumber values of ν(N—H) in *trans*-amide bonds with individual partial conformations and to assign certain wavenumber ranges to a given partial conformation. This goal governed the selection of the substances measured; the series includes substances which are able to adopt all probable partial conformations.

EXPERIMENTAL

Melting points were determined on a Koffler block and are not corrected.

Materials

The substances used were synthesized according to published procedures. Acetyl derivatives were in general synthesized by using acetanhydride in acetic acid to react with the appropriate amine. The purity of the substances used was checked by gas chromatography and mass spectrometry. Melting points, or in the case of liquids boiling points, all agreed with published data: N-Methylhexadecanamide[14], m.p. 86°C; N-ethylhexanamide[15], b.p. 126–127°C/7 Torr; N-ethyloctadecanamide[16], m.p. 78°C; N-propylacetamide[17], b.p. 114–116°C/13 Torr; N-isopropylacetamide[17], b.p. 102–104°C/14 Torr; N-butylacetamide[17], b.p. 120°C/12 Torr; N-isobutylacetamide[17], b.p. 116°C/13 Torr; N-dodecylacetamide[18], m.p. 56°C; N-octadecyloctadecanamide[19], m.p. 95–96°C; N-cyclopentylacetamide[20], b.p. 146–149°C/22 Torr; N-cyclohexylacetamide[20], m.p. 107–109°C; N-(*trans*-4-tert-butylcyclohexyl)acetamide[21], m.p. 117–118°C; N-(*cis*-4-tert-butylcyclohexyl)acetamide[21], m.p. 170–171°C; N-adamantylacetamide[22], m.p. 149–150°C. N-(1-*Methyl*-1-*dodecyl*)*acetamide*: A mixture of 2-aminotridecane (0·16 g), acetic acid (20 ml) and acetanhydride (1·5 ml) was refluxed for 3 h, evaporated, water was added and again evaporated. The remainder was crystallised from a mixture of methanol and water with a yield of 0·17 g, m.p. 65–66°C. For $C_{15}H_{31}NO$ (241·4) calculated: 74·63% C, 12·94% H, 5·80% N; found: 75·24% C, 13·20% H, 6·08% N.

TABLE I

Spectroscopic Parameters of Bands of $\nu(N—H)_{free}$ and Percentage (% B) of Partial Conformations (in brackets standard deviation 1σ)

Measured in tetrachloromethane, concentration 0·0005M, 10 cm cells.

No	Compound	$\nu(N—H)^a$	$\Delta\nu_{1/2}{}^b$	$\varepsilon^a_{max}{}^c$	B^d	% B^e	Conformation
1	N-methylacetamide	3 476·1[f]	—	—	—	—	*A*
		3 433·0[f]	—	—	—	—	*cis*
2	N-methylhexadecanamide	3 472·9[f]	—	—	—	—	*A*
		3 431·9[f]	—	—	—	—	*cis*
3	N-ethylacetamide	3 465·1 (1·5)	10·5	16·7	275	13 (5)	*C*
		3 460·0 (0·3)	17·0	67·1	1 790	84 (5)	*D*
		3 413·5 (1·3)	22·7	2·1	90	3 (0·8)	*cis*
4	N-ethylhexanamide	3 463·2 (0·3)	13·4	30·7	650	29 (3)	*C*
		3 457·0 (0·2)	15·6	63·8	1 560	69 (3)	*D*
		3 408·6 (1·0)	18·4	1·4	40	2 (0·3)	*cis*
5	N-ethyloctadecanamide	3 464·1 (0·3)	12·9	24·4	495	20 (3)	*C*
		3 457·4 (0·2)	15·6	77·3	1 895	78 (3)	*D*
		3 408·6 (1·0)	14·9	1·6	38	2 (0·3)	*cis*
6	N-propylacetamide	3 468·9 (0·2)	11·0	24·3	420	19 (2)	*C*
		3 459·9 (0·2)	17·2	64·6	1 745	79 (2)	*D*
		3 412·4 (1·0)	17·6	1·9	50	2 (0·5)	*cis*
7	N-butylacetamide	3 469·2 (1·0)	11·0	25·6	445	19 (1)	*C*
		3 459·4 (0·1)	17·3	65·6	1 780	75 (1)	*D*
		3 412·0 (0·2)	29·0	3·4	150	6 (1)	*cis*
8	N-isobutylacetamide	3 469·6 (0·1)	10·6	46·2	770	33 (1)	*C*
		3 459·6 (0·2)	18·2	54·4	1 580	67 (1)	*D*
		3 422[f,g]	—	—	—	—	*cis*
9	N-dodecylacetamide	3 468·0 (0·1)	11·6	32·2	585	27 (1)	*C*
		3 458·1 (0·1)	15·8	61·4	1 525	70 (1)	*D*
		3 412·2 (1·3)	20·7	1·7	55	3 (0·5)	*cis*
10	N-octadecyloctadecanamide[h]	3 465·3 (0·2)	14·3	—	—	38 (2)	*C*
		3 455·3 (0·1)	15·2	—	—	62 (2)	*D*
11	N-isopropylacetamide	3 449·6 (0·1)	11·4	67·6	1 210	66 (6)	*E*
		3 444·7 (0·9)	18·3	20·1	580	32 (6)	*T*
		3 399·3 (1·0)	18·9	1·5	40	2 (0·4)	*cis*
12	N-(1-methyl-1-dodecyl)acetamide	3 446·2 (0·1)	16·7	80·7	2 115	96 (1)	*E*
		3 392·1 (1·5)	20·5	2·9	95	4 (1)	*cis*
13	N-cyclopentylacetamide	3 451·2 (0·1)	11·8	85·8	1 585	84 (2)	*E*
		3 439·6 (0·1)	22·2	8·2	290	15 (1)	*T*
		3 402·5 (1·6)	8·2	1	15	1 (1)	*cis*

TABLE I (*Continued*)

No	Compound	ν(N—H)[a]	$\Delta\nu_{1/2}$[b]	ε^{a}_{max}[c]	B[d]	% B[e]	Conformation
14	N-cyclohexylacetamide	3 459·0 (0·1)	8·3	9·1	120	6 (1)	*E* axial
		3 447·5 (0·1)	11·4	91·3	1 630	84 (2)	*E* equatorial
		3 440·8 (0·5)	13·4	7·9	170	9 (1)	*T*
		3 399·9 (0·6)	10·9	1	20	1 (0·1)	*cis*
15	N-(*trans*-4-tert-butylcyclohexyl)acetamide	3 447·8 (0·1)	10·1	87·0	1 380	77 (3)	*E* equatorial
		3 441·3 (0·7)	16·2	15·3	390	22 (4)	*T*
		3 399·6 (1·1)	14·1	1·3	30	2 (0·4)	*cis*
16	N-(*cis*-4-tert-butylcyclohexyl)acetamide	3 456·9 (0·1)	11·1	87·2	1 515	78 (3)	*E* axial
		3 448·2 (1·3)	17·3	9·0	250	13 (4)	*E*[i]
		3 410·7 (2·4)	39·4	2·9	170	9 (3)	*cis*
17	N-adamantylacetamide	3 441·0 (0·1)	8·7	80·8	1 110	70 (2)	*E*
		3 436·8 (0·1)	9·5	17·9	265	17 (1)	*T*
		3 422·7 (0·9)	13·6	9·6	205	13 (1)	*cis*

[a] The standard deviation does not involve the systematic measurement error (±0·5 cm); [b] half-width of the band in cm^{-1}; [c] in 1 mol^{-1} cm^{-1}; [d] integrated intensity in 1 mol^{-1} cm^{-2}; [e] percentage calculated from the integrated intensity; [f] wavenumber values read directly from the spectrum; [g] slight sign; [h] saturated solution; [i] probably a flexible conformation (see text).

Methods

Spectra were measured on a Perkin-Elmer model 621 instrument with precision ±0·5 cm^{-1}, calibrated with gaseous ammonia. Band separation was carried out numerically with an Elliott 503 computer using an Algol 503 Mk 1 programme. Measurements of concentration effects in a number of substances showed that at 0·0005M there is no intermolecular association in tetrachloromethane. Such solutions were therefore used for standard measurements (Table I). Infrasil cells with a 10 cm optical path length were used. Temperature effects were measured in cells with a thermocouple in a glass probe penetrating the cover, output to a Zeiss Jena model 1 galvanometer. The cells were surrounded by an electric heating element, had an optical path length 2 cm, and solutions in this case were in tetrachloroethylene. Deuteration was carried out with D_2O and repeated freeze drying, or by boiling. All manipulations with deuterated substances were carried out in a dry-box.

RESULTS AND DISCUSSIONS

Data from band separation in the spectra of 17 secondary amides in the 3200 to 3500 cm^{-1} region are presented in Table I. The spectra of some substances in the ν(NH) region are shown in Fig. 1. With the exception of N-methylamides (compounds *1* and *2*) the separation was satisfactory using bands of the Lorentz type. Compounds *1* and *2* in the 3440 – 3480 cm^{-1} region showed marked asymmetry

in the lower wavenumbers which could not be approximated in either doublet or triplet bands of the Lorentz type. With increased temperature the band maximum decreased and the asymmetry increased in the lower wavenumbers.

In order to assign the measured bands to stretching vibrations of nonassociated N—H bonds in various partial conformations, we have to exclude other factors which might influence the plurality of bands: *1.* To exclude intermolecular effects we measured spectra in such low concentration that wavenumbers, relative intensities and band shape were independent of concentration. *2.* A satisfactory explanation cannot involve Fermi resonance since deuteration of N-methyl- and N-butylacetamide

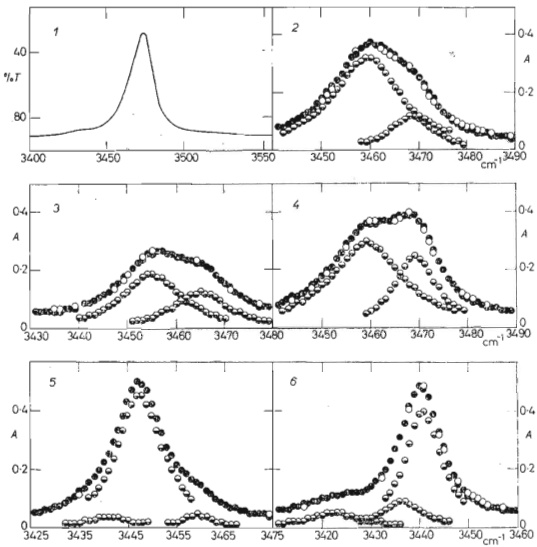


FIG. 1

Spectra of Some Amides

1 N-Methylacetamide, non-separated spectrum; *2* N-propylacetamide; *3* N-octadecyloctadecanamide; *4* N-isobutylacetamide; *5* N-cyclohexylacetamide; *6* N-adamantylacetamide *2*, *3*, *4*, *5*, *6* are spectra drawn directly by the computer.

● Points on the experimental curve; ○ points on the calculated envelope curve if they are not identical with points on the experimental curve; ◒ points of bands determined by separation. For conditions of measurement see Experimental.

did not change the number of the ν(N—H,D) bands; a shift to lower wavenumbers resulting from deuteration corresponds to the shift calculated for proton substitution by deuterium at the nitrogen atom and the difference between calculated and measured values of $\nu(N—D)_{free}$ are not different from those usually observed[23] (Table II). In addition, an increased temperature resulted in changes of intensity of some bands of free ν(N—H), *e.g.* N-butyl- and N-isobutylacetamide in Table III. This behaviour is not in agreement with that to be expected from Fermi resonance, but is typical for spectral changes in a mixture of conformers. *3.* The course of the temperature effect also negates the possibility of a solute–solvent complex. *4.* The most satisfactory explanation of band multiplicity of $\nu(N—H)_{free}$ would be conformational factors, *i.e.* multiplicity of bands corresponds to multiplicity of conformers in an equilibrium mixture.

TABLE II

Comparison of Wavenumbers (cm^{-1}) of Vibrations ν(N—H) and ν(N—D) in Representative Compounds

Measured in 0·004M concentration in tetrachloromethane; 1 cm-NaCl cells.

$\nu(N—H)_{exp}$	$\nu(N—D)_{exp}$	$\nu(N—D)_{calc}$	$\Delta\nu(N—D)$[a]	Assignment
		N-Butylacetamide[b]		
3 412·0	2 534·8	2 490·5	44·3	*cis*, free
3 459·4	2 565·3	2 525·1	40·2	*trans*, free
3 469·2	2 576·6	2 532·3	44·3	*trans*, free
3 360·0	2 479·1	2 452·7	26·6	bound[c]
		N-Methylacetamide[d]		
3 433·2	2 540·0	2 506·0	34·0	*cis*, free
3 475·5	2 578·8	2 536·6	41·9	*trans*, free
3 368·2	2 500	2 458·5	41·5	bound[c]

[a] Difference between measured (after separation) and calculated wavenumbers; [b] bands separated by means of a computer; [c] remnant of association bands; [d] wavenumber values read directly from the spectrum.

For rotation of substituents about the N—C_α bond in conformational analysis one most frequently uses the curve of potential energy with 6 minima[24]. This corresponds to the same number of partial conformations of N—H and C_α—H bonds. If we consider various substitutions at the C_α atom (in a series of substituents at the N atom: methyl, n-alkyl, sec-alkyl, tert-alkyl) all of the possible partial conformat-

ions are expressed in projectional formulae $A-F$ (Scheme 1). It cannot be excluded that this concept is an oversimplification, particularly for the peptide chain[9] *per se* where the final arrangement is the result of the combined effect of a large number of amide bonds. However, for compounds with a single amide bond, the simplification is justified. The wavenumbers of stretching vibrations of N—H bonds in partial conformation *A*, with a *syn*-periplanar arrangement of N—H and C_α—H bonds, is deduced from the spectrum of N-methylamide (Compounds *1* and *2*). Pullman and coworkers[25] determined by quantum chemical calculations that this conformation in N-methylacetamide is more stable (by 0·6 – 0·8 kcal mol^{-1}) than a *syn*-clinal arrangement (conformation *B*) which lies at maximum potential energy. The wavenumber of the absorption maximum, 3476·5 cm^{-1}, is therefore considered to be the wavenumber of most stable conformation *A*. Band asymmetry in the lower wavenumbers can be explained by a statistical representation of less stable conformations

TABLE III

Temperature Dependence of the Wavenumbers (cm^{-1}) of Stretching Vibrations of Free N—H Bonds in Tetrachloroethylene

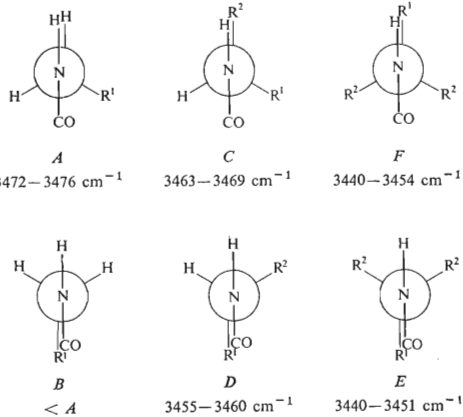
Values obtained by separation, concentration 0·0024M, 2 cm cells.

T °C	ν(N—H)	$\Delta\nu_{1/2}$ [a]	ε^a_{max}	% ε^a_{max} [b]	B [c]	% B [d]
			N-Isobutylacetamide			
36·2	3 468·4	10·9	49·2	45	845	34
	3 458·2	17·1	52·2	48	1 400	56
	3 419·4	18·8	2·6	2	78	3
	3 403·2	24·7	4·3	4	165	7
101·5	3 469·4	12·1	30·0	38	570	26
	3 459·4	20·5	44·0	56	1 420	64
	3 418·7	23·0	1·9	2	70	3
	3 402·7	33·7	3·0	4	160	7
			N-Butylacetamide			
37·3	3 467·8	10·9	26·6	26	455	17
	3 458·1	17·4	69·0	68	1 890	71
	3 407·4	37·8	5·5	5	330	12
99·5	3 468·7	11·9	14·3	19	270	12
	3 459·0	21·1	55·8	75	1 850	79
	3 410·1	31·7	4·24	6	210	9

[a] Half-width of band; [b] percentage of bands according to ε^a_{max}; [c] apparent integrated intensity; [d] percentage of bands according to integrated intensity.

with a dihedral angle of the N—H and C_α—H bonds not equal to zero, because of the low potential barriers to the rotation about the N—CH bond[25]. Minority conformations with dihedral angles not equal to zero of necessity have lower wavenumbers of stretching vibrations of the N—H bond than in conformation *A*. The lowest value should be observed in conformation *B*.

Larger alkyl substituents without branching at C_α can in principle assume conformations *A* – *D*. From an analysis of models conformation *A* does not come into consideration because of the marked interaction between O and CH_2 or CH_3 groups in the *syn*-periplanar position. Conformation *B* is also not suitable because of the marked 1,3-interaction between carbonyl oxygen atom and CH_2 or CH_3 groups. As possible partial conformations we suggest only *C* and *D*, the first of which has been shown by crystal X-ray studies in N,N′-bis(propionyl)-1,6-hexanediamine[26] and both of them were detected in nylon[27]. In the spectra of N-n-alkylamides (compounds *3* – *10*) we find in the given regions two bands, the higher wavenumber of which can be assigned (in analogy to N-methylamide) to conformation *C*, with *syn*-periplanar N—H and C_α—H bonds. In agreement with this interpretation is the case of ε-caprolactam (1-aza-2-cycloheptanone) even if in this case there is a *cis*-amide group. If we compare the calculated conformations[28] of ε-caprolactam and 2-piperidone we can see that the angles at the amide bonds in both rings are practically the same. This is confirmed by the fact that both these lactams[29] have the same ν(C=O) values: ε-caprolactam 1676 cm^{-1}, 2-piperidone 1677 cm^{-1}. In both substances the



SCHEME 1

amide bonds are basically planar. The only difference between both substances is the varied orientation of the NH bond in relation to the C—H at the carbon atom next to the nitrogen atom. In ε-caprolactam the NH bond is *syn*-periplanar with C—H, in 2-piperidone it is *syn*-clinal. The wavenumber of the free ν(N—H) for ε-caprolactam is 3429 cm^{-1}, for 2-piperidone 3419 cm^{-1}. ε-Caprolactam with an NH bond *syn*-periplanar to C—H absorbs at 10 cm^{-1} higher than 2-piperidone with a *syn*-clinal NH bond. The band with the lower wavenumber remains to be assigned to the stretching vibration of the N—H bond in partial conformation *D*.

Amides substituted at the nitrogen atom by alkyls branched in the α position can assume only partial conformation *E* without marked non-bonding interactions with the carbonyl oxygen atom. However, the spectra of such amides display two (compounds *11*–*13*) or three (compound *14*) bands which must be assigned to the stretching vibrations of free N—H in the *trans*-amide group. It is felt that the most intense band with the highest wavenumber (about 3450 cm^{-1}) belongs to N—H in the stable *E* conformation, the much weaker band with a lower wavenumber (type *T* in Table I) to *C* or *D* conformations, however with a somewhat distorted amide group (compare *e.g.*[7]). The third band in N-cyclohexylacetamide (compound *14*) must be assigned, on the basis of comparison with *trans*- and *cis*-N-(4-tert-butylcyclohexyl)-acetamide (compound *15* and *16*) to a conformer with its acetamide group in axial position. In this arrangement the N—H bond interacts with H in the axial position at $C_{(3)}$ and $C_{(5)}$ of the cyclohexane ring (Scheme 2). The wavenumber characteristic for partial conformation *E* of the N—H bond and the hydrocarbon residue is thus increased, similarly as with the wavenumber of vibration ν(O—H) in axial alcohols of the cyclohexane series[30]. In the spectrum of *cis*-isomer (*16*), in addition to bands assigned to conformers with a cyclohexane ring in chair conformation and with a planar amide bond, and in addition to bands associated with very rare conformers with a *cis*-amide grouping, there is also a third band (3447 cm^{-1}) which indicates the presence of a further conformer. In this case it could contain a cyclohexane ring in the flexible conformation. The N—H bond in this case is located in a similar environment as the equatorial acetamide substituent in the chair conformation of the cyclohexane ring (partial conformation *E*). The N—H bond in conformation *E* as the major component is also represented in N-tert-butylacetamide, for which the literature gives wavenumbers ν(N—H) 3448 cm^{-1} (ref.[5]), 3452 cm^{-1} (ref.[6]) and 3451 cm^{-1} (ref.[7]). In this same region are also the stretching vibrations of the N—H bond of the predominant conformation of N-(1,1-dimethylpropyl)acetamide (3450 cm^{-1}) and N-(1,1-diethylpropyl)acetamide (3445 cm^{-1})[7]. Further conformations in these amides have a non-planar amide bond[7]. In a series of N-tert-alkylamides we observe a decrease in wavenumber of ν(N—H) associated with increasing effective steric volume of the alkyl. The extreme case here is N-adamantylacetamide (compound *17*) in which the wavenumber of ν(N—H) reaches a value of only 3440 cm^{-1}. In the spectrum of N-adamantylacetamide there are two further bands which can be assigned, in ana-

logy with the spectra of compounds *11*, *13–15*. The band at 3436·6 cm^{-1} is considered as a band of a conformation with a non-planar amide bond. This is also supported by a side-band maximum in the ν(C=O) band with an increased wavenumber (1692 cm^{-1} as opposed to the main maximum at 1684·6 cm^{-1}) in agreement with concepts on changes in spectroscopic parameters which accompany deviations in the amide grouping from planarity[7]. The third band at 3422 cm^{-1} can be tentatively assigned to a conformer with a *cis*-amide bond. This is a striking finding since a similar band in the spectrum of N-tert-butylacetamide has not been found[6] and since the size of the adamantyl substituent argues against previous views on the possible formation of a *cis*-amide grouping[6]. The presence of a conformer with a *cis*-amide bond becomes the more probable when considering the effect of concentration on spectrum. At higher concentrations in addition to a band of an associated *trans*-amide there is also present a distinct band corresponding to the dimer of a *cis*-amide. Further, in the carbonyl region of the spectrum, measured under conditions in which the substance is nonassociated, there is a clear side band at a lower wavenumber (1671 cm^{-1}).

In conclusion it is possible on the basis of these data to present ranges of wavenumbers for stretching vibrations of nonassociated N—H groups of *trans*-amide bonds in individual partial conformations (see diagram 1). We assume that these values can be used to determine conformation at least of secondary *trans*-amides which cannot interact intermolecularly through the N—H group with another amide bond or another proton accepting group. In this sense we have already made use of these values for conformational analysis of lactams with medium-sized rings[31]. For possible application in peptides further studies of models with alterations in the acyl components would be necessary.

We should like to thank Academician F. Šorm for the interest he has shown in this work. Mrs H. Janešová assisted in the synthetic work, and Mr P. Formánek helped to measure the spectra.

REFERENCES

1. Luck W.: Naturwissenschaften *52*, 25 (1965).
2. Hallam H. E., Jones C. M.: J. Mol. Structure *1*, 413 (1967—1968).
3. Nyquist R. A.: Spectrochim. Acta *19*, 509 (1963).
4. McLachlan R. D., Nyquist R. A.: Spectrochim. Acta *20*, 1397 (1964).
5. Jones R. L.: Spectrochim. Acta *22*, 1555 (1966).
6. Jones R. L.: Spectrochim. Acta *23A*, 1745 (1967).
7. Jones R. L., Smith R. E.: J. Mol. Structure *2*, 475 (1968).
8. Marraud M., Neel J., Avignon M., Huong P. V.: J. Chim. Phys. *67*, 959 (1970).
9. Scheraga H. A.: Chem. Rev. *71*, 195 (1971).
10. Karle I. J., Karle J.: Acta Cryst. *16*, 969 (1963).
11. Bystrov V. F., Portnova S. L., Tsetlin V. I., Ivanov V. T., Ovchinnikov Yu. A.: Tetrahedron *25*, 493 (1969).
12. Ramachandran G. N., Chandrasekaran R., Kopple K. D.: Biopolymers *10*, 2113 (1971).

13. Donzell B.: *Thesis.* Eidgenössische Technische Hochschule, Zürich 1971.
14. Davies M., Jones A. H.: Trans. Faraday Soc. *55*, 1329 (1959).
15. Jurjev J., Beljakova Z. V., Kostetskij P. V., Prokofjev A. I.: Ž. Obšč. Chim. *29*, 2494 (1959).
16. Braun J. v., Jostes F., Münch W.: Ann. *453*, 1113 (1927).
17. Gertler S. I., Yerington A. P.: U.S. Dept. Agr., Agr. Research Service, Entomol. Research Branch ARS-33-14, 1955; Chem. Abstr. *50*, 7111 (1956).
18. Goto R., Watanabe A., Hojo K., Kosaka M.: J. Chem. Soc. Japan *87*, 1220 (1966).
19. Agre C. L., Dinga G., Pflaum R.: J. Org. Chem. *20*, 695 (1955).
20. Harvill E. K., Herbst R. M., Schreiner E. C., Roberts C. W.: J. Org. Chem. *15*, 662 (1950).
21. Hückel W., Heyder K.: Chem. Ber. *96*, 220 (1963).
22. Dolejšek Z., Hála S., Hanuš V., Landa S.: This Journal *31*, 435 (1966).
23. Krueger P. J., Jan J.: Can. J. Chem. *48*, 3236 (1970).
24. Yan J. F., Momany F. A.: Hoffmann R., Scheraga H. A.: J. Phys. Chem. *74*, 420 (1970).
25. Maigret B., Pullman B., Dreyfus M.: J. Theoret. Biol. *26*, 321 (1970).
26. Jensen L. H.: Acta Cryst. *15*, 433 (1962).
27. Kinoshita Y.: Makromol. Chem. *33*, 1 (1959).
28. Warschel A., Levitt M., Lifson S.: J. Mol. Spectry *33*, 84 (1970).
29. Chen C. Y. S., Swenson C. A.: J. Phys. Chem. *73*, 2999 (1969).
30. Joris L., von Ragué-Schleyer P., Osawa E.: Tetrahedron *24*, 4759 (1968).
31. Smolíková J., Havel M., Vašíčková S., Vítek A., Svoboda M., Bláha K.: This Journal, in press.

Translated by J. H. Cort.