CRYSTAL STRUCTURE AND CHIROPTICAL PROPERTIES OF (+)-(3S)-4-AZATRICYCLO[4,3,1,0³,⁷]DECAN-5-ONE

Karel BLÁHA[a], Petr MALOŇ[a], Miloš TICHÝ[a], Ivo FRIČ[a], Ramakrishnan USHA[b], Suryanarayana RAMAKUMAR[b] and Kailasam VENKATESAN[b]

[a]*Institute of Organic Chemistry and Biochemistry,*
Czechoslovak Academy of Sciences, 166 10 Prague 6 and
[b] *Department of Organic Chemistry,*
Indian Institute of Sciences, Bangalore 560012, India

X-Ray crystal structure of the title lactam *I* was solved using direct methods (space group $P2_1/c$; $a = 10.680$ (2) Å, $b = 6.153$ (2) Å, $c = 12.432$ (2) Å, $\beta = 110.40$ (2)°, $V = 766$ Å³, $Z = 4$) and refined to the final R value of 0·053. The result attests the presence of an only slightly non-planar *cis*-amide group ($\omega = +1.2$ (6)°, $\chi_C = +2$ (1)°, $\chi_N = +10$ (4)°, and an envelope conformation of the five-membered lactam ring. CD spectra of (+)-*I*, measured in solvents of various polarity at various concentrations and temperatures, exhibit a negative Cotton effect of the $n-\pi^*$ transition and a positive Cotton effect of the $\pi-\pi^*$ transition. The rotatory strength of the $n-\pi^*$ dichroic band is substantially smaller than in the case of (−)-(3S)-4-azatricyclo[4,4,0,0³,⁸]decan-5-one (*II*) with a strongly non-planar *cis*-amide group.

In the course of our studies[1-7] on the potential occurrence of non-planar amide groups in amides and peptides we have presented data on the molecular geometry and chiroptical properties of (−)-(3S)-4-azatricyclo[4,4,0,0³,⁸]decan-5-one (*II*).* In this model compound, the non-planar *cis*-amide group is embedded in a rigid polycyclic skeleton. Molecular geometry of the lactam *II* was determined by X-ray analysis[7] and the signs of the experimentally observed CD bands were related to the specified chirality of this structural entity with an inherently chiral non-planar amide chromophore. In order to compare with the real peptide and amide moieties it would be useful to add to the set of model structures a compound with a fixed planar amide group. There are sound indications that (+)-(3S)-4-azatricyclo--[4,3,1,0³,⁷]decan-5-one (*I*), which is isomeric with lactam *II*, could fulfil this requirement. The *cis*-amide group in this compound is part of a five-membered ring and if this ring assumes the envelope conformation due to the junction to the bicyclo-[2,2,2]octane system, the amide group should be at least approximately planar.

---

* In some of our previous communications[4-6] the absolute configuration of the lactam (−)-*II* has been improperly designated as (−)-(2S,5S). The right symbol is (−)-(3S). The error is nevertheless related to the symbol denomination only and does not influence the results at all.

Moreover, comparison with monocyclic five-membered lactams would allow us to estimate the limitation of conformational flexibility in the polycyclic lactam *I*. Generally, the lactam *I* offers an opportunity to study the geometry and properties of the *cis*-amide unit in nearly planar conformation.

EXPERIMENTAL

Material: The synthesis of the lactam *I* was described earlier[2]. The (+)-(3*S*)-enantiomer was used for CD measurements, crystals of the racemic compound for X-ray analysis. All data presented in this paper are related to the (+)-(3*S*) enantiomer.

Crystal data: ($\pm$)-4-azatricyclo[4,3,1,0^{3,7}]decan-5-one (*I*), $C_9H_{13}NO$, molecular weight 151·2; monoclinic (unique axis *b*), space group $P2_1/c$; $a = 10\cdot680 \pm 0\cdot002$ Å, $b = 6\cdot153 \pm$ $\pm 0\cdot002$ Å, $c = 12\cdot432 \pm 0\cdot002$ Å, $\beta = 110\cdot40 \pm 0\cdot02°$, $V = 766$ Å^3; $D_m = 1\cdot304$ g cm^{-3}, $D_c = 1\cdot311$ g cm^{-3}, $Z = 4$; F(0,0,0) = 328. Approximate dimensions of the crystal used in the data collection were $0\cdot8 \times 0\cdot2 \times 0\cdot2$ mm. Linear absorption coefficient $\mu = 0\cdot88$ cm^{-1} (MoK$_\alpha$ radiation). The data were collected on a CAD-4 diffractometer in the $\omega/2\Theta$ mode using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0\cdot7107$ Å). Corrections were made for Lorentz and polarization factors but not for absorption. A total of 961 reflections was collected of which 881 were significant [$|F| > 2\sigma(|F|)$].

Structure solution and refinement: The structure was solved using the MULTAN programme[8]. All eleven non-hydrogen atoms could be identified in the E-map based on the set of signs with the highest figure-of-merit. The positional and isotropic thermal parameters were refined block-diagonally using the programme written by Shiono[9] and modified by B.S. Reddy. Hydrogen atoms were then located at stereochemically reasonable positions from a difference map. Further

TABLE I

Fractional Coordinates (10^5) of the Heavy Atoms (with e.s.d.'s in parentheses)

Atom[a]	X	Y	Z
C(1)	−76 489 (58)	−34 789 (95)	+14 323 (47)
C(2)	−87 087 (56)	−20 800 (100)	+ 5 656 (51)
C(3)	−83 283 (59)	−17 729 (89)	− 4 999 (48)
N(4)	−89 754 (47)	−33 841 (81)	−13 889 (39)
C(5)	−82 572 (59)	−51 936 (91)	−12 733 (48)
C(6)	−70 237 (52)	−48 461 (96)	− 2 068 (47)
C(7)	−73 288 (55)	−54 994 (96)	+ 8 687 (46)
C(8)	−68 596 (54)	−23 923 (100)	− 2 081 (45)
C(9)	−59 466 (58)	−14 094 (101)	+ 9 091 (49)
C(10)	−63 734 (57)	−21 368 (103)	+19 045 (47)
O(11)	−85 403 (43)	−68 268 (70)	−18 728 (34)

[a] The atoms are numbered according to Fig. 2.

TABLE II

Anisotropic Temperature Factors ($\beta_{ij} . 10^4$) of the Heavy Atoms (with e.s.d.'s in parentheses)
The temperature factor is of the form

$$T = \exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}).$$

Atom	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
C(1)	78 (7)	210 (19)	53 (5)	−10 (9)	23 (5)	5 (7)
C(2)	64 (6)	227 (19)	75 (5)	15 (9)	22 (5)	− 9 (8)
C(3)	80 (7)	136 (17)	60 (5)	10 (8)	6 (4)	12 (7)
N(4)	76 (6)	216 (16)	56 (4)	− 3 (7)	−3 (4)	3 (6)
C(5)	77 (6)	171 (17)	54 (4)	−25 (9)	18 (4)	− 7 (7)
C(6)	50 (6)	186 (18)	65 (5)	17 (8)	13 (4)	−23 (7)
C(7)	78 (7)	170 (17)	56 (5)	5 (9)	4 (5)	18 (7)
C(8)	70 (6)	220 (19)	54 (5)	−27 (9)	30 (4)	− 4 (8)
C(9)	64 (6)	219 (19)	70 (5)	−16 (9)	21 (5)	−29 (8)
C(10)	82 (7)	227 (19)	55 (5)	− 3 (10)	14 (5)	−24 (8)
O(11)	114 (6)	239 (14)	73 (4)	−41 (7)	12 (4)	−40 (6)

TABLE III

Fractional Coordinates (. 10^4) of Hydrogen Atoms (with e.s.d.'s in parentheses)
The temperature factors are of the form $T = \exp(-B . \sin^2 \Theta/\lambda^2)$.

Atom	X	Y	Z	$B(\text{Å}^2)$
H(Cl)	−8 058 (54)	−3 922 (93)	+2 007 (44)	3·1 (1·2)
H(C2)	−9 659 (56)	−2 812 (96)	+ 275 (47)	4·0 (1·3)
H'(C2)	−8 830 (50)	− 665 (86)	+ 908 (42)	2·8 (1·1)
H(C3)	−8 533 (53)	− 338 (91)	− 751 (42)	3·0 (1·2)
H(N4)	−9 815 (67)	−3 170 (107)	−1 856 (53)	5·1 (1·6)
H(C6)	−6 397 (53)	−5 688 (95)	− 233 (43)	2·9 (1·2)
H(C7)	−6 459 (53)	−6 222 (96)	+1 435 (45)	3·4 (1·2)
H'(C7)	−8 094 (57)	−6 549 (93)	+ 671 (45)	3·2 (1·3)
H(C8)	−6 674 (56)	−1 962 (93)	− 831 (45)	3·6 (1·3)
H(C9)	−5 193 (56)	−1 981 (100)	+1 075 (45)	4·2 (1·5)
H'(C9)	−6 058 (52)	+ 189 (86)	+ 837 (40)	2·5 (1·1)
H(Cl0)	−6 512 (56)	− 898 (95)	+2 249 (44)	3·3 (1·2)
H'(Cl0)	−5 591 (57)	−3 019 (95)	+2 434 (49)	4·0 (1·4)

refinement of positional and anisotropic thermal parameters of C, N and O atoms and of positional and isotropic thermal parameters of hydrogen atoms led to a final R value of $0\cdot053$ (significant reflections only). Scattering factors for non-hydrogen atoms were taken from ref.[10], for hydrogen atoms from ref.[11]. The quantity minimized was $\sum \omega(|F_0| - K|F_c|)^2$ with $\omega = 1/\sigma^2(F_0)$. Final positional and thermal parameters for non-hydrogen atoms are listed in Tables I and II, those for hydrogen atoms in Table III. A table of observed and calculated structure factors can be obtained from one of the authors (K. V.). Bond angles involving heavy atoms are given in Table IV. The numbering of atoms in the crystallographic description differs somewhat from that of systematic nomenclature and is evident from the figures.

Chiroptical measurements: The CD spectra were measured on a Roussel–Jouan CD 185/II Dichrographe equipped with a cryostat. The measurements were performed at 25°C in about $6 \cdot 10^{-3}$M solutions, unless specified explicitly. The experimental curves were digitized and simulated by a sum of Gaussian bands approximate parameters of which were optimized in the next step using an algorithm described by Fletcher and Powell[12]. For all the mentioned transformations of experimental data we used a Hewlett–Packard 9830A calculator equipped with an HP 9864A digitizer and an HP 9862A digital $x - y$ plotter. The data for the lactam *II* used for comparison were processed in the same way. (CD data given in ref.[4] were processed by another procedure and are therefore slightly different from those given in this paper.) CD data of the lactam *I* are collected in Table V.

RESULTS

Crystal packing: The crystal packing is shown in Fig. 1. The spiral chains, running parallel to the b axis, consist of hydrogen-bonded molecules related by two-fold screw axes. A similar pattern is found in the crystal structure of cyclo(L-prolyl- -D-phenylalanyl)[13] and also in glutarimide[14]. It is noteworthy that the b axis lengths in these three cases are quite close to each other $\left(6\cdot153 \text{ Å in lactam } I, 6\cdot638 \text{ Å in cyclo-} \left(\text{L-prolyl-D-phenylalanyl}\right)^{13}, 7\cdot416 \text{ Å in glutarimide}^{14}\right)$. In the crystal structure of the isomeric lactam *II* (ref.[7]), hydrogen bonding takes place between molecules

TABLE IV

Bond Angles (°) Involving the Heavy Atoms

C(2)—C(1)—C(7)	111·4 (5)		C(5)—C(6)—C(7)	109·9 (5)
C(2)—C(1)—C(10)	108·1 (5)		C(5)—C(6)—C(8)	101·7 (5)
C(7)—C(1)—C(10)	107·8 (5)		C(7)—C(6)—C(8)	108·7 (5)
C(1)—C(2)—C(3)	109·1 (5)		C(1)—C(7)—C(6)	109·7 (5)
C(2)—C(3)—N(4)	111·9 (5)		C(6)—C(8)—C(9)	115·6 (5)
C(2)—C(3)—C(8)	108·9 (5)		C(3)—C(8)—C(9)	113·4 (5)
N(4)—C(3)—C(8)	100·7 (5)		C(3)—C(8)—C(6)	97·9 (5)
C(3)—N(4)—C(5)	112·4 (5)		C(8)—C(9)—C(10)	110·4 (5)
N(4)—C(5)—C(6)	105·5 (5)		C(9)—C(10)—C(1)	109·0 (5)
N(4)—C(5)—O(11)	127·5 (5)		C(6)—C(5)—O(11)	126·9 (5)

related by an inversion centre. The hydrogen bond in the present structure is rather weak (N...O = 2·944 Å, ∡ N—H...O = 161·7° and ∡ H—N...O = 12·8°), in accord with the observation of Marsh and Donohue[15] on other hydrogen-bonded amides.
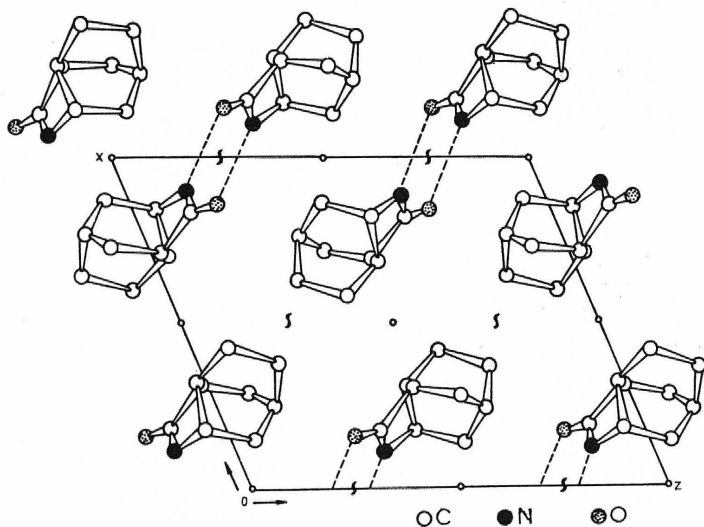

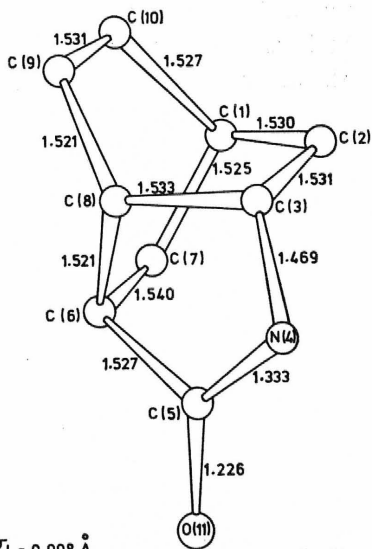FIG. 1

Packing of the Molecule as Viewed down the *b* Axis

FIG. 2

Bond Lengths (Å) Involving the Heavy Atoms $\sigma_l = 0.008$ Å

Molecular geometry: Bond distances involving the C, N and O atoms are shown in Fig. 2, bond angles in Table IV. The $C(sp)^3$—$C(sp^3)$ bonds linking methine carbon atoms do not show the lengthening observed in other bridged systems[7,16,17]. The standard dimensions of the *cis*-amide group are: C'—O = 1·24 Å, C'—N = 1·32 Å, $\sphericalangle$ N—C'—O = 123°, $\sphericalangle$ N—C'—$C_{(1)}^\alpha$ = 118°, $\sphericalangle$ O—C'—$C_{(1)}^\alpha$ = 119° and $\sphericalangle$ C'—N—$C_{(2)}^\alpha$ = 126° (ref.[18]). In the present structure, the angles C(6)—C(5)—N(4) $(105·5(5)°)$ and C(5)—N(4)—C(3) $(112·4(5)°)$ are significantly smaller than the corresponding values quoted above. The bond angle strain is obviously due to the constraints imposed by the bridging. The deviations from the standard values for these angles become more and more pronounced as we go from a seven-membered ring [for ε-caprolactam[19] $\sphericalangle$ N—C'—C_1^α = 118·5(2)° and $\sphericalangle$ C'—N—C_2^α = 125·5(2)°] to a four-membered ring [for cephalosporin[20] $\sphericalangle$ N—C'—C_1^α = 92·2(5)° and $\sphericalangle$ C'—N—C_2^α = 95·6(4)°]through a six-membered ring [lactam *II* where $\sphericalangle$ N—C'—C_1^α = = 110·4(3)° and $\sphericalangle$ C'—N—C_2^α = 115·4(3)°] and a five-membered ring [present case where $\sphericalangle$ N—C'—C_1^α = 105·5(5)° and $\sphericalangle$ C'—N—C_2^α = 112·4(5)°] in which the *cis*-amide group is embedded. The four torsion angles about the C'—N bond are: $\omega_1(C_1^\alpha$—C'—N—$C_2^\alpha)$ = +1·2(6)°, $\omega_2(O$—C'—N—H) = +9(6)°, $\omega_3(O$—C'—N—$C_2^\alpha)$ = +179·2(6)° and $\omega_4(C_1^\alpha$—C'—N—H) = −169(6)°. The deformation of the *cis*-amide group is then described by the values: $\Delta\omega = \omega_1$ = +1·2(6)° (torsional strain), $\chi_C = \omega_1 − \omega_3 + \pi$ = +2(1)° and $\chi_N = \omega_2 − \omega_3 + \pi$ = +10(4)°, characterizing the out-of-plane deformation at C' and N, respectively, the pyramidal distortion at the C' atom being smaller than that at the nitrogen atom in accordance with the observations of Dunitz and Winkler[21]. However, the predicted correlation between $\Delta\omega$ and χ_N through the relation $\chi_N = −2\,\Delta\omega\,(\chi_N \equiv \Theta_N$ ref.[22]) does not exist in the present structure. Calculations show that the magnitude of χ_N is not in the direction of the best hydrogen bond either. This adds further support to the
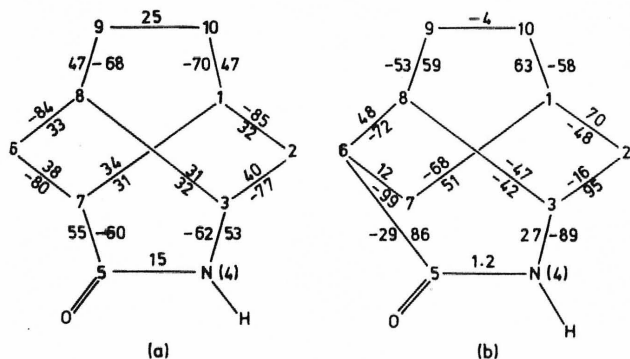

FIG. 3

Torsion Angles (°) in Lactam *II* (*a*) and in Lactam *I* (*b*)

earlier conclusion that deformations of the amide group are to be attributed to the strain in the bridged system.

The torsion angles in the skeleton of the lactam *I* and those of the lactam *II* (ref.[7]) are given in Fig. 3. The differences between torsion angles in these two isomers are considerable. A projection of the lactam *I* molecule down the axis C(1)...(C8) (Fig. 4) shows the twisted bicyclo[2,2,2]octane moiety with three unequal twist angles, the smallest being the one opposite the amide group. This trend is also seen in the lactam *II* (ref.[7]), but the twist angles are all larger than those of the present structure. In the lactam *II* all the three branches of the bicyclo[2,2,2]octane moiety are twisted in the same direction whereas in the lactam *I*, two are twisted in one direction and the third in the opposite sense. This can be clearly seen by comparing Fig. 4 with the corresponding figure for lactam *II* (ref.[7]).

(+)-*I*

(−)-*II*
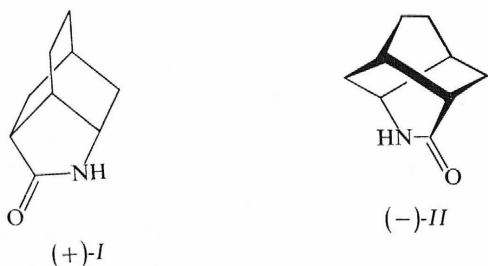
The sum of the internal angles for the five-membered ring formed by atoms C(3), N(4), C(5), C(6) and C(8) in the present structure is 518·2°. In fact, the deviations
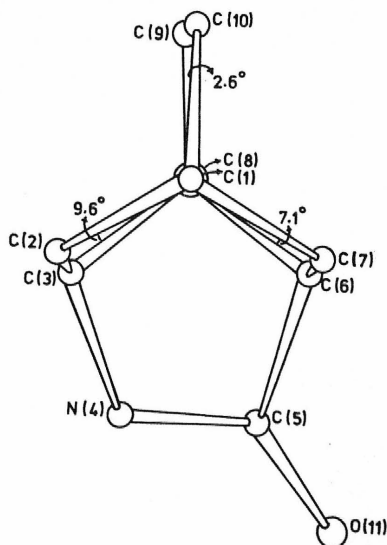

FIG. 4

View of the Molecule down the C(1)—C(8) Direction

of atoms C(3), N(4), C(5), C(6) and C(8) from the least-squares plane passing through them show that the five-membered ring is non-planar. However, atoms C(3), N(4), C(5) and C(6) define a better plane. The deviation of C(8) from this plane is 0·71 Å, suggesting that the five-membered ring possesses an envelope conformation comparable to that in pyroglutamic acid[23].

Chiroptical properties: CD data of the lactam (+)-*I* in several solvents are presented in Table V and Figs 5, 6. In all cases, the $n - \pi^*$ transition is characterized by a negative, the $\pi - \pi^*$ transition by a positive Cotton effect. A third dichroic

TABLE V
CD Spectra of the Lactam (+)-*I* Measured in Various Solvents

Solvent	Direct readings[a]		Values obtained upon separation[a]			
	λ_{max}	$[\Theta]_{max} \cdot 10^{-3}$	λ_{max}	$[\Theta]_{max} \cdot 10^{-3}$	Δ_{max}	$R \cdot 10^{39}$
			$n - \pi^*$ Transition			
Cyclohexane	227·0	−14·5	228·2	−14·1	16·0	−1·22
Dioxan	227·0	−16·9	226·0	−16·9	16·1	−1·48
Acetonitrile	226·0	−18·4	225·6	−18·5	16·5	−1·67
Methanol[b]	220·0	−20·8	216·4	−24·6	15·2	−2·12
Water	218·0	−18·7	214·6	−31·0	12·8	−2·28
TFE[c]	216·0	−18·0	212·2	−23·8	13·2	−1·83
HFP[d]	215·0	−11·3	211·1	−15·9	12·1	−1·12
			$\pi - \pi^*$ Transition			
Cyclohexane	192·0	61·3	191·9	62·1	12·8	5·09
Dioxan	e	e	193·6	68·0	11·9	5·14
Acetonitrile	193·0	67·8	193·2	68·0	13·2	5·72
Methanol[b]	194·0	63·0	194·7	66·9	13·6	5·76
Water	193·0	58·1	194·0	60·8	17·9	6·89
TFE[c]	193·0	59·9	193·7	63·7	13·3	5·39
HFP[d]	193·0	47·8	193·2	49·4	13·3	4·19
			Rydberg transition			
Cyclohexane	e	e	203·9	−2·4	13·2	−0·19

[a] $[\Theta]_{max}$ maximum molar ellipticity (deg cm^2 dmol^{-1}), Δ_{max} band halfwidth in nm, R rotatory strength in cgs (esu^2 cm^2); [b] the measurement was performed also in 1-pentanol, 1-propanol and 2-propanol. The data show no significant deviations from the values found in methanol; [c] TFE 2,2,2-trifluoroethanol; [d] HFP 1,1,1,3,3,3-hexafluoro-2-propanol; [e] the band maximum was not directly observed.

band was very distinct in the CD spectra of $(-)$-II in cyclohexane and was assigned to a transition of the Rydberg type $(cf.^{4,24,25})$. This band is discernible in the CD spectra of $(+)$-I only after the separation into Gaussian bands and is very weak even in cyclohexane (in more polar solvents it cannot be recognized at all). The apparent maximum of the $n-\pi^*$ band is red-shifted with decreasing solvent polarity. This shift is smaller than for the lactam II (for the extreme members of the solvent scale — 1,1,1,3,3,3-hexafluoro-2-propanol and cyclohexane — the shift is 12 and 25 nm with the lactams I and II, respectively). However, the positions of maxima of the $n-\pi^*$ bands are disfigured by overlapping with the intense $\pi-\pi^*$ band. More reliable data for the solvent shift mentioned can be obtained from the separated Gaussian bands: 17·1 nm for lactam I and 22·6 for lactam II. In a non-polar solvent (cyclohexane) the $n-\pi^*$ band in the CD spectrum of I is blue-shifted by about 4 nm relative to II. Also the wavelength of the $\pi-\pi^*$ dichroic band is significantly shifted to lower values with the lactam I. However, this value is not sensitive to the solvent polarity. The main feature in which the CD spectra of lactams I and II differ is the relation of rotatory strengths of the $n-\pi^*$ and $\pi-\pi^*$ transitions (approximately 1 : 3 for I and 1 : 1 for II). With the lactam I, the rotatory strengths of both transitions reach their maximum values in water (Table V) in contrast to the situation with lactam II in which the rotatory strengths increase monotonously with increasing solvent polarity.
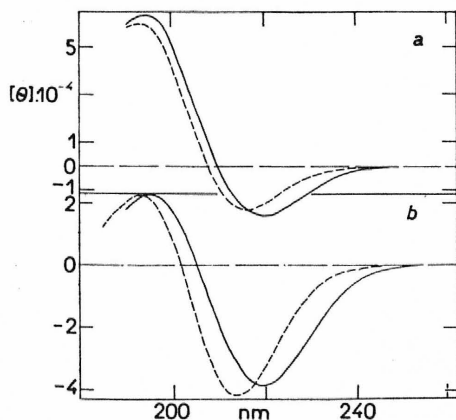

Fɪɢ. 5

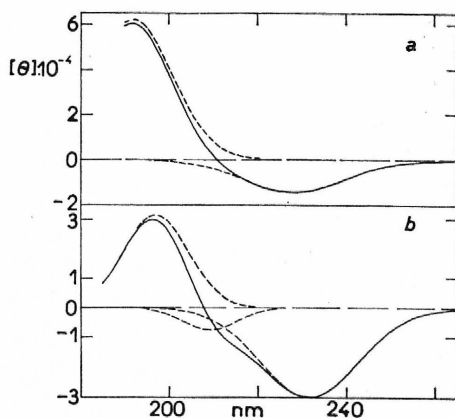CD Spectra of Lactams $(+)$-I (a) and $(-)$-II (b) in Methanol (———) and in 2,2,2-Trifluoroethanol ($- - -$)

Fɪɢ. 6

CD Spectra of Lactams $(+)$-I (a) and $(-)$-II (b) in Cyclohexane

——— Experimental curves, $- - -$ Gaussian bands obtained by separation. For the lactam I, the Gaussian band at about 205 nm due to the Rydberg transition is not shown because it is too weak.

The temperature dependences of the CD curves of $(+)$-I were measured in aceto-nitrile $(-40°$ to $+40°C)$ and in a mixture of methanol–ethanol $(1:1)$ $(-120°$ to $+40°C)$. At low temperatures only a hypsochromic shift was observed, as with $(-)$-II. The concentration dependence of the CD spectra (in the range from 10^{-3} to 10^{-4} mol l^{-1} in cyclohexane) does not reveal the presence of intermolecular as-sociates.

DISCUSSION

The *cis*-amide group in the crystalline lactam shows only slight deviations from planarity $[\Delta\omega = +1\cdot2(6)°,\ \chi_C = +2(1)°$ and $\chi_N = +10(4)°]$. We may suppose that the *cis*-amide group assumes a nearly planar conformation also in solutions. Therefore, the CD data of I can be used for finding out features characteristic for a fixed planar *cis*-amide group (built in a five-membered ring in an evelope con-formation). Comparison of the CD spectra of both rigid lactams, I with a planar and II with a non-planar amide group, should be informative. With the lactam I we can find a hypsochromic shift of the $n-\pi^*$ transition (in cyclohexane) and a de-crease in intensity of this transition, absolutely and also relatively with respect to the $\pi-\pi^*$ transition intensity. This observation is in accord with quantum chemical calculations[5,26] which predict the same sense of shifts for the conformational change non-planar amide group $\rightarrow$ planar amide group. Some features of the CD spectra of I, mainly the low intensity of the $n-\pi^*$ band with respect to that of the $\pi-\pi^*$ band and location of the maxima of both bands at short wavelengths are common also to the CD spectra of other amides with a virtually planar amide group[27-29]. However, the lactam I exhibits higher rotatory strengths of both electronic transitions when compared with monocyclic five-membered lactams mentioned in the literature (absolute values of the rotatory strength are usually $1-7 \cdot 10^{-40}$ and $1-2 \cdot 10^{-39}$ esu^2 cm^2 for the $n-\pi^*$ and $\pi-\pi^*$ transitions, respectively[28-31]). Lower intensities of CD bands of flexible lactams may be connected with their conformational mobility and with the presence of several conformational species with opposite Cotton effects. On the contrary, all molecules of I assume in solutions virtually the same conforma-tion and any compensation is excluded. Moreover, the rigid bicyclo[2,2,2]octane skeleton which is chirally oriented towards the amide group can further enhance the optical activity. The sign of the $n-\pi^*$ band of the lactam I obeys the Schellman's quadrant rule[32] and, consequently, a significant contribution of the one-electron mechanism to the origin of optical activity in this compound is possible. Nevertheless, the difference in twisting the bicyclo[2,2,2]octane skeleton does not influence the signs of Cotton effects of both the lactam I and II if enantiomers with the same absolute configuration at the bridgehead atom $C_{(3)}$ are considered.

REFERENCES

1. Tichý M., Dušková E., Bláha K.: Tetrahedron Lett. *1974*, 237.
2. Tichý M., Hamšíková E., Bláha K.: This Journal *41*, 1935 (1976).
3. Smolíková J., Tichý M., Bláha K.: This Journal *41*, 413 (1976).
4. Frič I., Maloň P., Tichý M., Bláha K.: This Journal *42*, 678 (1977).
5. Maloň P., Bláha K.: This Journal *42*, 687 (1977).
6. Maloň P., Frič I., Tichý M., Bláha K.: This Journal *42*, 3105 (1977).
7. Ramakumar S. R., Venkatesan K., Weber H. P.: Helv. Chim. Acta *60*, 1691 (1977).
8. Germain G., Main P., Woolfson M. M.: Acta Crystallogr. *A27*, 368 (1971).
9. Shiono R.: Unpublished results.
10. Cromer D. T., Waber J. T.: Acta Crystallogr. *18*, 104 (1965).
11. Stewart R. F., Davidson G. R., Simpson W. T.: J. Chem. Phys. *42*, 3175 (1965).
12. Fletcher R., Powell M. J. D.: Comput. J. *6*, 163 (1963).
13. Ramani R., Venkatesan K., Marsh R. E., Hu Kung W. J.: Acta Crystallogr. *B32*, 1051 (1976).
14. Peterson C. S.: Acta Chem. Scand. *25*, 379 (1971).
15. Marsh R. E., Donohue J.: Advan. Protein Chem. *22*, 235 (1967).
16. Potenza J., Mastropaolo D., Gallaher D., Henderson T.: Acta Crystallogr. *B31*, 1975 (1975).
17. Rao S. T., Sundaralingam M.: Acta Crystallogr. *B28*, 694 (1972).
18. Ramachandran G. N., Sasisekharan V.: Advan. Protein Chem. *23*, 288 (1968).
19. Winkler F. K., Dunitz J. D.: Acta Crystallogr. *B31*, 268 (1975).
20. Sweet R., Dahl L. F.: J. Amer. Chem. Soc. *92*, 5489 (1970).
21. Dunitz J. D., Winkler F. K.: Acta Crystallogr. *B31*, 251 (1975).
22. Ramachandran G. N., Lakshminarayanan A. V., Kolaskar A. S.: Biochim. Biophys. Acta *303*, 8 (1973).
23. Vasantha Pattabhi, Venkatesan K.: J. Chem. Soc., Perkin Trans. 2, *1974*, 1085.
24. Basch H., Robin M. B., Kuebler N. A.: J. Chem. Phys. *47*, 1201 (1967).
25. Basch H., Robin M. B., Kuebler N. A.: J. Chem. Phys. *49*, 5007 (1968).
26. Maloň P., Bystrický S., Bláha K.: This Journal *43*, 781 (1978).
27. Goodman M., Toniolo C., Falcetta J.: J. Amer. Chem. Soc. *91*, 1816 (1969).
28. Urry D. W.: J. Phys. Chem. *72*, 3035 (1968).
29. Greenfield N. J., Fasman G. D.: J. Amer. Chem. Soc. *92*, 177 (1970).
30. Geiger R. E., Wagnière G. H.: Helv. Chim. Acta *58*, 738 (1975).
31. Greenfield N. J., Fasman G. D.: Biopolymers *7*, 595 (1969).
32. Schellman J. A.: Accounts. Chem. Res. *1*, 144 (1968).
33. Yeh C.-Y., Bush C. A.: J. Phys. Chem. *78*, 1829 (1974).