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## Medium-Ring Compounds. XXII. Caprylolactam

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**Abstract.** Monoclinic,  $Cc$ ,  $a=5.000(5)$ ,  $b=23.15(2)$ ,  $c=7.21(1)$  Å,  $\beta=104.76(10)^\circ$ ,  $C_8H_{15}ON$ ,  $M=141.21$ ,  $Z=4$ ,  $D_m=1.16$ ,  $D_x=1.161$  g cm $^{-3}$ . Caprylolactam has a non-planar *transoid* amide group with a torsion angle of  $148^\circ$ . The ring skeleton shows approximate  $C_2$  symmetry. The crystal is built from hydrogen-bonded (N-H...O=C) chains along  $a$ .

**Introduction.** Crystals were prepared by slow evaporation of a solution of caprylolactam in ether/hexane at room temperature and were sealed in capillaries for X-ray analysis.

Intensities from a crystal of dimensions  $0.50 \times 0.40 \times 0.20$  mm were collected on an automated Hilger-Watts Y290 diffractometer with Mo  $K\alpha$  radiation ( $\lambda=0.71069$  Å,  $\mu=0.79$  cm $^{-1}$ ) and Sr/Zr balanced filters. All reflexions with scattering angle  $\theta < 27^\circ$  were measured, only those above background in the range  $27^\circ < \theta < 35^\circ$ . The measurements led to 1038 independent  $|F_o|$  values. Inspection of a sharpened Patterson synthesis gave coordinates for the five non-hydrogen atoms of the amide group. A subsequent Fourier synthesis showed the remaining five carbon atoms of the ring. The structure was refined by full-matrix least-squares calculations (two cycles isotropic, seven cycles anisotropic). All hydrogen atoms were located in a difference synthesis (only reflexions with  $\sin\theta/\lambda \leq 0.45$  Å $^{-1}$ ) and their parameters (including isotropic  $B$ 's) refined by four additional least-squares cycles with Huber-Buser's (1971) criteria. The final  $R$  was 0.031.

Final positions and vibrational parameters are given in Tables 1 and 2; bond distances, bond angles and torsion angles in Table 3. Scattering factors were taken

from *International Tables for X-ray Crystallography* (1962).\*

Table 2. *Caprylolactam*: atomic coordinates ( $\times 10^3$ ), e. s. d.'s in parentheses and isotropic  $B$  values for hydrogen atoms

E.s.d.'s for the  $B$  values are in the range 0.6–0.9 Å $^2$ .

	$x/a$	$y/b$	$z/c$	$B(\text{Å}^2)$
H(1) C(2)	-136 (6)	61 (1)	-285 (4)	1.7
H(2) C(2)	188 (7)	60 (1)	-229 (5)	3.0
H(1) C(3)	-149 (6)	159 (1)	-177 (5)	1.7
H(2) C(3)	-1 (6)	150 (1)	-344 (5)	2.3
H(1) C(4)	338 (6)	199 (1)	-178 (5)	2.1
H(2) C(4)	426 (6)	144 (1)	-51 (4)	1.3
H(1) C(5)	116 (7)	241 (1)	41 (6)	4.5
H(2) C(5)	426 (6)	229 (2)	136 (5)	3.7
H(1) C(6)	-5 (6)	157 (2)	197 (5)	3.1
H(2) C(6)	136 (6)	208 (1)	332 (5)	3.7
H(1) C(7)	418 (7)	142 (1)	505 (5)	3.3
H(2) C(7)	563 (5)	140 (1)	326 (4)	2.0
H(1) C(8)	132 (6)	64 (1)	360 (5)	1.8
H(2) C(8)	461 (6)	43 (1)	405 (5)	3.0
H(N)	403 (4)	58 (1)	87 (3)	0.9

**Discussion.** In the crystalline state the caprylolactam molecule adopts a conformation in which the amide group is *transoid* but markedly non-planar, the out-of-plane parameters (Winkler & Dunitz, 1971) being  $\chi_N=23.1^\circ$  (e. s. d. 2.2),  $\chi_C=-5.8(0.5)^\circ$  and  $\tau=162.9^\circ$  (1.1). All three kinds of out-of-plane deformation are

\* A list of structure factors is given by Winkler (1973) and has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30620 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Caprylolactam*: atomic coordinates (e. s. d.'s in parentheses) and vibrational tensor components for non-hydrogen atoms (all  $\times 10^4$ )

The  $U_{ij}$  values (in Å $^2$ ) correspond to the temperature factor expression  $T = \exp[-2\pi^2(U_{11}h^2a^{*2} \dots + 2U_{12}hka^*b^* \dots)]$  and have e.s.d.'s in the range 0.0008–0.0027 Å $^2$ .

	$x/a$	$y/b$	$z/c$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O	-2050 (0)	579 (1)	547 (0)	363	650	934	-25	250	65
N	2601 (4)	568 (1)	1308 (3)	355	418	587	26	176	33
C(1)	135 (4)	614 (1)	57 (4)	383	353	635	-13	151	-16
C(2)	215 (5)	768 (1)	-1949 (4)	541	568	515	-19	74	-86
C(3)	211 (5)	1428 (1)	-2122 (4)	524	579	521	74	121	104
C(4)	2797 (5)	1730 (1)	-903 (4)	555	473	683	-23	200	117
C(5)	2480 (6)	2077 (1)	811 (5)	803	420	828	-29	159	20
C(6)	1697 (6)	1762 (1)	2466 (5)	716	514	687	39	214	-154
C(7)	3856 (6)	1341 (1)	3635 (4)	594	726	495	-68	111	-76
C(8)	3056 (5)	708 (1)	3322 (4)	543	619	514	-0	133	95

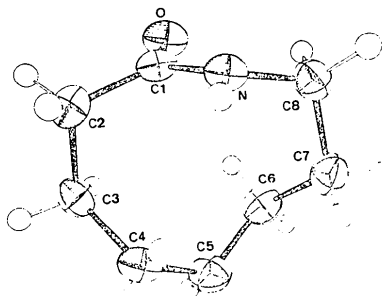


Fig. 1. The caprylactam molecule (with atom numbering shown) viewed along a direction perpendicular to the mean plane of the nine-membered ring. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

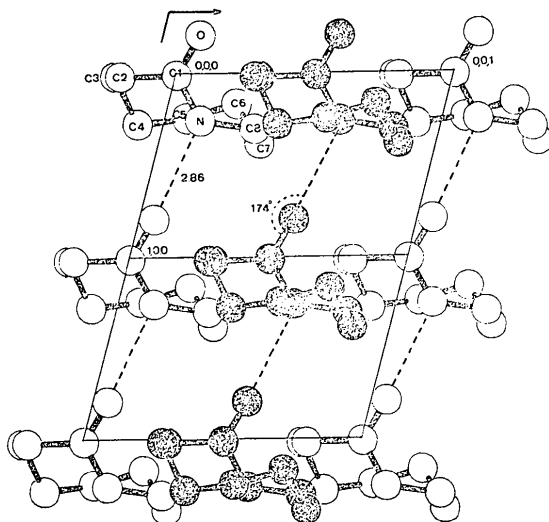


Fig. 2. Caprylactam; crystal structure projected down [010]. Only the molecules corresponding to the equivalent positions  $x, y, z$  and  $x, \bar{y}, \frac{1}{2} + z$  (black circles) are drawn.

working in cooperation to bring the ring members C(2) and C(8) closer together than they would be for a *trans*-planar conformation of the amide group. Bond lengths and angles observed in the *transoid* amide group are within 0.02 Å and 2° of the standard values (Marsh & Donohue, 1967).

The ring skeleton shows an approximate twofold axis passing through C(5) and the middle of the amide bond (Fig. 1). The observed torsion angles agree well with those calculated for *trans*-cyclononene by Ermer & Lifson (1973).

Analysis of the experimental thermal-motion tensors in terms of rigid-body translational and librational motion (Schomaker & Trueblood, 1968) results in significant disagreement between observed and calculated tensor components [ $\langle (\Delta U_{ij})^2 \rangle^{1/2} = 0.00246 \text{ Å}^2$ ,  $\langle \sigma(U_{ij}) \rangle^{1/2} = 0.00166 \text{ Å}^2$ ]. Since the observed  $U_{ij}$  values are fairly accurate the discrepancy must be due to internal motion within the molecule. The libration corrections amount to between 0.009 and 0.012 Å for bond lengths and are negligible for bond angles and torsion angles.

Whereas the *cis*-form of caprylactam is favoured in dilute solution, the free-energy difference being less than 1 kcal mole<sup>-1</sup> (Hallam & Jones, 1970), the *trans*-form seems to form a more stable crystal structure. As could be expected from the short 5 Å periodicity, the molecules are linked by N-H...O=C hydrogen bonds building infinite chains along *a* (Fig. 2). It has been claimed from nuclear magnetic resonance studies of *N*-monosubstituted amides (Graham & Chang, 1971) that the free energy of a single hydrogen bond in a linear chain is 1–2 kcal mole<sup>-1</sup> lower than that in a dimer. This would be enough to account for the occurrence of the *trans*-form in the crystalline state.

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Table 3. *Caprylactam*: molecular parameters

Typical e.s.d.'s are 0.003–0.004 Å for bond lengths, 0.25° for bond angles and 0.5° for torsion angles not involving H atoms. Bond angles and torsion angles calculated for *trans*-cyclononene (Ermer & Lifson, 1973) are in parentheses.

	Corrected for libration					
C(1)–O	1.233 Å	1.242 Å	O—C(1)–N	122.4°	C(8)–N—C(1)–C(2)	148.4 (150.5)°
N—C(1)	1.334	1.342	O—C(1)–C(2)	122.3	N—C(1)–C(2)–C(3)	–88.8 (–88.8)
C(1)–C(2)	1.500	1.510	N—C(1)–C(2)	115.0 (120.5)	C(1)–C(2)–C(3)–C(4)	65.8 (59.4)
C(2)–C(3)	1.535	1.545	C(1)–C(2)–C(3)	108.4 (107.9)	C(2)–C(3)–C(4)–C(5)	–109.2 (–108.1)
C(3)–C(4)	1.534	1.545	C(2)–C(3)–C(4)	115.1 (114.0)	C(3)–C(4)–C(5)–C(6)	64.2 (65.8)
C(4)–C(5)	1.515	1.527	C(3)–C(4)–C(5)	117.4 (117.0)	C(4)–C(5)–C(6)–C(7)	66.7 (66.8)
C(5)–C(6)	1.531	1.541	C(4)–C(5)–C(6)	119.0 (120.7)	C(5)–C(6)–C(7)–C(8)	–109.3 (–108.1)
C(6)–C(7)	1.537	1.547	C(5)–C(6)–C(7)	116.5 (117.0)	C(6)–C(7)–C(8)–N	58.3 (59.4)
C(7)–C(8)	1.522	1.532	C(6)–C(7)–C(8)	114.1 (114.0)	C(7)–C(8)–N—C(1)	–90.5 (–88.8)
C(8)–N	1.448	1.458	C(7)–C(8)–N	109.4 (107.9)	C(8)–N—C(1)–O	–25.8
C–H	0.95–1.04 (4)		C(8)–N—C(1)	122.8 (120.5)		
N–H	0.85		H—C–H	101–113 (3)	H(N)–N–C(1)–O	177
			H(N)–N–C(8)	116	H(N)–N–C(1)–C(2)	–9
			H(N)–N–C(1)	118		

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### Medium-Ring Compounds. XXIII. Caprylolactam Hydrochloride

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**Abstract.** Monoclinic,  $P2_1/c$ ,  $a = 12.79$  (1),  $b = 14.88$  (1),  $c = 10.84$  (1) Å,  $\beta = 109.60$  (10)°,  $C_8H_{15}ON \cdot HCl$ ,  $M = 177.67$ ,  $Z = 8$ ,  $D_m = 1.22$ ,  $D_x = 1.24$  g cm<sup>-3</sup>. The compound is very hygroscopic. Protonation of the lactam takes place at the oxygen atom. The protonated amide group has a nearly planar *cis* configuration in contrast to unprotonated caprylolactam which shows a non-planar *transoid* amide group in the crystalline state. The crystal structure of caprylolactam.HCl is built from hydrogen-bonded (N–H...Cl...H–O) helices running along [010] and associated by electrostatic interactions.

**Introduction.** The crystals, prepared in the same way as those of caprolactam hydrochloride (Winkler & Dunitz, 1975*a*), are extremely hygroscopic and could be handled only in a dry atmosphere. They were sealed in capillaries for X-ray analysis.

Intensities from a crystal of dimensions 0.40 × 0.40 × 0.15 were collected on an automated Hilger and Watts diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 3.45$  cm<sup>-1</sup>) and Sr/Zr balanced filters. All reflexions with scattering angle  $\theta < 23^\circ$  were measured, only those above background in the range  $23^\circ < \theta < 30^\circ$ . 2952 independent  $|F_o|$  values were obtained. The structure (Fig. 1) was solved by the heavy-atom method and refined by full-matrix least-squares analysis (four cycles isotropic, six cycles anisotropic). All hydrogen atoms were located in a difference synthesis (only reflexions with  $\sin \theta/\lambda \leq 0.4$  Å<sup>-1</sup>) and their parameters (including isotropic  $B$ 's) refined by five additional least-squares cycles with Huber-Buser's (1971) criteria. The final  $R$  was 0.056.

Final positional and vibrational parameters are given in Tables 1 and 2, bond distances, bond angles

and torsion angles in Table 3. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).\*

**Discussion.** In dilute solutions of caprylolactam the *cis* form predominates (Hallam & Jones, 1970). Since protonation on the amide oxygen is expected to increase the double-bond character of the amide bond, the non-planar *transoid* amide group observed in crystalline caprylolactam (Winkler & Dunitz, 1975*b*) should be

\* A list of structure factors is given by Winkler (1973) and has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30621 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

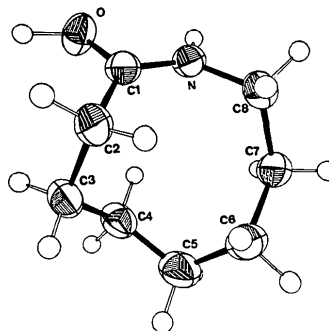


Fig. 1. The protonated caprylolactam molecule (mol 1) with atom numbering viewed along a direction perpendicular to the mean plane of the nine-membered ring. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).