

shows the broad pattern of absorption bands centred on 950 cm^{-1} that is characteristic of compounds containing short, symmetrical hydrogen bonds (Hadzi, 1962). The structure is built from helices of alternating chloride anions and protonated lactam dimers running along the 3_1 screw axes. Electrostatic interactions between the helices, as present in the caprylolactam hydrochloride structure (Winkler & Dunitz, 1975c), are here absent. In keeping with the large thermal motion in the aliphatic part of the molecule, no intermolecular $\text{H}_2\text{C}\cdots\text{CH}_2$ contacts shorter than $3\cdot90\text{ \AA}$ occur.

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Medium-Ring Compounds. XXVII.* Caprinolactam Hemihydrochloride

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Abstract. Tetragonal, $P4_22_1$ (or $P4_32_12$), $a=13\cdot45$ (1), $c=11\cdot85$ (1) \AA , $(\text{C}_{10}\text{H}_{19}\text{ON})_2\cdot\text{HCl}$, $M=374\cdot97$, $Z=4$, $D_m=1\cdot16$, $D_x=1\cdot161\text{ g cm}^{-3}$. The hemiprotonated amide group is *trans* and virtually planar. Two lactam molecules form a protonated dimer linked by a short symmetrical hydrogen bond of $2\cdot43\text{ \AA}$. The crystal structure is built from hydrogen-bonded ($\text{N}\cdots\text{H}\cdots\text{Cl}^-\cdots\text{H}\cdots\text{N}$ and $\text{C}=\text{O}\cdots\text{H}^+\cdots\text{O}=\text{C}$) chains in the $[001]$ direction, which are pairwise associated by electrostatic interactions.

Introduction. Caprinolactam (Fig. 1) was prepared from commercially available cyclodecanone (Aldrich, Milwaukee, U.S.A.) by the method of Ruzicka, Kobelt, Häfliger & Prelog (1949). Crystals of the hemihydrochloride were obtained in the same way as those of pelargolactam hemihydrochloride (Winkler & Dunitz, 1975a) and were sealed in capillaries for X-ray analysis.

Intensities from a cube-shaped crystal ($0\cdot40\text{ mm}$) were collected on an automated Hilger-Watts Y290 diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda=0\cdot71069\text{ \AA}$, $\mu=1\cdot96\text{ cm}^{-1}$) monochromatized by reflexion from graphite. All reflexions with scattering angle $\theta<26^\circ$ were measured, only those above background in the range $26^\circ<\theta<30^\circ$. The measurements led to 1373 independent $|F_o|$ values. The structure was solved by the heavy-atom method, the chloride anion occupying a special position on a twofold axis, and refined by full-matrix least-squares analysis (four cycles isotropic, three cycles anisotropic). All hydrogen atoms (except that involved in the $\text{O}\cdots\text{O}$ hydrogen bond) were located in a difference synthesis (only reflexions with $\sin\theta/\lambda\leq 0\cdot40\text{ \AA}^{-1}$) and their parameters (including isotropic B 's) refined by four additional least-squares cycles with Huber-Buser's (1971) criteria. The final R was $0\cdot037$.

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

* For part XXVI see p. 264.

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

Discussion. Caprinolactam itself crystallizes in an OD-structure with a supercell containing 48 molecules and no attempt was made to solve this structure (Winkler, 1973*b*). In the hemihydrochloride the molecule adopts a conformation related to the one of pelargolactam observed in its hemihydrochloride (Winkler & Dunitz, 1975*a*); the two conformations have a sequence of eight torsion angles in common. The *trans*-amide group is almost planar, the out-of-plane parameters (Winkler & Dunitz, 1971) being $\chi_N = -9.7(3.0)^\circ$, $\chi_C = 1.4(0.5)^\circ$ and $\tau = 180.0(1.5)^\circ$. Whereas the bond lengths of the hemiprotonated amide group agree well with those observed in pelargolactam hemihydrochloride,

* A list of structure factors is given by Winkler (1973*a*) and has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30625 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

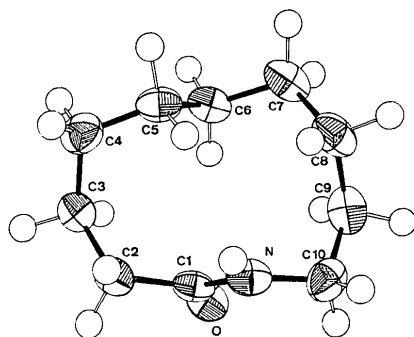


Fig. 1. The hemiprotonated caprinolactam molecule (with atom numbering) viewed along a direction perpendicular to the mean plane of the eleven-membered ring. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

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

		E.s.d.'s for the given <i>B</i> 's are in the range 1.0–2.0 Å ² .			
		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
H(1)	C(2)	55 (4)	117 (4)	177 (5)	4.4
H(2)	C(2)	148 (3)	–12 (4)	371 (5)	1.9
H(1)	C(3)	161 (4)	6 (4)	242 (5)	3.5
H(2)	C(3)	271 (3)	129 (3)	404 (3)	2.0
H(1)	C(4)	308 (3)	10 (4)	365 (5)	2.4
H(2)	C(4)	397 (5)	138 (5)	267 (6)	4.5
H(1)	C(5)	343 (4)	60 (4)	174 (4)	3.7
H(2)	C(5)	333 (4)	213 (4)	106 (5)	2.2
H(1)	C(6)	215 (3)	171 (3)	131 (4)	2.6
H(2)	C(6)	223 (3)	274 (3)	309 (3)	1.0
H(1)	C(7)	326 (4)	316 (4)	255 (5)	2.9
H(2)	C(7)	202 (4)	434 (4)	214 (4)	1.1
H(1)	C(8)	247 (5)	389 (4)	95 (4)	4.3
H(2)	C(8)	63 (4)	399 (4)	91 (5)	5.5
H(1)	C(9)	99 (3)	281 (3)	93 (3)	1.1
H(2)	C(9)	63 (4)	345 (3)	315 (4)	1.4
H(1)	C(10)	–34 (4)	384 (4)	244 (5)	2.7
H(2)	C(10)	–71 (4)	234 (4)	314 (4)	2.1
H(N)		–76 (3)	228 (3)	185 (4)	1.6

there are significant differences in the bond angles at the carbonyl carbon. Referred to the standard *trans* unit (Marsh & Donohue, 1967), an opening of 4° is observed for the N–C(1)–C(2) angle, reminiscent of the comparable effect observed for protonated *cis*-amide groups (Winkler & Dunitz, 1975*b*). The torsion angles of the eleven-membered ring agree well with those calculated by Ermer (1973) for the corresponding *trans*-cycloundecene conformation by means of a consistent force field (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 [$\langle(\Delta U_{ij})^2\rangle^{1/2} = 0.00234 \text{ Å}^2$, $\langle\sigma^2(U_{ij})\rangle^{1/2} = 0.00130 \text{ Å}^2$]. The discrepancies are probably due to internal motions in the molecule, although the mean isotropic temperature factor ($\langle B \rangle = 4.4 \text{ Å}^2$)

Table 1. *Caprinolactam hemihydrochloride*: 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 Å²) correspond to the temperature-factor expression $T = \exp[-2\pi^2(U_{11}h^2a^2 + 2U_{12}hka^*b^* + \dots)]$ and have e.s.d.'s in the range 0.0006–0.0020 Å² (except for Cl, where they are smaller).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	553 (0)	553 (1)	0000 (0)	800	800	300	–257	78	–78
O	820 (1)	1642 (1)	4214 (1)	683	602	244	–20	8	–9
N	380 (2)	1492 (2)	2414 (2)	540	604	293	–118	1	–6
C(1)	917 (2)	1202 (2)	3267 (2)	525	482	290	–143	30	33
C(2)	1655 (2)	375 (2)	3121 (2)	646	421	425	–42	40	4
C(3)	2733 (2)	720 (2)	3343 (2)	587	553	575	31	7	94
C(4)	3298 (2)	1131 (2)	2344 (2)	579	583	644	11	118	–90
C(5)	2807 (2)	1955 (2)	1678 (2)	564	606	380	–115	87	–38
C(6)	2599 (2)	2896 (2)	2357 (2)	618	506	390	–149	–29	–19
C(7)	2049 (2)	3688 (2)	1697 (2)	833	529	528	–171	–114	94
C(8)	976 (2)	3430 (2)	1403 (2)	816	613	523	–84	–159	156
C(9)	265 (2)	3328 (2)	2432 (3)	724	628	652	125	–75	9
C(10)	–289 (2)	2346 (2)	2466 (2)	481	810	441	44	–45	40

Table 3. *Caprinolactam hemihydrochloride: molecular parameters*

Typical e.s.d.'s are 0.004 Å for bond lengths, 0.2–0.3° for bond lengths and 0.5° for torsion angles not involving hydrogen atoms. Torsion angles for the corresponding *trans*-cycloundecene conformation (Ermer, 1973) are in parentheses.

		Corrected for libration					
C(1)—O	1.275 Å	1.281 Å	O—C(1)—N	119.2°	C(10)—N—C(1)—C(2)	−174.5	(−175.4)°
N—C(1)	1.302	1.308	O—C(1)—C(2)	120.9	N—C(1)—C(2)—C(3)	117.8	(116.6)
C(1)—C(2)	1.500	1.508	N—C(1)—C(2)	120.0	C(1)—C(2)—C(3)—C(4)	−88.8	(−84.0)
C(2)—C(3)	1.545	1.550	C(1)—C(2)—C(3)	112.2	C(2)—C(3)—C(4)—C(5)	52.5	(55.6)
C(3)—C(4)	1.511	1.517	C(2)—C(3)—C(4)	116.7	C(3)—C(4)—C(5)—C(6)	61.2	(60.3)
C(4)—C(5)	1.513	1.520	C(3)—C(4)—C(5)	117.2	C(4)—C(5)—C(6)—C(7)	−176.4	(−177.9)
C(5)—C(6)	1.526	1.533	C(4)—C(5)—C(6)	114.3	C(5)—C(6)—C(7)—C(8)	68.5	(65.4)
C(6)—C(7)	1.514	1.521	C(5)—C(6)—C(7)	113.6	C(6)—C(7)—C(8)—C(9)	65.2	(64.5)
C(7)—C(8)	1.526	1.531	C(6)—C(7)—C(8)	114.9	C(7)—C(8)—C(9)—C(10)	−126.0	(−126.0)
C(8)—C(9)	1.556	1.562	C(7)—C(8)—C(9)	115.0	C(8)—C(9)—C(10)—N	54.3	(56.9)
C(9)—C(10)	1.517	1.523	C(8)—C(9)—C(10)	113.5	C(9)—C(10)—N—C(1)	75.1	(70.8)
C(10)—N	1.461	1.469	C(9)—C(10)—N	112.4	C(10)—N—C(1)—O	4.1	
			C(10)—N—C(1)	123.0			
C—H	0.94–1.12 (6)		H—C—H	103–111 (4)	H(N)—N—C(1)—O	174	
N—H	0.91		H(N)—N—C(10)	125	H(N)—N—C(1)—C(2)	−4	
			H(N)—N—C(1)	111			

is smaller than usual in this series and does not allow large vibrational amplitudes.

The crystal structure is built from hydrogen-bonded chains of alternating chloride anions and protonated caprinolactam dimers running along *c* (Fig. 2). As in pelargolactam hemihydrochloride the dimers are held together by a short symmetrical O...O hydrogen bond of 2.43 Å, and each chloride anion is hydrogen-bonded to two amide nitrogens. In pelargolactam hemihydrochloride electrostatic interaction between the negative and positive charge centres, both located on twofold axes, is weak, and the hydrogen-bonded species are arranged in a helix. Here they are arranged in linear chains which are pairwise associated by electrostatic interactions, the distance of a chloride anion from the midpoint of the O...H...O hydrogen bond being 3.36 Å.

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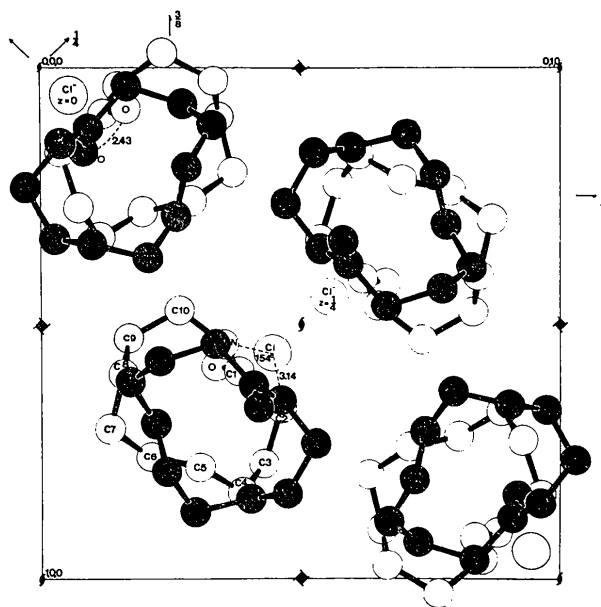


Fig. 2. The crystal structure of caprinolactam hemihydrochloride projected down [001]. Atoms of the upper molecules are marked with black circles.

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