

In all electron-density maps and in the various least-squares refinements the amide group came out as slightly non-planar, with a torsion angle C(2)–C(1)–N–C(9) in the range 165–170°.

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Medium-Ring Compounds. XXV. Pelargolactam Hemihydrochloride

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Abstract. Trigonal, $P3_121$ (or $P3_221$), $a=7.26$ (1), $c=32.71$ (3) Å, $(C_9H_{17}ON)_2 \cdot HCl$, $M=346.92$, $Z=3$, $D_m=1.17$, $D_x=1.158$ g cm⁻³. The hemiprotonated *trans*-amide group is non-planar, the torsion angle C–C–N–C being 168°. The amide oxygen atoms of pairs of lactam molecules, related by a twofold axis, are linked by a short, symmetrical hydrogen bond (O···O, 2.43 Å). The crystal structure is built from helices of alternating chloride anions and protonated lactam dimers around the threefold screw axes, anions and cations being linked by Cl···H–N hydrogen bonds.

Introduction. Pelargolactam was prepared from commercially available cyclononane (Aldrich, Milwaukee, U.S.A.) by the method described by Ruzicka, Kobelt, Häfliger & Prelog (1949). When dry HCl gas

was passed into an ethereal solution of pelargolactam, the solution became turbid, but after a short time it cleared, yielding an aqueous phase at the bottom of the flask. After removal of ether the residual liquid was dried in an evacuated desiccator over phosphorus pentoxide. The remaining solid was washed several times with ether and then dissolved in warm acetone. Slow evaporation of the solvent yielded crystals of the hemihydrochloride as trigonal plates, frequently twinned. For X-ray analysis the crystals were sealed in capillaries.

Intensities from a crystal of dimensions 0.40 × 0.40 × 0.15 Å were collected on an automated Hilger–Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å, $\mu=2.1$ cm⁻¹). All reflexions with scattering angle $\theta < 20^\circ$ were measured,

Table 1. *Pelargolactam hemihydrochloride: atomic coordinates (e. s. d.'s in parentheses) and vibrational tensor components for non-hydrogen atoms (all × 10⁴)*

The U_{ij} values (in Å²) correspond to the temperature-factor expression $T = \exp [-2\pi(U_{11}h^2a^{*2} \dots + 2U_{12}hka^*b^* \dots)]$ and have e.s.d.'s in the range 0.002–0.020 Å² (except for Cl, where they are smaller).

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	5954 (0)	5954 (4)	0000 (0)	894	894	379	564	–56	56
O	–497 (7)	8788 (8)	2026 (1)	838	940	428	529	–119	–60
N	584 (9)	8904 (9)	2670 (1)	772	696	429	343	–2	–42
C(1)	1007 (12)	9279 (10)	2281 (2)	729	497	487	338	45	21
C(2)	3292 (13)	10257 (12)	2158 (2)	790	836	562	246	7	–6
C(3)	3835 (16)	8595 (23)	2025 (3)	870	2104	801	818	74	–181
C(4)	3206 (20)	6713 (22)	2291 (3)	1445	1926	963	1311	–429	–462
C(5)	907 (19)	4888 (16)	2233 (3)	1685	1186	923	1022	–711	–647
C(6)	–156 (22)	3627 (17)	2622 (4)	2244	1195	1377	1133	–680	–136
C(7)	–956 (15)	4538 (16)	2911 (3)	1052	849	1147	319	–199	220
C(8)	–2373 (13)	5362 (13)	2767 (2)	727	799	753	192	51	166
C(9)	–1556 (13)	7619 (14)	2833 (2)	717	982	573	360	126	59

only those above background in the range $20^\circ < \theta < 24^\circ$, leading to 630 independent $|F_o|$ values. The structure was solved by the heavy-atom method and refined by full-matrix least-squares analysis (three cycles isotropic, six cycles anisotropic). All hydrogen atoms were located in a difference synthesis (only reflexions with $\sin \theta/\lambda \leq 0.4 \text{ \AA}^{-1}$) and their parameters (including isotropic B 's) refined by four additional least-squares cycles with Huber-Buser's (1971) criteria. The final R was 0.039. The limited amount of data is expressed in the rather low value of around 4 for the number of reflexions per parameter.

Final positional and vibrational parameters are given in Tables 1 and 2, bond distances, bond angles and torsion angles in Table 3. Scattering factors for C, N, O, Cl^- were taken from *International Tables for*

X-ray Crystallography (1962) and those for H from Stewart, Davidson & Simpson (1965).*

Discussion. In contrast to the highly disordered crystal structure of pelargolactam (Winkler & Dunitz, 1975a), the hemihydrochloride has a structure in which disorder is expressed only in the rather large and anisotropic temperature factors of some atoms. The conformation of the ten-membered ring (Fig. 1) is similar to that of the minor component (occupation factor *ca* 20%) found in the disordered structure of *trans*-cyclodec-5-enyl-*p*-nitrobenzoate (Ermer, 1970). Bond angles and torsion angles calculated with the consistent force field of Ermer & Lifson (1973) for the corresponding conformation of *trans*-cyclodecene (Ermer, 1973) agree reasonably well with those observed in the hemiprotonated lactam (Table 3): the r.m.s. deviations between observed and calculated parameters are 3.0° and 6.1° for the ten bond angles and torsion angles respectively. The largest discrepancies involve the atoms in the middle of the saturated hydrocarbon chain, which show anisotropic thermal motions (see Fig. 1 and Table 1) with B values approaching 20 \AA^2 for their largest components. Such large thermal motions may arise from low-energy torsional vibrations or from disorder: in either case the separations between mean atomic positions do not correspond to interatomic distances, and systematic errors in molecular parameters, such as shortened bond lengths [e.g. C(3)–C(4), C(6)–C(7), C(8)–C(9)] and opened C–C–C angles [e.g. at C(3) and C(7)], may be produced.

Table 2. *Pelargolactam 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 B 's are in the range $1.5\text{--}2.3 \text{ \AA}^2$.

	x/a	y/b	z/c	$B(\text{\AA}^2)$
H(N)	185 (10)	931 (10)	282 (2)	6.5
H(1) C(2)	351 (11)	1137 (10)	197 (2)	8.2
H(2) C(2)	414 (9)	1099 (9)	238 (2)	7.6
H(1) C(3)	339 (11)	827 (10)	179 (2)	9.0
H(2) C(3)	546 (10)	934 (10)	199 (2)	5.8
H(1) C(4)	427 (9)	618 (10)	223 (2)	7.2
H(2) C(4)	335 (13)	737 (12)	255 (2)	10.5
H(1) C(5)	16 (12)	553 (13)	209 (2)	9.9
H(2) C(5)	104 (11)	393 (11)	206 (2)	9.0
H(1) C(6)	–130 (11)	234 (11)	249 (2)	10.0
H(2) C(6)	103 (11)	353 (11)	275 (2)	10.4
H(1) C(7)	–176 (10)	350 (10)	314 (2)	7.0
H(2) C(7)	48 (13)	571 (12)	301 (2)	10.5
H(1) C(8)	–262 (11)	492 (10)	248 (2)	7.9
H(2) C(8)	–378 (10)	463 (10)	291 (2)	7.8
H(1) C(9)	–258 (10)	810 (11)	270 (2)	7.2
H(2) C(9)	–138 (11)	786 (11)	312 (2)	8.5

* 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 30623 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Pelargolactam hemihydrochloride*: molecular parameters

E. s. d.'s are in the range $0.006\text{--}0.018 \text{ \AA}$ for bond lengths, $0.6\text{--}1.1^\circ$ for bond angles and $1.0\text{--}2.0^\circ$ for torsion angles not involving H atoms. Bond angles and torsion angles calculated for the corresponding *trans*-cyclodecene conformation (Ermer, 1973) are in parentheses.

	Corrected for libration					
C(1)–O	1.277 \AA	1.289 \AA	O—C(1)—N	120.1°	C(9)—N—C(1)—C(2)	–168.3 (–167.9)°
N—C(1)	1.305	1.318	O—C(1)—C(2)	123.1	N—C(1)—C(2)—C(3)	95.4 (95.6)
C(1)—C(2)	1.496	1.515	N—C(1)—C(2)	116.8 (121.1)	C(1)—C(2)—C(3)—C(4)	–49.5 (–49.9)
C(2)—C(3)	1.509	1.528	C(1)—C(2)—C(3)	111.7 (111.6)	C(2)—C(3)—C(4)—C(5)	84.1 (89.7)
C(3)—C(4)	1.488	1.505	C(2)—C(3)—C(4)	118.8 (113.2)	C(3)—C(4)—C(5)—C(6)	–147.1 (–157.0)
C(4)—C(5)	1.538	1.557	C(3)—C(4)—C(5)	114.9 (112.9)	C(4)—C(5)—C(6)—C(7)	78.5 (73.3)
C(5)—C(6)	1.533	1.551	C(4)—C(5)—C(6)	114.6 (114.9)	C(5)—C(6)—C(7)—C(8)	50.2 (59.8)
C(6)—C(7)	1.431	1.449	C(5)—C(6)—C(7)	118.1 (116.2)	C(6)—C(7)—C(8)—C(9)	–118.5 (–116.4)
C(7)—C(8)	1.500	1.516	C(6)—C(7)—C(8)	119.8 (114.4)	C(7)—C(8)—C(9)—N	52.1 (43.3)
C(8)—C(9)	1.453	1.472	C(7)—C(8)—C(9)	115.4 (115.2)	C(8)—C(9)—N—C(1)	75.5 (62.3)
C(9)—N	1.455	1.474	C(8)—C(9)—N	111.8 (112.3)	C(9)—N—C(1)—O	10.7
			C(9)—N—C(1)	123.7 (124.5)		
C—H	0.82–1.06 (6)		H—C—H	103–118 (6)	H(N)—N—C(1)—O	178
N—H	0.95		H(N)—N—C(9)	125	H(N)—N—C(1)—C(2)	–1
			H(N)—N—C(1)	110		

On the other hand, the vibrational tensors of C(3)–C(7) (Fig. 1) suggest that the main molecular motion is a libration around an axis passing through the amide bond in a direction approximately perpendicular to the best plane through the ten ring atoms. Analysis of

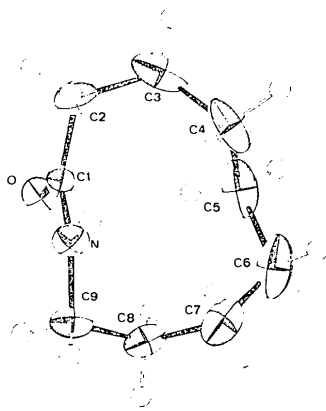


Fig. 1. The hemiprotonated pelargolactam molecule (with atom numbering) viewed along a direction perpendicular to the mean plane of the ten-membered ring. The vibration ellipsoids are drawn at the 25% probability level (Johnson, 1965).

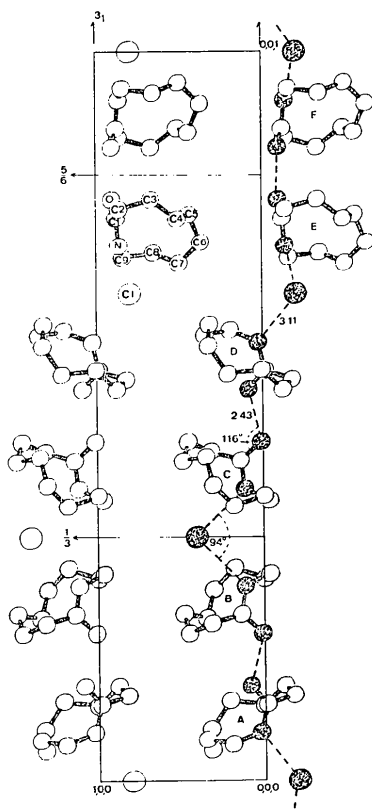


Fig. 2. The crystal structure of pelargolactam hemihydrochloride projected on the (010) plane. Black atoms (N, O, Cl) are involved in hydrogen bonding.

the experimental thermal motion tensors in terms of rigid-body translational and librational motion (Schoemaker & Trueblood, 1968) supports this impression and leads to fairly good agreement between observed and calculated tensor components [$\langle(\Delta U_{ij})^2\rangle^{1/2} = 0.0106 \text{ \AA}^2$, $\langle\sigma^2(U_{ij})\rangle^{1/2} = 0.0096 \text{ \AA}^2$]. The largest eigenvalues of C(2)–C(9) are well reproduced by a librational motion of amplitude 7.4° about an axis passing approximately through the amide oxygen atom and the amide hydrogen H(N). Such a libration hardly affects the hydrogen bonds, which seem to provide the main interaction between the molecules and their environment. The libration corrections are more than 0.02 \AA in bond lengths, not nearly large enough to explain apparent C–C bond lengths of $1.43\text{--}1.45 \text{ \AA}$. We suspect that the observed parameters in this part of the molecule are in error because of low-energy internal motions or disorder connected with the presence of a second, minor conformation, as was shown to be the case for 1,1,5,5-tetramethylcyclodecane-8-carboxylic acid (Dunitz, Eser, Bixon & Lifson, 1967) where similar anomalies were observed. These difficulties in interpretation do not appear to affect the dimensions of the hemi-protonated *trans*-amide group, which differ from those of the standard *trans*-amide unit (Marsh & Donohue, 1967) in a way that seems quite consistent with the effects of protonation. The C–N bond becomes slightly shorter, the C–O bond slightly longer. These changes are in the same sense as, but smaller than those that accompany full protonation of the *cis*-amide group (Winkler & Dunitz, 1975*b*). The opening of the N–C(1)–C(2) angle amounts to about 5° in protonated *cis*-amide groups but is much smaller (0.9°) and barely significant for the hemi-protonated *trans*-amide group of pelargolactam.

The hemi-protonated amide group in the ten-membered ring is significantly non-planar, the out-of-plane deformations (Winkler & Dunitz, 1971) being $\chi_C = 1.0 (1.2)^\circ$, $\chi_N = -12.7 (5.0)^\circ$ and $\tau = -175.2 (2.5)^\circ$. The 11.7° deviation of the C(9)–N–C(1)–C(2) torsion angle from 180° is composed mainly from bending at nitrogen and twisting [$\pi + \tau - \chi_N/2 = 11.2 (0.5)$], although the uncertainty in the amide-hydrogen position does not allow their relative contributions to be determined very accurately.

In the crystal structure (Fig. 2) the chloride anions lie on twofold axes ($z=0, \frac{1}{3}$ and $\frac{2}{3}$). Each is linked to two lactam molecules by N–H...Cl hydrogen bonds. The lactam molecules among themselves are linked by short, symmetrical O...H⁺...O hydrogen bonds into protonated dimers also centred on twofold axes ($z = \frac{1}{6}, \frac{1}{2}$ and $\frac{5}{6}$). The short O...O distance of 2.43 \AA is close to the corresponding distances of 2.42 and 2.48 \AA reported in the structures of acetamide hemihydrochloride (Takei, 1957) and hemihydrobromide (Wiemann, Gillier-Pandraud, Thoai & Beauté, 1969) and is typical of symmetrical hydrogen bonding [see Speakman (1972) for a review]. We have confirmed that the infrared spectrum of pelargolactam hydrochloride also

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 3.90 \AA occur.

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Medium-Ring Compounds. XXVII.* Caprinolactam Hemihydrochloride

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Abstract. Tetragonal, $P4_22$ (or $P4_32_12$), $a=13.45(1)$, $c=11.85(1)\text{ \AA}$, $(\text{C}_{10}\text{H}_{19}\text{ON})_2\cdot\text{HCl}$, $M=374.97$, $Z=4$, $D_m=1.16$, $D_x=1.161\text{ g cm}^{-3}$. The hemiprotonated amide group is *trans* and virtually planar. Two lactam molecules form a protonated dimer linked by a short symmetrical hydrogen bond of 2.43 \AA . The crystal structure is built from hydrogen-bonded ($\text{N}-\text{H}\cdots\text{Cl}^-\cdots\text{H}-\text{N}$ 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 (0.40 mm) were collected on an automated Hilger-Watts Y290 diffractometer with $\text{Mo K}\alpha$ radiation ($\lambda=0.71069\text{ \AA}$, $\mu=1.96\text{ cm}^{-1}$) 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 $\sin\theta/\lambda\leq 0.40\text{ \AA}^{-1}$) and their parameters (including isotropic B 's) refined by four additional least-squares cycles with Huber-Buser's (1971) criteria. The final R was 0.037 .

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

* For part XXVI see p. 264.