

## Medium-Ring Compounds. XXVI.\* Tripelargolactam Oxonium Chloride

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Triclinic,  $PT$ ,  $a = 12.26$  (1),  $b = 12.74$  (1),  $c = 12.09$  (1) Å,  $\alpha = 108.06$  (10),  $\beta = 120.39$  (10),  $\gamma = 81.74$  (10)°,  $(C_9H_{17}ON)_3 \cdot H_2O \cdot HCl$ ,  $M = 520.17$ ,  $Z = 2$ ,  $D_m = 1.14$ ,  $D_x = 1.150$  g cm<sup>-3</sup>. All three molecules assume the same general type of conformation with a slightly non-planar *trans*-amide group. There is evidence for the occurrence of minor amounts of other conformations. The crystal structure is built from hydrogen-bonded layers showing approximate trigonal symmetry with chlorine anions hydrogen-bonded to three amide nitrogens and oxonium cations to three amide oxygens related by the approximate threefold axis. Attractive electrostatic interactions between anions and cations help to form double layers showing approximately  $\bar{3}$  point symmetry. It is only in the association of the double layers, which have non-polar surfaces, that the trigonal symmetry is lost.

### Introduction

Crystals of irregular shape were sometimes obtained as a by-product in the attempt to crystallize pelargolactam hemihydrochloride (Winkler & Dunitz, 1975) at temperatures around 0°. For X-ray analysis they were sealed in capillaries.

Intensities from a crystal of dimensions 0.50 × 0.50 × 0.20 mm were collected on an automated Hilger-Watts Y290 diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å,  $\mu = 1.65$  cm<sup>-1</sup>) monochromatized by reflexion from graphite. All reflexions with scattering angle  $\theta < 20^\circ$  were measured, only those above background in the range  $20^\circ < \theta < 24^\circ$ . The measurements led to 3289 independent  $|F_o|$  values. Analysis of a sharpened Patterson synthesis gave positions for the chlorine anion and the 15 atoms (C, N and O) of the three amide moieties. An  $F_o$  synthesis based on phases calculated from these 16 atomic positions showed most of the remaining ring atoms and a stronger peak at the centre of three amide oxygens. This peak was attributed to a water molecule, whose presence in the crystal had not been recognized before. Although the electron density was diffuse in some parts of the hydrocarbon chains, all ring atoms were located unambiguously in a second  $F_o$  synthesis. Four cycles of full-matrix least-squares refinement (isotropic temperature factors) reduced the initial  $R$  of 0.33 to 0.19. With 51 hydrogen atoms (CH<sub>2</sub> and NH) at calculated positions ( $B_H = 12$  Å<sup>2</sup> assumed and held constant) included, seven cycles of block-diagonal least-squares refinement (anisotropic temperature factors for non-hydrogen atoms) led to the final  $R$  of 0.096. An  $(F_o - F_c)$  synthesis, including only the non-hydrogen atoms, showed positive peaks (0.15–0.30 e Å<sup>-3</sup>) for all H atoms of molecules 1 and 2, for some H atoms of molecule 3, and also spurious peaks of up to 0.7 e Å<sup>-3</sup> in the region of molecule 3. Around the O atom of the water molecule

the residual electron density is very diffuse, and it was not possible to determine the positions of the three remaining hydrogen atoms involved in O...O hydrogen bonds.

Final positional and vibrational parameters are given in Tables 1 and 2, bond angles, bond lengths and torsion angles in Table 3. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).\*

### Discussion

All three molecules of the asymmetric unit assume the same general type of conformation as found in the analysis of pelargolactam hemihydrochloride (Winkler & Dunitz, 1975). As in that analysis, the molecular parameters (Table 3) show certain features (abnormally short bond lengths, opened bond angles) characteristic of disordered structures. For the four independent pelargolactam molecules in the two crystal structures, the mean differences between observed and standard bond lengths increase with the mean isotropic temperature factor of the molecule. For all these molecules, but especially for molecule 3 with its residual electron density and large vibrational motion, it seems likely that the averaged structure actually corresponds to a superposition of different molecular orientations and/or conformations. The highest peak (0.7 e Å<sup>-3</sup>) observed in the final  $(F_o - F_c)$  synthesis in the region of molecule 3 could well correspond to an alternative amide oxygen position, since it is found at a distance of 2.5 Å from the water oxygen. Although a second residual peak of 0.5 e Å<sup>-3</sup> is compatible with a corresponding amide nitrogen position, it was not possible to locate additional atoms.

\* Parts XIX–XXV and XXVII appear as Short Structural Papers on pp. 268–288.

\* 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 30624 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Analysis of the experimental thermal motion tensors in terms of rigid-body translational and librational motion (Schomaker & Trueblood, 1968), also yields a level of disagreement between observed and calculated vibration tensor components that increases with the mean isotropic temperature factor:

	$\langle(\Delta U_{ij})^2\rangle^{1/2}$	$\langle\sigma^2(U_{ij})\rangle^{1/2}$	$\langle B_{ii}\rangle$
Pelargolactam			
hemihydrochloride	0.0106 Å <sup>2</sup>	0.0096 Å <sup>2</sup>	7.5 Å <sup>2</sup>
Molecule 2	0.0128	0.0076	9.3
Molecule 1	0.0151	0.0083	9.6
Molecule 3	0.0270	0.0107	12.6

Table 1. *Tripelargolactam oxonium chloride: 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<sup>2</sup>) 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 0.003–0.020 Å<sup>2</sup> (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	1693 (2)	2530 (2)	2626 (2)	546	1817	570	-67	219	449
O(H <sub>2</sub> O)	1641 (5)	6117 (7)	3622 (6)	672	2353	918	99	373	766
1O	259 (5)	4117 (5)	6260 (5)	716	954	814	47	453	189
1N	1374 (6)	3728 (6)	5187 (6)	709	954	805	49	399	404
1C(1)	365 (7)	3615 (7)	5249 (7)	558	935	701	52	248	381
1C(2)	-622 (8)	2822 (9)	4064 (8)	775	1436	708	-109	277	231
1C(3)	-433 (11)	1674 (10)	4282 (12)	1228	1526	1327	-584	433	-263
1C(4)	747 (12)	1158 (9)	4733 (11)	1880	946	1321	27	932	157
1C(5)	1651 (12)	1546 (9)	6224 (12)	1843	1187	1516	150	1050	650
1C(6)	3009 (15)	1590 (12)	6631 (16)	2145	1753	2376	691	1330	685
1C(7)	3555 (10)	2472 (11)	6684 (12)	1010	2186	1769	666	825	1147
1C(8)	3259 (8)	3633 (10)	7300 (9)	730	1863	924	-301	194	329
1C(9)	2526 (8)	4312 (8)	6353 (9)	851	1113	1156	-264	531	291
2O	6269 (4)	4029 (5)	4477 (5)	629	997	685	-166	237	226
2N	4174 (5)	3665 (5)	3240 (6)	627	916	702	81	331	184
2C(1)	5300 (7)	3558 (7)	4226 (7)	683	883	563	20	312	125
2C(2)	5361 (8)	2782 (9)	4973 (8)	778	1545	696	-256	229	397
2C(3)	5766 (10)	1655 (10)	4482 (11)	1273	1535	1362	-155	253	861
2C(4)	5055 (11)	1122 (9)	3026 (14)	1335	889	2164	45	637	541
2C(5)	5554 (10)	1401 (10)	2193 (12)	938	1442	1573	139	671	29
2C(6)	4566 (12)	1451 (12)	804 (12)	1337	2000	1341	-156	551	-110
2C(7)	3751 (10)	2357 (11)	633 (10)	1126	2023	819	197	443	170
2C(8)	4347 (10)	3521 (9)	1274 (9)	1248	1548	901	-674	425	618
2C(9)	3982 (8)	4216 (8)	2282 (9)	761	955	1053	128	262	501
3O	1559 (6)	6054 (6)	1566 (6)	986	1753	1070	215	520	648
3N	632 (7)	6391 (8)	-385 (7)	932	1838	757	-231	317	284
3C(1)	631 (9)	6521 (10)	688 (9)	949	1984	969	128	495	847
3C(2)	-246 (10)	7261 (11)	1027 (11)	1152	2162	1234	531	655	953
3C(3)	156 (14)	8372 (14)	1682 (16)	1722	2292	2241	-183	1212	-24
3C(4)	646 (12)	9068 (12)	1327 (12)	1639	2099	1471	705	910	959
3C(5)	2073 (13)	8869 (13)	1788 (11)	1760	2565	820	-1009	129	107
3C(6)	2446 (16)	8833 (15)	839 (18)	2258	2513	2424	-739	1175	521
3C(7)	2451 (14)	7919 (13)	-92 (23)	2112	2507	1490	-784	840	680
3C(8)	2705 (10)	6753 (12)	-12 (11)	860	2347	1330	2	554	368
3C(9)	1635 (9)	5990 (9)	-681 (9)	977	1567	727	137	448	209

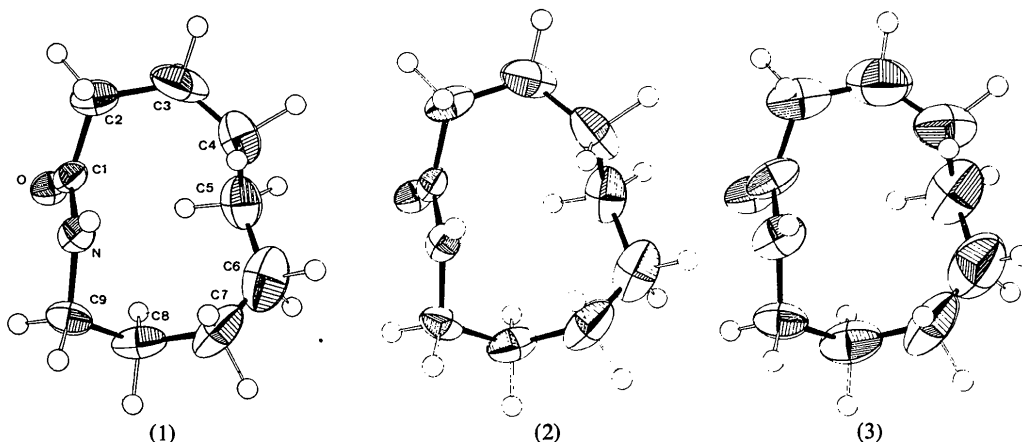


Fig. 1. The three pelargolactam molecules (from left to right: 1, 2 and 3) viewed along a direction perpendicular to the mean plane of the ten-membered ring. The vibration ellipsoids are drawn at the 25% probability level (Johnson, 1965).

Table 2. *Tripelargolactam oxonium chloride*: calculated hydrogen positions ( $\times 10^3$ )Assumptions:  $\text{CH}_2$ , C-H, 1.09 Å, HCH,  $106^\circ$ , local  $C_{2v}$  symmetry; N-H, 1.00 Å along bisector C(1)NC(9).

	$x/a$	$y/b$	$z/c$
H(1N)	136	340	431
H(1) 1C(2)	-157	312	388
H(2) 1C(2)	-58	278	316
H(1) 1C(3)	-76	171	499
H(2) 1C(3)	-109	111	333
H(1) 1C(4)	59	26	445
H(2) 1C(4)	120	128	420
H(1) 1C(5)	137	237	662
H(2) 1C(5)	153	100	671
H(1) 1C(6)	355	146	763
H(2) 1C(6)	318	87	596
H(1) 1C(7)	459	237	723
H(2) 1C(7)	331	242	566
H(1) 1C(8)	273	358	780
H(2) 1C(8)	415	407	809
H(1) 1C(9)	227	510	687
H(2) 1C(9)	312	453	602
H(2N)	342	335	315
H(1) 2C(2)	602	312	604
H(2) 2C(2)	443	273	488
H(1) 2C(3)	677	170	478
H(2) 2C(3)	571	111	500
H(1) 2C(4)	507	22	285
H(2) 2C(4)	406	136	265
H(1) 2C(5)	606	220	275
H(2) 2C(5)	626	79	212
H(1) 2C(6)	506	140	24
H(2) 2C(6)	398	70	32
H(1) 2C(7)	314	225	-44
H(2) 2C(7)	312	232	102
H(1) 2C(8)	538	346	175
H(2) 2C(8)	407	393	49
H(1) 2C(9)	453	499	280
H(2) 2C(9)	298	445	177
H(3N)	-17	660	-112
H(1) 3C(2)	-115	723	11
H(2) 3C(2)	-44	694	166
H(1) 3C(3)	-66	881	174
H(2) 3C(3)	88	838	271
H(1) 3C(4)	11	894	24
H(2) 3C(4)	50	994	177
H(1) 3C(5)	263	952	271
H(2) 3C(5)	233	809	207
H(1) 3C(6)	185	943	29
H(2) 3C(6)	341	918	142
H(1) 3C(7)	151	789	-98
H(2) 3C(7)	313	810	-35
H(1) 3C(8)	335	640	-41
H(2) 3C(8)	323	677	105
H(1) 3C(9)	125	579	-177
H(2) 3C(9)	197	521	-41

As can be seen from Fig. 1, molecules 1 and 2 seem to librate around an axis running approximately through the atoms O and H(N). The calculated mean-square librational amplitudes are  $7.8$  and  $8.6^\circ$  for molecules 1 and 2 respectively (a value of  $7.4^\circ$  was found for an equivalent libration in pelargolactam hemihydrochloride). For molecule 3 the rigid-body analysis gives a large translational component with  $U=0.186 \text{ \AA}^2$  in a direction approximately perpendicular to the plane of the amide group.

The dimensions of the amide group in molecules 1 and 2 differ very little from those of the standard *trans*-peptide group (Marsh & Donohue, 1967). The

$pK_a$  of the protonated amide group in the medium-ring lactams is about the same as that of  $\text{H}_3\text{O}^+$  (Huisgen, Brade, Walz & Glogger, 1957). In any case, the amide groups can be at most  $\frac{1}{2}$  protonated, and their dimensions should not differ too much from those of the unprotonated pelargolactam molecule.

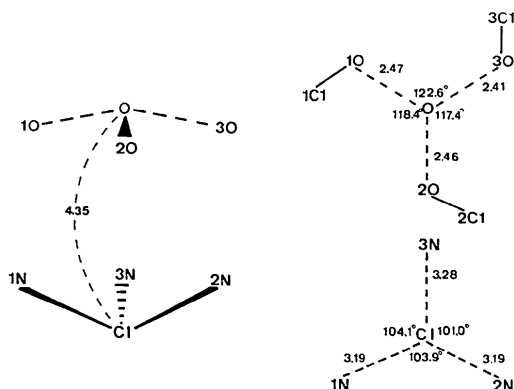


Fig. 2. *Tripelargolactam oxonium chloride*. Pyramidal coordination and hydrogen-bonding parameters of chloride anion and oxonium cation.

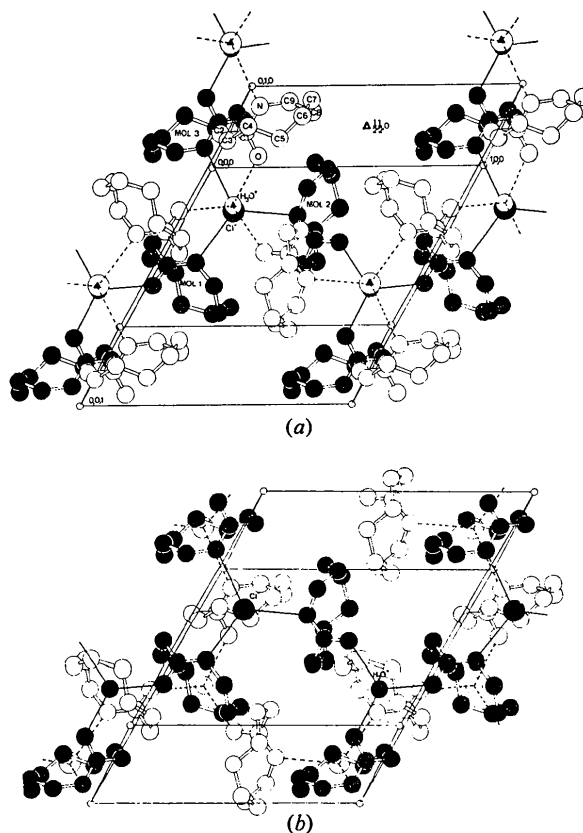


Fig. 3. The crystal structure of *tripelargolactam oxonium chloride* projected on the (010) plane. Atoms of the layer common to (a) and (b) are marked with black circles and its hydrogen bonds with full lines: (a) double layer with approximate  $\bar{3}$  point symmetry (electrostatic interaction  $\text{H}_3\text{O}^+\cdots\text{Cl}^-$ ); (b) double layer with  $\bar{1}$  point symmetry (hydrophobic contact).

Table 3. *Tripelargolactam oxonium chloride: molecular parameters (Å and degrees)*

E.s.d.'s are in the range 0.007–0.020 Å for bond lengths, 0.7–1.5° for bond angles and 1.5–3.0° for torsion angles. Values in parentheses are strongly affected by large thermal motion or disorder (see Discussion).

C(1)–O	1.254	1.260	(1.322)	O—C(1)–N	121.6	122.1	(116.5)	C(9)–N—C(1)–C(2)	–168.6	–168.9	(–158.9)
N—C(1)	1.307	1.315	(1.257)	O—C(1)–C(2)	122.6	122.6	121.1	N—C(1)–C(2)–C(3)	93.2	96.4	87.1
C(1)–C(2)	1.495	1.504	(1.459)	N—C(1)–C(2)	115.8	115.3	(121.9)	C(1)–C(2)–C(3)–C(4)	–48.4	–52.2	–49.3
C(2)–C(3)	1.530	(1.492)	(1.409)	C(1)–C(2)–C(3)	110.5	112.3	115.8	C(2)–C(3)–C(4)–C(5)	79.2	87.0	81.1
C(3)–C(4)	(1.405)	(1.482)	(1.407)	C(2)–C(3)–C(4)	(122.7)	116.6	(128.5)	C(3)–C(4)–C(5)–C(6)	–144.3	–146.9	(–136.6)
C(4)–C(5)	1.518	1.556	1.552	C(3)–C(4)–C(5)	115.5	115.0	111.8	C(4)–C(5)–C(6)–C(7)	85.1	73.9	89.1
C(5)–C(6)	(1.482)	1.509	(1.422)	C(4)–C(5)–C(6)	116.0	115.9	115.5	C(5)–C(6)–C(7)–C(8)	44.0	54.6	(32.8)
C(6)–C(7)	(1.357)	(1.408)	(1.347)	C(5)–C(6)–C(7)	(122.8)	119.6	(125.3)	C(6)–C(7)–C(8)–C(9)	–112.4	–118.8	(–102.5)
C(7)–C(8)	1.520	1.536	1.496	C(6)–C(7)–C(8)	119.7	118.0	(128.8)	C(7)–C(8)–C(9)–N	51.7	50.4	50.2
C(8)–C(9)	(1.488)	(1.496)	(1.457)	C(7)–C(8)–C(9)	115.4	112.5	118.6	C(8)–C(9)–N—C(1)	75.7	76.3	71.6
C(9)–N	1.474	1.438	1.433	C(8)–C(9)–N	111.8	112.5	114.7	C(9)–N—C(1)–O	9.2	7.5	13.4
				C(9)–N—C(1)	122.6	122.4	(127.9)				

The crystal structure is built from hydrogen-bonded layers which show approximate trigonal symmetry. Each chloride anion is hydrogen bonded to three amide nitrogens and each oxonium cation to three amide oxygens related by the approximate threefold axis. Again molecules 1 and 2 show almost identical hydrogen-bond lengths (Fig. 2) but, for above-mentioned reasons, distances involving atoms of molecule 3 are less reliable. Although the analysis did not permit location of the hydrogen atoms involved in the short O...O hydrogen bonds and fast proton exchange between the four oxygens of comparable basicity is likely to occur, the almost trigonal environment of the central oxygen atom makes it seem more appropriate to speak of an oxonium cation rather than of a water molecule. The oxonium ion is expected to be pyramidal, and in a recent neutron-diffraction analysis of an oxonium salt an H–O–H angle of 110.4° has been observed (Lundgren & Williams, 1973). The coordination of the central oxygen by the three amide oxygens in the present compound is only very slightly pyramidal if we take the O(1)–O–O(2) angle of 118.4° as a reference value. The coordination of the chlorine anion is, however, strongly pyramidal, the N(1)–Cl–N(2) angle being 103.9°.

The layers, which are parallel to the (010) plane, have a polar side consisting of amide groups, chloride anions and oxonium cations, and an apolar side consisting of methylene groups. The next layer on the polar side is obtained by inversion at a centre of symmetry. As can be seen from Fig. 3(a) chloride anions and oxonium cations of the two layers are nearly superimposed in projection along the threefold axes, the O...Cl distance being 4.35 Å. A similar arrangement of chloride anions and oxonium cations has been observed in the crystal structure of hydrochloric acid monohydrate (Yoon & Carpenter, 1959) with a corresponding distance of 4.22 Å.

The attractive electrostatic interactions between anions and cations thus lead to the formation of double layers, which show approximately  $\bar{3}$  point symmetry. Both sides of such a double layer are dominated by the hydrocarbon chains to give non-polar surfaces that contain cavities at their intersections with the threefold axes. Two double layers, related by inversion at centres with  $y=0$ , are packed together in such a way that the

hydrocarbon chains of one layer penetrate into the cavities of the other. Thereby the trigonal symmetry is lost and the surroundings of the three molecules become different [Fig. 3(b)]. The hydrocarbon chain of molecule 1 lies above an oxonium ion, that of molecule 3 above a chloride ion, and that of molecule 2 above an empty region of the structure. For molecule 1 the shortest distance of a methylene carbon to the oxonium oxygen is more than 6 Å, whereas for molecule 3 the C(5)...Cl<sup>–</sup> distance is around 4.5 Å. It is interesting to note that the oxonium cation and the chloride anion show large mean-square vibrational amplitudes of 0.485 and 0.425 Å respectively in the direction of the threefold axis. It seems plausible to attribute this to an inversion vibration of the oxonium ion, analogous to the well known NH<sub>3</sub> inversion vibration. This motion would be transmitted most strongly in the direction of the vibration so that the chloride anions above and below the oxonium oxygen would be most affected. Since a large translational vibration in the same direction with mean-square amplitude of 0.43 Å was found for molecule 3 in the rigid-body analysis and since molecule 3 lies above or below a chlorine anion, the transmission of this motion to molecule 3 seems possible.

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