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Medium-Ring Compounds. XXIII. Caprylolactam Hydrochloride

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Abstract. Monoclinic, $P2_1/c$, $a=12\cdot79$ (1), $b=14\cdot88$ (1), $c=10\cdot84$ (1) Å, $\beta=109\cdot60$ (10)°, $C_8H_{15}ON.HCl$, $M=177\cdot67$, $Z=8$, $D_m=1\cdot22$, $D_x=1\cdot24$ g cm^{-3}. 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 atomosphere. They were sealed in capillaries for X-ray analysis.

Intensities from a crystal of dimensions $0\cdot40 \times 0\cdot40 \times 0\cdot15$ were collected on an automated Hilger and Watts diffractometer with Mo $K\alpha$ radiation ($\lambda=0\cdot71069$ Å, $\mu=3\cdot45$ cm^{-1}) and Sr/Zr balanced filters. All reflexions with scattering angle $\theta < 23°$ were measured, only those above background in the range $23° < \theta < 30°$. 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 $\theta/\lambda \le 0\cdot4$ Å^{-1}) and their parameters (including isotropic B's) refined by five additional least-squares cycles with Huber-Buser's (1971) criteria. The final R was $0\cdot056$.

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
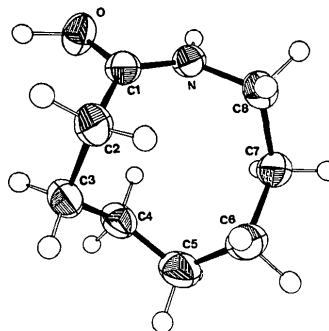

Fig. 1. The protonated caprylolactam molecule (mol 1) with atom numbering viewed along a direction perpendicular to the mean plane of the nine-membered ring. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).

further destabilized relative to a planar *cis*-amide group. Hence the occurrence of the latter in the hydrochloride is not surprising.

The molecular parameters of the two protonated *cis*-caprylolactam molecules in the asymmetric unit are almost identical. As in the case of the eight-membered ring (Winkler & Dunitz, 1975c), there is again remarkably close agreement between bond angles and torsion angles observed here and those calculated by Ermer & Lifson (1973) for *cis*-cyclononene. The r.m.s. diviations are only 1·1° for the 18 = 2 × 9 bond angles and 2·2° for the torsion angles. Since the ring skeleton shows no symmetry, the formal interchange of N–H and C=O groups leads to a non-identical but rather similar conformation, which can be expected to be of comparable stability and which has been observed in the crystal structure of *N*-methylthiocaprylolactam (Flippen, 1972).

The dimensions of the protonated *cis*-amide group compare well with those observed in enantholactam hydrochloride (Winkler & Dunitz, 1974c) and show the same changes with respect to the standard dimensions of the unprotonated *cis*-amide group (Ramachandran & Sasisekharan, 1968).

The out-of-plane deformations (Winkler & Dunitz, 1971) of the two protonated amide groups are small but some are significant [$\chi_N = -2\cdot3\ (3\cdot0)°$ and $6\cdot4\ (4\cdot0)°$, $\chi_C = -4\cdot1\ (0\cdot6)°$ and $-4\cdot0\ (0\cdot6)°$, $\tau = -8\cdot3\ (1\cdot5)°$ and $-4\cdot3\ (2\cdot0)°$ for molecules 1 and 2, respectively]. The poorly determined amide-hydrogen position does not allow a good estimate of τ and χ_N [but $\tau - \chi_N/2 = -7\cdot2\ (0\cdot6)°$ and $-7\cdot5\ (0\cdot6)°$].

Table 2. *Caprylolactam hydrochloride: atomic coordinates* (× 10), *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 1–2 Å².

	x/a	y/b	z/c	B (Å²)
H(1) 1C(2)	179 (3)	276 (3)	549 (4)	2·8
H(2) 1C(2)	262 (3)	193 (3)	621 (4)	3·1
H(1) 1C(3)	43 (3)	190 (3)	413 (4)	3·3
H(2) 1C(3)	73 (3)	148 (3)	560 (4)	3·5
H(1) 1C(4)	168 (3)	79 (3)	365 (4)	3·6
H(2) 1C(4)	44 (4)	42 (3)	373 (4)	3·3
H(1) 1C(5)	171 (4)	−60 (3)	476 (4)	4·8
H(2) 1C(5)	125 (4)	−17 (3)	591 (5)	5·8
H(1) 1C(6)	316 (4)	−49 (3)	676 (5)	5·2
H(2) 1C(6)	297 (3)	62 (3)	698 (4)	4·7
H(1) 1C(7)	357 (4)	−4 (3)	468 (5)	5·7
H(2) 1C(7)	447 (4)	−7 (3)	603 (4)	3·6
H(1) 1C(8)	498 (3)	124 (3)	548 (4)	2·5
H(2) 1C(8)	422 (4)	151 (3)	636 (4)	3·3
H(1N)	374 (3)	178 (3)	371 (4)	3·4
H(1O)	155 (5)	316 (4)	335 (6)	6·6
H(1) 2C(2)	311 (3)	39 (3)	−28 (4)	2·9
H(2) 2C(2)	235 (3)	−47 (3)	−118 (4)	2·4
H(1) 2C(3)	449 (4)	−46 (3)	107 (5)	4·6
H(2) 2C(3)	434 (4)	−81 (3)	−33 (4)	4·2
H(1) 2C(4)	326 (3)	−171 (3)	129 (4)	2·6
H(2) 2C(4)	453 (4)	−198 (3)	130 (5)	5·1
H(1) 2C(5)	332 (4)	−301 (3)	−4 (5)	6·1
H(2) 2C(5)	394 (4)	−240 (4)	−92 (5)	7·7
H(1) 2C(6)	199 (4)	−281 (4)	−199 (5)	6·1
H(2) 2C(6)	215 (4)	−170 (3)	−202 (4)	5·3
H(1) 2C(7)	143 (4)	−252 (3)	0 (4)	3·5
H(2) 2C(7)	61 (4)	−255 (3)	−143 (5)	4·7
H(1) 2C(8)	−1 (3)	−133 (3)	−75 (4)	2·8
H(2) 2C(8)	84 (4)	−95 (4)	−159 (5)	5·8
H(2N)	99 (4)	−73 (3)	113 (5)	6·3
H(2O)	326 (6)	64 (5)	184 (7)	9·6

Table 1. *Caprylolactam hydrochloride: 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 $T = \exp\ [-2\pi^2(U_{11}h^2a^{2*}\ldots + 2U_{12}hka^*b^*\ldots)]$ and have e.s.d.'s in the range 0·0015–0·0068 Å² (except for Cl, where they are much smaller).

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1Cl	4327 (1)	1447 (1)	2077 (1)	594	541	732	−23	302	−55
1O	2221 (2)	2733 (2)	3378 (2)	979	749	745	307	507	260
1N	3499 (2)	1781 (2)	4478 (3)	604	514	703	18	322	14
1C(1)	2622 (3)	2237 (2)	4416 (3)	617	497	691	−11	327	−38
1C(2)	2044 (3)	2171 (2)	5390 (3)	598	587	615	48	318	−27
1C(3)	1011 (3)	1563 (2)	4846 (3)	539	755	721	46	280	24
1C(4)	1206 (3)	654 (2)	4299 (4)	601	720	930	−110	274	−118
1C(5)	1733 (3)	−69 (3)	5322 (5)	843	639	1352	−103	544	39
1C(6)	2912 (3)	75 (2)	6227 (4)	869	661	922	125	487	217
1C(7)	3789 (3)	247 (2)	5583 (4)	635	603	933	114	339	141
1C(8)	4181 (3)	1219 (2)	5574 (3)	514	660	806	36	214	18
2Cl	426 (1)	1071 (1)	−1790 (1)	642	544	784	−62	293	−3
2O	2528 (2)	197 (2)	1695 (2)	851	736	845	−212	468	−260
2N	1344 (2)	−759 (2)	402 (3)	591	561	712	−47	258	−28
2C(1)	2212 (3)	−256 (2)	603 (3)	605	463	770	27	282	−8
2C(2)	2882 (3)	−222 (2)	−284 (3)	627	503	758	−42	353	−14
2C(3)	3941 (3)	−790 (2)	279 (4)	613	682	977	−12	363	−88
2C(4)	3771 (3)	−1744 (3)	687 (4)	701	698	1129	130	254	107
2C(5)	3350 (4)	−2418 (3)	−436 (5)	1009	579	1621	40	588	−150
2C(6)	2185 (4)	−2286 (3)	−1406 (4)	1116	704	1191	−200	598	−351
2C(7)	1234 (3)	−2211 (2)	−843 (4)	895	674	928	−230	352	−157
2C(8)	764 (3)	−1276 (2)	−793 (4)	611	704	894	−121	254	−107

Analyses of the experimental thermal motion tensors in terms of rigid-body translational and librational motion (Schomaker & Trueblood, 1968) lead to better agreement between observed and calculated tensor components $[\langle(\Delta U_{ij})^2\rangle^{1/2}=0{\cdot}00261$ and $0{\cdot}00317$ Å^2, $\langle\sigma^2(U_{ij})\rangle^{1/2}=0{\cdot}00296$ and $0{\cdot}00333$ for molecules 1 and 2 respectively] than expected. The rigid-body model thus accounts adequately for the averaged molecular motion. The eigenvalues and eigenvectors (referred to principal molecular axes) of the libration tensors of the two molecules are very similar, indicating a corresponding similarity in the interaction of the molecules with their surroundings. Libration corrections amount to 0·006–0·014 Å for bond lengths but are negligible for bond angles and torsion angles.

The crystal structure (Fig. 2) shows the same general features, especially with respect to the surroundings of the protonated cis-amide group, as that of enantholactam hydrochloride (Winkler & Dunitz, 1974c). Alternating caprylolactam cations and chloride anions (N–H⋯Cl, 3·16 and 3·14 Å; Cl⋯H–O, 2·86 and 2·88 Å) form hydrogen-bonded helices around the twofold screw axes, with four cations and four anions per turn. Left- and right-handed helices (related by inversion centres at $x=0$) are arranged in such a way that chloride anions of one helix lie directly above the planes of protonated amide groups of another helix running in the opposite direction. The corresponding distances are given in Fig. 2. Although the C(1)⋯Cl distances are 0·1–0·2 Å longer than in

Table 3. *Caprylolactam hydrochloride: molecular parameters* (Å *and degrees*)

Typical e.s.d.'s are 0·003–0·006 Å for bond lengths, 0·2–0·4° for bond angles and 0·4–0·8° for torsion angles not involving H atoms. Bond angles and torsion angles calculated for cis-cyclononene (Ermer & Lifson, 1973) are in brackets.

	Mol. 1	Corr. for libration	Mol. 2	Corr. for libration		Mol. 1	Mol. 2		Mol. 1	Mol. 2
C(1)–O	1·299	1·309	1·303	1·313	O——C(1)–N	115·2	116·0	C(8)–N——C(1)–C(2)	−9·2	−9·5 (−5·6)
N——C(1)	1·293	1·299	1·295	1·302	O——C(1)–C(2)	120·6	119·9	N——C(1)–C(2)–C(3)	−100·4	−100·9 (−101·7)
C(1)–C(2)	1·482	1·491	1·487	1·497	N——C(1)–C(2)	124·1	124·0 (125·7)	C(1)–C(2)–C(3)–C(4)	49·8	50·4 (47·0)
C(2)–C(3)	1·545	1·558	1·538	1·552	C(1)–C(2)–C(3)	109·5	110·3 (110·4)	C(2)–C(3)–C(4)–C(5)	78·2	78·0 (78·3)
C(3)–C(4)	1·532	1·541	1·524	1·535	C(2)–C(3)–C(4)	115·8	115·7 (115·3)	C(3)–C(4)–C(5)–C(6)	−66·1	−66·4 (−65·0)
C(4)–C(5)	1·530	1·541	1·529	1·540	C(3)–C(4)–C(5)	115·5	115·3 (116·9)	C(4)–C(5)–C(6)–C(7)	−55·1	−54·0 (−58·0)
C(5)–C(6)	1·513	1·526	1·521	1·534	C(4)–C(5)–C(6)	118·2	117·9 (119·1)	C(5)–C(6)–C(7)–C(8)	103·2	104·1 (104·9)
C(6)–C(7)	1·528	1·537	1·537	1·547	C(5)–C(6)–C(7)	116·9	117·2 (117·0)	C(6)–C(7)–C(8)–N	−85·8	−87·4 (−87·4)
C(7)–C(8)	1·532	1·543	1·524	1·536	C(6)–C(7)–C(8)	117·0	117·1 (115·4)	C(7)–C(8)–N——C(1)	86·2	86·4 (85·0)
C(8)–N	1·475	1·486	1·475	1·485	C(7)–C(8)–N	115·7	114·8 (114·5)	C(8)–N——C(1)–O	174·9	174·5
					C(8)–N——C(1)	127·3	126·8 (126·8)			
C–H		0·94–1·13 (5)			H——C–H	101–117 (3)		H(N)–N–C(1)–O	−7	1
N–H	0·98		1·03		H(N)–N–C(8)	114	118	H(N)–N–C(1)–C(2)	168	177
O–H	1·05		1·11		H(N)–N–C(1)	118	115			
					H(O)–O–C(1)	116	115			

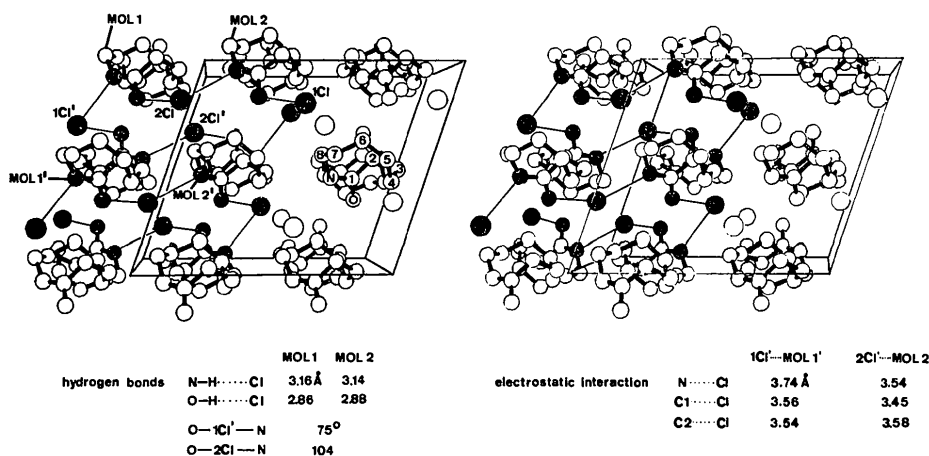| hydrogen bonds		MOL 1	MOL 2		electrostatic interaction		1Cl'···MOL 1'	2Cl'···MOL 2'
	N–H⋯Cl	3.16 Å	3.14		N⋯Cl		3.74 Å	3.54
	O–H⋯Cl	2.86	2.88		C1⋯Cl		3.56	3.45
	O—1Cl'—N	75°			C2⋯Cl		3.54	3.58
	O—2Cl—N	104						

Fig. 2. Stereographic view down [010] of the crystal structure of caprylolactam hydrochloride. The axial directions are a→, c↓, and b out of the plane of the paper. Chloride anions, oxygen and nitrogen atoms involved in the indicated hydrogen bonds (light lines) are marked with black circles. The following relationships hold with respect to the coordinates given in Table 1: MOL 1 $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; MOL 1' $\bar{x},1-y,1-z$; MOL 2 $x,1+y,z$; MOL 2' $x,\frac{1}{2}-y,\frac{1}{2}+z$; 1 Cl $x,1+y,z$; 1 Cl' $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; 2 Cl $x,1+y,z$; 2 Cl' $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$.

enantholactam hydrochloride the carbonyl carbon is again displaced from the plane of its three neighbours [N,O,C(2)] towards the Cl⁻ anion by approximately the same amount [0·029 (4) Å]. Referring to Fig. 2, the two molecules MOL1 and MOL2 (not the standard molecules described in Table 1) are approximately related by a non-crystallographic translation of circa $\frac{1}{2},\frac{1}{4},0$. Pairs of chloride ions are also related by this translation (e.g. 2 Cl and 1 Cl; or 1 Cl' and 2 Cl' by $\frac{1}{2}, -\frac{1}{4},0$). However, the chloride ions 1 Cl' and 2 Cl (hydrogen bonded to the two amide nitrogens of MOL1 and MOL2) are not simply related, and as a result the directions of the N–H···Cl hydrogen bonds are clearly different, the C(1)–N–Cl angle being 124° for MOL1 and 136° for MOL2.

Despite this difference the general pattern of interactions with chloride anions remains rather similar for both molecules, which may account for the observed similarity in their librational tensors. However, the observed differences in molecular parameters, χ_N and τ, involving the amide hydrogen positions might be real although they are of low statistical significance.

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Medium-Ring Compounds. XXIV. Pelargolactam

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Abstract. Orthorhombic, $Pna2_1$ or $Pnam$ (disordered structure), $a=13·71$ (1), $b=4·918$ (5), $c=13·98$ (1) Å, $C_9H_{17}ON$, $M=155·23$, $Z=4$, $D_m=1·10$, $D_x=1·093$ g cm⁻³. The crystal structure consists of hydrogen-bonded chains running along b. The structure is disordered and only an approximate description could be obtained. The pelargolactam molecule can adopt various energetically similar conformations, which associate to different types of ordered hydrogen-bonded chains, and it is suggested that these different types of chains associate in a disordered way.

Introduction. Pelargolactam was prepared from commercially available cyclononanone (Aldrich, Milwaukee, U.S.A.) by the method described by Ruzicka, Kobelt, Häfliger & Prelog (1949). Single crystals were obtained by recrystallization from a 1:1:1 mixture of heptane, octane and benzene. They were sealed in capillaries for X-ray analysis.

Intensities from a crystal of dimensions 0·40 × 0·33 × 0·24 mm were collected on an automated Hilger–Watts Y290 diffractometer with Mo $K\alpha$ radiation ($\lambda=0·71069$ Å, $\mu=0·71$ cm⁻¹) and Sr/Zr balanced filters. All reflexions with scattering angle $\theta<23°$ were measured, and 686 independent $|F_o|$ values obtained.

Statistical tests (Wilson, 1949) yielded a mean isotropic B value of around 10 Å² and indicated that the structure is centrosymmetric (disordered). However, an ordered, non-centrosymmetric structure can simulate a centrosymmetric one if a large fragment contains an approximate, non-crystallographic centre of symmetry.

The short b translation (4·92 Å) hints at association of trans-amide groups into hydrogen-bonded chains running in that direction. On this basis the orientation of the amide group was determined from a sharpened Patterson synthesis. The mean plane of the group was found to be perpendicular to a and a strong peak at $0,\frac{1}{2},\frac{1}{2}$ (Harker line $\frac{1}{2}+2x,\frac{1}{2},\frac{1}{2}$) suggested an x coordinate of approximately 0·25 for its five non-hydrogen atoms. This interpretation was also consistent with other features of the Patterson function, but the position of the five-atom fragment along b could not be determined so easily. The best fit to the Harker peaks was obtained with the y coordinate of the carbonyl