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Medium-Ring Compounds. XX. Caprolactam Hydrochloride

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Abstract. Orthorhombic, $Pca2_1$ or $Pcam$ (disordered structure), $a=10{\cdot}18$ (1), $b=10{\cdot}43$ (1), $c=7{\cdot}61$ (1) Å, $C_6H_{11}ON.HCl$, $M=149{\cdot}62$, $Z=4$, $D_m=1{\cdot}22$, $D_x=1{\cdot}230$ g cm^{-3}. The compound is very hygroscopic. Structure analysis shows that protonation of the lactam takes place at the oxygen atom. The molecular conformation is similar to that of caprolactam. The crystal structure is built from hydrogen-bonded (O–H···Cl···H–N) chains in the [100] direction with polar columns of alternating cations and anions along [001]. Disorder arises from reversal of the polarity direction accompanied by parallel displacement of the columns.

Introduction. The compound was prepared by passing dry HCl gas into an ethereal solution of the lactam. The resulting precipitate was filtered, washed with dry ether and recrystallized from dry acetone. Crystals for X-ray examination were sealed in capillaries to protect them from moisture.

Intensities from a crystal of dimensions $0{\cdot}40\times0{\cdot}35\times0{\cdot}45$ mm were collected on an automated Hilger–Watts Y290 diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å, $\mu=4{\cdot}03$ cm^{-1}) monochromatized by reflexion from graphite. In the θ range out to 25° all reflexions were measured, in the range $25°<\theta<30°$ only those significantly above background. In the course of the measurements intensity variations for some reflexions occurred. Although the more obvious possible sources of fluctuation (movement of crystal, instability of X-ray generator and counter, *etc.*) were checked, the reason for these intensity variations remains obscure. To guard against major errors two independent sets were collected. For about 90% of the reflexions the individual intensities were within 10% of their mean values. For the remaining reflexions, two additional intensity measurements were carried out and the results averaged. The measurements led ultimately to 866 independent $|F_o|$ values of somewhat dubious accuracy. Intensity statistics and systematic absences ($0kl$, l odd; $h0l$, h odd) indicated a centrosymmetric distribution of atoms in the space group $Pcam$ and hence pointed to a disordered crystal structure (since $Z=4$ would require twofold molecular symmetry). However, the possibility of an ordered structure in the lower space group $Pca2_1$ had to be considered.

From the Patterson function the x and y coordinates of the chlorine atom could be derived. The z coordinate is fixed by symmetry in $Pcam$ at $z=\frac{1}{4}$ and can be chosen to have this value in $Pca2_1$. The first F_o synthesis, phased on the Cl positions, showed an arrangement of peaks corresponding to the superposition of a caprolactam molecule with its image reflected across $z=\frac{1}{4}$. Four peaks [O, N, C (1), C (4)] lay on the mirror plane. An arrangement corresponding to one enantiomorph with reasonable molecular parameters was selected and refined by least-squares calculations in $Pca2_1$. Three cycles with isotropic temperature factors lowered R to 0·17, but the z coordinates of the four atoms close to $z=\frac{1}{4}$ failed to converge. An (F_o-F_c)-synthesis calculated at this stage showed that all the atom peaks were markedly elongated in the z direction. With 11 hydrogen atoms at calculated positions ($B_H=7$ Å^2 assumed and held constant) included, several

Table 1. *Caprolactam hydrochloride: atomic coordinates (e. s. d.'s in parentheses) and vibrational tensor components for non-hydrogen atoms (all* $\times10^4$)

The U_{ij} values (in Å^2) correspond to the temperature-factor expression $T=\exp[-2\pi^2(U_{11}h^2a^{2*}+\ldots+2U_{12}hka^*b^*\ldots)]$ and have standard deviations in the range 0·002–0·011 Å^2 (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}
Cl	509 (1)	2122 (1)	7500 (0)	468	514	808	−18	0	0
O	1076 (3)	145 (3)	2840 (7)	558	514	903*	30	−39	32
N	1410 (4)	2178 (3)	2235 (10)	464	529	903*	−1	−11	38
C(1)	596 (4)	1262 (4)	2334 (5)	524	467	903*	81	−94	9
C(2)	−833 (5)	1419 (5)	1906 (7)	548	546	814	−80	−29	−2
C(3)	−1528 (5)	2350 (6)	3150 (8)	429	899	758	20	39	6
C(4)	−1233 (5)	3779 (6)	2799 (11)	719	658	903*	229	20	−71
C(5)	198 (6)	4148 (5)	3031 (8)	803	464	814	23	−36	−40
C(6)	1106 (5)	3513 (5)	1756 (8)	681	450	903	−95	−25	−1

* These values were set equal to U_{33} of C(6) (see text).

cycles of anisotropic least-squares refinement lowered R to 0·086. However, a subsequent (F_o-F_c) synthesis showed negative density at all the atomic positions (except those close to $z=\frac{1}{4}$) and positive density at positions related by reflexion across $z=\frac{1}{4}$, a clear indication that a disordered model in *Pcam* should lead to still better agreement between F_o and F_c.

The difficulty with least-squares refinement of a disordered structure in *Pcam* is that the correlation coefficient between U_{33} and z is almost unity for the atoms that overlap most strongly with their mirror images across $z=\frac{1}{4}$. To get around this problem we assume that the U_{33} parameters of all the atoms are approximately equal, as would be the case if the elongation of the peaks in the z direction were attributed mainly to a translatory vibration of the whole structure in this direction. For the subsequent refinements the U_{33} parameters of O, N, C(1) and C(4) were set equal to that of C(6), the atom furthest away from the mirror plane. With this constraint the mean value of U_{33} over the eight atoms of the molecule dropped from 0·14 to 0·086 Å^2 (close to U_{33} of Cl) and R was reduced to 0·062. Although the nominal e.s.d.'s in the z coordinates of O, N, C (1) and C (4) were reduced in this way to less than 0·008 Å, the actual uncertainties in these coordinates are many times larger, of the order of 0·1 Å, corresponding to the e. s. d. of about 0·01 Å^2 in U_{33} of C (6). The bond lengths and angles of the amide group are relatively insensitive to these uncertainties but its planarity is strongly affected. A final series of least-squares refinements with the O atom constrained to lie in the plane of N, C (1) and C (2) with an algorithm involving Lagrangian undetermined multipliers (Dover, 1968) reduced R to 0·052. Final positional and vibrational parameters are given in Tables 1 and 2, bond lengths, bond angles and torsion angles in Table 3. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

* 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 30618 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Caprolactam hydrochloride: calculated hydrogen coordinates* ($\times 10^3$)

Assumptions: CH_2, C–H, 1·09 Å, HCH, 106°, local C_{2v} symmetry; N–H, 1·00 Å along bisector C(1)NC(6).

	x/a	y/b	z/c
H(N)	235	198	251
H(1) C(2)	−132	49	196
H(2) C(2)	−94	175	56
H(1) C(3)	−125	212	450
H(2) C(3)	−258	219	307
H(1) C(4)	−183	436	367
H(2) C(4)	−154	402	147
H(1) C(5)	51	392	436
H(2) C(5)	29	518	291
H(1) C(6)	201	406	167
H(2) C(6)	67	354	45

An (F_o-F_c) synthesis calculated at the end of the analysis showed only one prominent peak of 0·35 e Å^{-3}, situated 0·9 Å from the O atom in the direction of the chloride anion. This peak can be identified with the acidic H atom that was omitted from the structure model.

Discussion. The chair conformation of the seven-membered ring is very similar to that in unprotonated caprolactam (Winkler & Dunitz, 1975). The only major differences are in the dimensions of the amide group where protonation on O leads to a shortening of 0·07 Å in the C(1)–N bond, a corresponding lengthening of 0·07 Å in the C(1)–O bond and to changes of 4–5° in the bond angles at C(1). These changes are all consistent with the expected increase in double-bond character of the amide bond. In this connexion it is interesting that the pattern of torsion angles round the ring is even closer to mirror symmetry than in caprolactam itself. The pattern obtained for cycloheptene by force-field calculations (Ermer & Lifson, 1973) is exactly mirror-symmetric and the individual values agree well with those observed in caprolactam (r. m. s. $\Delta=6{\cdot}1°$) but even better with those observed here (r. m. s. $\Delta=4{\cdot}0°$).

Fig. 1 shows the crystal structure in projection down **c** (this projection is not affected by the disorder). The protonated caprolactam cations and chloride anions

Table 3. *Caprolactam hydrochloride: bond distances, bond angles and torsion angles*

Typical e.s.d.'s in bond angles and torsion angles are 0·6 and 1·0° respectively.

C(1)–O	1·321 (6) Å	O—C(1)–N	116·1°	C(6)–N—C(1)–C(2)*	2·0°
N—C(1)	1·267 (6)	O—C(1)–C(2)	121·2	N—C(1)–C(2)–C(3)	−63·5
C(1)–C(2)	1·500 (7)	N—C(1)–C(2)	122·7	C(1)–C(2)–C(3)–C(4)	75·8
C(2)–C(3)	1·530 (8)	C(1)–C(2)–C(3)	112·5	C(2)–C(3)–C(4)–C(5)	−62·6
C(3)–C(4)	1·543 (9)	C(2)–C(3)–C(4)	114·6	C(3)–C(4)–C(5)–C(6)	64·2
C(4)–C(5)	1·517 (8)	C(3)–C(4)–C(5)	114·3	C(4)–C(5)–C(6)–N	−78·6
C(5)–C(6)	1·494 (8)	C(4)–C(5)–C(6)	113·9	C(5)–C(6)–N—C(1)	63·0
C(6)–N	1·472 (6)	C(5)–C(6)–N	112·9	C(6)–N—C(1)–O*	−178·0
		C(6)–N—C(1)	126·2		

* These values are strongly dependent on the constrained refinement (see text).

are linked by hydrogen bonds (N–H···Cl, 3·14; Cl···H–O, 2·88 Å) into infinite chains running in the **a** direction at $z = \pm 0{\cdot}25$. Chloride ions of one set of chains lie midway between amide groups of the other set (Fig. 2), so the structure can also be regarded as being built from columns of alternating anions and cations in the **c** direction. In an ordered structure in $Pca2_1$ these columns are polar, but it is clear from Figs. 1 and 2 that changing the polarity sense of a given column by reflecting it across $z = \pm\frac{1}{4}$ does not alter the hydrogen-bonding arrangement. It does, however, lead to changes in the distances between methylene groups of neighbouring molecules; in particular, the distances C(3)···C(3) and C(5)···C(5) are reduced from over 4 Å to 3·44 and 3·51 Å, respectively, appreciably shorter than the normal contact distance of about 3·65 Å. The simplest way to increase these too short contacts is to displace the whole reflected column along +**c** so that the z coordinates of the reflected atoms change from $-z$ to $-z+\Delta z$. Both of the short contacts are thereby lengthened by *circa* $0{\cdot}8 \times \Delta z$.

As mentioned above the electron-density peaks of all the atoms, including chlorine, are elongated in the z direction. This is also evident from the vibrational tensors listed in Table 1 ($\langle U_{11}\rangle = 0{\cdot}058$ Å^2, $\langle U_{22}\rangle = 0{\cdot}056$ Å^2, $\langle U_{33}\rangle = 0{\cdot}082$ Å^2). The difference of 0·025 Å^2 in mean-square-amplitude may correspond to an additional translatory vibration parallel to **c**, but it is just as compatible with a disordered model in which each anisotropic atom is replaced by two isotropic half-weight atoms separated by $\Delta z \sim 0{\cdot}32$ Å $= 2(0{\cdot}025$ Å$^2)^{1/2}$. This would be sufficient to avoid the unfavourable C···C contacts.

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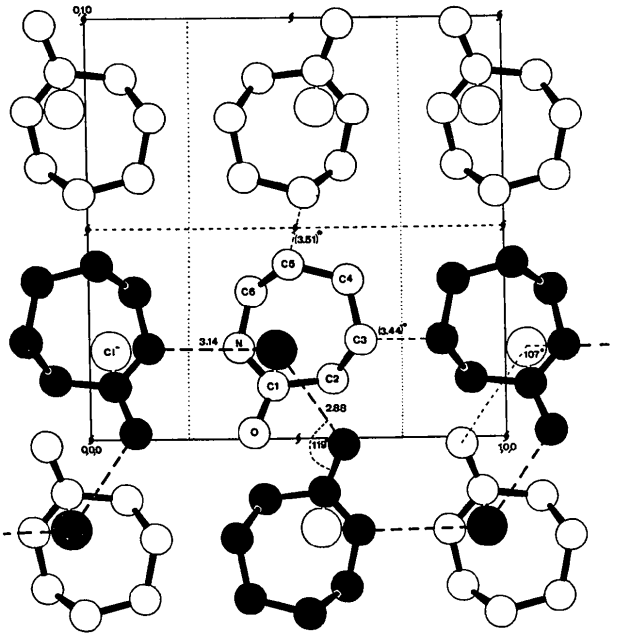

Fig. 1. The caprolactam hydrochloride structure projected down [001]. The atoms marked by black circles form part of a hydrogen-bonded chain at $z \sim 0{\cdot}25$. The distances marked with an asterisk correspond to short C···C contacts produced by reflecting the central column across the plane $z = \pm\frac{1}{4}$ without parallel displacement.

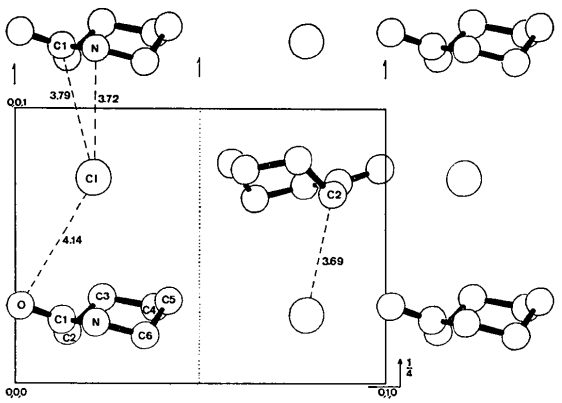

Fig. 2. The caprolactam hydrochloride structure projected down [100]. For clarity the ordered structure in $Pca2_1$ is shown. In the disordered model each column of cations and anions parallel to [001] may be reflected across $z = \pm\frac{1}{4}$ and displaced by $\Delta z \sim 0{\cdot}3$ Å.

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