

enantholactam hydrochloride the carbonyl carbon is again displaced from the plane of its three neighbours [N, O, C(2)] towards the Cl<sup>-</sup> 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*  $\frac{1}{2}, \frac{1}{2}, 0$ . Pairs of chloride ions are also related by this translation (*e.g.* 2 Cl and 1 Cl; or 1 Cl' and 2 Cl' by  $\frac{1}{2}, -\frac{1}{2}, 0$ ). 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,  $\chi_N$  and  $\tau$ , 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<sup>-3</sup>. 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 cyclononane (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 ( $\lambda = 0.71069$

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Å,  $\mu = 0.71$  cm<sup>-1</sup>) and Sr/Zr balanced filters. All reflexions with scattering angle  $\theta < 23^\circ$  were measured, and 686 independent  $|F_o|$  values obtained.

Statistical tests (Wilson, 1949) yielded a mean isotropic  $B$  value of around 10 Å<sup>2</sup> 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

carbon close to zero, but other possibilities could not be eliminated with certainty.

An  $F_o$  synthesis (F1) based on this model in  $Pna2_1$  ( $R=0.59$ ) showed an approximate mirror plane perpendicular to  $c$  and passing through the midpoint of the line C(2)–C(9) [Fig. 1(a)]. The next two atoms C(3) and C(8) appeared as single peaks at reasonable positions, but the remaining four carbon atoms could not be located. The electron density in the region where they were expected to occur was very diffuse, and a second  $F_o$  synthesis (F2), based on the larger seven-atom model ( $R=0.49$ ), did not yield any improvement in resolution.

In another approach, using the tangent formula (Karle & Karle, 1966), 40 strong reflexions, with large contributions from the five atoms of the amide group, were chosen as a starting set for four cycles of tangent refinement, leading to 160 consistently phased reflexions with  $E_o \geq 1.2$ . The corresponding  $E$  map showed the same features as observed in the synthesis F2.

It was therefore concluded that the structure is disordered in  $Pnam$  and should be considered as a superposition of two arrangements related by reflexion across the mirror plane. On this basis, a model incorporating the conformation of the ten-membered ring observed in pelargolactam hemihydrochloride (Winkler & Dunitz, 1975a) fitted the observed electron density (F2) reasonably well, although it did not explain all its features. Several other models, based on different conformations of the ten-membered ring, were also considered but none of them fitted any better. All of them, however, led to some unacceptable molecular parameters, especially in the polymethylene chain, which may show some further kind of disorder. Only for the amide group and its next two carbon atoms, C(3) and C(8), does the simple disorder model seem completely compatible with the electron density and lead to not unreasonable molecular parameters. Approximate coordinates for these seven atoms are given in Table 1.\*

Table 1. Approximate fractional coordinates for the seven-atom fragment in  $Pnam$  (disordered)

C(2), C(9) and C(3), C(8) are related by the mirror plane at  $z=0.25$ .

	$x/a$	$y/b$	$z/c$
O	0.24	-0.24	0.22
N	0.24	0.20	0.29
C(1)	0.24	0.02	0.21
C(2)	0.23	0.10	0.11
C(3)	0.13	0.08	0.08
C(8)	0.13	0.08	0.42
C(9)	0.23	0.10	0.39

\* 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 30622 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

**Discussion.** The difficulties described above in the interpretation of the electron-density maps for pelargolactam were not entirely unexpected since a previous study of *trans*-cyclodec-5-enyl-*p*-nitrobenzoate had indicated that more than one conformation of the cycloolefin must be present in the crystal (Ermer, 1970; Dunitz, 1971). It has subsequently been shown by force-field calculations (Ermer & Lifson, 1973) that there are at least six conformations of *trans*-cyclodecene with approximately equal (within 2.5 kcal mole<sup>-1</sup>) strain enthalpies.

As in the crystal structure of caprylolactam (Winkler & Dunitz, 1975b) chains of hydrogen-bonded lactam molecules are held together by much weaker van der Waals attraction. This would suggest that the statistical mirror plane of the disordered structure results from mistakes in chain-chain association rather than from mistakes in the propagation of a given chain. The observed disorder in the structure of *trans*-cyclodec-enyl-*p*-nitrobenzoate (Ermer, 1970) requires the presence of two similar ring conformations related by a rotation of the *trans* double-bond system, as shown for the amide group of pelargolactam in Fig. 1. For the unsymmetrical amide group, an additional operation involving formal interchange of N–H and C=O has to be considered. There are thus four similar conformations related by the group of operations shown in Fig. 1 and since they are all compatible with the observed electron density distribution, the crystal may well consist of a disordered arrangement of four kinds of ordered hydrogen-bonded chains.

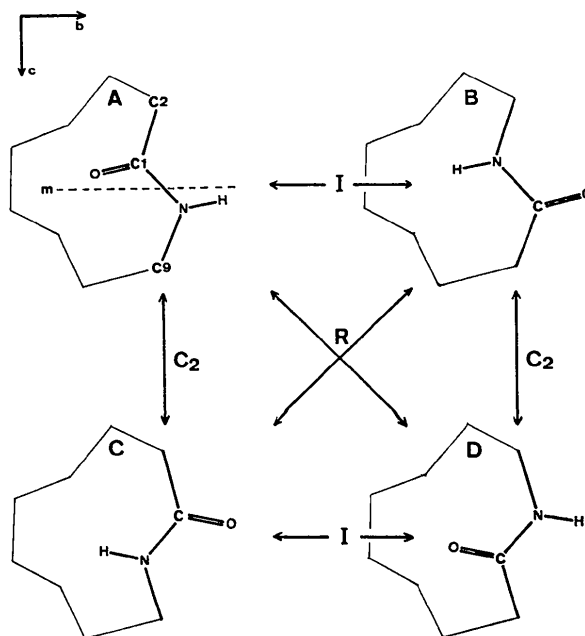


Fig. 1. Four different, energetically similar conformations of pelargolactam related by reorientation of the amide group as indicated by  $C_2$  (rotation),  $\bar{I}$  (inversion or formal interchange of N–H with C=O) and  $R$  (reflexion).

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<sup>-3</sup>. 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<sup>-1</sup>). 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 × 10<sup>4</sup>)*

The  $U_{ij}$  values (in Å<sup>2</sup>) 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 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	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