which appears to be more important. The O(10)···C(3) distance is 2·992 (2) Å, which is short enough to be considered as an interaction of the type described by Bürgi, Dunitz & Shefter (1974) (BDS) as incipient nucleophilic attack by the epoxide O atom on the carbonyl of the lactone. In confirmation of this C(3) is displaced from the plane of C(4), O(2), O(9) by 0·010 (2) Å towards O(10). These parameters exactly fit the relationship of BDS and the O(10)···C(3)—O(9) angle of 118·8° is close to optimum. The strongest interactions found by BDS had an O···C distance of about 2·6 Å whereas at 3·1 Å the interaction seemed to be negligible. A model of (I) shows that the C(3)···O(10) distance is longer for the envelope configuration of the lactone ring so that the oxygen–carbonyl interaction may well influence the conformation of the lactone ring.

We have observed this transannular interaction in other derivatives of (II) and (IV) and shall review the effect synoptically elsewhere.

### References

Bürgi, H. B., Dunitz, J. D. & Shefter, E. (1974). *Acta Cryst.* B30, 1517–1527.

Hildebrandt, R. L. & Wieser, J. D. (1974). *J. Mol. Struct.* 22, 247–255.

*International Tables for X-ray Crystallography* (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.

Morris, D. G., Murray-Rust, J. & Murray-Rust, P. (1977). *J. Chem. Soc. Perkin Trans.* 2, pp. 1577–1580.

Newton, R. F., Howard, C. C., Reynolds, D. P., Wadsworth, A. H., Crossland, N. M. & Roberts, S. M. (1978). *J. Chem. Soc. Chem. Commun.* pp. 662–664.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

# Enantholactam (7-Heptanelactam) at 98 K*

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**Abstract.** $C_7H_{13}NO$, $M_r = 127·18$, monoclinic, $C2/c$, $Z = 8$, $a = 21·998$ (15), $b = 7·204$ (3), $c = 9·107$ (5) Å, $\beta = 102·89$ (6)°, $V = 1406·8$ Å³, $D_c = 1·201$ Mg m⁻³. Significant differences in bond lengths and angles between the protonated and unprotonated forms of enantholactam occur only for the amide moiety.

**Introduction.** In a previous study of the deformations of the secondary amide group caused by ring strain and protonation, the crystal structures of a number of medium-ring lactams and of their adducts with hydrochloric acid have been determined (Dunitz & Winkler, 1975). Since enantholactam could not be crystallized at that time the dimensions of the protonated amide group in the corresponding hydrochloride (Winkler & Dunitz, 1975) had to be compared to those of the standard *cis* amide group. It was thus left uncertain to what extent the observed deformations were caused by incor-

poration of the *cis* amide group in an eight-membered ring. The present analysis allows a more reliable determination of the effects of protonation because protonated and unprotonated forms of the molecule show essentially the same conformation in their respective crystals. This similarity could not be taken for granted since the infrared spectrum of enantholactam in dilute chloroform solution suggests the presence of two conformers of about equal free energy (Hallam & Jones, 1967).

Crystals of enantholactam (Fluka AG, m.p. 301 K) were obtained by sublimation of a small amount of material within an evacuated capillary of 0·5 mm diameter. Slight warming of the sample over a period of 48 h yielded a single crystal, about 0·25 mm in edge, at one end of the capillary cooled to about 273 K by a nitrogen gas stream. After further slow cooling to 98 K intensities were collected on an automated Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å); 1684 independent reflections ($\theta \leq 27°$) were measured of which 1067 were observed $[I \geq 3\sigma(I)]$. The structure was solved by direct methods (*MULTAN*; Germain,

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Main & Woolfson, 1970) and refined by full-matrix least squares (XRAY system; Stewart, Kruger, Ammon, Dickinson & Hall, 1972). In the final cycles all positional and thermal parameters (anisotropic for non-hydrogen atoms) were refined with a modified weighting system (Dunitz & Seiler, 1973) with $r = 2.5$ Å$^2$. Including isotropic extinction corrections the final $R$ for the observed reflections was 0.030. Positional and isotropic thermal parameters are given in Table 1,* bond distances, bond angles and torsion angles in Fig. 2. Fig. 1 is a stereoview of a molecule of enantholactam.

**Discussion.** Significant differences in bond lengths and angles (Fig. 2) between the protonated and unprotonated forms occur only for the amide moiety. Changes in ring torsion angles amount only to a few degrees and are likely to be secondary effects. After correction for rigid-body libration for both molecules the lengthening

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* Lists of structure factors, anisotropic thermal parameters (for C, N and O atoms) and bond lengths not corrected for molecular vibration have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34428 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
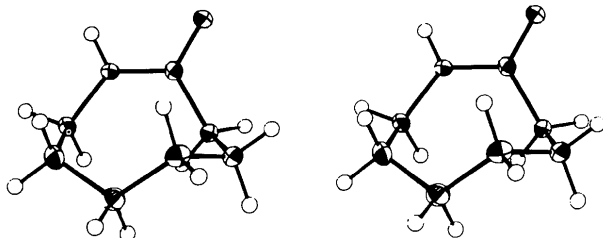


Fig. 1. Stereoscopic view of the molecule drawn by *ORTEP* (Johnson, 1965). The thermal-vibration ellipsoids are drawn at the 50% probability level.

of the C—O bond on protonation is 0.065 Å and the shortening of the C—N bond is 0.039 Å (e.s.d.'s ~0.004 Å). The C(1)—C(2) and the N—C(7) lengths differ by 0.047 Å in the unprotonated molecule whereas they are almost equal in the protonated molecule. This trend to a more symmetric, more double-bond-like geometry on protonation is also seen in the bond angles.

The out-of-plane parameters $\chi_N$, $\chi_C$ and $\tau$ (Dunitz & Winkler, 1975) are small for both molecules but otherwise do not have much in common:

|        | enantholactam | enantholactam.HCl |
|--------|---------------|-------------------|
| $\chi_C$ | 1.4 (0.3)°    | 4.4 (0.5)°        |
| $\chi_N$ | −4.8 (1.2)    | −1.6 (3.0)        |
| $\tau$   | −4.5 (0.6)    | 2.6 (1.5).        |

The small value of $\chi_C$ in enantholactam confirms that the unusually large value in the hydrochloride is due to interaction with the nearby anion (Cl⁻) and not to some intramolecular constraint. In enantholactam the amide H atom lies 0.07 Å (e.s.d. <0.02 Å) above the plane
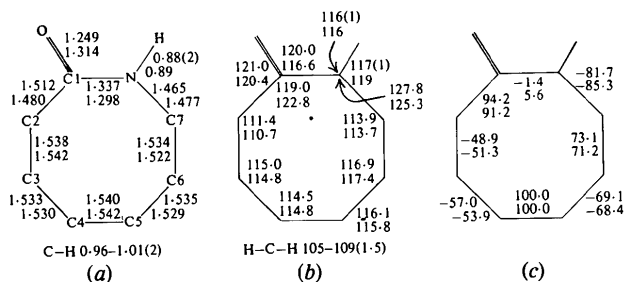


Fig. 2. (a) Bond lengths (Å) corrected for molecular vibration, (b) bond angles (°), and (c) torsion angles (°). E.s.d.'s are 0.002 Å for bond lengths, 0.10 to 0.13° for bond angles and somewhat larger for torsion angles not involving H atoms; those involving H atoms are given in parentheses. The values given on a second line refer to enantholactam hydrochloride (Winkler & Dunitz, 1975).

Table 1. *Atomic coordinates* ($\times 10^5$ *for* C, N *and* O, $\times 10^4$ *for* H *atoms; e.s.d.'s in parentheses*) *and isotropic* $U$ *values* ($\times 10^4$)

$\bar{U}$ is the average of the three eigenvalues of each anisotropic vibration tensor.

|       | $x$      | $y$       | $z$       | $\bar{U}$ (Å$^2$) |        | $x$      | $y$       | $z$        | $U$ (Å$^2$) |
|-------|----------|-----------|-----------|--------|--------|----------|-----------|------------|--------|
| O     | 74029 (4) | 18705 (13) | 26335 (11) | 207    | HN     | 7153 (8) | 4725 (26) | 1381 (22)  | 298 (46) |
| N     | 69395 (5) | 38370 (16) | 8304 (13)  | 157    | H(1)C(2) | 6705 (8) | 836 (22)  | −652 (20)  | 232 (42) |
| C(1)  | 70599 (6) | 21176 (18) | 13610 (15) | 148    | H(2)C(2) | 7062 (7) | −508 (24) | 602 (19)   | 236 (42) |
| C(2)  | 67637 (6) | 4972 (19)  | 4136 (15)  | 171    | H(1)C(3) | 5941 (8) | −1020 (23) | 44 (20)   | 240 (12) |
| C(3)  | 61544 (6) | −1033 (20) | 8311 (17)  | 198    | H(2)C(3) | 6242 (8) | −762 (24) | 1805 (21)  | 282 (45) |
| C(4)  | 56984 (6) | 14736 (21) | 9202 (16)  | 205    | H(1)C(4) | 5315 (8) | 912 (22)  | 1139 (20)  | 274 (44) |
| C(5)  | 55041 (6) | 26213 (20) | −5307 (17) | 207    | H(2)C(4) | 5869 (8) | 2317 (21) | 1773 (19)  | 208 (40) |
| C(6)  | 58402 (6) | 44798 (20) | −5551 (17) | 216    | H(1)C(5) | 5561 (7) | 1846 (22) | −1406 (22) | 219 (42) |
| C(7)  | 65315 (6) | 44001 (20) | −5958 (16) | 180    | H(2)C(5) | 5053 (8) | 2884 (20) | −720 (18)  | 223 (40) |
|       |          |           |           |        | H(1)C(6) | 5634 (7) | 5193 (26) | −1417 (21) | 281 (45) |
|       |          |           |           |        | H(2)C(6) | 5778 (7) | 5200 (23) | 327 (20)   | 209 (40) |
|       |          |           |           |        | H(1)C(7) | 6594 (7) | 3563 (22) | −1422 (18) | 159 (37) |
|       |          |           |           |        | H(2)C(7) | 6665 (8) | 5691 (23) | −799 (19)  | 221 (41) |
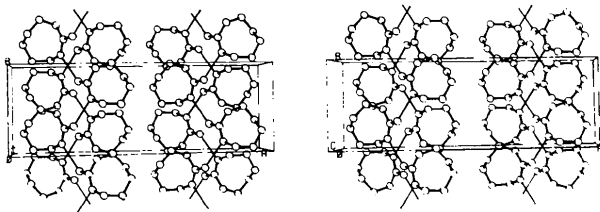
Fig. 3. Stereoscopic view down [001] of the crystal structure. H atoms are not drawn. The N···O hydrogen bonds are drawn slightly thinner.

through C(7), N and C(1). The O atom to which it is hydrogen bonded is 0·28 Å above this plane so optimization of the hydrogen-bond geometry might be the major driving force for the observed out-of-plane deformation. A final difference map shows maxima of 0·14 to 0·28 e Å$^{-3}$ at or close to the mid-points of bonds not involving H atoms. No significant density attributable to the amide O atom lone pairs is observed.

The packing is shown in Fig. 3. Hydrogen-bonded chains of molecules related by a twofold screw axis run along the **b** direction. Lateral association of these chains in the **c** direction leads to double layers of molecules with their polar amide groups buried in the middle of each double layer and with non-polar

methylene groups on the two surfaces. The hydrogen bond is nearly linear ($\angle$N–H···O 174°; N···O 2·81 Å) and the C(1)–O···H angle is 134°.

### References

DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* B29, 589–595.
DUNITZ, J. D. & WINKLER, F. K. (1975). *Acta Cryst.* B31, 251–263.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.
HALLAM, H. E. & JONES, C. M. (1967). *J. Mol. Struct.* 1, 413–423.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
WINKLER, F. K. & DUNITZ, J. D. (1975). *Acta Cryst.* B31, 273–275.
WINKLER, F. K., SEILER, P., CHESICK, J. & DUNITZ, J. D. (1976). *Helv. Chim. Acta*, 59, 1417–1423.

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# (17S)-Spiro[(androstène-4)-17:5'-(oxathiolane-1',2')] One-3 Oxyde-2' (Isomère A)*

### PAR EVELYNE SURCOUF

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**Abstract.** $C_{21}H_{30}O_3S$, orthorhombic, $P2_12_12_1$, $a = 23\cdot367$ (3), $b = 13\cdot156$ (1), $c = 6\cdot180$ (1) Å, $Z = 4$. The structure was solved by direct methods. The parameters were refined by full-matrix least-squares calculations using 1877 observed reflexions. The H atoms were included in the calculation. The refinement converged at $R = 0\cdot051$ and $R_w = 0\cdot041$. The molecule shows a planar conformation. The bond lengths and angles are in good agreement with the expected values.

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* Conformations Cristallines d'Hormones Stéroïdes de Synthèse. XII. Parties I: Lepicard, Delettré & Mornon (1973); II: Lepicard, Delettré & Mornon (1974); III: Mornon, Lepicard & Delettré (1974); IV: Delettré, Mornon & Lepicard (1975a); V: Delettré, Mornon & Lepicard (1975b); VI: Mornon, Lepicard & Delettré (1976); VII: Delettré, Mornon & Bally (1977); VIII: Bally, Lepicard & Surcouf (1977); IX: Lepicard, Delettré & Mornon (1977); X: Mornon, Lepicard & Bally (1977); XI: Surcouf (1978).

**Introduction.** Les spirosultines, stéroïdes en 17, manifestent chez l'animal d'intéressantes propriétés antiminéralocorticoïdes (Nedelec *et al.*, 1978). Par rapport aux spirolactones correspondantes, ces composés présentent la particularité d'exister sous deux formes isomères au niveau de l'atome de soufre et, il a été observé que, *in vitro*, seule une des deux formes présente une affinité pour le récepteur de l'aldostérone. Il était donc intéressant de connaître la structure moléculaire de ces composés. Cet article concerne l'étude de l'isomère *A*, inactif *in vitro* (RU22454).

Les mesures d'intensités ont été effectuées sur un diffractomètre automatique Philips PW 1100 en utilisant la radiation Cu $K\alpha$. Seules les intensités des réflexions ont été mesurées, le fond continu résultant d'une série unique de mesures effectuées en fonction de l'angle $\theta$.