Fig. 3. Packing diagram viewed normal to the *ab* plane (*ORTEP*, Johnson, 1965).

the phenyl ring in the direction away from the other phenyl ring [C(2) −0·03, C(5) −0·10 Å]. The bond distances and angles within the half molecule appear normal except for the C—C—C angles across C(1) and C(5) which average 114·1°; these are the bridgehead atoms in the tricyclic ring system. The ring formed by atoms C(1), C(5)—C(8), and O(9) is in the 'boat' form; an examination of models indicates that this form is preferable to the 'chair' form in which one of the methyl groups would interact strongly with the phenyl ring. The packing of the molecules is shown in Fig. 3. There are no indications of intermolecular hydrogen bonds.

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Structure of the Racemic Pair of Lactones of (2S,3S)-4-Hydroxyvaline and its Optical Isomer (as their Hydrochlorides)

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Abstract. $C_5H_9NO_2.HCl$, monoclinic, $C2/c$, $a = 16\cdot536$ (10), $b = 5\cdot656$ (10), $c = 15\cdot68$ (1) Å, $\beta = 105\cdot2$ (1)°, $D_m = 1\cdot40$, $D_c = 1\cdot42$ g cm⁻³ for $Z = 8$. The methyl and ammonium substituents on the lactone ring are *trans*; the ring itself is puckered although four of the ring atoms are coplanar with the O atom of the carbonyl group.

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Introduction. As part of a study of the biosynthesis of cephalosporin it was necessary to prepare the four isomers of 4-hydroxyvaline, a mixture of which was obtained by the method of Galantay, Szabo & Fried (1963). Conversion of the free amino acids to a corresponding mixture of lactones (as their hydrochlorides) and recrystallization from ethanol and ether led to a mixture of a less-soluble pair of enantiomers (unpublished results). An X-ray crystallographic analysis was performed to establish the configuration of these enantiomers.

A crystal 0·27 × 0·10 × 0·06 mm was used for data collection. The cell parameters were determined by least squares from the settings of 25 reflexions measured on a four-circle diffractometer with Mo $K\alpha$ radiation.

Systematic absences hkl: $h + k = 2n + 1$, $h0l$: $l = 2n + 1$ ($h = 2n + 1$), $0k0$: $k = 2n + 1$ indicated either Cc or $C2/c$; successful refinement in the latter vindicated its choice, based on an inspection of E statistics. Intensities were collected out to $2\theta = 46°$ on a Philips PW 1100 computer-controlled diffractometer operating in the ω–2θ scan mode [scan width 1·2° (θ), scan speed 0·04° (θ) s^{-1}], with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Three reference reflexions were monitored after every 68 reflexions measured; their intensities had a mean deviation of 2%. Of 1075 measured intensities, 602 unique observed reflexions [$I_{rel} > 2.45\sigma(I_{rel})$] were employed in the analysis. The data were corrected for Lorentz–polarization effects but not for absorption.

The Cl atom was located both from a Patterson map and from an E map. A difference map phased on the refined position of the Cl atom showed peaks which could be ascribed to all the non-hydrogen atoms; R was 0·46. Full-matrix least-squares refinement of the positions of all the non-hydrogen atoms with isotropic temperature factors reduced R to 0·08. At this stage peaks corresponding to the H atoms appeared in a difference map.

In a final full-matrix least-squares refinement with a unit weighting scheme, the bond lengths between C atoms of the ring and H atoms attached to them were held at 1·080 Å. The methyl and ammonium H atoms were constrained to ride on their parent C and N atoms with idealized tetrahedral geometry and C–H and N–H distances fixed at 1·080 Å. The isotropic temperature factors of the ring, methyl and ammonium H atoms were refined as three independent variables which converged to $U = 0.049$, 0·072 and 0·074 Å^2 respectively. All the non-hydrogen atoms were assigned anisotropic temperature factors in the final refinement, which converged to $R = 0.041$ and $R_w = 0.041$ with $w = 1/\sigma^2$. Table 1 lists the final atomic positions, Table 2 the molecular parameters.*

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

E.s.d.'s are given in parentheses.

C(1)–C(2)	1·523 (7)	O(2)–C(1)	1·341 (6)
C(2)–C(3)	1·519 (7)	C(1)–O(1)	1·189 (6)
C(3)–C(4)	1·519 (8)	C(2)–N	1·483 (6)
C(4)–O(2)	1·464 (7)	C(3)–C(5)	1·506 (8)
C(1)–C(2)–C(3)	103·7 (4)	O(2)–C(1)–O(1)	123·7 (5)
C(2)–C(3)–C(4)	100·6 (4)	C(1)–C(2)–N	110·4 (4)
C(3)–C(4)–O(2)	105·6 (4)	C(3)–C(2)–N	116·1 (4)
C(4)–O(2)–C(1)	110·5 (4)	C(2)–C(3)–C(5)	115·7 (5)
O(2)–C(1)–C(2)	108·4 (5)	C(4)–C(3)–C(5)	113·7 (5)
C(2)–C(1)–O(1)	127·9 (5)		
C(1)–C(2)–C(3)–C(4)	−31·6	C(4)–O(2)–C(1)–C(2)	−2·8
C(2)–C(3)–C(4)–O(2)	30·7	O(2)–C(1)–C(2)–C(3)	22·7
C(3)–C(4)–O(2)–C(1)	−18·3		

Table 1. *Final atomic coordinates* ($\times 10^4$)

H(21) is bound to C(2), H(31) to C(3) *etc.*; HN(1), HN(2) and HN(3) are bound to the N atom.

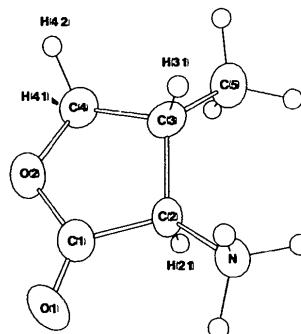|	x	y	z
C(1)	2175 (4)	8316 (10)	1549 (3)
C(2)	1736 (3)	5995 (9)	1222 (3)
C(3)	841 (3)	6401 (10)	1269 (4)
C(4)	988 (4)	8070 (11)	2054 (4)
C(5)	355 (4)	4213 (11)	1369 (4)
N	1845 (2)	5393 (9)	338 (3)
O(1)	2808 (2)	9062 (8)	1428 (3)
O(2)	1740 (2)	9419 (7)	2043 (2)
Cl	1216 (1)	509 (3)	9520 (1)
H(21)	2027	4570	1653
H(31)	507	7313	676
H(41)	1121	7064	2660
H(42)	480	9315	1995
H(51)	641	3392	1998
H(52)	303	2932	847
H(53)	−261	4850	1366
HN(1)	1595	6783	−129
HN(2)	1565	3727	82
HN(3)	2516	5294	439

Fig. 1. Structure of the asymmetric unit [with R configuration at both C(2) and C(3)]. H(41) is hidden behind C(4).

Discussion. The asymmetric unit of the structure is the hydrochloride of 4-hydroxyvaline lactone whose cation is depicted in Fig. 1, which also gives the atomic nomenclature. The isomer shown has the R configuration at both C(2) and C(3).

Bond lengths in the cation do not depart dramatically from conventional values, and, from bond-angle values, little strain is present in the ring, although O(2)–C(1)–C(2) = 108·4 (5)° indicates a marked deviation from ideal sp^2 geometry at C(1). The CH_3 and NH_3^+ groups are *trans*-disposed; this is shown in Fig. 2, where the cation is viewed approximately along C(1)–C(2). Fig. 2 also emphasizes the pucker of the lactone ring, which has an envelope configuration. The four ring atoms C(4), O(2), C(1) and C(2) are almost coplanar with the carbonyl O atom (Table 3) whereas C(3) is situated some 0·5 Å above the mean
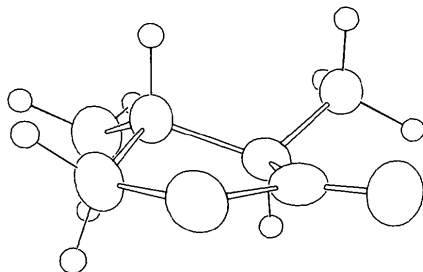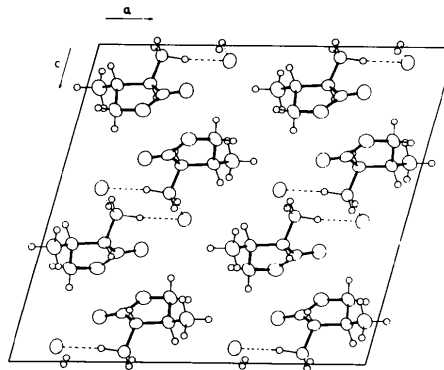

Fig. 3. Packing in the unit cell. Hydrogen bonding (involving N and Cl atoms) is represented by dashed lines.

Fig. 2. View of the lactone with the ring atom O(2) closest to the observer.

Table 3. *Least-squares plane*

The equation of the plane is expressed in orthogonalized space as $PI + QJ + RK = S$. The plane through C(2), C(1), O(1), O(2) is given by: $5·4757I - 2·6499J + 11·0293K = 0·7067$.

Atoms included in the calculation	Distance from plane (Å)	Atoms not included in the calculation	Distance from plane (Å)
C(2)	−0·003	C(3)	0·542
C(1)	0·011	C(4)	0·040
O(1)	−0·004	C(5)	0·118
O(2)	−0·003	N	0·753

plane defined by the latter four atoms. The N atom of the NH_3^+ group and, surprisingly, the methyl C atom both lie on the same side of the plane as C(3).

Fig. 3 shows the packing of the molecules. Each Cl^- ion is hydrogen-bonded to three ammonium H atoms in such a way that infinite spiralling chains of cations alternating with anions are formed round the twofold screw axes. No intermolecular close contacts other than these $N-H \cdots Cl$ bonds were detected.

All calculations were carried out with *SHELX* and *XANADU* (Sheldrick, 1976; Rogers & Sheldrick, 1975) on a Univac 1106 Computer at the University of Cape Town.

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