

Structure of (–)-Lupinine Hydrochloride

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Abstract. $C_{10}H_{20}NO^+ \cdot Cl^-$, $M_r = 205.6$, orthorhombic, $P2_12_12_1$, $a = 7.108$ (1), $b = 11.634$ (2), $c = 13.470$ (1) Å, $Z = 4$, $D_x = 1.23$ Mg m $^{-3}$, $\mu(Cu K\alpha) = 2.75$ mm $^{-1}$. The structure was refined to $R = 0.042$ for 824 unique reflexions. The alkaloid cations are hydrogen bonded through the Cl^- ions ($N-H \cdots Cl \cdots H'-O'$) to form infinite chains along the b axis. The absolute configuration of the lupinine skeleton has been established as (1*R*,5*R*,10*R*).

Introduction. The crystal structure of lupinine hydrochloride has been determined as part of systematic studies on the structure of lupinine and its derivatives.

Crystals for X-ray analysis were obtained from ethanol–diethyl ether solution. A single crystal with dimensions 0.30 × 0.25 × 0.25 mm was used for diffractometer data collection. Intensities of reflexions were measured by the θ – 2θ scan method on a Syntex $P2_1$ diffractometer with Cu $K\alpha$ radiation (graphite monochromator). Lorentz and polarization corrections were applied, but no absorption correction was made. 824 reflexions with $I \geq 1.96\sigma(I)$ were used in the structure determination. The structure was solved by direct methods. 106 reflexions with $E \geq 1.5$ were used in *MULTAN* (Germain, Main & Woolfson, 1971) for phase determination. The E map computed for the set of phases with the best figures of merit showed the Cl atom position $x = 0.5$, $y = 0.476$, $z = 0.343$, which was also deduced from the Patterson synthesis. The above E map and the Fourier map based on the Cl atom both possessed a mirror symmetry plane perpendicular to the a axis. However, the spurious mirror plane in the maps did not prevent us finding the correct locations of most of the non-hydrogen atoms. The remaining non-hydrogen atoms were found from a subsequent Fourier synthesis. The structure was refined by full-matrix least squares with anisotropic temperature factors. All H atoms were identified in a difference Fourier map and were included in the last cycles of refinement. Their parameters were held constant (B_{iso} for an H atom was one unit greater than the isotropic temperature factor of its carrier). Reflexions were weighted as follows: $w = (F_o/F_{low})^2$ if $F_o < F_{low}$, $w = 1$ if $F_{low} \leq F_o \leq F_{high}$, $w = (F_{high}/F_o)^2$ if $F_o > F_{high}$, with

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Table 1. Atomic positional parameters ($\times 10^4$) and isotropic thermal parameters (\AA^2)

	x	y	z	B
Cl	4989 (2)	4782 (1)	3430 (1)	3.21 (8)
C(1)	8105 (7)	3696 (4)	756 (3)	2.6 (3)
C(2)	10115 (8)	3799 (5)	1191 (4)	3.9 (3)
C(3)	10020 (9)	4430 (5)	2176 (4)	4.3 (4)
C(4)	9183 (8)	5612 (5)	2042 (4)	3.8 (4)
N(5)	7248 (5)	5539 (3)	1611 (3)	2.2 (2)
C(6)	6438 (8)	6709 (4)	1485 (4)	3.2 (3)
C(7)	4454 (8)	6699 (5)	1066 (4)	3.4 (4)
C(8)	4430 (9)	6059 (5)	95 (4)	3.6 (4)
C(9)	5227 (8)	4861 (5)	247 (3)	3.8 (3)
C(10)	7234 (7)	4880 (4)	644 (3)	2.0 (3)
C(11)	6916 (7)	2837 (4)	1306 (4)	2.4 (3)
O(1)	7897 (5)	1788 (3)	1398 (3)	4.1 (3)

$F_{low} = 4.5$ and $F_{high} = 20.5$. Structure factors with anomalous-scattering corrections for the Cl atom ($f' = 0.348$, $f'' = 0.702$) were calculated for two possible enantiomorphs. The final $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$ were $R(-) = 0.042$, $R_w(-) = 0.050$ and $R(+)$ = 0.050, $R_w(+)$ = 0.059. The ratio of the two R_w values is $\mathcal{R} = 1.180$, and application of Hamilton's (1965) \mathcal{R} test strongly indicates that the first enantiomorph is correct ($\mathcal{P}_{1.706, 0.005} \approx 1.0056$).

The atomic parameters for the correct (–)-lupinium cation are given in Table 1.*

The calculations were carried out using the *Syntex XTL* (1973) structure determination system.

Discussion. The atom-numbering scheme is shown in Fig. 1. Bond lengths and angles in the lupinium cation (Tables 2 and 3, respectively) are close to those found in lupinine (Kozioł, Kosturkiewicz & Podkowińska, 1978), except for $N^+ - C_{sp^3}$ bonds. The average $N^+ - C$ distance of 1.499 Å is in good agreement with the

* Lists of structure factors, anisotropic thermal parameters of the non-hydrogen atoms and all H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34918 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

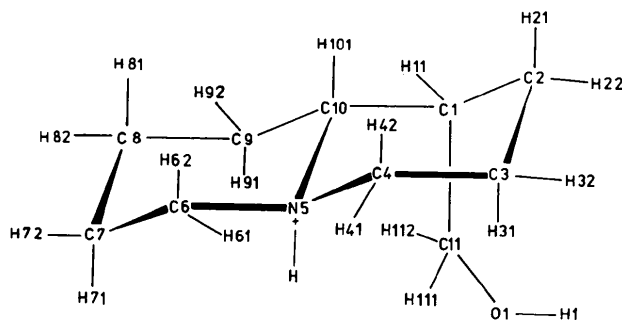


Fig. 1. The atom-numbering scheme in the lupininium cation.

Table 2. Bond lengths (Å)

C(1)—C(2)	1.549 (8)	C(6)—C(7)	1.519 (8)
C(2)—C(3)	1.519 (8)	C(7)—C(8)	1.506 (8)
C(3)—C(4)	1.511 (8)	C(8)—C(9)	1.519 (8)
C(4)—N(5)	1.495 (7)	C(9)—C(10)	1.524 (8)
N(5)—C(10)	1.512 (6)	C(1)—C(11)	1.505 (7)
C(10)—C(1)	1.519 (7)	C(11)—O(1)	1.412 (6)
N(5)—C(6)	1.489 (6)		

Table 3. Bond angles (°)

C(1)—C(2)—C(3)	109.1 (4)	C(8)—C(9)—C(10)	112.5 (4)
C(2)—C(3)—C(4)	110.7 (5)	C(9)—C(10)—N(5)	108.4 (4)
C(3)—C(4)—N(5)	110.9 (4)	C(9)—C(10)—C(1)	113.7 (4)
C(4)—N(5)—C(10)	111.7 (4)	C(1)—C(10)—N(5)	111.9 (4)
C(4)—N(5)—C(6)	110.3 (4)	C(10)—C(1)—C(2)	110.1 (4)
C(6)—N(5)—C(10)	111.3 (4)	C(10)—C(1)—C(11)	115.0 (4)
N(5)—C(6)—C(7)	113.2 (4)	C(2)—C(1)—C(11)	112.5 (4)
C(6)—C(7)—C(8)	109.8 (5)	C(1)—C(11)—O(1)	109.9 (4)
C(7)—C(8)—C(9)	109.4 (5)		

Table 4. Torsion angles (°) (e.s.d.'s for torsion angles are between 0.5 and 0.6°)

C(10)—C(1)—C(2)—C(3)	56.9	C(7)—C(8)—C(9)—C(10)	-58.9
C(1)—C(2)—C(3)—C(4)	-58.8	C(8)—C(9)—C(10)—N(5)	57.8
C(2)—C(3)—C(4)—N(5)	58.9	C(9)—C(10)—N(5)—C(6)	-55.2
C(3)—C(4)—N(5)—C(10)	-55.7	C(10)—N(5)—C(6)—C(7)	56.4
C(4)—N(5)—C(10)—C(1)	54.6	O(1)—C(11)—C(1)—C(2)	-50.6
N(5)—C(10)—C(1)—C(2)	-54.9	O(1)—C(11)—C(1)—C(10)	-177.6
N(5)—C(6)—C(7)—C(8)	-56.1	N(5)—C(10)—C(1)—C(11)	73.3
C(6)—C(7)—C(8)—C(9)	55.4	C(3)—C(2)—C(1)—C(11)	-72.7

values characteristic of a protonated amino N (Birnbaum, 1967).

The lupininium cation has the same conformation as the lupinine molecule in crystals of the free base: both rings of the *trans*-quinolizidine nucleus form chairs and the —CH₂OH group is axial (Table 4). Fig. 2 is a Newman projection along the C(1)—C(11) bond and shows the hydroxyl-group orientation which is almost the same as that in lupinine (Kozioł *et al.*, 1978). The configuration, established as (1*R*,5*R*,10*R*), confirms the work of Cookson (1953).

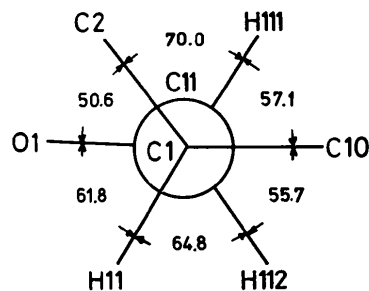


Fig. 2. A Newman projection along the C(1)—C(11) bond.

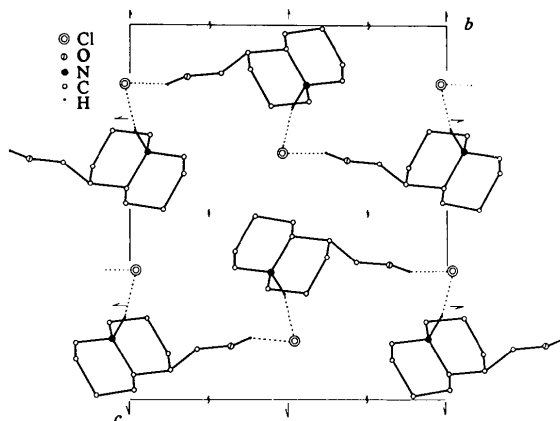


Fig. 3. Molecular packing on the (100) plane [H atoms, except H and H(1), are omitted for clarity].

Table 5. Hydrogen bonds

N(5)···Cl	3.060 (4) Å	∠N(5)—H···Cl	157.6°
N(5)—H	0.99		
H···Cl	2.12		
O(1')···Cl	3.117 (4)	∠O(1')—H(1')···Cl	164.7
O(1')—H(1')	0.93		
H(1')···Cl	2.21		
		∠N(5)···Cl···O(1')	100.9 (1)

Symmetry code: superscript: none *x, y, z*, (i) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

The packing of the molecules is shown in Fig. 3. The lupininium cations and Cl anions are linked by hydrogen bonds. The hydrogen-bond geometry is reported in Table 5.

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