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(+)-Lupanine Hydrochloride Dihydrate

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Abstract. $[C_{15}H_{25}N_2O]^+Cl^-.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}900$ (3), $b = 15{\cdot}286$ (3), $c = 7{\cdot}478$ (1) Å, $Z = 4$, $d_x = 1{\cdot}25$ g cm^{-3}, μ(Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å) = 20·9 cm^{-1}. The structure was solved by direct methods and refined by least-squares calculations to an R of 0·050 for 1243 unique diffractometer data. Ring C in the lupanine cation has the boat conformation. The molecules are linked together by a network of hydrogen bonds: $N(16)^+\cdots Cl^-\cdots O(water)\cdots O(2)'$.

Introduction. Spectroscopic (Wiewiórowski, Edwards & Bratek-Wiewiórowska, 1967) and X-ray photographic (Doucerain, Chiaroni & Riche, 1976) investigations of the lupanine molecule had shown a boat conformation for the ring *C* in the solid and liquid states. However, the problem of the conformation of the lupanine cation was still unsolved. After protonation of the free base, ring *C* in the resulting cation can remain unchanged (*i.e.* in the boat conformation) or by inversion at N(16) it can form a chair, as was observed in sparteine (Skolik, Wiewiórowski & Krueger, 1970). The reactivity and conformation of the protonated quinolizidine derivatives are being studied by Wiewiórowski, Skolik and their co-workers, and they suggested that we determine the molecular and crystal structure of a hydrated (+)-lupanine hydrochloride, $[\alpha]^{20}_D = +56{\cdot}8°$ (Wiewiórowski & Perkowska, 1978).

The title compound was crystallized from dry acetone. A crystal 0·2 × 0·2 × 0·3 mm was mounted on a Syntex $P2_1$ diffractometer and 1355 intensities were collected with Cu $K\alpha$ radiation (graphite monochromator) up to $2\theta = 114°$. After application of Lp corrections (no correction was made for absorption) 1243 reflections with $I > 1{\cdot}96\sigma(I)$ were employed for the structure calculation. The structure was solved by direct methods using *MULTAN* for 318 reflections with $E > 1{\cdot}2$. The phase solution with the best figures of merit gave an E map from which the positions of 17 non-hydrogen atoms were found. A Fourier synthesis (R = 32%) revealed the missing C(13), C(14) and O(water) atoms. The structure was refined to an R of 8·5% by a full-matrix least-squares method, first with isotropic and then anisotropic temperature factors for all atoms. At this stage two successive difference syntheses revealed all the H atoms except for two from

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3)

	x	*y*	*z*
Cl	1511 (1)	1681 (1)	5149 (3)
N(1)	5232 (3)	1 (3)	5575 (6)
C(2)	6114 (4)	266 (4)	5563 (10)
O(2)	6493 (4)	481 (3)	6944 (7)
C(3)	6580 (5)	280 (5)	3760 (10)
C(4)	6166 (5)	−326 (5)	2403 (11)
C(5)	5172 (5)	−120 (5)	2242 (8)
C(6)	4696 (4)	−273 (4)	3992 (8)
C(7)	3776 (4)	206 (4)	4075 (8)
C(8)	3305 (4)	−35 (4)	5850 (9)
C(9)	3881 (4)	329 (4)	7343 (8)
C(10)	4793 (5)	−139 (4)	7312 (8)
C(11)	4013 (4)	1320 (4)	7235 (8)
C(12)	3626 (5)	1809 (5)	8828 (9)
C(13)	3762 (6)	2787 (5)	8705 (12)
C(14)	3379 (5)	3124 (5)	7002 (12)
C(15)	3738 (4)	2645 (4)	5388 (11)
N(16)	3570 (3)	1669 (3)	5565 (6)
C(17)	3864 (4)	1204 (4)	3893 (8)
O(*w*1)	599 (4)	2718 (3)	8429 (8)
O(*w*2)	1704 (6)	2857 (4)	1653 (7)
H(1)	723	10	393
H(2)	657	99	311
H(3)	620	−103	292
H(4)	650	−17	100
H(5)	493	−48	129
H(6)	517	53	161
H(7)	458	−102	419
H(8)	352	5	289
H(9)	267	29	583
H(10)	329	−72	562
H(11)	354	17	858
H(12)	466	−83	761
H(13)	527	14	840
H(14)	473	144	706
H(15)	298	160	923
H(16)	414	164	3
H(17)	359	318	2
H(18)	451	289	873
H(19)	273	308	703
H(20)	360	384	670
H(21)	441	269	519
H(22)	335	289	419
H(23)	291 (4)	154 (4)	586 (8)
H(24)	460	137	370
H(25)	356	152	295
H(26)	89	308	946
H(27)	113	249	765

the second molecule of water. Fixed parameters for H atoms were included in the calculations with B_j one unit greater than the isotropic value for the atoms to which they were bonded. Only the parameters for H(23) attached to N(16) were allowed to vary. Refinement converged to $R = 0.050$ with a corresponding $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o| = 0.053$ for 1243 observed reflections.* The function minimized was $\sum w|F_o - F_c|^2$ where $w = 1/\sigma^2(F_o)$. The final positional parameters are given in Table 1. All calculations were performed on a Nova 1200 computer with the programs included in the syntex XTL/E-XTL structure determination system (Syntex, 1976). Neutral-atom scattering factors used were those listed in *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows a perspective view of the alkaloid cation, the intramolecular bond lengths and valency angles with their e.s.d.'s and the endocyclic torsion angles. The lupanine skeleton consists of two *trans* quinolizidine systems. The presence of a lactam group causes ring *A* to adopt a half-chair conformation. C(2)=O(2) (1·222 Å) and C(2)–N(1) (1·376 Å) show the characteristic changes in lengths associated with an interaction between the free pair of electrons on N(1) and the attached carbonyl group. The values cited above and the angle between the planes defined by C(3), C(2), O(2), N(1) and C(2), N(1), C(6), C(10) (Table 2) are comparable within 2σ with the values found in (±)-lupanine (Doucerain *et al.*, 1976). On the other hand, the values of Doucerain *et al.* for the torsion angles around C(3)–C(2), C(2)–N(1) and N(1)–C(6) (–34, 15 and –18°) differ by 10–15° from those reported here (Fig. 1*c*). Consequently, this fragment is flat, which could indicate that conjugation in the lactam group is stronger in the (+)-lupanine cation than in (±)-lupanine. Rings *B* and *D* are in the chair conformation. Ring *C* forms a boat as in (±)-lupanine and lupanine *N*-oxide perchlorate (Kałuski, Gusiev, Struchkov, Skolik, Baranowski & Wiewiórowski, 1972), while in 13-hydroxylupanine (Kałuski, Garbarczyk, Gusiev, Struchkov, Skolik & Wiewiórowski, 1978) and 13-*epi*-hydroxy-15-[2′-(5′-hydroxymethylfuryl)]lupanine hydrobromide (Garbarczyk,

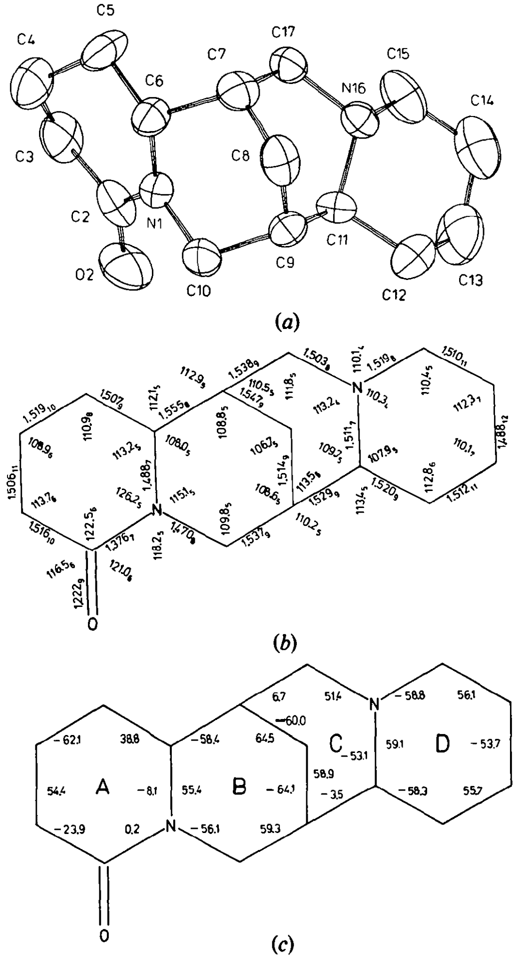

Fig. 1. The lupanine cation. (*a*) An *ORTEP* drawing (Johnson, 1965) with 50% vibration ellipsoids. (*b*) Bond lengths (Å) and valency angles (°) with e.s.d.'s. (*c*) Endocyclic torsion angles (°).

Table 2. *Least-squares planes*

Equations to planes

Plane 1: $-0.3367X + 0.9398Y - 0.0584Z + 2.9008 = 0$
Plane 2: $-0.2940X + 0.9458Y - 0.1382Z + 2.8667 = 0$
Plane 3: $-0.2932X + 0.9462Y - 0.1367Z + 2.8546 = 0$

Deviations of atoms from the planes (Å)

Plane	N(1)	C(2)	O(2)	C(3)	C(4)	C(5)	C(6)	C(10)	χ^2
1	0·034	–0·027	0·032*	–0·162*			–0·022	–0·022	102·33
2	0·000	–0·002	0·001	0·001					0·13
3	0·000	–0·001	0·004*	0·001	–0·557*	0·193*	–0·000		0·03

The angle between planes 1 and 2 is 5·2°.

* Atoms not included in plane calculations.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33531 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

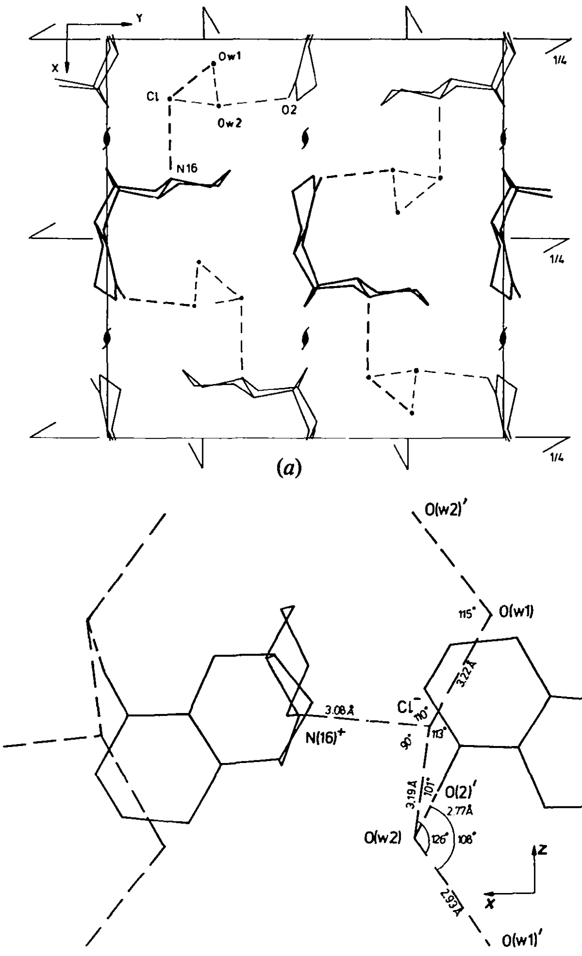
Kałuski, Bratek-Wiewiórowska, Skolik & Wiewiórowski, 1974) this ring is a chair.

The average C—N$^+$ (1·511 Å) and C—C (1·522 Å) bond lengths (with r.m.s. deviations of 0·011 and 0·019 Å respectively) are in good agreement with the values of 1·500 and 1·537 Å cited by Birnbaum (1967). The mean values for C—H bonds and C—C—H, H—C—H angles are 1·08 Å and 109°. Thus, all observed bond distances and angles in the lupanine cation agree well with the values expected from the known structures of lupanine and angustifoline derivatives (Kałuski *et al.*, 1972, 1978; Garbarczyk *et al.*, 1974; Doucerain *et al.*, 1976; Birnbaum, Cheung, Wiewiórowski & Bratek-Wiewiórowska, 1967; Rychlewska, 1977; and references therein).

The molecules of (+)-lupanine hydrochloride are linked together by a three-dimensional hydrogen-bond lattice formed by the molecules of water (see Fig. 2). The values

$$\mathrm{N(16)^+} \overset{3\cdot08\ \text{Å}}{\cdots\cdots\cdots} \mathrm{Cl^-} \overset{3\cdot19\ \text{Å}}{\cdots\cdots\cdots} \mathrm{O}(w2) \overset{2\cdot77\ \text{Å}}{\cdots\cdots\cdots} \mathrm{O(2)'}$$

[where O(2)′ is at $\frac{1}{2}+x, \frac{1}{2}-y, -z$] fall well within the usually accepted ranges (Kitaigorodsky, 1976; Stout & Jensen, 1970). The distances Cl$^-\cdots$O(w1) (3·22 Å) and O(w1)′$\cdots$O(w2) (2·93 Å) are equal to the upper limits cited by Stout & Jensen (1970): 2·86–3·21 Å for O—H$\cdots$Cl and 2·65–2·93 Å for O—H$\cdots$O [where O(w1)′ is at $1+z$]. N(16)$^+$—H(23) is 1·02 (6) Å and H(23)$\cdots$Cl$^-$ is 2·171 (6) Å, with ∠N(16)—H(23)—Cl 148 (4)°.



(*b*)

Fig. 2. (*a*) The crystal structure projected along the *z* axis. The hydrogen bonds are shown as dashed lines. (*b*) A schematic drawing of the hydrogen-bond system viewed along the *y* axis.

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