

Table 5. *Least-squares plane of the benzene ring and deviations of atoms (Å) from the plane*

Equation of the plane in the standard orthogonal system			
$0.87282X - 0.45256Y - 0.19075Z - 3.2835 = 0$			
C(1)	0.002	Cl(1)*	0.003
C(2)	-0.002	Cl(2)*	0.006
C(3)	-0.002	O(1)*	0.070
C(3')	0.002	C(4)*	-1.190
C(1')	-0.002	Weighted standard deviation	
C(2')	0.002	of plane: 0.003 Å.	
$\chi^2 = 2.67$		$\alpha = 0.5$	

The benzene ring is nearly ideally planar within experimental error.

\* Not included in the calculation of the plane.

& Domenicano, 1978); differences for those with a non-hydrogen *ortho* substituent are 1.4–3.0°.

The dihedral angle between the mean plane through the benzene ring and the plane through C(3), O(1) and C(4) is 84.0 (3)°. The differences in angles for the compounds with and without H as the *ortho* substituent are 0.5–12.0 and 84–88° respectively.

Deviations of atoms from the mean plane of the benzene ring are given in Table 5.

The angle C(3)–O(1)–C(4) is 115.2 (3)°. Analogous angles for the tetramethyl and tetrabromo derivatives are 114.7 (16) and 114.5 (7)° respectively.

Intermolecular distances do not indicate any interactions stronger than normal van der Waals.

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## Anhydrous (+)-Lupanine Perchlorate

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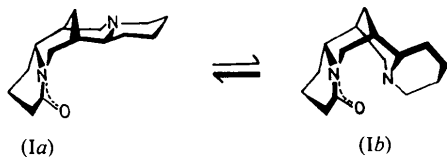
(Received 9 October 1979; accepted 1 February 1980)

**Abstract.**  $C_{15}H_{25}N_2O^+ \cdot ClO_4^-$ ,  $M_r = 348.9$ , orthorhombic,  $P2_12_12_1$ ,  $a = 12.551$  (2),  $b = 10.332$  (1),  $c = 12.369$  (1) Å,  $Z = 4$ ,  $d_x = 1.44$  Mg m<sup>-3</sup>. The structure was solved by the heavy-atom method and refined by full-matrix least squares to an  $R_F$  of 0.035 for 1249 observed reflections. Unlike lupanine, lupanine hydrochloride dihydrate and lupanine perchlorate monohydrate the lupanine cation in the anhydrous perchlor-

ate has the *trans-cis* configuration and a significantly different conformation. Rings *A*, *B*, *C* and *D* have chair forms. The lupanine cation and perchlorate anion are linked by a weak hydrogen bond:  $N(16)^+ \cdots OClO_3^- = 3.026$  (4) Å.

**Introduction.** This work is a continuation of an X-ray investigation of the structures of lupanine derivatives.

The spectroscopic data (Wiewiórowski, Edwards & Bratek-Wiewiórowska, 1967) and the X-ray analyses of ( $\pm$ )-lupanine (Doucerain, Chiaroni & Riche, 1976), (+)-lupanine hydrochloride dihydrate (Skrzypczak-Jankun & Kałuski, 1978) and (+)-lupanine perchlorate monohydrate (Małuszyńska, Hoser & Kałuski, 1979) have shown that the lupanine free base and its protonated cation exist in the same boat-chair conformation (1a). From these facts one can infer that inversion at N(16) in (1a), leading to the full-chair conformer (1b), proceeds with difficulty.



However, the results of the spectroscopic investigation appeared to indicate that the cation of the anhydrous lupanine perchlorate had the full-chair conformation (1b) (Perkowska, Pieczonka & Wiewiórowski, 1980).

This work is intended to verify this hypothesis concerning the molecular structure of anhydrous lupanine perchlorate. If this hypothesis were correct, our studies should also answer the question as to whether there are intramolecular factors stabilizing the all-chair conformation of the lupanine cation, as was the case in sparteine perchlorate (Borowiak, Boki & Struchkov, 1980).

Crystallization was carried out in special anhydrous conditions. Lupanine perchlorate monohydrate was dissolved in dry acetone with 3 Å molecular sieves. After 24 h the solution was decanted. Crystals were obtained by slow evaporation of the acetone solution or of an acetone/*n*-hexane mixture (10:1 v/v).

Data were collected on a Syntex P2<sub>1</sub> diffractometer to  $2\theta = 115^\circ$  with Cu  $K\alpha$  ( $\lambda = 1.54178$  Å) radiation (graphite monochromator) and a  $\theta$ - $2\theta$  scan technique with scan speeds varying linearly between 2.00 and 29.30° min<sup>-1</sup>. Of 1279 unique reflections, 1249 and  $I > 1.96\sigma(I)$  and were used in subsequent calculations. No corrections for absorption were applied [ $\mu_1(\text{Cu } K\alpha) = 2.4 \text{ mm}^{-1}$ ].

The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method to  $R = 0.078$ . The H atoms were easily located on two subsequent difference Fourier maps. They were included in the calculations with all parameters fixed. The final discrepancy factors were  $R_F = 0.035$  and  $R_w = \sum w^{1/2}|F_o - F_c| / \sum w^{1/2}|F_o| = 0.045$  for 1249 reflections. The function minimized was  $\sum w|F_o - F_c|^2$  with the weights  $w = (F_o/F_L)^2$  for  $F_o < F_L$ ;  $w = 1$  for  $F_L < F_o < F_H$ ;  $w = (F_H/F_o)^2$  for  $F_o > F_H$ , where  $F_L = 3.65$ ,  $F_H = 17.80$ .

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub>
Cl	2737 (1)	2837 (1)	2431 (1)	2.9 (1)
O(1)	2617 (3)	2654 (3)	1295 (2)	4.5 (2)
O(2)	3549 (3)	1992 (4)	2804 (4)	6.9 (3)
O(3)	1757 (3)	2494 (5)	2931 (3)	6.1 (3)
O(4)	2974 (4)	4140 (4)	2641 (4)	8.3 (3)
O(C2)	3974 (2)	8251 (3)	3546 (2)	4.0 (2)
N(1)	4825 (2)	7034 (3)	4797 (2)	2.0 (2)
N(16)	6489 (2)	5074 (3)	4427 (2)	2.4 (2)
C(2)	4602 (3)	8185 (4)	4311 (3)	2.7 (2)
C(3)	5170 (4)	9400 (4)	4660 (4)	3.7 (3)
C(4)	5521 (4)	9393 (4)	5840 (4)	3.8 (3)
C(5)	6030 (3)	8099 (3)	6111 (3)	3.2 (2)
C(6)	5237 (3)	7013 (4)	5932 (3)	2.4 (2)
C(7)	5666 (3)	5678 (4)	6213 (3)	2.7 (2)
C(8)	4806 (3)	4669 (4)	6032 (3)	2.9 (2)
C(9)	4576 (3)	4625 (4)	4825 (3)	3.2 (2)
C(10)	4146 (3)	5938 (4)	4461 (3)	3.3 (2)
C(11)	5559 (3)	4180 (4)	4184 (3)	2.5 (2)
C(12)	5866 (4)	2772 (4)	4391 (3)	3.6 (3)
C(13)	6894 (4)	2360 (4)	3845 (4)	4.6 (3)
C(14)	7780 (4)	3272 (4)	4134 (3)	3.8 (3)
C(15)	7491 (4)	4654 (4)	3847 (4)	3.4 (3)
C(17)	6678 (3)	5274 (4)	5611 (3)	2.9 (2)
H(C3)	4723	10127	4434	5.0
H(C3')	5825	9295	4290	5.0
H(C4)	4802	9342	6330	5.0
H(C4')	6023	10070	6013	5.0
H(C5)	6656	7921	5700	5.0
H(C5')	6307	8031	6885	5.0
H(C6)	4647	7204	6457	5.0
H(C7)	5863	5642	6997	5.0
H(C8)	4961	3865	6244	5.0
H(C8')	4134	4822	6422	5.0
H(C9)	3997	3939	4619	5.0
H(C10)	3312	6033	4922	5.0
H(C10')	4037	6018	3695	5.0
H(C11)	5407	4341	3469	5.0
H(C12)	5842	2621	5078	5.0
H(C12')	5293	2233	4269	5.0
H(C13)	7006	1435	4055	5.0
H(C13')	6862	2373	3012	5.0
H(C14)	8379	2993	3816	5.0
H(C14')	8087	3079	4860	5.0
H(C15)	8031	5438	3982	5.0
H(C15')	7282	4740	3064	5.0
H(N16)	6312	5835	4106	5.0
H(C17)	7222	5914	5663	5.0
H(C17')	7039	4444	5832	5.0

Positional parameters are listed in Table 1.\* The XTL/E-XTL system of programs (Syntex, 1976) was used during the calculations. Bond distances, bond angles and torsion angles are given in Fig. 1.

**Discussion.** The X-ray analysis has shown that the cation of anhydrous lupanine perchlorate has the

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35079 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

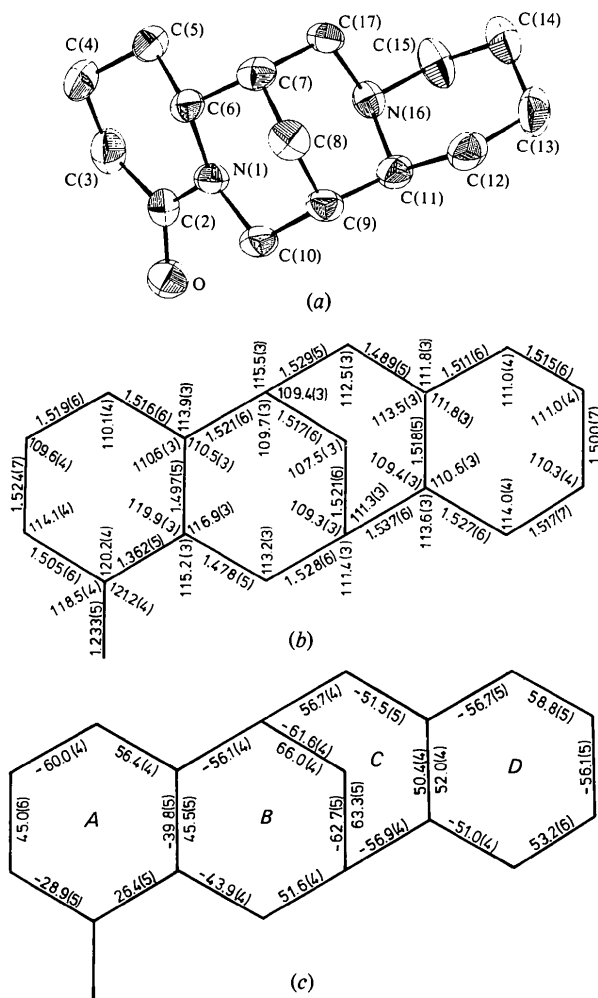


Fig. 1. The structure of the cation of anhydrous (+)-lupanine perchlorate. (a) An ORTEP drawing (Johnson, 1965) showing thermal ellipsoids with 50% probability. (b) Bond lengths (Å) and valency angles (°) with e.s.d.'s. (c) Endocyclic torsion angles (°).

*trans-cis* configuration and adopts a full-chair conformation. These facts confirm the hypothesis that the molecular structure of the lupanine cation in its anhydrous perchlorate significantly differs from the atomic arrangements in ( $\pm$ )-lupanine (Doucerain, Chiaroni & Riche, 1976), (+)-lupanine hydrochloride dihydrate (Skrzypczak-Jankun & Kałuski, 1978) and (+)-lupanine perchlorate monohydrate (Małuszyńska, Hoser & Kałuski, 1979). In both the above-mentioned salts ring C has a boat form as in ( $\pm$ )-lupanine. It now becomes evident that the removal of one water molecule from (+)-lupanine perchlorate monohydrate causes prototropism and changes the configuration and conformation of the lupanine cation. The change is such as to impose a *transoidal*\* conformer [as in

\* *transoidal* or *cisoidal* conformers mean a quasi-*trans* or quasi-*cis* position of the lactam function in relation to the tertiary amine group (see Ia,b).

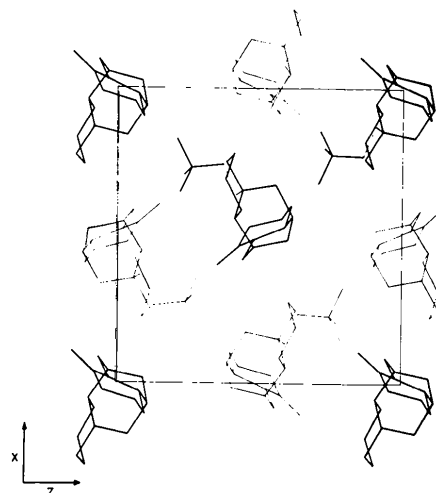


Fig. 2. Molecular packing in the unit cell ( $xOz$  projection). The hydrogen bonds are shown as dashed lines.

( $\pm$ )-lupanine, (+)-lupanine hydrochloride dihydrate, and (+)-lupanine perchlorate monohydrate] on a *cisoidal* one.

Comparing the molecular structures of lupanine and its salts cited here, one can see the differences in conformation of rings A. In ( $\pm$ )-lupanine this ring has a sofa form, in (+)-lupanine hydrochloride dihydrate an intermediate form between sofa and half-chair, in (+)-lupanine perchlorate monohydrate a half-chair, and in anhydrous (+)-lupanine perchlorate a chair flattened in the region of a carbonyl group. The asymmetry parameters for ring A in the last structure are:  $\Delta C_s^2 = 3.92$ ,  $\Delta C_s^{3,4} = 30.55$ ,  $\Delta C_s^{1,2} = 11.15$ .

All bond lengths and valency angles agree with their expected values. The mean values for  $N(1)-C_{sp^3}$ ,  $N(16)^+-C_{sp^3}$  and  $C_{sp^3}-C_{sp^3}$  in the lupanine cation are 1.487 [9],\* 1.509 [8] and 1.521 [8] Å respectively. Bond distances and angles in the perchlorate anion varied from 1.403 (4) to 1.425 (3) Å for O-Cl (av. 1.417 [8] Å) and from 107.8 (2) to 112.2 (2)° for O-Cl-O (av. 109.4 [1.4]°). We have observed that the temperature factors of the Cl and O atoms in the anion are relatively small in comparison with the other perchlorates of the lupin alkaloids. This probably improves the accuracy of all structural parameters.

Anhydrous (+)-lupanine perchlorate has a structure similar to that of sparteine perchlorate (Borowiak, Bokiy & Struchkov, 1980). In the sparteine salt an intramolecular  $N(1)\cdots N(16)^+$  hydrogen bond is a predominant factor which stabilizes the molecular structure. Such an interaction in a lupanine salt could not occur as the free pair of electrons on N(1) is engaged in conjugation with the carbonyl group. The

\* The numbers in square brackets are r.m.s. deviations.

only intramolecular interaction is that between  $N(16)^+$  and  $OCIO_3^-$  [ $N(16)^+ \cdots O(1Cl) = 3.026$  (4) Å].

In the crystal structure of (+)-lupanine perchlorate, which is much the same as sparteine perchlorate, no intermolecular contacts (apart from normal van der Waals contacts) are observed (Fig. 2).

We thank Professor M. Wiewiórowski for suggesting this structure determination. The study was supported by the Polish Academy of Sciences (MRI-9).

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## 4,5,9,10,11,12-Hexafluoropentacyclo[6.4.0.0<sup>3,6</sup>.0<sup>4,12</sup>.0<sup>5,9</sup>]dodec-10-ene\*

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**Abstract.**  $C_{12}H_8F_6$ ,  $M_r = 266.2$ , triclinic,  $P\bar{1}$ ,  $a = 6.625$  (3),  $b = 7.176$  (4),  $c = 11.427$  (6) Å,  $\alpha = 79.43$  (4),  $\beta = 78.67$  (4),  $\gamma = 67.56$  (4)°,  $V = 488.8$  Å<sup>3</sup>,  $D_m = 1.85$  (5) (floatation),  $D_x = 1.808$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.202$  mm<sup>-1</sup>,  $Z = 2$ , at 293 (1) K; final  $R = 0.048$  for 1700 observed reflexions [ $I > 2.5\sigma(I)$ ]. There is considerable strain in the molecule resulting in two rather long C–C distances of 1.567 (4) and 1.581 (3) Å.

**Introduction.** The title compound was prepared by cycloaddition between hexafluorobenzene and 1,4-cyclohexadiene by Drs M. Zupan and B. Šket, Chemistry Department, University E. Kardelj, Ljubljana, Yugoslavia. An inspection of Weissenberg photographs and the mean value of  $|E^2 - 1| = 0.977$  indicated the space group  $P\bar{1}$ . The cell parameters and their e.s.d.'s were obtained by least squares from  $2\theta$  values of 45 centered reflexions (Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å) at 293 (1) K. A prismatic single crystal  $0.4 \times 0.4 \times 0.5$  mm, sealed in a Lindemann-glass capillary, was used for data collection on an automated Enraf-Nonius CAD-4 diffractometer with graphite-mono-

chromatized Mo  $K\alpha$  radiation. A summary of the data collection and reduction is given in Table 1. The data were corrected for variation in reference reflexions and Lorentz-polarization effects, but not for absorption. Multisolution  $\sum_2$  sign expansion (Sheldrick, 1976) located all non-hydrogen atoms. Isotropic full-matrix

Table 1. *Data-collection summary*

Temperature (K)	293 (1)
Diffractometer	CAD-4, automated, four-circle
Radiation	Mo $K\alpha$ (graphite monochromator) ( $\lambda = 0.71069$ Å)
Scan method	$\omega$ - $2\theta$
$2\theta$ scan width (°)	$0.8 + 0.2 \tan \theta$
Scan rate (deg min <sup>-1</sup> )	Minimum 1.8; maximum 20.1
Background	$\frac{1}{4}$ of the scan time at each of the scan limits
$2\theta_{\max}$ (°)	54
Maximum scan time (s)	40
Aperture (mm)	$2.5 + 0.9 \tan \theta$
Reference reflexions	115, 214, 332
Intensity decrease (%)	12
Measured reflexions	3834 ( $\pm h, \pm k, \pm l$ )
Averaged reflexions	2035
Mean discrepancy on $I$ (%)	2.0
Observed reflexions	1700 [ $I > 2.5\sigma(I)$ ]
Unobserved reflexions	335
$\sigma(I)$ base	Counting statistics
$\mu$ (mm <sup>-1</sup> )	0.202 for Mo $K\alpha$

\* It should be noted that the numbering scheme used for naming the title compound differs from the crystallographic numbering.