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Structure of the Alkaloid Lupinine

By Anna Kozioł and Zofia Kosturkiewicz

Department of Crystallography, Institute of Chemistry, A. Mickiewicz University, ul. Grunwaldzka 6,
60-780 *Poznań, Poland*

and Halina Podkowińska

Department of Chemistry, College of Economics, ul. Marchlewskiego 146, 60-967 *Poznań, Poland*

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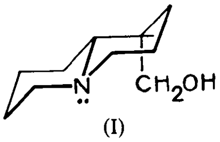
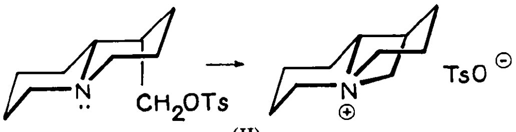
Abstract. $C_{10}H_{19}NO$, $M_r = 169{\cdot}3$, monoclinic, $P2_1$, $a = 6{\cdot}746\,(1)$, $b = 8{\cdot}245\,(2)$, $c = 10{\cdot}079\,(2)$ Å, $\beta = 114{\cdot}04\,(2)°$, $V = 512{\cdot}1\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}10$ g cm^{-3}, $F(000) = 188$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 5{\cdot}5$ cm^{-1}. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to a final $R = 0{\cdot}045$. The lupinine molecules are bonded by intermolecular O—H···N hydrogen bonds to form infinite chains parallel to the *b* axis. The O···N distance is 2·868 (4) Å and the O—H···N angle is 169·8 °.

Introduction. Lupinine was first isolated from yellow lupin (*Lupinus luteus*) seeds by Cassola (1835). Its formula and structure (I) were chemically established by Willstätter & Fourneau (1902) and by numerous subsequent investigators (Manske & Holmes, 1953, 1960; Boit, 1961).



(I)

Thomas, Vipond & Marion (1955) studied IR spectra of lupinine and found that in extremely dilute carbon disulfide solution, lupinine showed a broad ν_{OH} absorption band at 3270 cm^{-1}. This observation was regarded as strong evidence for intramolecular hydrogen bonding in lupinine. Formation of such a bond requires the hydroxymethylene group, attached to a *trans*-quinolizidine nucleus, to be axially oriented and *cis* to the lone electron pair of the N atom. Evidence for the axial orientation of the $-CH_2OH$ group in lupinine was obtained from quaternization of the tosyl ester of lupinine (Galinovsky & Nesvadba, 1954; Huber, 1969) (II).



(II)

Although the structure and conformation of lupinine were established, some questions concerned with its ν_{OH} absorption still remained unanswered. In the IR spectra of lupinine in the solid state, the absorption band of the hydroxyl group was broad and situated at 3170 cm^{-1}. In chloroform and carbon tetrachloride solutions the same band was still broad and shifted to 3200 and to 3290 cm^{-1}, respectively (Wiewiórowski, 1977; Aaron & Ferguson, 1974). The stability of the absorption frequency in the course of dilution in CCl_4 was interpreted as the intramolecular hydrogen bonding in lupinine also being present in concentrated solutions. In the spectra of lupinine in solution (in any concentration), apart from the ν_{OH} band assigned to the bonded hydroxyl group, a very small band due to a 'free' hydroxyl group exists at about 3600 cm^{-1}. Aaron & Ferguson (1974) explained that the absorption of a 'free' hydroxyl group in lupinine is due to the presence of rotamers.

An X-ray investigation of lupinine was undertaken in order to explain some ambiguities in the interpretation of spectra and to study the hydrogen-bond arrangement in the solid state.

Lupinine (m.p. 69 °C) was isolated from yellow lupin seeds. Single crystals of lupinine suitable for X-ray analysis were obtained from *n*-heptane solution. A crystal with dimensions 0·3 × 0·3 × 0·35 mm selected for intensity measurements was sealed in a glass capillary since the crystals were unstable in air.

The cell parameters were preliminarily measured from precession photographs. Their precise values were obtained by least-squares refinement of 2θ, ω and χ settings of 12 reflexions measured on a diffractometer.

The space group $P2_1$ was established from systematic absences $0k0$ for k odd and symmetry requirements of the molecule.

Intensities of reflexions were collected on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation to $2\theta_{max} = 120°$. The θ–2θ scan technique was used with a variable scan rate of 2·02–29·30° min^{-1}. Two standard reflexions were monitored at intervals of 30 reflexions. There was no systematic variation of intensity with time. Of 734 independent reflexions measured, 710 had $I > 1{\cdot}96\,\sigma(I)$ and were used in the calculations. The intensities were corrected for Lorentz and polarization factors but not for absorption. The reflexions were adjusted to an absolute scale by Wilson statistics (Wilson, 1942).

The structure was solved using the direct-method computer program *MULTAN* (Germain, Main & Woolfson, 1971). 103 normalized structure factors with $|E| \geq 1{\cdot}4$ were introduced in the calculations and then 16 sets of phases were generated. An E map calculated for one of the sets showed the positions of all non-hydrogen atoms. The structure was refined with isotropic and then anisotropic thermal parameters, to an R value of 0·112, using block-diagonal and full-matrix least-squares methods.

All H atoms were found from a subsequent difference Fourier synthesis. The isotropic temperature factor assigned to an H atom was one unit greater than the isotropic temperature factor of the heavy atom to which it was bonded. H atoms were included in the subsequent cycles of least-squares refinement, but their positional and thermal parameters were kept fixed. The next difference map was calculated and improved positions of the H atoms were found and included in the refinement.

The function minimized in least-squares calculations was $\sum w(F_o - F_c)^2$. The weighting scheme used was: $w = (F_o/F_{\rm low})^2$ if $F_o < F_{\rm low}$, $w = 1$ if $F_{\rm low} \leq F_o \leq F_{\rm high}$, $w = (F_{\rm high}/F_o)^2$ if $F_o > F_{\rm high}$, with $F_{\rm low} = 1{\cdot}6$ and $F_{\rm high} = 6{\cdot}5$.

The final refinement gave $R = 0{\cdot}045$ and $R_w = 0{\cdot}052$, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$.

All calculations were performed with the *Syntex XTL* (1973) structure determination system on a Nova 1200 minicomputer. The atomic parameters are given in Tables 1 and 2.*

Table 1. *Positional parameters* (×10⁴) *for non-hydrogen atoms*

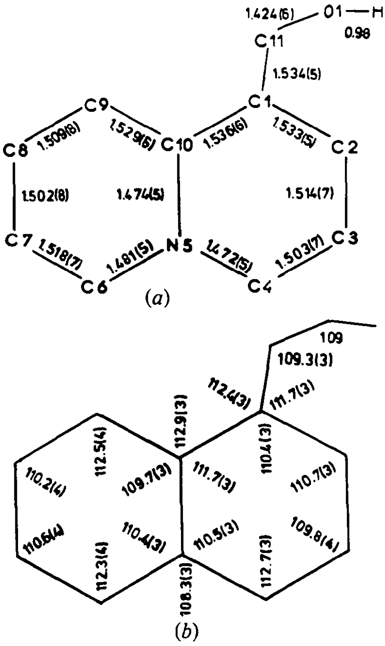
	x	y	z
N(5)	2297 (4)	2613*	2864 (3)
C(1)	1873 (4)	−388 (5)	2625 (4)
C(2)	85 (5)	−299 (6)	3193 (4)
C(3)	402 (6)	1167 (6)	4162 (4)
C(4)	531 (6)	2675 (7)	3365 (4)
C(6)	2279 (7)	4148 (6)	2095 (4)
C(7)	4054 (8)	4199 (7)	1535 (5)
C(8)	3874 (6)	2772 (8)	566 (4)
C(9)	3802 (6)	1214 (7)	1331 (4)
C(10)	2010 (5)	1216 (6)	1891 (4)
C(11)	4062 (6)	−884 (6)	3824 (4)
O(1)	6774 (4)	−2294 (5)	4541 (3)

* Position fixed to define y coordinates in this polar space group.

Table 2. *Positional parameters* (×10³) *and isotropic B values* (Å²) *for hydrogen atoms*

	x	y	z	$B_{\rm iso}$
H(11)	152	−128	196	4·6
H(21)	−141	−17	243	5·7
H(22)	36	−143	393	5·7
H(31)	173	123	503	6·0
H(32)	−81	117	451	6·0
H(41)	−107	275	233	5·2
H(42)	81	339	397	5·2
H(61)	78	411	99	6·1
H(62)	242	520	279	6·1
H(71)	574	422	248	7·8
H(72)	393	541	107	7·8
H(81)	247	278	−30	6·8
H(82)	487	274	8	6·8
H(91)	526	114	215	6·2
H(92)	321	14	49	6·2
H(101)	67	130	99	4·6
H(111)	489	−7	466	4·9
H(112)	520	−117	346	4·9
H(1)	505	−244	546	6·3

Discussion. The atom-numbering sequence and the bond distances and angles are shown in Fig. 1. The mean C–H bond length is 1·04 Å. Torsion angles (Table 3) confirm the chair conformation of both rings in lupinine. The quinolizidine nucleus is in the *trans*



(*a*)

(*b*)

Fig. 1. (*a*) Bond lengths (Å) and (*b*) angles (°) with their e.s.d.'s.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33690 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°) *in lupinine*

O(1)–C(11)–C(1)–C(2)	50·0
O(1)–C(11)–C(1)–C(10)	174·8
C(10)–C(1)–C(2)–C(3)	−53·6
C(1)–C(2)–C(3)–C(4)	54·9
C(2)–C(3)–C(4)–N(5)	−58·0
C(3)–C(4)–N(5)–C(10)	58·8
C(4)–N(5)–C(10)–C(1)	−56·5
N(5)–C(10)–C(1)–C(2)	54·6
N(5)–C(6)–C(7)–C(8)	56·2
C(6)–C(7)–C(8)–C(9)	−52·9
C(7)–C(8)–C(9)–C(10)	54·3
C(8)–C(9)–C(10)–N(5)	−56·7
C(9)–C(10)–N(5)–C(6)	57·7
C(10)–N(5)–C(6)–C(7)	−58·9

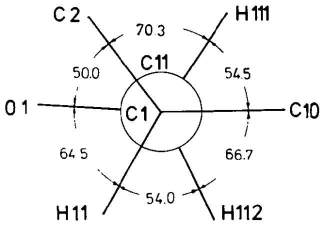


Fig. 2. A Newman projection along the C(1)–C(11) bond.

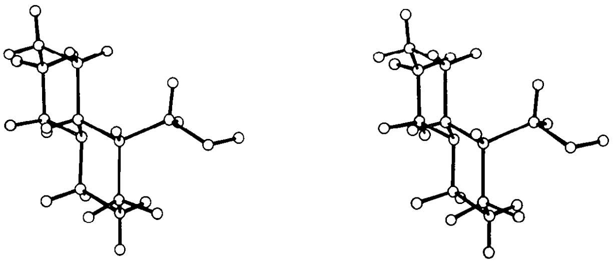


Fig. 3. Stereoscopic view of lupinine molecule.

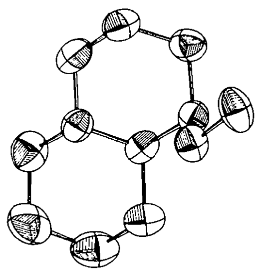
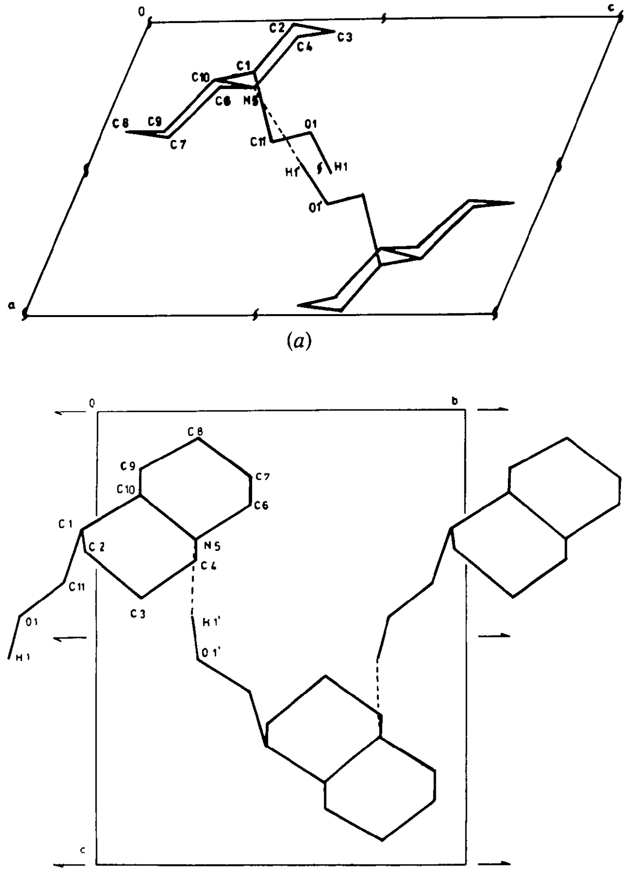


Fig. 4. View of molecule with thermal ellipsoids.



(*a*)

(*b*)

Fig. 5. Crystal structure projection (*a*) on (010) plane, (*b*) on (100) plane. The hydrogen bond is shown with broken lines.

conformation and the $-CH_2OH$ group is in the axial position. A Newman projection along the C(1)–C(11) bond (Fig. 2) illustrates the orientation of the hydroxyl group towards the *trans*-quinolizidine nucleus. The stereopair and the thermal ellipsoid drawings of the lupinine molecule are presented in Figs. 3 and 4 respectively.

The molecular packing is shown in Fig. 5. The molecules are linked by the intermolecular N(5)···H(1')–O(1') hydrogen bond. The N(5)···O(1'), N(5)···H(1') and H(1')–O(1') distances are 2·868 (4), 1·89 and 0·98 Å respectively and the N(5)···H(1')–O(1') angle is 169·8°. The lupinine molecules form infinite chains related by a 2_1 symmetry axis. There are no significant short intermolecular contacts besides this hydrogen bond.

The presence of the intermolecular hydrogen bond was unexpected since on the basis of spectroscopic data the intramolecular hydrogen bond was suggested as existing in the solid state. Probably bands which are due to the inter- and intramolecular hydrogen bonds appear in the IR spectrum so close to each other that it was not possible to establish unambiguously the character of this bond.

The formation of an intramolecular hydrogen bond would require the molecule to exist in the form of a different rotamer in which the N(5)···O(1) distance would be about 2·6 Å.

Further spectroscopic investigations will be carried out in order to explain the nature of the hydrogen bond in solution.

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SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1978). B**34**, 3494

Refinement of Nb_3Si and Nb_3As: errata.

By R. M. WATERSTRAT, K. YVON, H. D. FLACK and E. PARTHÉ, *Laboratoire de Cristallographie aux Rayons X, Université de Genève,* 32 *bd. d'Yvoy, CH-*1211 *Genève* 4, *Switzerland*

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In Table 5 of the paper by Waterstrat, Yvon, Flack & Parthé [*Acta Cryst.* (1975), B**31**, 2765–2769] the positional parameters which are presented for the compound Ta_3P (reference 11) are, in fact, those of the compound Zr_3P.

All the relevant information is contained in the Abstract.

Acta Cryst. (1978). B**34**, 3494–3496

The crystal structure of tetrakis(pentafluorophenyl)silane.

By ANASTAS KARIPIDES and BARBARA FOERST, *Department of Chemistry, Miami University, Oxford, Ohio* 45056, *USA*

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The crystal structure of $(C_6F_5)_4Si$ has been determined from three-dimensional single-crystal X-ray data collected on a computer-automated diffractometer. The compound crystallizes in space group $I4_1/a$ with cell dimensions of a = 17·165 (12), c = 8·125 (8) Å and Z = 4. The $(C_6F_5)_4Si$ molecules have S_4 crystallographically imposed symmetry. Full-matrix least-squares refinement yielded a conventional R factor of 0·070.

The molecular symmetry, crystal packing and energetics of tetra(aryl) Group IVa compounds have been the object of numerous recent investigations (Karipides & Oertel, 1977; Hutchings, Andose & Mislow, 1975; Robbins, Jeffrey, Chesick, Donohue, Cotton, Frenz & Murillo, 1975; Hutchings, Nourse & Mislow, 1974; Ahmed, Kitaigorodsky & Mirskaya, 1971). As part of our program to study the structural characteristics of such compounds we have determined the crystal structures of the pentafluorophenyl derivatives of Ge and Sn (Karipides, Forman, Thomas & Reed, 1974) and in this paper report on the crystal structure of tetrakis(pentafluorophenyl)silane.

The title compound was kindly supplied by Dr C. Tamborski (Tamborski, Soloski & Dec, 1965) and suitable crystals were obtained by recrystallization from benzene. Indexed Weissenberg photographs revealed tetragonal symmetry and the observed absences $h + k + l = 2n + 1$ for hkl; h, (k) = $2n + 1$ for $hk0$; $l = 4n + 1$ for $00l$ uniquely determined the space group to be $I4_1/a$. The pertinent crystal data are given in Table 1.