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Structure (Neutron) of 4,9-Dihydro-7-methoxy-1-methyl-3*H*-pyrido[3,4-*b*]indole (Harmaline), $C_{13}H_{14}N_2O$

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Abstract. $M_r = 214{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}709\ (5)$, $b = 13{\cdot}576\ (6)$, $c = 7{\cdot}541\ (4)$ Å, $V = 1096{\cdot}4\ (9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}30$ Mg m^{-3}, room-temperature neutron diffraction study, $\lambda = 0{\cdot}9203\ (3)$ Å, final $R = 0{\cdot}076$ for 976 reflections. The framework of the molecule is built up of three rings (benzene, pyrrole and fused dihydropyridine). The substituted dihydropyridine ring is rather puckered. One molecule is connected to two other molecules by one N—H···N hydrogen bond each; hydrogen-bond length 1·989 (12) Å, angle 170·3 (14)°.

Introduction. The crystal and molecular structure of the title compound was investigated by neutron diffraction at room temperature. The purpose was a reliable determination of the C(3)—N(4) bond length (see Fig. 1) and of the hydrogen positions. These data shall be compared with the results of a planned study of harmine, $C_{13}H_{12}N_2O$. In contrast to harmaline this latter compound is used in medicine and the efficiency of both compounds shall be discussed as a function of the crystal-structure data.

Experimental. Natural alkaloidal constitutuent of *Peganum hamala*, redissolved in dehydrated ethyl alcohol, prismatic crystals then grown at room temperature, 3 × 1 × 1 mm, four-circle diffractometer for neutron diffraction P110/FR2, Kernforschungszentrum Karlsruhe (Heger, Massing, Guth, Reimers & Paulus, 1981), 12 reflections used for measuring lattice parameters, 1885 independent *hkl* with $2\theta \leq 90°$, $h_{max} = 16$, $k_{max} = 20$, $l_{max} = 9$, one standard – no systematic intensity variation, ω-scan technique, 909 with $I \leq 2\sigma(I)$, linear background and Lorentz correction, absorption ignored, starting atomic positions for C,N,O taken from former structure determination (Atta-Ur-Rahman, Foresti Serantoni & Riva di Sanseverino, 1971), program system *SHELXTL* (Sheldrick, 1978) on a Nova 3 computer (Data General), block-diagonal refinement on F, scattering lengths $b_C = 6{\cdot}65$, $b_N = 9{\cdot}40$, $b_O = 5{\cdot}80$, $b_H = -3{\cdot}74$ fm (Bacon, 1977), H from ΔF synthesis, all atoms anisotropic, scaling factor, isotropic extinction parameter $g = 0{\cdot}0064\ (5)$, final $R = 0{\cdot}076$, $R_w = 0{\cdot}061$ with $w = 1/\sigma^2(F)$, max. LS shift/error = 0·5, average LS shift/error = 0·18, max. and min. height in final ΔF synthesis = 1·5 and 1·2 fm.

Discussion. Final atomic parameters are given in Table 1,† bond lengths and angles in Table 2.

As can be seen from Fig. 1 the framework of the molecule is built up of three rings. In the planar benzene ring a bond order of $n = 1{\cdot}5$ (Allmann, 1975) is realized with a mean bond length of 1·406 (10) Å for C(sp^2)—C(sp^2) bonds. In the pyrrole ring the C(13)—N(1), N(1)—C(2) and C(8)—C(7) bonds exhibit π-bonding contributions with a bond order of $n \sim 1{\cdot}3$. With $n = 1{\cdot}7$ C(7)—C(2) tends to a double bonding. The best plane through this ring is inclined by 1·5 (2)° with respect to the benzene ring plane. The substituted dihydropyridine ring is rather puckered. Its conformation is twisted with two pseudo-twofold axes along the middle of the bonds C(2)—C(3) and C(6)—C(5) and along the vertices C(7)···N(4). Nearly double bonds are found for C(3)(sp^2)—N(4) and the already cited C(7)—C(2) bondings. Otherwise only single bonds exist in this ring. C(5) is displaced by 0·536 (8) Å out of the least-squares plane through the benzene and pyrrole rings.

The mean bond lengths involving H are as follows: C(sp^3)—H = 1·082 (15), C(sp^2)—H = 1·093 (12), N—H = 1·023 (10) Å.

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† Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39201 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}(U_{11}+U_{22}+U_{33})$.

	x	y	z	U_{eq}
C(2)	−1162 (4)	6288 (4)	357 (8)	24 (1)
C(3)	−2065 (5)	7064 (4)	−31 (9)	32 (2)
C(5)	−3381 (6)	6291 (5)	2042 (11)	40 (2)
C(6)	−2863 (5)	5274 (4)	1545 (9)	36 (2)
C(7)	−1517 (5)	5407 (4)	1090 (9)	29 (2)
C(8)	−468 (5)	4782 (4)	1023 (8)	25 (2)
C(9)	−239 (5)	3785 (4)	1551 (10)	36 (2)
C(10)	958 (6)	3399 (4)	1343 (10)	38 (2)
C(11)	1919 (6)	3972 (4)	605 (10)	35 (2)
C(12)	1725 (5)	4931 (4)	33 (9)	32 (2)
C(13)	524 (5)	5322 (3)	256 (8)	27 (2)
C(15)	4099 (6)	4055 (5)	62 (12)	51 (3)
C(16)	−1736 (7)	7840 (5)	−1344 (12)	47 (3)
N(1)	82 (4)	6248 (3)	−154 (6)	33 (1)
N(4)	−3168 (4)	7047 (3)	670 (6)	34 (1)
O(14)	3036 (7)	3503 (5)	510 (12)	44 (2)
H(1)	4259 (16)	4650 (14)	864 (41)	102 (9)
H(2)	4029 (17)	4355 (16)	−1278 (26)	85 (8)
H(3)	4898 (13)	3510 (13)	128 (40)	108 (8)
H(4)	−994 (19)	8309 (17)	−837 (37)	110 (9)
H(5)	−2495 (18)	8250 (13)	−1730 (35)	91 (8)
H(6)	−1260 (24)	7545 (15)	−2501 (27)	106 (9)
H(7)	1169 (16)	2659 (12)	1775 (24)	67 (6)
H(8)	−975 (15)	3344 (10)	2165 (27)	68 (6)
H(9)	2474 (11)	5374 (9)	−585 (23)	60 (5)
H(10)	647 (11)	6830 (8)	−474 (23)	49 (4)
H(11)	−3014 (15)	4754 (11)	2662 (22)	62 (5)
H(12)	−3379 (13)	4945 (11)	401 (20)	59 (5)
H(13)	−4390 (13)	6226 (12)	2311 (25)	65 (6)
H(14)	−2956 (16)	6527 (10)	3220 (28)	62 (6)

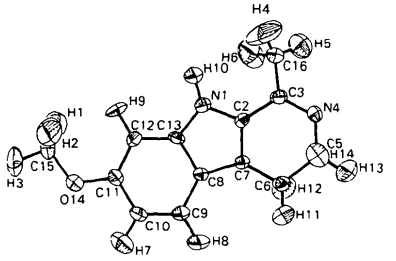

Fig. 1. Molecular structure of harmaline. Projection onto the least-squares plane of the benzene ring (50% probability thermal ellipsoids).

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

C(2)–C(3)	1·460 (7)	C(9)–H(8)	1·094 (17)
C(2)–C(7)	1·372 (8)	C(10)–C(11)	1·406 (9)
C(2)–N(1)	1·388 (6)	C(10)–H(7)	1·081 (16)
C(3)–C(16)	1·488 (10)	C(11)–C(12)	1·387 (8)
C(3)–N(4)	1·295 (7)	C(11)–O(14)	1·357 (9)
C(5)–C(6)	1·535 (9)	C(12)–C(13)	1·402 (7)
C(5)–N(4)	1·475 (9)	C(12)–H(9)	1·105 (15)
C(5)–H(13)	1·103 (15)	C(13)–N(1)	1·379 (6)
C(5)–H(14)	1·048 (20)	C(15)–O(14)	1·405 (10)
C(6)–C(7)	1·493 (8)	C(15)–H(1)	1·024 (25)
C(6)–H(11)	1·111 (17)	C(15)–H(2)	1·092 (22)
C(6)–H(12)	1·118 (17)	C(15)–H(3)	1·132 (17)
C(7)–C(8)	1·409 (7)	C(16)–H(4)	1·088 (23)
C(8)–C(9)	1·432 (8)	C(16)–H(5)	1·028 (21)
C(8)–C(13)	1·414 (8)	C(16)–H(6)	1·086 (23)
C(9)–C(10)	1·394 (9)	N(1)···H(10)	1·023 (12)
C(11)–C(10)–C(9)	120·7 (6)	C(10)–C(11)–C(12)	122·2 (5)
C(10)–C(11)–O(14)	114·0 (6)	C(12)–C(11)–O(14)	123·8 (6)
C(11)–C(12)–C(13)	117·1 (5)	O(14)–C(15)–H(1)	114·5 (15)
O(14)–C(15)–H(2)	111·4 (12)	H(1)–C(15)–H(2)	105·2 (20)
O(14)–C(15)–H(3)	104·7 (11)	H(1)–C(15)–H(3)	111·3 (17)
H(2)–C(15)–H(3)	109·7 (19)	C(11)–O(14)–C(15)	118·5 (6)
C(12)–C(13)–C(8)	122·8 (5)	C(12)–C(13)–N(1)	129·3 (5)
C(8)–C(13)–N(1)	107·9 (5)	C(13)–C(8)–C(9)	118·4 (5)
C(13)–C(8)–C(7)	107·6 (4)	C(9)–C(8)–C(7)	134·1 (5)
C(10)–C(9)–C(8)	118·8 (5)	C(5)–N(4)–C(3)	116·1 (5)
C(7)–C(2)–N(1)	110·1 (4)	C(7)–C(2)–C(3)	121·7 (5)
N(1)–C(2)–C(3)	127·5 (5)	N(4)–C(5)–C(6)	113·5 (6)
C(5)–C(6)–C(7)	107·2 (5)	C(8)–C(7)–C(2)	106·8 (5)
C(8)–C(7)–C(6)	134·9 (5)	C(2)–C(7)–C(6)	117·8 (5)
C(13)–N(1)–C(2)	107· (4)	N(4)–C(3)–C(2)	120·7 (5)
N(4)–C(3)–C(16)	120·0 (5)	C(2)–C(3)–C(16)	119·1 (5)
H(4)–C(16)–H(5)	111·1 (17)	H(4)–C(16)–H(6)	99·0 (20)
H(5)–C(16)–H(6)	110·1 (20)	H(4)–C(16)–C(3)	110·7 (16)
H(5)–C(16)–C(3)	112·6 (14)	H(6)–C(16)–C(3)	112·6 (12)
C(9)–C(10)–H(7)	120·5 (11)	H(7)–C(10)–C(11)	118·7 (11)
C(8)–C(9)–H(8)	120·8 (12)	H(8)–C(9)–C(10)	120·7 (9)
C(11)–C(12)–H(9)	122·3 (8)	H(9)–C(12)–C(13)	120·7 (8)
C(13)–N(1)–H(10)	123·7 (7)	H(10)–N(1)–C(2)	127·1 (7)
H(11)–C(6)–H(12)	105·0 (12)	H(11)–C(6)–C(7)	113·0 (10)
H(11)–C(6)–C(5)	109·6 (10)	H(12)–C(6)–C(5)	111·8 (9)
H(12)–C(6)–C(7)	110·4 (9)	H(13)–C(5)–H(14)	107·3 (12)
H(13)–C(5)–C(6)	109·1 (10)	H(13)–C(5)–N(4)	109·5 (11)
H(14)–C(5)–C(6)	109·1 (6)	H(14)–C(5)–N(4)	108·4 (5)

One harmaline molecule is connected to two other molecules by one N–H···N hydrogen bond each. This is illustrated by the dotted lines in Fig. 2. The hydrogen-bond length is 1·989 (12) Å with a bond angle N(1)–H(10)–N(4) of 170·3 (14)°.

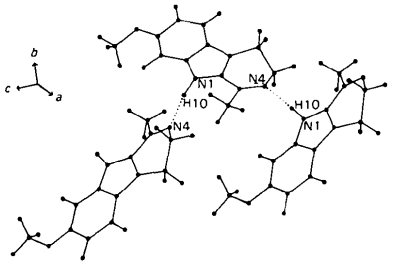

Fig. 2. Illustration of hydrogen bondings (dotted lines) in harmaline.

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