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Structure of Harman, 1-Methyl-9H-pyrido[3,4-*b*]indole

BY KARIMAT EL-SAYED

Physics Department, Ain Shams University, Cairo, Egypt

DAVID M. BARNHART

Department of Physical Sciences, Eastern Montana College, Billings, Montana 59101, USA

HERMAN L. AMMON

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, USA

AND GAMILA M. WASSEL

Pharmaceutical Science Laboratory, National Research Center, Cairo, Egypt

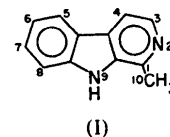
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Abstract. C₁₂H₁₀N₂, *M_r* = 182.23, orthorhombic, *P*2₁2₁2₁, *a* = 9.540 (4), *b* = 13.378 (7), *c* = 15.525 (7) Å, *V* = 1981.4 (1.6) Å³, *Z* = 8, *D_x* = 1.230 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 5.93 cm⁻¹, *F*(000) = 768, *T* = 295 K, *R* = 0.055 for 1169 *I*s 3σ above background. There are two molecules in the asymmetric unit, without any significant differences in bond lengths and angles. The average out-of-plane distances for the 13 ring atoms in the two molecules are 0.022 and 0.029 Å respectively. Each molecule is hydrogen-bonded to two others to form continuous spiral chains through the structure.

Introduction. The hallucinogenic plants and their constituents have been reviewed (Marderosian, 1967). The major botanical sources investigated constitute one or more members of the families Leguminosae, Malpighiaceae, Zygophyllaceae, Gramineae, and Convolvulaceae. In these surveys, the indolic bases *N,N*-dimethyltryptamine, 5-methoxy-*N*-methyltryptamine, 5-methoxy-*N,N*-dimethyltryptamine, bufotenine, harmine, harmaline, harmalol, harman, lysergic acid amides, psilocin and psilocybin were reported as the pharmacologically active constituents of the plants.

A few species of the family Zygophyllaceae, *viz* *Peganum*, *Tribulus* and *Zygophyllum*, were reported to

contain harmine-type alkaloids (Borkowski, 1959; Borkowski & Lutomski, 1960; Ivanov, Nikolov & Tonev, 1965; Ikram & Hug, 1966). The main alkaloids isolated from *Peganum harmala* are harmine and harmaline (Brimblecombe & Pinder, 1975). Ethanol extracts of *Peganum* were reported to show a broad spectrum of antimicrobial activity. Moreover, examination of each alkaloid of this group separately showed that only harmine, harman and harmalol had antimicrobial activity (Al Shamma, Drake, Flynn, Mitscher, Park, Rao, Simpson, Swayze, Veysoglu & Wu, 1981). Harman also has been identified in cigarette smoke (Poindexter & Carpenter, 1962). The crystal and molecular structure of harman (I), the major alkaloid isolated from *Fagonia cretica* L. (Zygophyllaceae) (Ahmed, Rizk, Hammouda & Abdel-Gawad, 1969), is reported.



Experimental. Isolated from wild-plant aerial parts of *Fagonia cretica* L., Egypt; prismatic crystals grown

from nitromethane solution; crystal $0.2 \times 0.2 \times 0.3$ mm; Picker FACS-I diffractometer with graphite monochromator (Cu $K\alpha$); cell constants by least squares from 12 reflections automatically centered at $\pm 2\theta$; intensity data measured with 2θ - θ scan technique: 2° min^{-1} in 2θ , 10 s backgrounds, 2θ -scan range = $1.45^\circ + 0.29^\circ \tan\theta$, $2\theta_{\text{max}}$ 126° ; h, k, l range 0,0,0–10,14,15; four standards measured every 100 data, average and maximum standard I variations 0.3% and 3.4%; no correction for absorption; 1537 total data, 1449 unique data, $R_{\text{int}} = 0.025$, 1169 data 3σ above background.

Structure solved with direct-methods subprogram of XTAL system (Stewart, Hall, Alden, Olthof-Hazekamp & Doherty, 1983). H atoms placed at idealized

locations with $\text{C-H} = 1.02 \text{ \AA}$. C- and N-atom positions, anisotropic temperature factors, and H-atom isotropic temperature factors refined by full-matrix least squares; $\sum w(F_o - F_c)^2$ minimized, $w = 1/\sigma^2(F)$; final R , wR and S 0.055, 0.051 and 1.060, respectively; average and max. shift/e.s.d. 0.0004 and 0.06 [U_{22} of N(2)]; max. and min. $\Delta\rho$ in final difference map 0.20 and -0.30 e \AA^{-3} .

Scattering factors from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974); XTAL programs (Stewart *et al.*, 1983); Univac 1100/82 computer.

Discussion. Final atomic parameters are given in Table 1.* Bond lengths and angles are listed in Table 2. There

Table 1. Atomic coordinates and equivalent isotropic temperature factors (\AA^2), with e.s.d.'s in parentheses

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

	x	y	z	U_{eq}
N(9)	0.3459 (6)	0.0803 (5)	0.0796 (4)	0.051 (4)
N(2)	0.5293 (6)	0.1660 (5)	0.2748 (5)	0.066 (5)
C(1)	0.5102 (8)	0.1146 (6)	0.2022 (5)	0.056 (5)
C(3)	0.4319 (9)	0.2332 (7)	0.2999 (6)	0.075 (7)
C(4)	0.3099 (9)	0.2530 (6)	0.2550 (6)	0.064 (6)
C(4a)	0.2886 (8)	0.1989 (5)	0.1798 (5)	0.051 (5)
C(4b)	0.1767 (8)	0.1923 (6)	0.1173 (5)	0.051 (5)
C(5)	0.0449 (8)	0.2416 (6)	0.1095 (7)	0.069 (6)
C(6)	-0.0376 (9)	0.2129 (8)	0.0402 (7)	0.088 (8)
C(7)	0.0034 (9)	0.1425 (8)	-0.0185 (7)	0.086 (8)
C(8)	0.1329 (9)	0.0920 (7)	-0.0123 (6)	0.072 (6)
C(8a)	0.2164 (8)	0.1187 (6)	0.0576 (5)	0.051 (7)
C(9a)	0.3880 (7)	0.1277 (6)	0.1545 (5)	0.048 (5)
C(10)	0.6221 (9)	0.0404 (8)	0.1750 (7)	0.089 (8)
N(9')	0.8031 (6)	0.2197 (5)	0.3330 (4)	0.046 (4)
N(2')	1.0271 (7)	0.0822 (5)	0.4864 (4)	0.057 (4)
C(1')	0.9173 (8)	0.0974 (6)	0.4337 (5)	0.052 (5)
C(3')	1.1231 (9)	0.1557 (7)	0.4960 (5)	0.065 (6)
C(4')	1.1172 (8)	0.2486 (7)	0.4567 (5)	0.058 (5)
C(4a')	1.0039 (7)	0.2653 (5)	0.4029 (4)	0.045 (5)
C(4b')	0.9616 (8)	0.3476 (6)	0.3481 (5)	0.047 (5)
C(5')	1.0160 (9)	0.4421 (6)	0.3299 (6)	0.061 (6)
C(6')	0.951 (1)	0.5012 (6)	0.2704 (6)	0.073 (7)
C(7')	0.829 (1)	0.4691 (7)	0.2298 (6)	0.075 (7)
C(8')	0.7696 (9)	0.3766 (7)	0.2452 (5)	0.064 (6)
C(8a')	0.8384 (8)	0.3163 (6)	0.3060 (5)	0.048 (5)
C(9a')	0.9044 (7)	0.1895 (5)	0.3913 (4)	0.042 (5)
C(10')	0.812 (1)	0.0145 (6)	0.4225 (6)	0.070 (6)

* Lists of structure factors and anisotropic thermal parameters for C and N atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43003 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

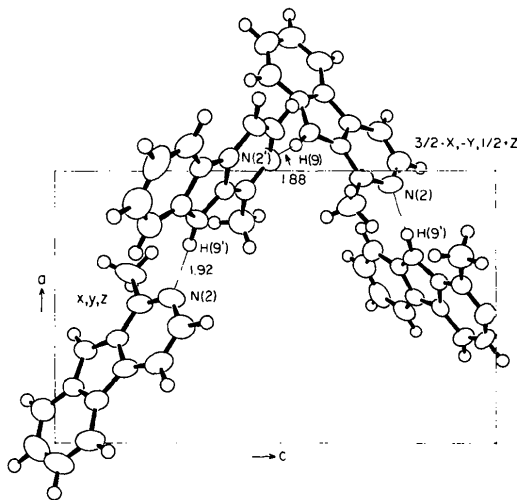


Fig. 1. ORTEP drawing (Johnson, 1976) normal to the ac plane. The C and N atoms are depicted as 50% ellipsoids, and the H atoms are shown as $B = 1.5 \text{ \AA}^2$ spheres.

Table 2. Bond lengths (\AA) and angles ($^\circ$), with e.s.d.'s in parentheses

Molecule A		Molecule B		Molecule A		Molecule B		Molecule A		Molecule B	
N(9)—C(8a)	1.38 (1)	1.40 (1)	C(3)—C(4)	1.38 (1)	1.38 (1)	C(4b)—C(5)	1.43 (1)	1.40 (1)			
N(9)—C(9a)	1.38 (1)	1.385 (9)	C(4)—C(4a)	1.39 (1)	1.38 (1)	C(5)—C(6)	1.39 (1)	1.37 (1)			
N(2)—C(1)	1.33 (1)	1.35 (1)	C(4a)—C(4b)	1.45 (1)	1.45 (1)	C(6)—C(7)	1.37 (2)	1.39 (1)			
N(2)—C(3)	1.35 (1)	1.35 (1)	C(4a)—C(9a)	1.40 (1)	1.40 (1)	C(7)—C(8)	1.41 (1)	1.38 (1)			
C(1)—C(9a)	1.39 (1)	1.40 (1)	C(4b)—C(8a)	1.40 (1)	1.41 (1)	C(8)—C(8a)	1.39 (1)	1.41 (1)			
C(1)—C(10)	1.52 (1)	1.50 (1)									
C(8a)—N(9)—C(9a)	107.2 (6)	107.3 (6)	C(4)—C(4a)—C(9a)	119.4 (7)	119.3 (7)	C(7)—C(8)—C(8a)	115.5 (8)	115.9 (8)			
C(3)—N(2)—C(1)	119.6 (7)	119.0 (7)	C(4b)—C(4a)—C(9a)	105.7 (6)	106.6 (6)	C(4b)—C(8a)—N(9)	109.8 (7)	109.7 (6)			
N(2)—C(1)—C(9a)	119.9 (7)	119.1 (7)	C(4a)—C(4b)—C(5)	132.8 (7)	134.7 (7)	C(8)—C(8a)—N(9)	127.5 (7)	128.2 (7)			
N(2)—C(1)—C(10)	118.5 (7)	118.5 (7)	C(4a)—C(4b)—C(8a)	106.7 (6)	106.2 (6)	C(8)—C(8a)—C(4b)	122.7 (7)	122.1 (7)			
C(9a)—C(1)—C(10)	121.6 (8)	122.5 (7)	C(5)—C(4b)—C(8a)	120.4 (7)	119.1 (7)	C(1)—C(9a)—N(9)	129.2 (7)	128.6 (6)			
N(2)—C(3)—C(4)	124.2 (8)	125.2 (7)	C(4b)—C(5)—C(6)	116.0 (8)	119.5 (8)	C(4a)—C(9a)—N(9)	110.5 (6)	110.2 (6)			
C(3)—C(4)—C(4a)	116.6 (8)	116.2 (7)	C(5)—C(6)—C(7)	123. (9)	120.5 (8)	C(4a)—C(9a)—C(1)	120.3 (7)	121.1 (6)			
C(4)—C(4a)—C(4b)	134.8 (7)	134.0 (7)	C(6)—C(7)—C(8)	122.3 (9)	122.9 (9)						

are no significant differences between bond lengths and angles in the two molecules (*A* and *B*). The average out-of-plane distances for the 13 ring atoms in the two molecules are 0.022 and 0.029 Å respectively. Bond lengths in the indole regions of (I) and harmaline (III) (7-methoxy-3,4-dihydroharmalin, Reimers, Guth & Wang, 1984) are quite similar with the exception of C(4a)–C(4b) [1.45 (1) in (I), 1.409 (7) Å in (II)]. Hydrogen bonding links the molecules together in spiral chains along the *z* direction of the unit cell (Fig. 1). The N...H distances are 1.88 and 1.92 Å respectively. (II) shows similar hydrogen-bonding links.

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Structures and Quantum-Mechanical Calculations of Two Polarized Nitroethylenes: C₉H₉ClN₂O₂S (I) and C₆H₁₃N₃O₂ (II)

BY FABIO GANAZZOLI AND STEFANO V. MEILLE

Dipartimento di Chimica del Politecnico, Piazza L. da Vinci 32, I-20133 Milano, Italy

AND PAOLO GRONCHI

Dipartimento di Chimica Industriale e Ingegneria Chimica del Politecnico, Piazza L. da Vinci 32, I-20133 Milano, Italy

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Abstract. (I) 1-(*o*-Chloroanilino)-1-methylthio-2-nitroethylene, $M_r = 244.70$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.135$ (3), $b = 9.563$ (2), $c = 10.291$ (3) Å, $\beta = 101.69$ (6)°, $V = 1073.1$ (5) Å³, $D_x = 1.514$ g cm⁻³, $D_m = 1.51$ g cm⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.21$ cm⁻¹, $F(000) = 504$, $T = 293$ K, $R = 0.0311$ (1147 observed reflections). (II) 1,1-Bis(dimethylamino)-2-nitroethylene, $M_r = 159.19$, monoclinic, $P2_1/n$, $Z = 4$, $a = 5.281$ (1), $b = 13.939$ (2), $c = 11.510$ (2) Å, $\beta = 98.74$ (3)°, $V = 837.4$ (3) Å³, $D_x = 1.263$ g cm⁻³, $D_m = 1.25$ g cm⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.90$ cm⁻¹, $F(000) = 344$, $T = 293$ K, $R = 0.0621$ (913 observed reflections). The C=C bond lengths are 1.375 (4) Å in (I) and 1.406 (5) Å in (II) with extensive π delocalization in

both molecules. The ethylenic moiety is significantly twisted in (II), while it is almost exactly planar in (I) where an intramolecular H bond between the aminic nitrogen and the nitro group is present. Semiempirical quantum-mechanical calculations have also been carried out on the title compounds and on related molecules to estimate charge densities and bond orders as well as the preferred geometries.

Introduction. Polarized 1,1-XY-disubstituted 2-nitroethylenes, with *X* and/or *Y* an electron-donating group, have been extensively investigated. They can be described as push-pull ethylenes, a class of compounds presenting an unusually low rotational barrier around the C=C double bond (Isaakson, Sandström &