

2,5-Bis(1-piperidinylmethyl)benzene-1,4-diol

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The title compound, $C_{18}H_{28}N_2O_2$, is a product of a Mannich reaction involving hydroquinone, formaldehyde and piperidine. The molecule occupies a special position on an inversion centre. The structure is stabilized by an intramolecular O—H···N hydrogen bond linking the phenol OH group and a piperidyl N atom.

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Key indicators

Single-crystal X-ray study

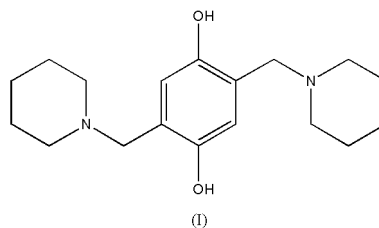
 $T = 293\text{ K}$ Mean $\sigma(C-C) = 0.003\text{ \AA}$ R factor = 0.051 wR factor = 0.128

Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

The Mannich reaction is extremely useful for the preparation of nitrogenous molecules (Arend *et al.*, 1998; Zhou *et al.*, 2000). Its popularity (Laobuthee *et al.*, 2001) is due to the widespread occurrence of nitrogen in drugs and natural products, as well as the diversity of this multicomponent reaction. 2,5-Bis(1-piperidinylmethyl)benzene-1,4-diol, (I), has been synthesized by the Mannich reaction (Miller *et al.*, 1965; Shriner *et al.*, 1946). The crystal structure of (I) is reported in this paper.



The molecular structure of (I) is shown in Fig. 1. The molecule occupies a special position on a crystallographic inversion centre. The piperidine ring has the usual chair conformation. Because of the steric hindrance between the benzene and piperidine rings, atom C4 has a distorted tetrahedral geometry, with the N1—C4—C3 angle [$112.28(17)^\circ$] deviating significantly from the regular tetrahedral value. Intramolecular O—H···N hydrogen bonds (Table 2) stabilize the crystal structure.

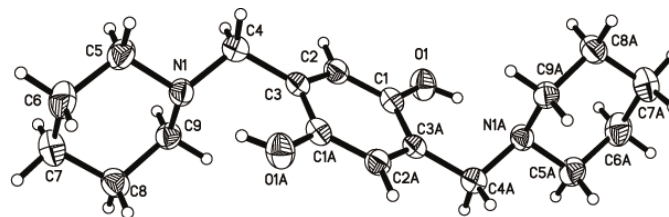


Figure 1

View of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level. The suffix A corresponds to symmetry code (i) in Table 1.

Experimental

To a suspension of 1 g (33 mmol) of paraformaldehyde and 0.2 g (1.8 mmol) of hydroquinone in 20 ml of stirred ethanol was cautiously added 0.31 g (3.6 mmol) of piperidine. A mildly exothermic reaction ensued. After reflux for 6 h, the solvent was evaporated. The crystalline product was separated and recrystallized from ethanol (yield 69%). Colourless prism-shaped single crystals suitable for X-ray structure analysis were obtained (m.p. 469–471 K). Spectroscopic analysis, IR (KBr, ν , cm^{-1}): 3432, 2947, 2858, 1480, 1453, 1378, 869; ^1H NMR (CDCl_3 , p.p.m.): 6.48 (s, 2H), 3.62 (s, 4H), 2.43–2.80 (m, 8H), 1.46–1.65 (m, 12H). Analysis calculated for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2$: C 71.02, H 9.27, N 9.20%; found: C 71.13, H 9.60, N 9.31%.

Crystal data

$\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_2$
 $M_r = 304.42$
 Triclinic, $P\bar{1}$
 $a = 6.372$ (2) Å
 $b = 8.184$ (3) Å
 $c = 8.649$ (3) Å
 $\alpha = 72.349$ (5)°
 $\beta = 81.745$ (6)°
 $\gamma = 80.865$ (5)°
 $V = 422.2$ (3) Å³
 $Z = 1$
 $D_x = 1.197$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 644 reflections
 $\theta = 2.6$ – 25.6 °
 $\mu = 0.08$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.20 \times 0.16 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ϕ and ω scans
 Absorption correction: none
 2215 measured reflections
 1487 independent reflections
 982 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 25.0$ °
 $h = -7 \rightarrow 7$
 $k = -8 \rightarrow 9$
 $l = -5 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.128$
 $S = 1.06$
 1487 reflections
 101 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.1017P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.372 (2)	N1–C5	1.464 (3)
N1–C4	1.475 (3)	N1–C9	1.463 (3)
O1–C1–C2	118.6 (2)	N1–C5–C6	111.31 (19)
O1–C1–C3 ⁱ	121.42 (19)	N1–C9–C8	111.57 (18)
N1–C4–C3	112.28 (17)		
O1–C1–C2–C3	−179.63 (18)	N1–C5–C6–C7	−56.3 (3)
C2–C3–C4–N1	138.2 (2)	C7–C8–C9–N1	57.1 (2)

Symmetry code: (i) $-x, -y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots N1 ⁱ	0.82	2.00	2.711 (2)	146

Symmetry code: (i) $-x, -y, -z$.

All H atoms were located in a difference map and included in the refinement in the riding-model approximation (O–H = 0.82 Å and C–H = 0.93–0.97 Å), with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ in the case of the hydroxyl H atom].

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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