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Piperidine Nitroxide Radicals with Heterocyclic Ring Substituents. I. Structure of 4-Hydroxy-2,2,6,6-tetramethyl-4-(2-pyridylmethyl)piperidine 1-Oxide

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Abstract. $C_{15}H_{23}N_2O_2$, $M_r = 263.4$, tetragonal, $P4_1$, $a = 8.4561$ (6), $c = 20.8204$ (29) Å, $V = 1488.8$ (3) Å^3, $Z = 4$, $D_x = 1.175$ g cm^{-3}, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 5.90$ cm^{-1}, $F(000) = 572.0$, room temperature, $R = 0.025$ for 943 reflections with $I > 3\sigma(I)$. The piperidine ring is in a chair conformation with the 2-pyridylmethyl substituent axial and the hydroxyl and oxo groups equatorial. There are intermolecular hydrogen bonds between the hydroxyl group and the 2-pyridylmethyl forming chains along the fourfold screw axis.

Experimental. Orange crystals obtained by slow evaporation from ethanol solution at room temperature, crystal dimensions 0.1 × 0.1 × 0.3 mm. Cell parameters and intensity data measured on AFC-5*S* Rigaku diffractometer using $\omega/2\theta$ scans. Unit cell from 20 reflections measured to $\theta_{\max} = 27°$. Range of *h*, *k* and *l*: 0–9, 0–9, 0–23, respectively; intensities measured for 1304 independent reflections to $\sin\theta/\lambda = 0.56$ Å^{-1}. Data not corrected for absorption, three standard reflections, no significant change. 943 reflections with $I > 3\sigma(I)$ used in refinement. $R_{\rm int} = 0.01$. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). The first *E* map revealed all non-H atoms. Least-squares refinement used *F* magnitudes in *SHELX*76 (Sheldrick, 1976), and the *CRYSRULER* package (Rizzoli, Sangermano, Calestani & Andreetti, 1986); 264 parameters, isotropic and then anisotropic temperature factors.

Table 1. *Final positional parameters* (× 10^4) *and isotropic or equivalent isotropic thermal parameters* (Å^2 × 10^4) *with e.s.d.'s in parentheses*

$U_{\rm iso}$ for H3; $U_{\rm eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for non-H.

	x	*y*	*z*	$U_{\rm iso}/U_{\rm eq}$
O1	7442 (3)	64 (2)	2866 (3)	744 (9)
N1	7016 (3)	1528 (2)	2862 (3)	477 (8)
C1	8224 (3)	2666 (3)	2627 (3)	475 (9)
C11	8566 (4)	2302 (4)	1922 (4)	673 (13)
C12	9734 (4)	2402 (4)	3023 (4)	778 (15)
C2	7662 (3)	4372 (3)	2734 (3)	444 (10)
C3	5924 (3)	4732 (3)	2611 (3)	360 (9)
O3	5518 (2)	4579 (2)	1946 (3)	437 (6)
C31	5573 (3)	6431 (3)	2840 (3)	405 (9)
C4	4935 (3)	3565 (3)	2985 (3)	368 (9)
C5	5281 (3)	1805 (3)	2865 (3)	413 (8)
C51	4588 (4)	870 (3)	3428 (4)	584 (12)
C52	4568 (4)	1206 (3)	2232 (4)	563 (12)
N100	3262 (3)	6840 (3)	3504 (3)	452 (8)
C200	3849 (3)	6840 (3)	2903 (3)	405 (9)
C300	2918 (4)	7234 (3)	2383 (3)	520 (11)
C400	1373 (4)	7669 (4)	2478 (3)	617 (13)
C500	773 (4)	7686 (4)	3086 (4)	608 (12)
C600	1746 (4)	7254 (4)	3580 (3)	552 (11)
H3	6066 (30)	5248 (33)	1733 (13)	590 (79)

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Interatomic distances and bond angles were calculated with the program *PARST* of the *CRYRULER* package (Rizzoli *et al.*, 1986).

N1—C1	1.486 (4)	N1—C5	1.486 (4)
N1—O1	1.289 (3)	C1—C2	1.535 (4)
C1—C11	1.527 (10)	C1—C12	1.536 (7)
C2—C3	1.523 (4)	C3—C4	1.510 (6)
C3—C31	1.543 (4)	C3—O3	1.432 (9)
C4—C5	1.537 (4)	C5—C51	1.531 (8)
C5—C52	1.535 (9)	C31—C200	1.504 (4)
C200—N100	1.346 (8)	C200—C300	1.380 (7)
C300—C400	1.372 (5)	C400—C500	1.364 (10)
C500—C600	1.367 (8)	C600—N100	1.338 (4)
O3—H3	0.86 (2)	O3—N100^{i}	2.903 (6)
N3—N100^{i}	2.08 (3)		
C1—N1—C5	125.3 (2)	C1—N1—O1	115.6 (2)
C5—N1—O1	115.3 (2)	C2—C1—N1	110.4 (2)
C2—C1—C11	112.8 (4)	C2—C1—C12	108.4 (3)
N1—C1—C11	108.4 (3)	N1—C1—C12	107.5 (3)
C11—C1—C12	109.2 (3)	C1—C2—C3	117.5 (2)
C2—C3—C4	108.5 (2)	C2—C3—O3	112.1 (3)
O3—C3—C31	109.7 (3)	C2—C3—C31	108.7 (2)
C4—C3—C31	110.0 (3)	C4—C3—O3	107.9 (3)
C3—C4—C5	116.3 (3)	C4—C5—N1	110.0 (2)
C4—C5—C51	107.6 (3)	C4—C5—C52	112.6 (3)
N1—C5—C51	107.5 (2)	N1—C5—C52	109.4 (3)
C51—C5—C52	109.7 (3)	C3—C31—C200	115.3 (2)
C300—C200—N100	121.3 (3)	C300—C200—C31	122.7 (4)
N100—C200—C31	116.0 (3)	C200—C300—C400	119.7 (5)
C300—C400—C500	119.4 (4)	C400—C500—C600	118.1 (4)
C500—C600—N100	123.9 (5)	C600—N100—C200	117.6 (5)
C3—O3—H3	108.0 (2)	O3—H3—N100^{i}	162 (3)

Symmetry code: (i) y, $-x+1$, $z-\frac{1}{4}$.

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H atoms located on difference Fourier map. Unit weights. Refinement converged with $R = 2.5\%$, $S = 0.37$; in the last cycle of refinement $(\Delta/\sigma)_{\max}$ was 0.036 for all parameters, maximum, minimum heights in final difference Fourier map were 0.072, $-0.092\,\text{e}\,\text{Å}^{-3}$. Scattering factors from the *CRYSRULER* package (Rizzoli *et al.*, 1986).

Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2. Atom numbering is shown in Fig. 1.*

Related literature. Piperidine nitroxides are under study, to explore the effect of substituents in the 4-position on the conformation of the piperidine ring (Rozantzev, 1970). An intramolecular hydrogen bond between the hydroxyl group and the piperidine N atom was expected, but instead an intermolecular hydrogen bond was found, joining the hydroxyl group to a neighbouring pyridine N atom. The synthesis and properties of this compound are described by Gwoździński, Skolimowski & Skowroński (1989).

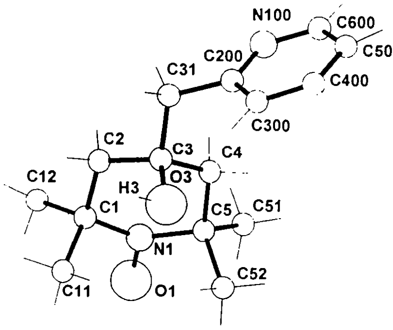

Fig. 1. Atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares planes, bond lengths and bond angles involving H atoms, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71162 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1044]