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The crystal structure of 2-[4-hydroxy-3-methoxyphenyl]-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl, $C_{14}H_{19}N_2O_4$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	$0.25 \times 0.23 \times 0.21$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.10 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
θ_{max} , completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4665, 2580, 0.056
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1715
$N(\text{param})_{\text{refined}}$:	188
Programs:	Bruker programs [1], SHELX [2]

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Abstract

$C_{14}H_{19}N_2O_4$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.263(10)$ Å, $b = 9.874(11)$ Å, $c = 15.431(16)$ Å, $V = 1407(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0542$, $wR_{\text{ref}}(F^2) = 0.1323$, $T = 296(2)$ K.

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The asymmetric unit of the title compound is in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

2,3-Dimethyl-2,3-bis(hydroxylamino) butane (1.48 g, 10.0 mmol) and 3-methoxy-4-hydroxybenzaldehyde (1.52 g, 10 mmol) were dissolved in methanol (30.0 mL). The reaction

mixture was filtered after stirring for 24 h at room temperature. The resulting white powder was washed by cool methanol and suspended in dichloromethane (30 mL). Then the reaction mixture was added to an aqueous solution of NaIO_4 (30 mL) and stirred for 15 min in an ice bath to give a dark blue solution. The aqueous phase was extracted with CH_2Cl_2 and the organic layer was combined and dried over Na_2SO_4 . Then the solvent was removed to give a dark blue residue, which was purified by flash column chromatography with *n*-hexane/ethyl acetate (1:2) to yield 1.42 g (51%) of the title compound as a dark blue powder. Crystals of the title compound were obtained from hexane/dichloromethane (2:1).

Experimental details

In the structure all the H atoms were positioned geometrically using a riding model, with $\text{C-H}_{\text{methyl}} = 0.96$ Å; $\text{C-H}_{\text{methylene}} = 0.97$ Å; $\text{C-H}_{\text{aryl}} = 0.93$ Å and $\text{O-H} = 0.82$ Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Comment

Nitronyl nitroxides, stable organic radicals, synthesized more than 30 years ago, which have characteristics of magnetism, anticancer, antiradiation and antioxidation [3]. They have received considerable attention recently because of their capability of scavenging free radical such as OH, H_2O_2 , and O_2 , protecting endothelial cells from the attack of free radicals [4, 5], and their structure [6]. The synthesis of nitronyl nitroxide radicals dates back to the seventies of the last century by Ullman [7, 8].

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.2595(3)	0.3343(3)	0.38307(19)	0.0326(7)
C2	0.3255(4)	0.5248(3)	0.4680(2)	0.0420(8)
C3	0.2938(3)	0.4030(3)	0.52915(19)	0.0378(8)
C4	0.2404(5)	0.6533(3)	0.4901(2)	0.0592(11)
H4A	0.2619	0.7227	0.4484	0.089*
H4B	0.2671	0.6842	0.5469	0.089*
H4C	0.1389	0.6337	0.4889	0.089*
C5	0.4854(4)	0.5560(3)	0.4551(3)	0.0607(11)
H5A	0.5358	0.4740	0.4404	0.091*
H5B	0.5247	0.5927	0.5077	0.091*
H5C	0.4964	0.6209	0.4092	0.091*
C6	0.4094(4)	0.3713(3)	0.5950(2)	0.0574(11)
H6A	0.3825	0.2918	0.6272	0.086*
H6B	0.4199	0.4468	0.6340	0.086*
H6C	0.4993	0.3552	0.5658	0.086*
C7	0.1455(4)	0.4067(4)	0.5733(2)	0.0576(11)
H7A	0.0723	0.4241	0.5307	0.086*
H7B	0.1443	0.4775	0.6161	0.086*
H7C	0.1272	0.3210	0.6007	0.086*
C8	0.2193(3)	0.2509(3)	0.30823(19)	0.0322(7)
C9	0.2801(4)	0.1224(3)	0.29620(19)	0.0356(7)
H9	0.3479	0.0896	0.3355	0.043*
C10	0.2396(3)	0.0438(3)	0.2261(2)	0.0360(8)
C11	0.1347(4)	0.0921(3)	0.16850(19)	0.0391(8)
C12	0.0714(4)	0.2164(3)	0.1828(2)	0.0402(8)
H12	−0.0011	0.2467	0.1458	0.048*
C13	0.1142(3)	0.2970(3)	0.25154(19)	0.0398(8)
H13	0.0725	0.3820	0.2597	0.048*
C14	0.4001(5)	−0.1376(4)	0.2635(2)	0.0669(12)
H14A	0.4871	−0.0854	0.2576	0.100*
H14B	0.4188	−0.2303	0.2478	0.100*
H14C	0.3674	−0.1338	0.3225	0.100*
N1	0.2726(3)	0.4701(2)	0.38260(17)	0.0399(7)
N2	0.2835(3)	0.2890(2)	0.46404(16)	0.0362(6)
O1	0.2622(3)	0.5465(2)	0.31572(16)	0.0616(8)
O2	0.2776(3)	0.16378(19)	0.48889(14)	0.0511(7)
O3	0.2913(3)	−0.0830(2)	0.20781(14)	0.0501(7)
O4	0.0938(3)	0.0177(2)	0.09778(15)	0.0544(7)
H4	0.0167	−0.0201	0.1078	0.082*

As shown in the figure, the nitronyl nitroxide ring and the phenyl rings are twisted with respect to each other making a dihedral angle of 43.37(11)°. The puckering parameters of the nitronyl nitroxide ring are $Q(2) = 0.216(3)$ Å and $\varphi = 123.6(8)^\circ$ [9]. The pseudorotation parameters [10] for the nitronyl nitroxide ring are $P = 285.1(6)^\circ$ and $\tau(M) = 22.1(2)^\circ$ for the C1–N1 reference bond with the closest puckering

descriptor being twisted on C2–C3. Geometric parameters are similar to that of a directly related structure [11].

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