4-(Benzenesulfonyloxy)-2,2,6,6-tetramethyl-piperidin-4-yl oxide

Bao-Han Zhou,[a] **Xiang-Gao Meng,**[b] **Guo-Dong Yin**[a] **and An-Xin Wu**[a]*

[a]Key Laboratory of Pesticides and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China, and [b]College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

Correspondence e-mail:
chwuax@mail.ccnu.edu.cn

Key indicators

Single-crystal X-ray study
$T = 273$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.146
Data-to-parameter ratio = 18.7

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

The title compound, $C_{15}H_{22}NO_4S$, is a nitroxyl radical, which is stable mainly because the N atom is surrounded by tertiary C atoms, preventing formation of the nitrone. More significantly, intermolecular C—H···O hydrogen bonding contributes to the stability of the structure with weak intramolecular C—H···π(arene) interactions. The N—O distance is 1.2816 (18) Å.

Comment

Nitroxyl radicals are compounds containing an NO group that has one unpaired electron. The structure of this fragment can be conceived as a superposition of two resonance structures:
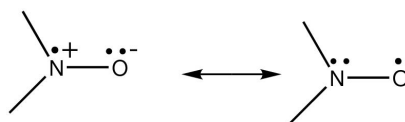

The contributions of the first and second structures to the ground state may be different, depending on the effects of conjugation and polarity of the medium. Piloty & Schwerin (1901) prepared the first organic nitroxyl. The structure of this nitroxyl free radical was later determined (Holden *et al.*, 1951). A widely used general procedure for the preparation of aromatic nitroxyls was developed (Wieland & Roth, 1920; Wieland & Kogl, 1922). A considerable amount of research, both theoretical and experimental, has been devoted to the electronic structure of nitroxyls (Stone *et al.*, 1965; Karimov *et al.*, 1969). It has been suggested that nitroxyl radicals are stable when the N atom is surrounded by tertiary C atoms, as formation of nitrones would not be possible in this case (Johnson *et al.*, 1956), the absence of α-H atoms ensuring the stability of nitroxyls.
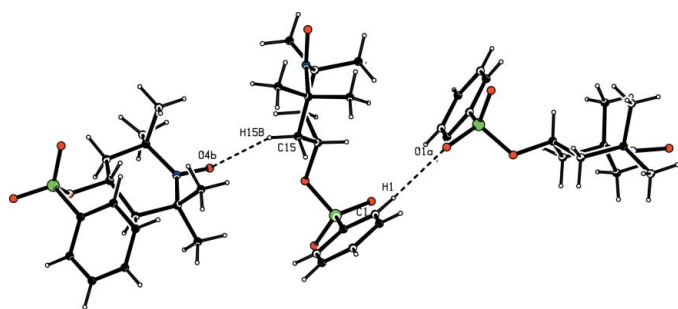

(I)
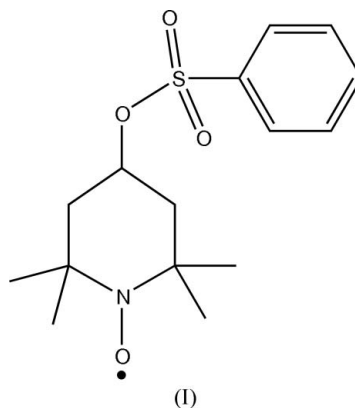
The title compound, (I) (Fig. 1), is a stable radical whose structure cannot be identified through ^{1}H NMR. Selected
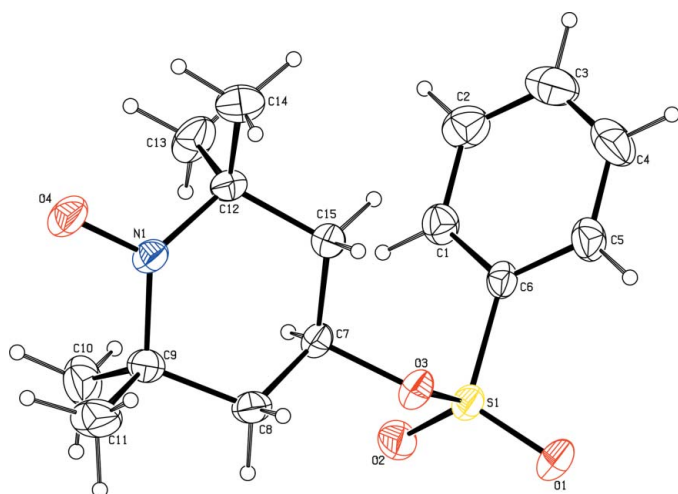
Figure 1
View of the molecule of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Figure 2
Intermolecular hydrogen bonding in the crystal structure of (I). Hydrogen-bonding interactions are indicated by dashed lines.

bond distances and angles describing the molecular conformation are listed in Table 1. The N1/C12/C15/C7–C9 ring exists as a chair conformation. The molecules are connected by intermolecular hydrogen bonding (Fig. 2 and Table 2). In addition, methyl atom C15 is involved in weak C—H···π interactions (C15—H15A···Cg2 = 3.1452 Å).

Experimental

The title compound was synthesized according to the literature procedure (Rozantsev & Sholle, 1971). Crystals suitable for data collection were obtained by slow evaporation from an acetone–hexane solution at 293 K.

Crystal data

$C_{15}H_{22}NO_4S$	Mo $K\alpha$ radiation
$M_r = 312.40$	Cell parameters from 3922
Orthorhombic, $Pbca$	reflections
$a = 11.4827 (9)$ Å	$\theta = 2.5$–$22.4°$
$b = 15.6864 (13)$ Å	$\mu = 0.21$ mm^{-1}
$c = 18.4671 (14)$ Å	$T = 273 (2)$ K
$V = 3326.3 (5)$ Å^3	Block, yellow
$Z = 8$	$0.30 \times 0.30 \times 0.20$ mm
$D_x = 1.248$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector	2525 reflections with $I > 2\sigma(I)$
diffractometer	$R_{int} = 0.034$
φ and ω scans	$\theta_{max} = 27.0°$
Absorption correction: none	$h = -12 \rightarrow 14$
18434 measured reflections	$k = -20 \rightarrow 19$
3629 independent reflections	$l = -23 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 0.3954P]$
$wR(F^2) = 0.146$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3629 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
194 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.366 (3)	C12—C15	1.526 (3)
C1—C6	1.374 (3)	C12—C14	1.527 (3)
C2—C3	1.372 (4)	C12—C13	1.530 (3)
C6—S1	1.755 (2)	N1—O4	1.2816 (18)
C7—O3	1.474 (2)	O1—S1	1.4224 (15)
C7—C15	1.499 (3)	O2—S1	1.4208 (15)
C12—N1	1.489 (3)	O3—S1	1.5649 (15)
O3—C7—C15	108.97 (14)	O4—N1—C9	115.77 (15)
N1—C9—C8	110.11 (15)	C12—N1—C9	125.03 (14)
N1—C12—C15	109.92 (14)	O3—S1—C6	104.09 (8)
O4—N1—C12	116.06 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O1^i	0.93	2.58	3.337 (3)	139
C15—H15B···O4^{ii}	0.97	2.46	3.351 (2)	153
C1—H1···O2	0.93	2.60	2.948 (3)	103
C7—H7···O2	0.98	2.54	2.949 (2)	105

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. All other H atoms were placed in geometrically idealized positions, with C—H distances in the range 0.93–0.98 Å, and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

References

Bruker (1997). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1999). *SAINT*. Version 6.01. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Holden, N., Yager, W. & Merrit, F. (1951). *J. Chem. Phys.* **19**, 1319–1320.

Johnson, D. H., Rogers, M. A. T. & Trappe, G. (1956). *J. Chem. Soc.* pp. 1093–1103.

Karimov, Y. S., Makova, M. K. & Grozantsev, E. (1969). *Theor. Eksp. Khim.* **5**, 701–705.

Piloty, O. & Schwerin, B. (1901). *Chem. Ber.* pp. 1870–1873.

Rozantsev, E. G. & Sholle, V. D. (1971), *Synthesis*, pp. 401–414.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Stone, T. I., Buckman, T., Nordio, P. L. & Mcconnell, H. M. (1965). *Proc. Natl Acad. Sci. USA*, **54**, 1010–1017.

Wieland, H. & Kogl, F. (1922). *Chem. Ber.* **55**, 1798–1780.

Wieland, H. & Roth, K. (1920). *Chem. Ber.* **53**, 210–212.