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## 2,2,6,6-Tetramethyl-4-(methylsulfonyloxy)piperidinyl 1-oxide

C. L. Homrighausen and J. A. Krause Bauer

### Abstract

2,2,6,6-Tetramethyl-4-(methylsulfonyloxy)piperidinyl 1-oxide, C<sub>10</sub>H<sub>20</sub>NO<sub>4</sub>S, is a stable radical with a nitroxyl bond length of 1.283 (2) Å. The N—O bond forms an angle of 19.9 (2)° with the CNC plane, the CNC angle is 124.5 (2)°. The piperidine ring adopts a chair conformation. Several C—H···O type intermolecular interactions are observed with C···O distances in the range 3.28–3.66 Å.

### Comment

2,2,6,6-Tetramethyl-4-(methylsulfonyl-oxyl)-1-piperidinoxy, 1, is a stable radical with the piperidine ring adopting a chair conformation. N1 and C4 are above and below the plane defined by C2—C3—C5—C6 with deviations of 0.36 and -0.72 Å, respectively. The nitroxyl bond length is 1.283 (2) Å which is comparable to 3-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 1.282 (2) Å (Cygler, 1979), 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl, 1.291 (7) Å (Berliner, 1970), 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy (MOTMP), 1.293 (5) Å and 4-acryloyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy (AOTMP), 1.288 (5) Å (Kajiwara *et al.*, 1994). The N—O bond forms an angle of 19.9° with the CNC plane, the CNC angle is 124.5 (2)°. Similar values are reported by Cygler (1979) for 3-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 19.7° and 124.7°, as well as by Berliner (1970) for 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl, 15.8° and 126.5°.

Several C—H···O type intermolecular interactions are observed with C···O distances in the range 3.278 (4)–3.660 (4) Å. The H···O distances ranging from 2.33 to 2.77 Å occur in the range that some consider to be moderate to weak nonconventional hydrogen bonding (Taylor & Kennard, 1982; Steiner, 1996; Jeffrey, 1997).

### Experimental

Crystals of a commercial sample (Aldrich Chemicals) of (1) were obtained as orange irregular blocks from slow evaporation of alcoholic solutions maintained at room temperature. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>NO</sub> 1361 (*m*), 1337 (*m*, *sh*) cm<sup>-1</sup>; m.p. 364–365 K.

### Refinement

Unit-cell dimensions were calculated from 30 reflections lying in a θ range of 5–15°. Intensity data were collected using variable speed (2–30° min<sup>-1</sup>) θ-2θ scans. A decay correction was applied (minimum 0.957, maximum 1.002) based on 3 standard reflections monitored every 300 reflections. The structure was solved by direct methods, expanded by the difference Fourier technique and refined by full-matrix least squares on F<sup>2</sup>. Positions of all the H atoms were either located directly or calculated based on geometric criteria and treated with a riding model (C—H = 0.96, 0.98 and 0.97 Å for -CH<sub>3</sub>, -CH

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and  $-\text{CH}_2$ , respectively). H-atom isotropic temperature factors were defined as  $aU(\text{C})$  where  $a = 1.5$  for  $-\text{CH}_3$  and 1.2 for all others.

### Computing details

Data collection: P3/P4-PC (Siemens, 1989); cell refinement: P3/P4-PC; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

### 2,2,6,6-tetramethyl-4-(methylsulfonyl-oxy)-1-piperidinoxy

#### Crystal data

$\text{C}_{10}\text{H}_{20}\text{NO}_4\text{S}$	$V = 1318.8 (5) \text{ \AA}^3$
$M_r = 250.33$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$
$a = 12.951 (3) \text{ \AA}$	$\mu = 0.25 \text{ mm}^{-1}$
$b = 9.977 (2) \text{ \AA}$	$T = 297 (2) \text{ K}$
$c = 11.131 (2) \text{ \AA}$	$0.40 \times 0.36 \times 0.30 \text{ mm}$
$\beta = 113.52 (3)^\circ$	

#### Data collection

Siemens P3 diffractometer	$R_{\text{int}} = 0.012$
Absorption correction: none	3 standard reflections
3200 measured reflections	every 300 reflections
3042 independent reflections	intensity decay: minimal
2024 reflections with $I > 2\sigma(I)$	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	145 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
3042 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

#### Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—O2	1.417 (2)	C2—C7	1.526 (4)
S1—O4	1.425 (2)	C2—C8	1.524 (4)
S1—O3	1.562 (2)	C2—C3	1.529 (3)
S1—C1	1.745 (3)	C3—C4	1.505 (3)
O1—N1	1.283 (3)	C4—C5	1.504 (3)
O3—C4	1.480 (3)	C5—C6	1.526 (3)

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N1—C2	1.495 (3)	C6—C10	1.529 (3)
N1—C6	1.496 (3)	C6—C9	1.530 (3)
O2—S1—O4	119.2 (1)	C7—C2—C3	111.5 (2)
O2—S1—O3	109.9 (1)	C8—C2—C3	109.3 (2)
O4—S1—O3	104.6 (1)	C4—C3—C2	113.0 (2)
O2—S1—C1	109.1 (2)	O3—C4—C5	110.4 (2)
O4—S1—C1	108.4 (1)	O3—C4—C3	105.6 (2)
O3—S1—C1	104.5 (1)	C5—C4—C3	108.8 (2)
C4—O3—S1	119.9 (1)	C4—C5—C6	111.8 (2)
O1—N1—C2	115.7 (2)	N1—C6—C5	109.8 (2)
O1—N1—C6	116.1 (2)	N1—C6—C10	106.8 (2)
C2—N1—C6	124.5 (2)	C5—C6—C10	109.5 (2)
N1—C2—C7	109.2 (2)	N1—C6—C9	109.5 (2)
N1—C2—C8	107.3 (2)	C5—C6—C9	111.5 (2)
C7—C2—C8	109.5 (2)	C10—C6—C9	109.7 (2)
N1—C2—C3	109.9 (2)		

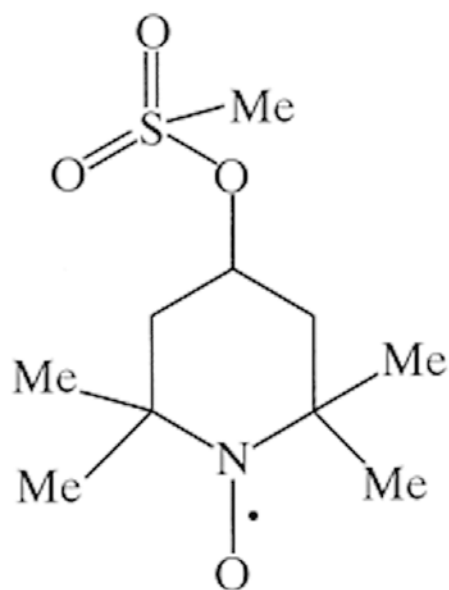
**Table 2***Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1B...O4 <sup>i</sup>	0.96	2.33	3.278 (3)	170
C7—H7A...O4 <sup>i</sup>	0.96	2.77	3.659 (4)	154
C8—H8C...O1 <sup>ii</sup>	0.96	2.68	3.544 (4)	150
C10—H10C...O2 <sup>iii</sup>	0.96	2.60	3.552 (3)	170

Symmetry codes: (i)  $x, -y+1/2, z+1/2$ ; (ii)  $-x+1, -y-1, -z$ ; (iii)  $-x+2, -y, -z$ .**References**

- Berliner, L. J. (1970). *Acta Cryst.* **B26**, 1198–1202.
- Cygler, M. (1979). *Acta Cryst.* **B35**, 195–197.
- Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding*. pp. 85–97. New York: Oxford University Press.
- Kajiwara, A., Sugimoto, H. & Kamachi, M. (1994). *Bull. Chem. Soc. Jpn.*, **67**, 2373–2377.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5.03. Program for Refinement of Crystal Structures. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1989). P3/P4-PC (Version 4.27) and *XDISK* (Version 4.27). Data Collection and Processing Programs. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steiner, T. (1996). *Crystallogr. Rev.* **6**, 1–57.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Scheme 1



**supplementary materials**

**2,2,6,6-tetramethyl-4-(methylsulfonyl-oxy)-1-piperidinoxy**

*Crystal data*

$C_{10}H_{20}NO_4S$	$D_x = 1.261 \text{ Mg m}^{-3}$
$M_r = 250.33$	Melting point: 91-92° C K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.951 (3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 9.977 (2) \text{ \AA}$	Cell parameters from 30 reflections
$c = 11.131 (2) \text{ \AA}$	$\theta = 5.0\text{--}15.0^\circ$
$\beta = 113.52 (3)^\circ$	$\mu = 0.25 \text{ mm}^{-1}$
$V = 1318.8 (5) \text{ \AA}^3$	$T = 297 (2) \text{ K}$
$Z = 4$	Irregular block, orange
$F_{000} = 540$	$0.40 \times 0.36 \times 0.30 \text{ mm}$

*Data collection*

Siemens P3 diffractometer	$R_{\text{int}} = 0.012$
Radiation source: normal-focus sealed tube	$\theta_{\text{max}} = 27.6^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.7^\circ$
$T = 297(2) \text{ K}$	$h = -16 \rightarrow 15$
$\theta$ - $2\theta$ scans	$k = 0 \rightarrow 12$
Absorption correction: none	$l = 0 \rightarrow 14$
3200 measured reflections	3 standard reflections
3042 independent reflections	every 300 reflections
2024 reflections with $I > 2\sigma(I)$	intensity decay: minimal

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.053$	H-atom parameters constrained
$wR(F^2) = 0.129$	$w = 1/[\sigma^2(F_o^2) + (0.0504P)^2 + 0.4212P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
3042 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
145 parameters	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
	Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

## supplementary materials

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between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement on  $F^2$  for ALL reflections except for 0 with very negative  $F^2$  or flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\text{sigma}(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.86464 (5)	0.29787 (7)	0.14934 (6)	0.0450 (2)
O1	0.62040 (15)	0.7505 (2)	0.3926 (2)	0.0627 (6)
O2	0.95838 (15)	0.3769 (2)	0.2272 (2)	0.0665 (6)
O3	0.75320 (13)	0.3775 (2)	0.11908 (15)	0.0466 (4)
O4	0.8566 (2)	0.2515 (2)	0.0248 (2)	0.0647 (6)
N1	0.6504 (2)	0.6670 (2)	0.3249 (2)	0.0427 (5)
C1	0.8547 (3)	0.1598 (3)	0.2404 (3)	0.0657 (8)
H1A	0.7914	0.1059	0.1881	0.098*
H1B	0.8451	0.1902	0.3171	0.098*
H1C	0.9224	0.1075	0.2662	0.098*
C2	0.5827 (2)	0.5410 (2)	0.2863 (3)	0.0443 (6)
C3	0.6138 (2)	0.4635 (3)	0.1869 (2)	0.0470 (6)
H3A	0.5843	0.3731	0.1793	0.056*
H3B	0.5782	0.5061	0.1018	0.056*
C4	0.7388 (2)	0.4569 (2)	0.2237 (2)	0.0377 (5)
H4	0.7767 (2)	0.4131 (2)	0.3090 (2)	0.045*
C5	0.7828 (2)	0.5969 (2)	0.2269 (2)	0.0427 (6)
H5A	0.7433	0.6388	0.1421	0.051*
H5B	0.8621	0.5929	0.2431	0.051*
C6	0.7678 (2)	0.6820 (2)	0.3326 (2)	0.0426 (6)
C7	0.6034 (3)	0.4576 (3)	0.4087 (3)	0.0665 (8)
H7A	0.6813	0.4322	0.4485	0.100*
H7B	0.5574	0.3785	0.3849	0.100*
H7C	0.5845	0.5096	0.4697	0.100*
C8	0.4590 (2)	0.5814 (3)	0.2230 (3)	0.0704 (9)
H8A	0.4461	0.6340	0.1461	0.106*
H8B	0.4402	0.6333	0.2840	0.106*
H8C	0.4130	0.5024	0.1991	0.106*
C9	0.8518 (2)	0.6423 (3)	0.4696 (3)	0.0612 (8)
H9A	0.8404	0.6975	0.5338	0.092*
H9B	0.9272	0.6544	0.4754	0.092*
H9C	0.8407	0.5499	0.4856	0.092*
C10	0.7833 (2)	0.8300 (3)	0.3081 (3)	0.0662 (9)
H10A	0.7738	0.8835	0.3746	0.099*
H10B	0.7283	0.8556	0.2237	0.099*
H10C	0.8575	0.8437	0.3106	0.099*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0479 (3)	0.0520 (4)	0.0413 (3)	0.0002 (3)	0.0245 (3)	-0.0062 (3)
O1	0.0539 (11)	0.0527 (11)	0.094 (2)	-0.0018 (9)	0.0424 (11)	-0.0185 (11)
O2	0.0436 (10)	0.0761 (14)	0.0796 (14)	-0.0062 (10)	0.0242 (10)	-0.0210 (11)
O3	0.0458 (10)	0.0549 (11)	0.0362 (9)	0.0032 (8)	0.0136 (7)	-0.0078 (8)
O4	0.0879 (14)	0.0726 (13)	0.0498 (11)	0.0026 (11)	0.0447 (10)	-0.0086 (10)
N1	0.0370 (10)	0.0386 (12)	0.0559 (12)	0.0006 (9)	0.0222 (9)	-0.0004 (9)
C1	0.096 (2)	0.055 (2)	0.055 (2)	0.013 (2)	0.040 (2)	0.0066 (14)
C2	0.0363 (12)	0.0370 (13)	0.064 (2)	-0.0005 (10)	0.0241 (11)	0.0003 (12)
C3	0.0384 (13)	0.0429 (14)	0.057 (2)	-0.0044 (11)	0.0160 (11)	-0.0034 (12)
C4	0.0378 (12)	0.0429 (14)	0.0331 (11)	0.0021 (10)	0.0148 (10)	-0.0018 (10)
C5	0.0388 (12)	0.0467 (15)	0.0457 (14)	-0.0026 (11)	0.0202 (11)	0.0023 (11)
C6	0.0334 (12)	0.0421 (14)	0.0522 (14)	-0.0048 (10)	0.0171 (10)	-0.0029 (11)
C7	0.081 (2)	0.055 (2)	0.088 (2)	0.006 (2)	0.060 (2)	0.014 (2)
C8	0.0345 (13)	0.057 (2)	0.117 (3)	-0.0053 (13)	0.028 (2)	-0.014 (2)
C9	0.0460 (15)	0.076 (2)	0.052 (2)	0.0043 (14)	0.0096 (12)	-0.0160 (15)
C10	0.060 (2)	0.043 (2)	0.110 (3)	-0.0099 (13)	0.049 (2)	-0.005 (2)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—O2	1.417 (2)	C2—C7	1.526 (4)
S1—O4	1.425 (2)	C2—C8	1.524 (4)
S1—O3	1.562 (2)	C2—C3	1.529 (3)
S1—C1	1.745 (3)	C3—C4	1.505 (3)
O1—N1	1.283 (3)	C4—C5	1.504 (3)
O3—C4	1.480 (3)	C5—C6	1.526 (3)
N1—C2	1.495 (3)	C6—C10	1.529 (3)
N1—C6	1.496 (3)	C6—C9	1.530 (3)
O2—S1—O4	119.2 (1)	C7—C2—C3	111.5 (2)
O2—S1—O3	109.9 (1)	C8—C2—C3	109.3 (2)
O4—S1—O3	104.6 (1)	C4—C3—C2	113.0 (2)
O2—S1—C1	109.1 (2)	O3—C4—C5	110.4 (2)
O4—S1—C1	108.4 (1)	O3—C4—C3	105.6 (2)
O3—S1—C1	104.5 (1)	C5—C4—C3	108.8 (2)
C4—O3—S1	119.9 (1)	C4—C5—C6	111.8 (2)
O1—N1—C2	115.7 (2)	N1—C6—C5	109.8 (2)
O1—N1—C6	116.1 (2)	N1—C6—C10	106.8 (2)
C2—N1—C6	124.5 (2)	C5—C6—C10	109.5 (2)
N1—C2—C7	109.2 (2)	N1—C6—C9	109.5 (2)
N1—C2—C8	107.3 (2)	C5—C6—C9	111.5 (2)
C7—C2—C8	109.5 (2)	C10—C6—C9	109.7 (2)
N1—C2—C3	109.9 (2)		
O2—S1—O3—C4	-42.3 (2)	C2—C3—C4—O3	179.2 (2)
O4—S1—O3—C4	-171.5 (2)	C2—C3—C4—C5	-62.3 (3)
C1—S1—O3—C4	74.7 (2)	O3—C4—C5—C6	179.2 (2)



## supplementary materials

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O1—N1—C2—C7	-67.4 (3)	C3—C4—C5—C6	63.8 (2)
C6—N1—C2—C7	90.4 (3)	O1—N1—C6—C5	-168.3 (2)
O1—N1—C2—C8	51.2 (3)	C2—N1—C6—C5	34.1 (3)
C6—N1—C2—C8	-151.0 (2)	O1—N1—C6—C10	-49.6 (3)
O1—N1—C2—C3	170.0 (2)	C2—N1—C6—C10	152.7 (2)
C6—N1—C2—C3	-32.3 (3)	O1—N1—C6—C9	69.0 (3)
N1—C2—C3—C4	44.5 (3)	C2—N1—C6—C9	-88.6 (3)
C7—C2—C3—C4	-76.7 (3)	C4—C5—C6—N1	-47.7 (3)
C8—C2—C3—C4	162.0 (2)	C4—C5—C6—C10	-164.7 (2)
S1—O3—C4—C5	88.9 (2)	C4—C5—C6—C9	73.8 (2)
S1—O3—C4—C3	-153.6 (2)		

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1B $\cdots$ O4 <sup>i</sup>	0.96	2.33	3.278 (3)	170
C7—H7A $\cdots$ O4 <sup>i</sup>	0.96	2.77	3.659 (4)	154
C8—H8C $\cdots$ O1 <sup>ii</sup>	0.96	2.68	3.544 (4)	150
C10—H10C $\cdots$ O2 <sup>iii</sup>	0.96	2.60	3.552 (3)	170

Symmetry codes: (i)  $x, -y+1/2, z+1/2$ ; (ii)  $-x+1, -y-1, -z$ ; (iii)  $-x+2, -y, -z$ .