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2-(Methylsulfinyl)benzamide

Zhou Yan

 College of Food Science and Biotechnology, Zhejiang Gongshang University,
 Hangzhou 310035, People's Republic of China

Correspondence e-mail: winter111852@yahoo.cn

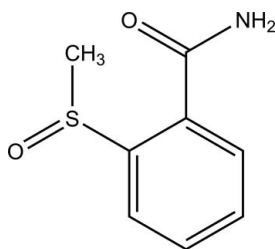
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
 R factor = 0.030; wR factor = 0.083; data-to-parameter ratio = 14.1.

In the crystal of the title compound, $\text{C}_8\text{H}_9\text{NO}_2\text{S}$, synthesized by the oxidation of 2-(methylsulfinyl)benzamide using NaOCl with 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) as the catalyst, molecules are linked *via* intermolecular N—H \cdots O_{amide} hydrogen bonds, forming centrosymmetric amide–amide dimers which are extended into a two-dimensional lamellar framework parallel to (100) through amide–sulfinyl N—H \cdots O hydrogen bonds. The benzene ring forms a dihedral angle of 25.6 (2) $^\circ$ with the amide group

Related literature

For general background to sulfoxides, see: Hernández-Torres *et al.* (2008); Padmanabhan *et al.* (2000); Nieves & Lang (2002); Wedel *et al.* (2008); Melzig *et al.* (2009); Huang *et al.* (2006, 2010). For selective oxidation of sulfides to sulfoxides, see: Huang *et al.* (2006); Karimi *et al.* (2005); Kirihara *et al.* (2009); Ruff *et al.* (2009). For related structures, see: Kobayashi *et al.* (2003).



Experimental

Crystal data

$\text{C}_8\text{H}_9\text{NO}_2\text{S}$
 $M_r = 183.22$
 Monoclinic, $P2_1/c$
 $a = 11.8497$ (5) Å
 $b = 5.0376$ (2) Å

$c = 14.8598$ (6) Å
 $\beta = 104.856$ (4) $^\circ$
 $V = 857.39$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.33$ mm⁻¹
 $T = 293$ K

0.46 × 0.26 × 0.23 mm

Data collection

Oxford Diffraction Gemini Ultra
 CCD-detector diffractometer
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Oxford
 Diffraction, 2009)
 $T_{\min} = 0.901$, $T_{\max} = 0.926$

3438 measured reflections
 1564 independent reflections
 1354 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.083$
 $S = 1.05$
 1564 reflections

111 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

 Hydrogen-bond geometry (Å, $^\circ$).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O2 ⁱ	0.86	2.08	2.934 (2)	175
N1—H1B \cdots O1 ⁱⁱ	0.86	2.18	2.991 (2)	157

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZS2076).

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supporting information

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2-(Methylsulfinyl)benzamide

Zhou Yan

S1. Comment

Sulfoxides are versatile synthetic intermediates in stereocontrol chemistry (Hernández-Torres *et al.*, 2008). They can be used to prepare chemically and biologically significant molecules, including therapeutic agents such as antiulcer (proton pump inhibitor), antibacterial, antifungal, antiatherosclerotic, antihypertensive, cardiogenic, psychotropic, and vasodilator agents (Padmanabhan *et al.*, 2000; Nieves & Lang, 2002; Wedel *et al.*, 2008; Melzig *et al.*, 2009). The versatility of sulfoxides as organic reagents continually motivate the development of efficient synthesis methods for sulfoxides (Huang *et al.*, 2006; Huang *et al.*, 2010). Although many methods for the synthesis of sulfoxides have been investigated, selective oxidation of sulfides to sulfoxides still remains a challenging task (Karimi *et al.*, 2005; Huang *et al.*, 2006; Kirihara *et al.*, 2009; Ruff *et al.*, 2009). Herein, we report the synthesis and the crystal structure of a sulfoxide, *viz.* the title compound, C₈H₉NO₂S (I). In the crystal structure (Fig. 1), the phenyl ring forms a dihedral angle of 25.6 (2)° with the amide group, similar to that found in benzamide (26.31°) (Kobayashi *et al.*, 2003). The amide groups in (I) give intermolecular N—H···O_{amide} hydrogen-bonding interactions (Table 1) forming centrosymmetric amide–amide dimers which are extended into a two-dimensional lamellar framework parallel to (100), through amide N—H···O_{sulfinyl} hydrogen bonds (Fig. 2).

S2. Experimental

To a stirred solution of 2-(methylthio)benzamide (167 mg, 1.0 mmol) and the catalyst 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) (1.6 mg, 0.01 mmol) in CH₂Cl₂ (8 ml), Bu₄NBr (16.1 mg, 0.05 mmol) and a saturated aqueous NaHCO₃ solution (5 ml) containing KBr (11.9 mg, 0.1 mmol) were added. This mixture was cooled to 273 K, a solution of 0.73 M NaOCl (0.91 ml, 1.25 mmol) in saturated aqueous NaHCO₃ was added dropwise over a period of 10 min. The mixture was stirred for a further 1 h at 273 K and for 0.5 h at room temperature. After the organic phase was separated, the aqueous phase was extracted with CH₂Cl₂ (3.5 ml) and the organic solution was washed with aqueous brine, dried over anhydrous Na₂SO₄ and filtered. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel with ethyl acetate/hexane as an eluant to afford the title compound as a white solid (160 mg, 87%). Colorless crystals were obtained by vapor diffusion of hexane into an ethyl acetate solution of (I) over a period of 7 d.

¹H NMR (400 MHz, CD₃OD, 295 K) δ (p.p.m.) 8.20–8.18 (1H, m), 7.92–7.89 (1H, m), 7.85–7.81 (1H, m), 7.66–7.62 (1H, m), and 2.89 (3H, s). ¹³C NMR (400 MHz, CD₃OD, 295 K) δ (p.p.m.) 168.9, 147.1, 132.4, 131.0, 130.5, 127.7, 123.4, and 43.7.

S3. Refinement

H atoms bonded to C or N were placed in geometrically calculated positions and were refined using a riding model, with C—H_{aromatic} = 0.93 Å, C—H_{methyl} = 0.96 Å and N—H = 0.86 Å, and with *U*_{iso}(H) = 1.2 or 1.5*U*_{eq}(C,N).

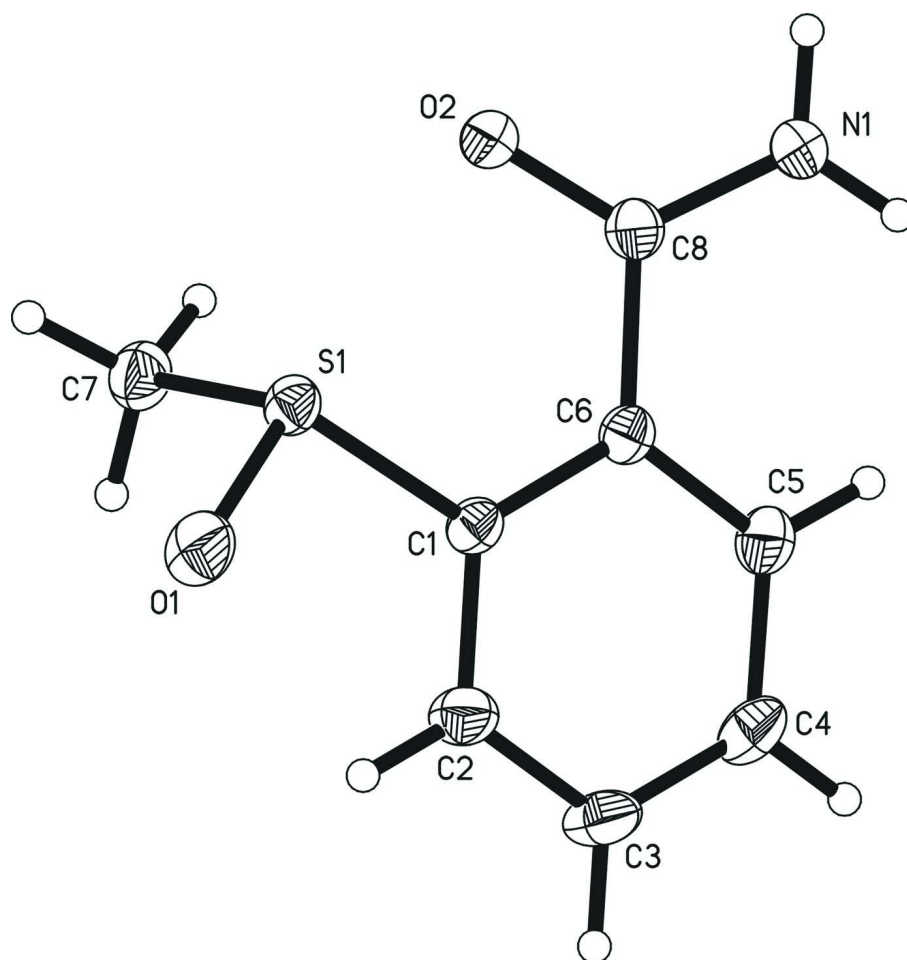


Figure 1

A view of the title compound with showing atom numbering and with displacement ellipsoids drawn at the 30% probability level

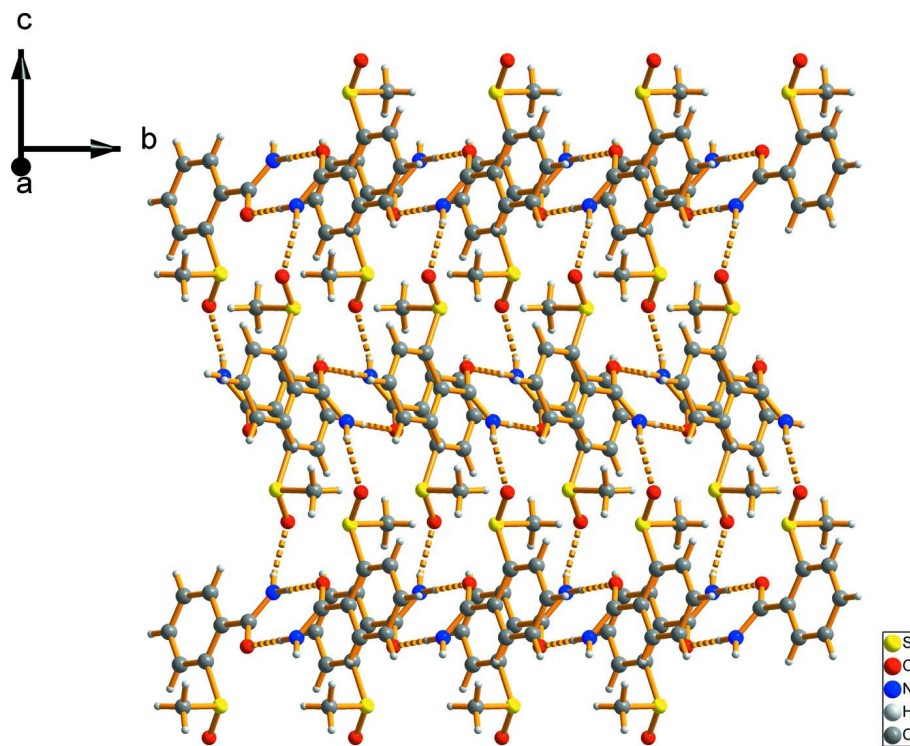


Figure 2

The two-dimensional layered structure of the title compound.

2-(Methylsulfinyl)benzamide

Crystal data

$C_8H_9NO_2S$

$M_r = 183.22$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 11.8497(5)\ \text{\AA}$

$b = 5.0376(2)\ \text{\AA}$

$c = 14.8598(6)\ \text{\AA}$

$\beta = 104.856(4)^\circ$

$V = 857.39(6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 384$

$D_x = 1.419\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2076 reflections

$\theta = 2.8\text{--}29.3^\circ$

$\mu = 0.33\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.46 \times 0.26 \times 0.23\ \text{mm}$

Data collection

Oxford Diffraction Gemini Ultra CCD-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $10.3592\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.901$, $T_{\max} = 0.926$

3438 measured reflections

1564 independent reflections

1354 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.3^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -14 \rightarrow 14$

$k = -4 \rightarrow 6$

$l = -14 \rightarrow 17$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.083$ $S = 1.05$

1564 reflections

111 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.2897P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.042 (3)

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 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 of F^2 against ALL reflections. The weighted R -factor wR and goodness 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.70440 (4)	0.05668 (9)	0.75213 (3)	0.03131 (18)
O1	0.78768 (11)	-0.0190 (3)	0.84272 (9)	0.0493 (4)
O2	0.56496 (11)	0.2416 (3)	0.58587 (9)	0.0443 (4)
N1	0.64197 (13)	0.4202 (3)	0.47654 (10)	0.0415 (4)
H1A	0.5843	0.5281	0.4588	0.050*
H1B	0.6982	0.4221	0.4497	0.050*
C1	0.77553 (14)	-0.0412 (3)	0.66326 (12)	0.0292 (4)
C2	0.86744 (15)	-0.2174 (4)	0.68979 (13)	0.0400 (5)
H2	0.8878	-0.2850	0.7500	0.048*
C3	0.92910 (16)	-0.2930 (4)	0.62648 (14)	0.0463 (5)
H3	0.9904	-0.4132	0.6440	0.056*
C4	0.89971 (16)	-0.1907 (4)	0.53778 (14)	0.0449 (5)
H4	0.9409	-0.2428	0.4952	0.054*
C5	0.80940 (16)	-0.0109 (4)	0.51166 (13)	0.0393 (5)
H5	0.7911	0.0593	0.4518	0.047*
C6	0.74535 (14)	0.0670 (3)	0.57362 (11)	0.0297 (4)
C7	0.59562 (16)	-0.1977 (4)	0.73172 (14)	0.0418 (5)
H7A	0.5457	-0.1791	0.6700	0.063*
H7C	0.5500	-0.1821	0.7763	0.063*
H7B	0.6328	-0.3685	0.7379	0.063*
C8	0.64414 (14)	0.2510 (4)	0.54531 (11)	0.0326 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0344 (3)	0.0335 (3)	0.0278 (3)	0.00090 (18)	0.01129 (18)	-0.00260 (18)
O1	0.0443 (8)	0.0777 (11)	0.0256 (7)	0.0052 (7)	0.0086 (6)	-0.0005 (7)
O2	0.0423 (7)	0.0527 (8)	0.0439 (8)	0.0163 (6)	0.0220 (6)	0.0167 (7)
N1	0.0389 (9)	0.0496 (10)	0.0386 (9)	0.0102 (8)	0.0147 (7)	0.0159 (8)
C1	0.0279 (8)	0.0322 (9)	0.0280 (9)	-0.0001 (7)	0.0084 (7)	-0.0029 (7)
C2	0.0363 (10)	0.0476 (12)	0.0350 (10)	0.0094 (9)	0.0069 (8)	0.0010 (9)
C3	0.0362 (10)	0.0525 (13)	0.0506 (12)	0.0148 (9)	0.0118 (9)	-0.0032 (10)
C4	0.0399 (10)	0.0554 (13)	0.0455 (12)	0.0041 (10)	0.0221 (9)	-0.0085 (10)
C5	0.0440 (10)	0.0466 (11)	0.0310 (10)	0.0022 (9)	0.0162 (8)	-0.0005 (8)
C6	0.0300 (9)	0.0317 (9)	0.0282 (9)	-0.0017 (7)	0.0088 (7)	-0.0019 (7)
C7	0.0428 (10)	0.0370 (11)	0.0498 (11)	-0.0030 (9)	0.0195 (9)	0.0003 (9)
C8	0.0350 (9)	0.0359 (10)	0.0269 (9)	0.0009 (8)	0.0080 (7)	-0.0009 (8)

Geometric parameters (\AA , $^\circ$)

S1—O1	1.5000 (13)	C3—C4	1.374 (3)
S1—C7	1.7875 (19)	C3—H3	0.9300
S1—C1	1.8078 (17)	C4—C5	1.380 (3)
O2—C8	1.239 (2)	C4—H4	0.9300
N1—C8	1.326 (2)	C5—C6	1.391 (2)
N1—H1A	0.8600	C5—H5	0.9300
N1—H1B	0.8600	C6—C8	1.488 (2)
C1—C2	1.382 (3)	C7—H7A	0.9600
C1—C6	1.398 (2)	C7—H7C	0.9600
C2—C3	1.384 (3)	C7—H7B	0.9600
C2—H2	0.9300		
O1—S1—C7	104.47 (9)	C5—C4—H4	119.9
O1—S1—C1	105.28 (8)	C4—C5—C6	120.95 (17)
C7—S1—C1	97.56 (8)	C4—C5—H5	119.5
C8—N1—H1A	120.0	C6—C5—H5	119.5
C8—N1—H1B	120.0	C5—C6—C1	118.09 (16)
H1A—N1—H1B	120.0	C5—C6—C8	121.68 (15)
C2—C1—C6	120.83 (16)	C1—C6—C8	120.18 (15)
C2—C1—S1	116.60 (13)	S1—C7—H7A	109.5
C6—C1—S1	122.44 (13)	S1—C7—H7C	109.5
C1—C2—C3	119.85 (17)	H7A—C7—H7C	109.5
C1—C2—H2	120.1	S1—C7—H7B	109.5
C3—C2—H2	120.1	H7A—C7—H7B	109.5
C4—C3—C2	120.01 (18)	H7C—C7—H7B	109.5
C4—C3—H3	120.0	O2—C8—N1	122.13 (16)
C2—C3—H3	120.0	O2—C8—C6	119.62 (15)
C3—C4—C5	120.24 (17)	N1—C8—C6	118.24 (15)
C3—C4—H4	119.9		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O2 ⁱ	0.86	2.08	2.934 (2)	175
N1—H1B \cdots O1 ⁱⁱ	0.86	2.18	2.991 (2)	157

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