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2,2′-[Methylenebis(sulfanediyl)]bis(pyridine 1-oxide)

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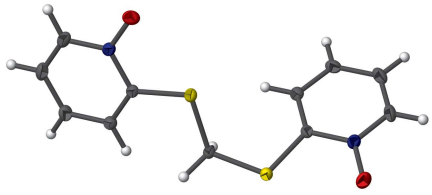
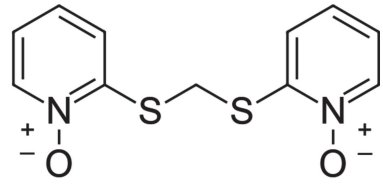
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{11}H_{10}N_2O_2S_2$, crystallizes with one complete molecule in the asymmetric unit. In the crystal, weak hydrogen bonding is observed between the N-oxide moieties and several C—H units.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) crystallizes in the $P2_1$ space group with a single molecule in the asymmetric unit. The two nitrogen–oxygen bonds in the N-oxide moiety exhibit similar lengths [1.307 (3) and 1.309 (3). The two pyridine N-oxide rings exist in a staggered conformation with respect to each other, forming a dihedral angle of 66.55 (9)° (Fig. 2).

In the extended network, molecules are arranged in a zigzag pattern when viewed along [101] (Fig. 3); this arrangement facilitates weak hydrogen-bonding interactions between adjacent molecules (Table 1). Both oxygen atoms participate in hydrogen bonding, interacting with hydrogen atoms bound to the aromatic rings of the N-oxide moieties. In addition to the interactions with aromatic H atoms, O1 is involved in hydrogen bonding with the methylene H atoms from the thioether moiety. As a result of the zigzag arrangement of molecules, no π–π stacking is observed.

For related N-oxide crystal structures, see: Rybarczyk-Pirek *et al.* (2018), Amoedo-Portela *et al.* (2002), and de Castro *et al.* (2002)

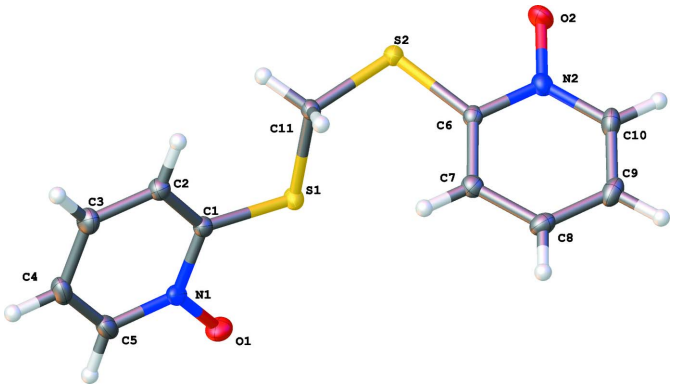


Figure 1
The molecular structure of the title compound shown with 50% probability ellipsoids.

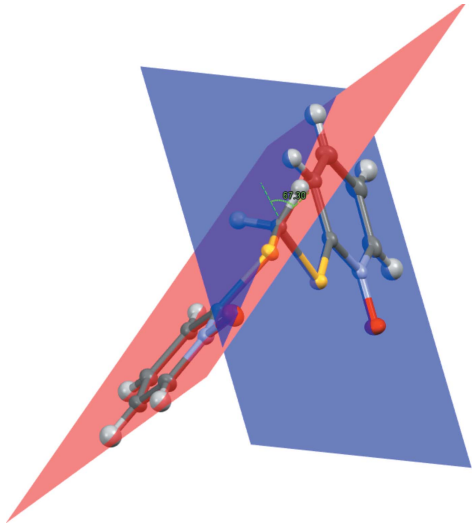


Figure 2
Depiction of the dihedral plane angle of the two pyridine N-oxide moieties visualized within *Mercury* (Macrae *et al.*, 2020).

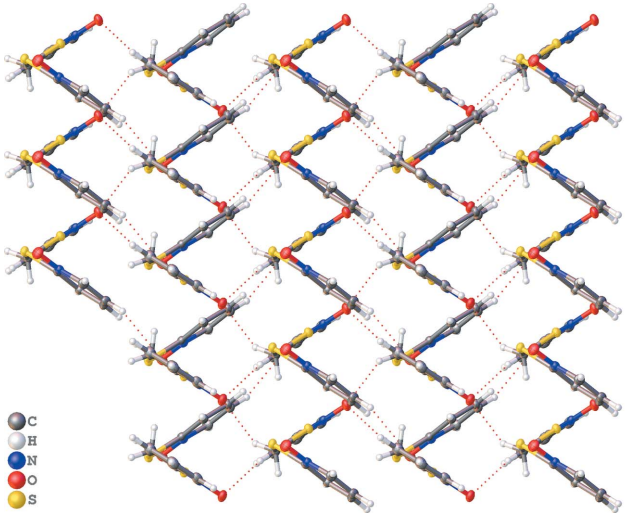


Figure 3
Packing diagram for the title compound as viewed from the [101] direction. Dotted red lines depict the weak hydrogen bonds.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.95	2.37	3.292 (3)	165
C9—H9···O2^{ii}	0.95	2.70	3.405 (4)	131
C11—H11A···O1^{iii}	0.99	2.33	3.159 (3)	141

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{10}N_2O_2S_2$
M_r	266.33
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, b, c (Å)	4.1658 (2), 10.4706 (6), 12.7624 (7)
β (°)	95.958 (2)
V (Å^3)	553.67 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.47
Crystal size (mm)	0.55 × 0.16 × 0.04
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.528, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17033, 4262, 3794
R_{int}	0.070
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.772
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.100, 1.06
No. of reflections	4262
No. of parameters	154
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.48
Absolute structure	Flack x determined using 1650 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.05 (4)

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015, 2018), *SHELXLE* (Hübschle *et al.*, 2011), *PLATON* (Spek, 2020), *OLEX2* (Dolomanov *et al.*, 2009), *Mercury* (Macrae *et al.*, 2008), *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).

Synthesis and crystallization

An oven-dried 100 ml, 24/40 single-necked, round-bottomed flask was charged with a 4 cm oval Teflon-coated stir bar and 2-mercaptopyridine *N*-oxide sodium salt (1.00 g, 1 equiv.). Dry CH_2Cl_2 (4.24 ml, 10 equiv.) was then added to the flask *via* syringe. The flask neck was equipped with a water-jacketed reflux condenser (30.0 cm height, 24/40 joint) with a constant flow of water. The reaction vessel was placed in a pre-heated oil bath and refluxed for an hour under stirring. After the allotted time, the reaction vessel was removed from the oil bath and cooled to room temperature and colorless plates of 2,2′-[methylenebis(sulfanediyl)]bis(pyridine-1-oxide) formed over 5 d. The crystals were vacuum filtered and the residual solvent was removed under vacuum (1.40 mm H g) for 12 h to

afford 2,2′-[methylenebis(sulfanediyl)]bis(pyridine-1-oxide) in high yield (89%).

Crystals suitable for diffraction formed slowly from a CD_2Cl_2 solution in an NMR tube.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

IUCrData (2020). **5**, x200171 [https://doi.org/10.1107/S2414314620001716]

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Crystal data

$C_{11}H_{10}N_2O_2S_2$
M_r = 266.33
Monoclinic, $P2_1$
a = 4.1658 (2) Å
b = 10.4706 (6) Å
c = 12.7624 (7) Å
β = 95.958 (2)°
V = 553.67 (5) Å^3
Z = 2
$F(000)$ = 276
D_x = 1.598 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9929 reflections
θ = 2.5–33.3°
μ = 0.47 mm^{-1}
T = 150 K
Plate, colourless
0.55 × 0.16 × 0.04 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer
Radiation source: fine focus sealed tube X-ray source
Triumph curved graphite crystal monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω and phi scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.528, T_{max} = 0.747
17033 measured reflections
4262 independent reflections
3794 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 33.3°, θ_{min} = 2.5°
h = −6→5
k = −16→16
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.100
S = 1.06
4262 reflections
154 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.1658P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Absolute structure: Flack x determined using 1650 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.05 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. C—H bond distances were constrained to 0.95 Å for aromatic C—H moieties. U_{iso}(H) values were set to 1.2 times U_{eq}(C).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.81710 (15)	0.68956 (6)	0.58939 (4)	0.01584 (13)
S2	0.86177 (15)	0.83538 (6)	0.79102 (4)	0.01541 (13)
O1	0.8980 (5)	0.5371 (2)	0.42557 (17)	0.0230 (4)
O2	1.0430 (5)	0.7815 (2)	0.99221 (16)	0.0224 (4)
N1	0.7052 (5)	0.6307 (2)	0.39242 (17)	0.0162 (4)
N2	0.8365 (5)	0.6943 (2)	0.95562 (16)	0.0162 (4)
C1	0.6300 (6)	0.7213 (2)	0.46299 (19)	0.0152 (4)
C2	0.4276 (6)	0.8217 (3)	0.43009 (19)	0.0178 (5)
H2	0.373352	0.884463	0.479079	0.021*
C3	0.3049 (7)	0.8300 (3)	0.3252 (2)	0.0221 (5)
H3	0.167937	0.899069	0.301822	0.026*
C4	0.3825 (8)	0.7369 (3)	0.2540 (2)	0.0241 (6)
H4	0.299597	0.741896	0.181928	0.029*
C5	0.5806 (8)	0.6380 (3)	0.2897 (2)	0.0225 (5)
H5	0.631713	0.573381	0.241816	0.027*
C6	0.7073 (6)	0.7022 (3)	0.85309 (18)	0.0139 (4)
C7	0.4827 (6)	0.6128 (3)	0.8125 (2)	0.0169 (5)
H7	0.391355	0.618626	0.741250	0.020*
C8	0.3922 (7)	0.5152 (3)	0.8762 (2)	0.0197 (5)
H8	0.236511	0.454000	0.849241	0.024*
C9	0.5303 (7)	0.5072 (3)	0.9797 (2)	0.0223 (5)
H9	0.471354	0.440113	1.024029	0.027*
C10	0.7527 (7)	0.5969 (3)	1.0173 (2)	0.0209 (5)
H10	0.849794	0.590692	1.087870	0.025*
C11	0.6603 (6)	0.8234 (3)	0.65943 (18)	0.0150 (4)
H11A	0.692061	0.903548	0.620641	0.018*
H11B	0.425731	0.811823	0.662873	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0192 (3)	0.0155 (3)	0.0129 (2)	0.0026 (2)	0.00225 (19)	0.0004 (2)
S2	0.0194 (3)	0.0138 (3)	0.0131 (2)	−0.0019 (2)	0.00204 (19)	0.0002 (2)
O1	0.0299 (10)	0.0159 (9)	0.0243 (10)	0.0048 (8)	0.0075 (8)	−0.0012 (7)
O2	0.0259 (10)	0.0239 (10)	0.0165 (9)	−0.0057 (8)	−0.0023 (7)	−0.0028 (7)
N1	0.0205 (10)	0.0149 (10)	0.0141 (9)	−0.0027 (8)	0.0061 (8)	−0.0010 (7)
N2	0.0176 (9)	0.0173 (9)	0.0140 (8)	0.0023 (9)	0.0029 (7)	−0.0005 (8)

C1	0.0188 (11)	0.0143 (11)	0.0129 (9)	−0.0018 (9)	0.0038 (8)	−0.0002 (8)
C2	0.0214 (11)	0.0162 (11)	0.0159 (10)	−0.0005 (9)	0.0030 (8)	−0.0001 (9)
C3	0.0259 (12)	0.0223 (12)	0.0171 (10)	−0.0003 (11)	−0.0020 (9)	0.0022 (11)
C4	0.0302 (14)	0.0280 (14)	0.0135 (11)	−0.0070 (12)	−0.0004 (9)	0.0016 (10)
C5	0.0315 (14)	0.0230 (13)	0.0139 (11)	−0.0070 (11)	0.0060 (10)	−0.0028 (9)
C6	0.0151 (10)	0.0138 (10)	0.0131 (9)	0.0021 (9)	0.0035 (7)	0.0007 (8)
C7	0.0183 (11)	0.0168 (11)	0.0159 (11)	0.0004 (9)	0.0031 (9)	−0.0006 (8)
C8	0.0212 (12)	0.0148 (11)	0.0237 (12)	−0.0018 (10)	0.0053 (9)	0.0003 (9)
C9	0.0259 (13)	0.0190 (12)	0.0235 (13)	0.0030 (10)	0.0093 (10)	0.0070 (10)
C10	0.0248 (13)	0.0229 (12)	0.0154 (11)	0.0031 (11)	0.0044 (9)	0.0063 (9)
C11	0.0186 (11)	0.0148 (11)	0.0119 (9)	0.0012 (9)	0.0022 (8)	−0.0006 (9)

Geometric parameters (Å, º)

S1—C1	1.749 (3)	C3—H3	0.9500
S1—C11	1.820 (3)	C4—C5	1.373 (4)
S2—C6	1.759 (3)	C4—H4	0.9500
S2—C11	1.802 (2)	C5—H5	0.9500
O1—N1	1.309 (3)	C6—C7	1.385 (4)
O2—N2	1.307 (3)	C7—C8	1.383 (4)
N1—C5	1.361 (3)	C7—H7	0.9500
N1—C1	1.366 (3)	C8—C9	1.388 (4)
N2—C10	1.356 (3)	C8—H8	0.9500
N2—C6	1.365 (3)	C9—C10	1.371 (4)
C1—C2	1.386 (4)	C9—H9	0.9500
C2—C3	1.385 (3)	C10—H10	0.9500
C2—H2	0.9500	C11—H11A	0.9900
C3—C4	1.393 (4)	C11—H11B	0.9900
C1—S1—C11	99.12 (11)	C4—C5—H5	119.4
C6—S2—C11	102.00 (12)	N2—C6—C7	120.1 (2)
O1—N1—C5	120.8 (2)	N2—C6—S2	110.72 (19)
O1—N1—C1	118.8 (2)	C7—C6—S2	129.16 (18)
C5—N1—C1	120.4 (2)	C8—C7—C6	119.6 (2)
O2—N2—C10	121.2 (2)	C8—C7—H7	120.2
O2—N2—C6	118.6 (2)	C6—C7—H7	120.2
C10—N2—C6	120.2 (2)	C7—C8—C9	119.5 (3)
N1—C1—C2	120.1 (2)	C7—C8—H8	120.2
N1—C1—S1	111.44 (18)	C9—C8—H8	120.2
C2—C1—S1	128.50 (19)	C10—C9—C8	119.4 (3)
C3—C2—C1	119.5 (2)	C10—C9—H9	120.3
C3—C2—H2	120.3	C8—C9—H9	120.3
C1—C2—H2	120.3	N2—C10—C9	121.1 (2)
C2—C3—C4	120.0 (3)	N2—C10—H10	119.4
C2—C3—H3	120.0	C9—C10—H10	119.4
C4—C3—H3	120.0	S2—C11—S1	110.79 (14)
C5—C4—C3	119.0 (3)	S2—C11—H11A	109.5
C5—C4—H4	120.5	S1—C11—H11A	109.5

C3—C4—H4	120.5	S2—C11—H11B	109.5
N1—C5—C4	121.2 (3)	S1—C11—H11B	109.5
N1—C5—H5	119.4	H11A—C11—H11B	108.1
O1—N1—C1—C2	179.7 (2)	C10—N2—C6—C7	1.9 (3)
C5—N1—C1—C2	−0.4 (4)	O2—N2—C6—S2	0.4 (3)
O1—N1—C1—S1	−0.4 (3)	C10—N2—C6—S2	−179.0 (2)
C5—N1—C1—S1	179.46 (19)	C11—S2—C6—N2	179.53 (17)
C11—S1—C1—N1	−179.00 (19)	C11—S2—C6—C7	−1.5 (3)
C11—S1—C1—C2	0.9 (3)	N2—C6—C7—C8	−0.5 (4)
N1—C1—C2—C3	−0.5 (4)	S2—C6—C7—C8	−179.4 (2)
S1—C1—C2—C3	179.6 (2)	C6—C7—C8—C9	−0.7 (4)
C1—C2—C3—C4	0.7 (4)	C7—C8—C9—C10	0.5 (4)
C2—C3—C4—C5	0.1 (4)	O2—N2—C10—C9	178.4 (3)
O1—N1—C5—C4	−179.0 (3)	C6—N2—C10—C9	−2.2 (4)
C1—N1—C5—C4	1.2 (4)	C8—C9—C10—N2	0.9 (4)
C3—C4—C5—N1	−1.0 (4)	C6—S2—C11—S1	−71.09 (14)
O2—N2—C6—C7	−178.7 (2)	C1—S1—C11—S2	−170.31 (14)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.95	2.37	3.292 (3)	165
C9—H9···O2^{ii}	0.95	2.70	3.405 (4)	131
C11—H11*A*···O1^{iii}	0.99	2.33	3.159 (3)	141

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