

2,2'-Disulfanediybis(pyridine *N*-oxide)–hydrogen peroxide (1/1)

Will Lynch* and Clifford W. Padgett

Georgia Southern University, 11935 Abercorn Street, Savannah, GA 31419, USA. *Correspondence e-mail: wlynch@georgiasouthern.edu

Received 30 January 2018

Accepted 23 February 2018

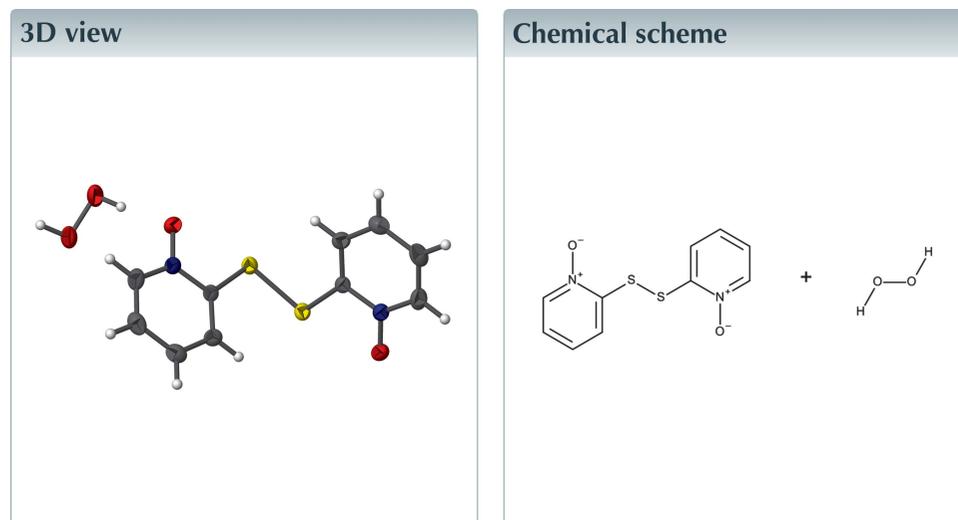
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; 2,2'-dithiobis(pyridine *N*-oxide); hydrogen peroxide; hydrogen bonding; co-crystal.

CCDC reference: 1825502

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

In the title co-crystal, $C_{10}H_8N_2O_2S_2 \cdot H_2O_2$, both molecules are generated by crystallographic twofold symmetry; the dihedral angle between the pyridine rings is $101.16(9)^\circ$. In the crystal, the components are linked by $O-H \cdots O$ hydrogen bonds to generate [010] chains of alternating 2,2'-dithiobis(pyridine *N*-oxide) and hydrogen peroxide molecules. The structure was refined as a two-component inversion twin.



Structure description

The antifungal and antibacterial properties of the bispyrithione family have made the compound 2,2'-dithiobis(pyridine *N*-oxide) of interest for many years (O'Donnell *et al.*, 2009; Paulus, 1993; Zhang *et al.*, 2001). A number of reports on the improved synthesis of the dithiobis compound have also been reported (*e.g.* Li *et al.*, 2012).

The title compound, $C_{10}H_8N_2O_2S_2 \cdot H_2O_2$, is a co-crystal (Fig. 1) formed *via* a hydrogen-bonding network interlinking the dithiobis(pyridine *N*-oxide) molecules with a $C_2^2(12)$ assembly. The hydrogen bond is formed between the peroxide OH moiety and the pyridine *N*-oxide O atom with $O \cdots O = 2.672(3)$ Å (Table 1). The hydrogen bonding network generates [010] chains (Fig. 2) of alternating dithiobis(pyridine *N*-oxide) and hydrogen peroxide molecules. The $O2-O2^{ii}$ and $S1-S1^i$ bond distances are 1.454(4) and 2.067(2) Å, respectively [symmetry codes: (i) $1-x, -y, z$; (ii) $1-x, 1-y, z$]. Both the hydrogen peroxide and the disulfide molecules are generated by crystallographic twofold symmetry. The torsion angle between the pyridine *N*-oxide rings is slightly greater than perpendicular at $101.16(9)^\circ$. The torsion angle $C1-S1-S1^i-C1^i$ that bridges the pyridine rings is slightly less at $100.43(13)^\circ$.

The hydrogen peroxide $H2A-O2-O2^{ii}-H2A^{ii}$ torsion angle is equal to $133.86(7)^\circ$. Similar compounds have been observed to have this torsion angle much closer to 90° . For example the hydrogen peroxide torsion angle in the (*Z*)-*N*-benzylidene-1-phenyl-

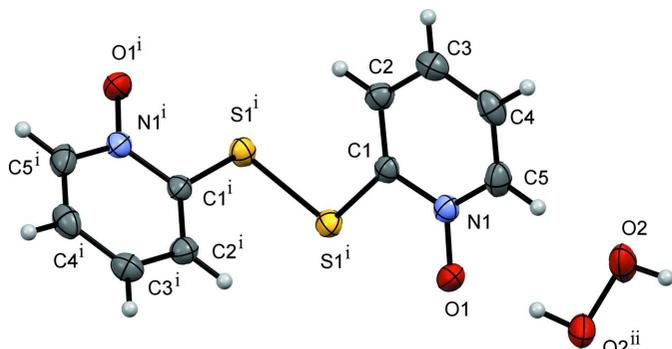


Figure 1
A view of the molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, z$; (ii) $1 - x, 1 - y, z$.]

methanamine oxide solvate is reported to be 88° (Churakov *et al.*, 2017) while a piperazine N-oxide derivative (Ravikumar *et al.*, 2005) is found to be 90° . Similar torsion angles of 101° and lower have been observed in phosphine oxide hydrogen peroxide adducts (see for example Ahn *et al.*, 2015). This large angle can be attributed to the lowest energy confirmation imposed by the solid-state supramolecular structure where the $O1 \cdots O2 - O2^{ii} \cdots O1^{ii}$ pseudo torsion angle (*via* the hydrogen bonds) is $140.06 (6)^\circ$.

Synthesis and crystallization

The title compound was synthesized by modification of the literature procedure (Bernstein & Losee, 1956): 2.0 g of 2-pyridinethiol-*N*-oxide was dissolved in 15 ml of water. To this was slowly added 1.9 ml of 30% hydrogen peroxide. The reaction mixture was stirred for 1 h and a white solid was collected by filtration. The white solid was determined to be 2,2'-dithiobis(pyridine *N*-oxide) as confirmed by ^1H NMR and

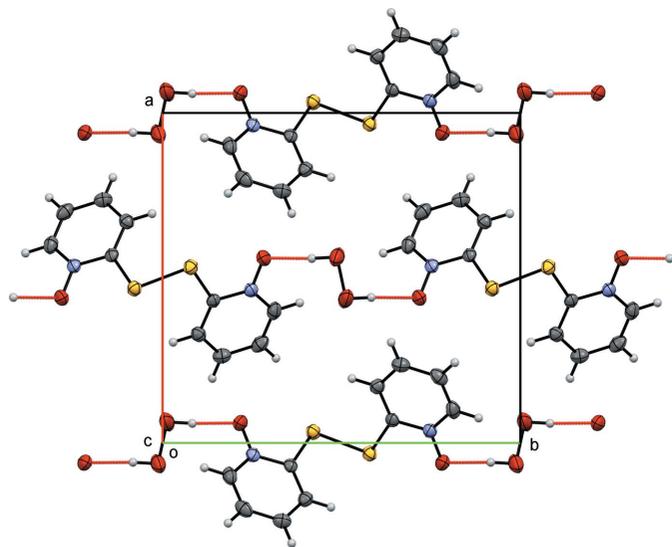


Figure 2
Crystal packing diagram of title compound viewed along $[001]$. Hydrogen bonds are colored red.

Table 1
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2A \cdots O1$	0.95 (3)	1.73 (3)	2.672 (3)	174 (3)

Table 2
Experimental details.

Crystal data	$C_{10}H_8N_2O_2S_2 \cdot H_2O_2$
Chemical formula	286.32
M_r	Orthorhombic, $P2_12_12$
Crystal system, space group	173
Temperature (K)	11.232 (2), 12.283 (3), 4.401 (1)
a, b, c (\AA)	607.2 (2)
V (\AA^3)	2
Z	Mo $K\alpha$
Radiation type	μ (mm^{-1})
μ (mm^{-1})	0.45
Crystal size (mm)	$0.60 \times 0.10 \times 0.10$
Data collection	
Diffractometer	Rigaku XtaLAB mini CCD
Absorption correction	Multi-scan (<i>REQAB</i> ; Rigaku, 1998)
T_{\min}, T_{\max}	0.890, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6396, 1386, 1316
R_{int}	0.045
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.059, 1.05
No. of reflections	1386
No. of parameters	87
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{\AA}^{-3}$)	0.13, -0.18
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.36 (10)

Computer programs: *CrystalClear* (Rigaku, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

melting point. The filtrate was allowed to stand for 4 days, at which time colorless prisms of the title compound were collected in a yield of 12%.

Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. The structure was refined with inversion twinning as the Flack parameter indicated racemic twinning.

Funding information

The authors acknowledge financial support from Armstrong State University.

References

- Ahn, S. H., Cluff, K. J., Bhuvanesh, N. & Blümel, J. (2015). *Angew. Chem. Int. Ed.* **54**, 13341–13345.
Bernstein, J. & Losee, K. A. (1956). US2742476[P]: 1956-04-17.

- Churakov, A. V., Prikhodchenko, P. V., Medvedev, A. G. & Mikhaylov, A. A. (2017). *Acta Cryst.* **E73**, 1666–1669.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Li, S., Li, R. L., Zhang, Z., Zhu, K. & Wang, G. (2012). *Adv. Mater. Res.* **554–556**, 868–873.
- O'Donnell, G., Poeschl, R., Zimhony, O., Gunaratnam, M., Moreira, J. B. C., Neidle, S., Evangelopoulos, D., Bhakta, S., Malkinson, J. P., Boshoff, H. I., Lenaerts, A. & Gibbons, S. (2009). *J. Nat. Prod.* **72**, 360–365.
- Paulus, W. (1993). In *Microbicides for the Protection of Materials: A Handbook*. London: Chapman and Hall.
- Ravikumar, K., Sridhar, B., Manjunatha, S. G. & Thomas, S. (2005). *Acta Cryst.* **E61**, o2515–o2517.
- Rigaku (1998). REQAB. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2009). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Zhang, Y. P., Fan, L. Y. & Tang, N. (2001). *Inorg. Chem.* **17**, 427–429.

full crystallographic data

IUCrData (2018). 3, x180320 [https://doi.org/10.1107/S2414314618003206]

2,2'-Disulfanediybis(pyridine *N*-oxide)–hydrogen peroxide (1/1)

Will Lynch and Clifford W. Padgett

2,2'-(Disulfanediy)bis(pyridine *N*-oxide)–hydrogen peroxide (1/1)*Crystal data*

$C_{10}H_8N_2O_2S_2 \cdot H_2O_2$

$M_r = 286.32$

Orthorhombic, $P2_12_12_1$

$a = 11.232$ (2) Å

$b = 12.283$ (3) Å

$c = 4.401$ (1) Å

$V = 607.2$ (2) Å³

$Z = 2$

$F(000) = 296$

$D_x = 1.566$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 1941 reflections

$\theta = 2.5$ – 27.5°

$\mu = 0.45$ mm⁻¹

$T = 173$ K

Prism, colorless

$0.60 \times 0.10 \times 0.10$ mm

Data collection

Rigaku XtaLAB mini CCD
diffractometer

Radiation source: Sealed Tube

Graphite Monochromator monochromator

Detector resolution: 13.6612 pixels mm⁻¹

profile data from ω -scans

Absorption correction: multi-scan

(*REQAB*; Rigaku, 1998)

$T_{\min} = 0.890$, $T_{\max} = 1.000$

6396 measured reflections

1386 independent reflections

1316 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 27.4^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -14 \rightarrow 14$

$k = -15 \rightarrow 15$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.059$

$S = 1.05$

1386 reflections

87 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 0.1P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.13$ e Å⁻³

$\Delta\rho_{\min} = -0.18$ e Å⁻³

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.36 (10)

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. Refined as a two-component inversion twin. Carbon-bound H-atoms were placed in calculated positions ($C-H = 0.95$ Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(H)$ set to $1.2U_{\text{equiv}}(C)$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.53255 (4)	0.07871 (4)	0.37729 (11)	0.02740 (14)
O1	0.56020 (13)	0.28267 (12)	0.5366 (4)	0.0341 (4)
N1	0.46320 (15)	0.24721 (13)	0.6798 (4)	0.0262 (4)
C1	0.43106 (16)	0.14203 (15)	0.6311 (5)	0.0238 (4)
C2	0.32900 (17)	0.10057 (17)	0.7678 (5)	0.0285 (4)
H2	0.305069	0.029391	0.729631	0.034*
C3	0.2635 (2)	0.16604 (18)	0.9608 (5)	0.0331 (5)
H3	0.195453	0.139037	1.054822	0.040*
C4	0.2999 (2)	0.27245 (19)	1.0134 (5)	0.0352 (5)
H4	0.256619	0.316832	1.144195	0.042*
C5	0.40004 (19)	0.31208 (17)	0.8720 (6)	0.0341 (5)
H5	0.424655	0.383244	0.907584	0.041*
O2	0.56329 (15)	0.48760 (13)	0.3328 (5)	0.0470 (5)
H2A	0.559 (3)	0.417 (2)	0.416 (6)	0.067 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0285 (2)	0.0256 (2)	0.0281 (2)	0.00163 (19)	0.0033 (2)	0.0034 (2)
O1	0.0291 (8)	0.0270 (8)	0.0460 (9)	-0.0033 (6)	0.0009 (7)	0.0068 (7)
N1	0.0260 (8)	0.0239 (8)	0.0286 (8)	0.0002 (7)	-0.0048 (7)	0.0020 (7)
C1	0.0246 (9)	0.0228 (9)	0.0241 (9)	0.0013 (7)	-0.0048 (8)	0.0020 (8)
C2	0.0276 (10)	0.0289 (10)	0.0290 (10)	-0.0025 (8)	-0.0022 (8)	-0.0004 (9)
C3	0.0279 (10)	0.0403 (13)	0.0310 (12)	0.0019 (9)	0.0013 (9)	0.0000 (9)
C4	0.0366 (12)	0.0379 (13)	0.0312 (11)	0.0110 (10)	-0.0020 (9)	-0.0083 (10)
C5	0.0401 (11)	0.0253 (10)	0.0369 (11)	0.0033 (8)	-0.0075 (11)	-0.0054 (10)
O2	0.0433 (9)	0.0287 (9)	0.0688 (11)	0.0072 (7)	0.0155 (9)	0.0110 (9)

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

S1—C1	1.775 (2)	C3—C4	1.389 (4)
S1—S1 ⁱ	2.067 (2)	C3—H3	0.9300
O1—N1	1.332 (2)	C4—C5	1.374 (3)
N1—C1	1.358 (3)	C4—H4	0.9300
N1—C5	1.362 (3)	C5—H5	0.9300
C1—C2	1.391 (3)	O2—O2 ⁱⁱ	1.454 (4)
C2—C3	1.382 (3)	O2—H2A	0.95 (3)
C2—H2	0.9300		
C1—S1—S1 ⁱ	100.52 (9)	C2—C3—C4	119.5 (2)
O1—N1—C1	117.00 (16)	C2—C3—H3	120.2
O1—N1—C5	121.92 (17)	C4—C3—H3	120.2
C1—N1—C5	121.07 (19)	C5—C4—C3	119.9 (2)
N1—C1—C2	119.93 (18)	C5—C4—H4	120.0
N1—C1—S1	110.19 (15)	C3—C4—H4	120.0

C2—C1—S1	129.85 (16)	N1—C5—C4	120.0 (2)
C3—C2—C1	119.5 (2)	N1—C5—H5	120.0
C3—C2—H2	120.3	C4—C5—H5	120.0
C1—C2—H2	120.3	O2 ⁱⁱ —O2—H2A	98.1 (18)

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

Hydrogen-bond geometry (Å, °)

<i>D—H···A</i>	<i>D—H</i>	<i>H···A</i>	<i>D···A</i>	<i>D—H···A</i>
O2—H2A···O1	0.95 (3)	1.73 (3)	2.672 (3)	174 (3)
