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5,5′-Dinitro-2,2′-dithiodipyridine

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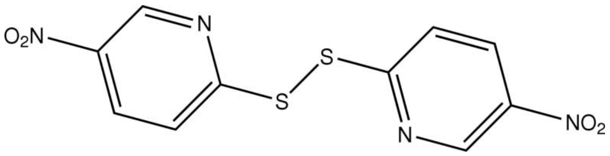
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.139; data-to-parameter ratio = 13.9.

In the title disulfide, (5-$O_2NC_5H_3N)_2S_2$ or $C_{10}H_6N_4O_4S_2$, the molecule has a center of inversion. All bond lengths and angles are within normal ranges, and the molecules are linked into centrosymmetric $R_2^2(22)$ dimers by a simple C—H···O interaction. In the crystal structure, there are no aromatic π–π stacking and no C—H···π(arene) interactions.

Related literature

For related literature, see: Allen (2002); Allen *et al.* (1987); Aupers *et al.* (1999); Bernstein *et al.* (1995); Boese *et al.* (1992); Boonstra (1963); Brito *et al.* (2006); Choi & Abel (1972); Cindric *et al.* (2001); Domenicano & Murray-Rust (1979); Etter *et al.* (1992); Glidewell *et al.* (2000); Herbstein & Kapon (1990); Kucsman *et al.* (1984); López-Rodríguez *et al.* (2006); Low *et al.* (2000); Sekine *et al.* (1994); Shefter (1970); Toma *et al.* (2004); Trotter & Williston (1966).



Experimental

Crystal data

$C_{10}H_6N_4O_4S_2$
M_r = 310.31
Monoclinic, $P2_1/n$
a = 5.2610 (15) Å
b = 6.0440 (13) Å
c = 18.8070 (19) Å
β = 92.839 (12)°
V = 597.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 293 (2) K
0.43 × 0.30 × 0.22 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min}$ = 0.842, $T_{\max}$ = 0.901
3529 measured reflections
1267 independent reflections
1122 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.139
S = 1.08
1267 reflections
91 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\min}$ = −0.31 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2$^{\rm ii}$	0.93	2.58	3.389 (4)	146

Symmetry code: (ii) $x + 1, y + 1, z$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This work was supported by a grant from the Universidad de Antofagasta (DI-1324–06). We thank the Spanish Research Council (CSIC) for providing us with a free-of-charge licence for the Cambridge Structural Database (Allen, 2002) system. AM thanks the Universidad de Antofagasta for a PhD fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2142).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Aupers, J. H., Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Low, J. N. & Wardell, J. L. (1999). *Main Group Chem.* **3**, 23–42.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Boese, R., Bläser, D., Nussbaumer, M. & Krygowski, T. M. (1992). *Struct. Chem.* **3**, 363–368.
Boonstra, E. G. (1963). *Acta Cryst.* **16**, 816–823.
Brito, I., López-Rodríguez, M., Cárdenas, A. & Vargas, D. (2006). *Acta Cryst.* C**62**, o461–o463.
Choi, C. S. & Abel, J. E. (1972). *Acta Cryst.* B**28**, 193–201.
Cindric, M., Strukan, N., Kajfez, T., Giester, G. & Kamenar, B. (2001). *Z. Anorg. Allg. Chem.* **627**, 2604–2608.
Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.
Etter, M. C., McDonald, J. C. & Wanke, R. A. (1992). *J. Phys. Org. Chem.* **5**, 191–200.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Glidewell, C., Low, J. N. & Wardell, J. L. (2000). *Acta Cryst.* B**56**, 893–905.
Herbstein, F. H. & Kapon, M. (1990). *Acta Cryst.* B**46**, 567–572.

doi:10.1107/S1600536807031091

Kucsman, A., Kapovits, I., Parkanyi, L., Argay, G. & Kalman, A. (1984). *J. Mol. Struct.* **125**, 331–347.

López-Rodríguez, M., Brito, I., Vargas, D. & Cárdenas, A. (2006). *Acta Cryst.* E**62**, m2690–m2692.

Low, J. N., Storey, E. J., McCarron, M., Wardell, J. L., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* B**56**, 58–67.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sekine, A., Ohashi, Y., Yoshimura, K., Yagi, M. & Higuchi, J. (1994). *Acta Cryst.* C**50**, 1101–1104.

Shefter, E. J. (1970). *J. Chem. Soc. B*, pp. 903–905.

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

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Toma, M., Sanchez, A., Castellano, E. E. & Ellena, J. (2004). *Rev. Chim.* **55**, 719–723.

Trotter, J. & Williston, C. S. (1966). *Acta Cryst.* **21**, 285–288.

supplementary materials

Acta Cryst. (2007). E**63**, o3351-o3352 [**doi:10.1107/S1600536807031091**]

5,5'-Dinitro-2,2'-dithiodipyridine

I. Brito, A. Mundaca, A. Cárdenas, M. López-Rodríguez and D. Vargas

Comment

This paper forms part of our continuing study of the synthesis and structural characterization of divalent sulfur compounds (Brito *et al.*, 2006 and references therein). We are particularly interested in the utility of the title compound, (Fig. 1 and Table 1), as a flexible ligand, and its binding modes, for the fabrication of different coordination polymer topologies. A database survey of C—S—S—C fragments (Allen *et al.*, 1987) found that S—S bond distances are bimodally distributed; for torsion angles in the ranges 75–105° and 0–20°, S—S bond-distance means were found to be 2.031 (15) and 2.070 (22) Å respectively. The corresponding value in the title compound is 2.0719 (11) Å, placing it in the upper quartile for Allen's first set. Further more, the torsion angles *X*—C—S—S, (where *X*=N or C), N2—C1—S1—S1^i = 5.2 (3)° (symmetry code (i): $-x + 1$, $-y + 1$, $-z$) are close to 0 or 180° and within the range found in other substituted aromatic disulfides with an equatorial conformation according to the Shefter classification (Shefter, 1970). A search in the Cambridge Structural Database (version 5.28; Allen 2002) for the pyridyl disulfide fragment yielded fifteen structures of those which only two have an equatorial conformation, namely *S*,*S*'-bis(3-(Ethoxycarbonyl)pyridin-2-yl)disulfide (refcode TATPUA; Toma *et al.*, 2004), and *S*,*S*'-bis(3-(n-Butoxycarbonyl)pyridin-2-yl)disulfide (refcode OCOYIO; Cindric *et al.*, 2001). The C—S bond length of 1.761 (3) Å is between the value for a C—S single-bond distance of about 1.81 (2) Å and that for a double-bond distance of about 1.56 (4) Å (Etter *et al.*, 1992) and is shorter than to those observed in organic disulfides with an equatorial conformation. Also noteworthy are the C—C—C, C—C—S and C—C—N angles at the *ipso* positions (Table 1), where the C—C—C angles, in particular, are consistent with the electron-donating and electron-withdrawing properties of thiolate and nitro substituents, respectively (Domenicano & Murray-Rust, 1979). The nitro group is nearly coplanar with the adjacent aryl ring (Fig. 1). The C4—N1 bond distance is 1.459 (4) Å; this value is typical of *C*(aryl)-NO_2 distances, where the mean value is 1.468 Å (Allen *et al.*, 1987) with upper and lower quartile values of 1.476 and 1.460 Å respectively.

Molecules of the title compound are linked into centrosymmetric $R_2^2(22)$ dimers by a simple C—H···O interaction,. [H···O = 2.58 Å, O···O = 3.389 (4) Å and C—H···O = 146°]. Nitro atom O_2 in the molecule at ($x + 1$, $y + 1$, $-z$) acts as hydrogen-bond acceptor to a C_2 atom H_2 in the molecule at (x, y, z), so generating a centro-symmetric dimer characterized by $R_2^2(22)$ motif and centred at (1/2, 1/2, 0), Fig. 2, (Bernstein *et al.*, 1995). Such interactions are generally the dominant feature of the crystal structures of compounds containing nitroarenethiolate ($O_2NC_6H_4SX$) fragments (Kucsman *et al.*, 1984; Aupers *et al.*, 1999; Low *et al.*, 2000; Glidewell *et al.*, 2000), as well as those of simple nitrobenzenes (Boonstra, 1963; Trotter & Williston, 1966; Choi & Abel, 1972, Herbstein & Kapon, 1990; Boese *et al.*, 1992; Sekine *et al.*, 1994). The title compound retains equatorial conformation in its complex formed with $AgNO_3$ (to within 22°) (López-Rodríguez *et al.*, 2006). The coordination of silver(I) ion to either sulfur or nitrogen atoms of the title compound has not required an unusual *X*—C—S—S angle (*X*=C or N) angle, therefore the S—S bond is unaffected by complexation (2.031 (2) for the complex and 2.0719 (15) Å for the title compound). The larger observed deviation due to complexation is in the phenyl ring orientation (C—S—S—C = 70.8 (2)° for the complex and 180° for the title compound).

Experimental

A sample of 2,2'-dithio-bis(5-nitropyridine) was purchased from Aldrich. Crystals suitable for single-crystal *x*-ray diffraction analysis were grown by slow evaporation of a solution in ethyl acetate. FT—IR (KBr pellet, cm^{-1}): ν (w, C– H) 3087, ν (s, N = O of NO_2 asymmetric) 1563, ν (v.s. N = O of NO_2 symmetric) 1343, ν (w, C - H disubstitution 1,4) 1958, ν (s, C - H disubstitution 1,4) 856, ν (w, C - N) 1101, ν (s, C = C) 1590, ν (w, C - H) 1006, (s, C = N) 1519, ν (w, C - S) 735, ν (w, S—S) 540.

Refinement

In the final cycles of the refinement, all H atoms were constrained to ride on their parent atoms, with aryl C - H distances of 0.93 Å, and with U_{iso}(H) = 1.2U_{eq}(C). 112 unique reflections were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction.

Figures

Fig. 1. A view of the molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are related to labeled atoms by the symmetry code (−*x* + 1, −*y* + 2, −*z*).

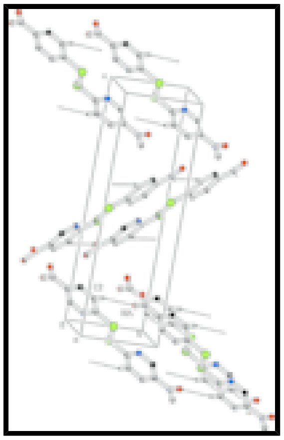


Fig. 2. The molecular packing. Dashed lines indicate hydrogen bond [Symmetry code: (i) *x* + 1, *y* + 1, *z*]. H atoms not involved in hydrogen bonds have been omitted for clarity.

5,5'-Dinitro-2,2'-dithiodipyridine

Crystal data

$C_{10}H_6N_4O_4S_2$
M_r = 310.31
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 5.2610 (15) Å
b = 6.0440 (13) Å

F_{000} = 316
D_x = 1.725 Mg m^{-3}
Melting point: 428-430 K
Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 2999 reflections
θ = 3.5–27.5°

$c = 18.8070$ (19) Å	$\mu = 0.47$ mm^{-1}
$\beta = 92.839$ (12)°	$T = 293$ (2) K
$V = 597.3$ (2) Å^3	Prism, colourless
$Z = 2$	0.43 × 0.30 × 0.22 mm

Data collection

Nonius KappaCCD area-detector diffractometer	1122 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.067$
Monochromator: graphite	$\theta_{\text{max}} = 27.5°$
φ scans, and ω scans with κ offsets	$\theta_{\text{min}} = 3.5°$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$h = -6 \rightarrow 6$
$T_{\text{min}} = 0.842$, $T_{\text{max}} = 0.901$	$k = -6 \rightarrow 7$
3529 measured reflections	$l = -19 \rightarrow 24$
1267 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + 1.3711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$(\Delta/\sigma)_{\text{max}} = 0.014$
$wR(F^2) = 0.139$	$\Delta\rho_{\text{max}} = 0.48$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{\text{min}} = -0.31$ e Å^{-3}
1267 reflections	Extinction correction: none
91 parameters	

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 > 2sigma(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 (Å^2)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
S1	0.64977 (15)	0.47850 (13)	0.03722 (4)	0.0348 (3)
O1	0.4118 (5)	−0.4104 (4)	0.22547 (13)	0.0486 (7)
O2	0.0696 (5)	−0.3958 (5)	0.15797 (16)	0.0615 (9)

N1	0.2791 (5)	−0.3234 (5)	0.17826 (13)	0.0345 (6)
N2	0.3161 (5)	0.1460 (4)	0.05263 (13)	0.0314 (6)
C1	0.5303 (6)	0.2418 (5)	0.07878 (15)	0.0285 (6)
C2	0.6740 (6)	0.1634 (5)	0.13849 (16)	0.0328 (7)
H2	0.8211	0.2363	0.155	0.039*
C3	0.5917 (6)	−0.0239 (5)	0.17193 (16)	0.0322 (7)
H3	0.6816	−0.0821	0.2114	0.039*
C4	0.3700 (6)	−0.1227 (5)	0.14469 (15)	0.0281 (6)
C5	0.2369 (6)	−0.0362 (5)	0.08584 (16)	0.0309 (6)
H5	0.0886	−0.1061	0.0688	0.037*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0363 (5)	0.0301 (4)	0.0372 (4)	−0.0081 (3)	−0.0048 (3)	0.0063 (3)
O1	0.0510 (15)	0.0434 (15)	0.0504 (14)	−0.0051 (12)	−0.0078 (11)	0.0192 (11)
O2	0.0546 (17)	0.0570 (18)	0.0706 (18)	−0.0317 (15)	−0.0185 (13)	0.0224 (15)
N1	0.0384 (15)	0.0303 (14)	0.0346 (13)	−0.0055 (11)	0.0002 (11)	0.0023 (11)
N2	0.0293 (13)	0.0298 (14)	0.0347 (13)	−0.0020 (11)	−0.0022 (10)	0.0018 (10)
C1	0.0319 (15)	0.0249 (14)	0.0289 (14)	−0.0001 (12)	0.0037 (11)	−0.0011 (11)
C2	0.0306 (15)	0.0326 (17)	0.0347 (15)	−0.0058 (13)	−0.0029 (12)	−0.0004 (12)
C3	0.0338 (16)	0.0321 (16)	0.0300 (14)	0.0016 (13)	−0.0042 (11)	0.0025 (12)
C4	0.0298 (15)	0.0236 (14)	0.0311 (14)	0.0000 (12)	0.0026 (11)	−0.0002 (11)
C5	0.0299 (15)	0.0299 (16)	0.0327 (15)	−0.0043 (12)	−0.0006 (11)	−0.0007 (12)

Geometric parameters (Å, °)

S1—C1	1.761 (3)	C1—C2	1.405 (4)
S1—S1^{i}	2.0719 (15)	C2—C3	1.375 (4)
O1—N1	1.221 (3)	C2—H2	0.93
O2—N1	1.229 (4)	C3—C4	1.386 (4)
N1—C4	1.459 (4)	C3—H3	0.93
N2—C1	1.339 (4)	C4—C5	1.383 (4)
N2—C5	1.343 (4)	C5—H5	0.93
C1—S1—S1^{i}	97.22 (11)	C1—C2—H2	120.9
O1—N1—O2	123.0 (3)	C2—C3—C4	117.7 (3)
O1—N1—C4	119.0 (3)	C2—C3—H3	121.2
O2—N1—C4	118.0 (3)	C4—C3—H3	121.2
C1—N2—C5	117.3 (3)	C5—C4—C3	121.1 (3)
N2—C1—C2	123.9 (3)	C5—C4—N1	119.8 (3)
N2—C1—S1	120.0 (2)	C3—C4—N1	119.1 (3)
C2—C1—S1	116.0 (2)	N2—C5—C4	121.7 (3)
C3—C2—C1	118.3 (3)	N2—C5—H5	119.1
C3—C2—H2	120.9	C4—C5—H5	119.1
C5—N2—C1—C2	−0.3 (5)	C2—C3—C4—N1	179.1 (3)
C5—N2—C1—S1	178.9 (2)	O1—N1—C4—C5	172.6 (3)
S1^{i}—S1—C1—N2	5.2 (3)	O2—N1—C4—C5	−8.2 (4)
S1^{i}—S1—C1—C2	−175.5 (2)	O1—N1—C4—C3	−6.4 (4)

N2—C1—C2—C3	0.6 (5)	O2—N1—C4—C3	172.8 (3)
S1—C1—C2—C3	−178.6 (2)	C1—N2—C5—C4	0.0 (4)
C1—C2—C3—C4	−0.5 (5)	C3—C4—C5—N2	0.1 (5)
C2—C3—C4—C5	0.2 (5)	N1—C4—C5—N2	−178.9 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2^{ii}	0.93	2.58	3.389 (4)	146

Symmetry codes: (ii) *x*+1, *y*+1, *z*.

Fig. 1

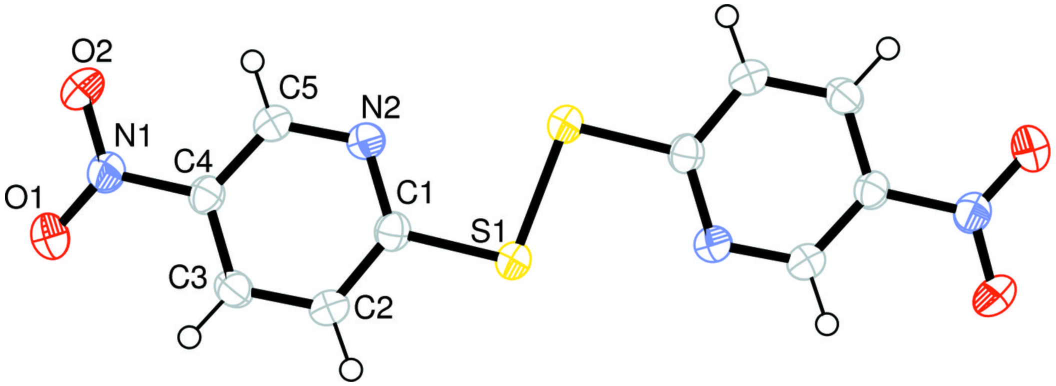


Fig. 2