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3,3′-Dinitro-2,2′-dithiodipyridine

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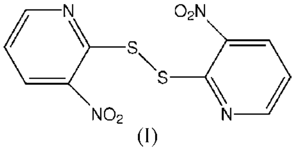
In the title compound, $C_{10}H_6N_4O_4S_2$, (I), the molecule has a centre of inversion. The structure is a positional isomer of 5,5′-dinitro-2,2′-dithiodipyridine [Brito, Mundaca, Cárdenas, López-Rodríguez & Vargas (2007). *Acta Cryst.* E**63**, o3351–o3352], (II). The 3-nitropyridine fragment of (I) shows excellent agreement with the bonding geometries of (II). The most obvious differences between them are in the S—S bond length [2.1167 (12) Å in (I) and 2.0719 (11) Å in (II)], and in the $C—C_{ipso}—N_{ring}$ [119.8 (2)° in (I) and 123.9 (3)° in (II)] and S—C—C [122.62 (18)° in (I) and 116.0 (2)° in (II)] angles. The crystal structure of (I) has an intramolecular C—H···O interaction, with an H···O distance of 2.40 (3) Å, whereas this kind of interaction is not evident in (II). The molecules of (I) are linked into centrosymmetric $R_4^4(30)$ motifs by a C—H···O interaction. There are no aromatic π–π stacking and no C—H···π(arene) interactions. Compound (I) can be used as a nucleophilic tecton in self-assembly reactions with metal centres of varying lability.

Comment

This paper forms part of our continuing study of the synthesis and structural characterization of divalent sulfur compounds (Brito *et al.*, 2007, and references therein). We report here the structure of the title compound, (I), isolated during attempts to synthesize coordination polymers with 5,5′-dinitro-2,2′-dithiodipyridine, (II), and silver trifluoromethanesulfonate. Compound (II) was purchased from Aldrich (purity 96%, CAS No. 2127-10-8). Impurities were not identified in the technical information accompanying the compound, but we believe that (I) was probably an impurity in the commercial sample of (II). To our knowledge, compound (I) is not commercially available.



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The asymmetric unit of (I) consists of one half-molecule on an inversion centre. A 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°, the mean S—S bond distances are 2.031 (15) and 2.070 (22) Å, respectively. The corresponding value in (I) is 2.1166 (10) Å, placing it in the upper quartile for Allen's first set. In both isomers, the *X*—C—S—S torsion angles (where *X* = N or C) 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 of the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) for the pyridyl disulfide fragment yielded 15 structures, of which only two have an equatorial conformation and S—S and C—S bond lengths similar to those of (I), namely *S*,*S*′-bis[3-(ethoxycarbonyl)pyridin-2-yl] disulfide (CSD refcode TATPUA; Toma *et al.*, 2004), and *S*,*S*′-bis[3-(*n*-butoxycarbonyl)pyridin-2-yl] disulfide (CSD refcode OCOYIO; Cindric *et al.*, 2001). The C1—S1 bond length of 1.771 (2) Å in (I) is between the C—S single-bond distance of 1.81 (2) Å and the double-bond distance of 1.56 (4) Å (Etter *et al.*, 1992) and is similar 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-withdrawing properties of nitro substituents (Domenicano & Murray-Rust, 1979). The nitro group is rotated 11.0 (3)° out of the plane of the pyridine ring (Fig. 1). The molecular conformations are dominated by the near orthogonality of the lone pairs on the two adjacent S atoms (Glidewell *et al.*, 2000).

The molecular packing of (I) (Fig. 2) is completely different from that of the 5,5′-isomer. Only in the 3,3′-isomer, (I), does the nitropyridine ring participate in significant intramolecular C—H···O interactions, with an H···O distance of 2.40 (3) Å. These interactions may stabilize the conformation adopted by the molecule in the solid state (Fig. 1). The molecules are

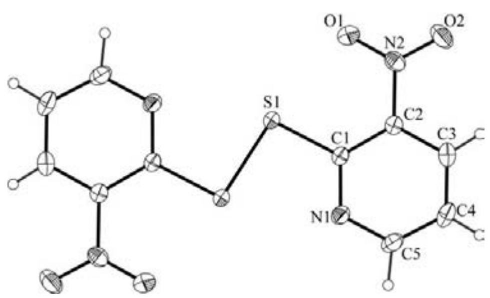


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x$, $-y$, $-z + 1$).

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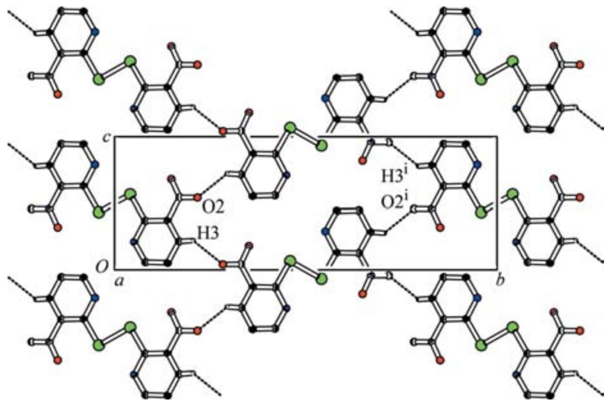

Figure 2
Part of the crystal structure of (I), showing the formation of a cyclic $R_4^4(30)$ pattern. H atoms not involved in the motif shown have been omitted. [Symmetry code: (i) $-x$, $-y + 1$, $-z + 1$.]

linked into centrosymmetric rings with an $R_4^4(30)$ motif (Bernstein *et al.*, 1995) centred at $(0, \frac{1}{2}, \frac{1}{2})$ (Fig. 2 and Table 2).

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. 5,5′-Dinitro-2,2′-dithiodipyridine and silver trifluoromethanesulfonate were purchased from Aldrich and used without further purification. The title compound was obtained in an attempt to prepare coordination polymers with silver trifluoromethanesulfonate and the ligand. A mixture of 5,5′-dinitro-2,2′-dithiodipyridine (1 mmol, 310 mg) and silver trifluoromethanesulfonate (1 mmol, 256.9 mg) in methanol (20 ml) was refluxed for 8 h. After slow cooling of the reaction system to room temperature, pale-yellow prismatic crystals of (II) and colourless needle-shaped crystals of (I) were formed. Samples of the two isomers were isolated manually at ambient temperature. The spectroscopic properties of (I) were not determined due to the small amount of sample available.

Crystal data

$C_{10}H_6N_4O_4S_2$
$M_r = 310.31$
Monoclinic, $P2_1/c$
$a = 3.8320$ (17) Å
$b = 21.4002$ (12) Å
$c = 7.8301$ (14) Å
$\beta = 108.339$ (10)°
$V = 609.5$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.46$ mm^{-1}
$T = 298$ (2) K
0.20 × 0.05 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.970$, $T_{\max} = 0.987$
4650 measured reflections
1335 independent reflections
1177 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.100$
$S = 1.22$
1335 reflections
103 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

All H atoms were located in a difference map and their positional and isotropic displacement parameters were refined.

Table 1
Selected bond and torsion angles (°).

N1—C1—C2	119.8 (2)	C4—C3—C2	118.1 (3)
N1—C1—S1	117.62 (18)	C3—C4—C5	118.4 (3)
C2—C1—S1	122.62 (18)	N1—C5—C4	124.3 (3)
C3—C2—C1	121.0 (2)		
S1^i—S1—C1—N1	3.70 (19)	S1^i—S1—C1—C2	−176.16 (18)

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

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O2	0.89 (3)	2.40 (3)	2.714 (4)	101 (2)
C3—H3···O2^{ii}	0.89 (3)	2.58 (3)	3.335 (4)	143 (2)

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

Data collection: *COLLECT* (Nonius, 1998); cell refinement and data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3134). Services for accessing these data are described at the back of the journal.

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