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5-(5-Nitropyridin-2-yldithio)-1-phenyl-1*H*-tetrazole

Iván Brito,[a]* Aldo Mundaca,[a] Alejandro Cárdenas[b] and Matías López-Rodríguez[c]

[a]Departamento de Química, Facultad de Ciencias Básicas, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile, [b]Departamento de Física, Facultad de Ciencias Básicas, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile, and [c]Instituto de Bio-Orgánica 'Antonio González', Universidad de La Laguna, Astrofísico Francisco Sánchez No. 2, La Laguna, Tenerife, Spain.
Correspondence e-mail: ivanbritob@yahoo.com

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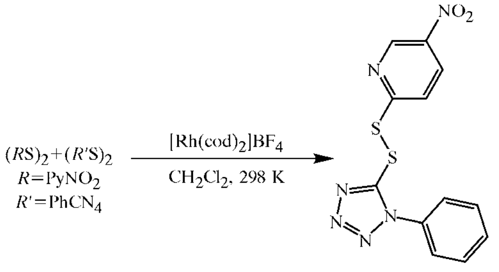
In the title disulfide, $C_{12}H_8N_6O_2S_2$, all bond lengths and angles are within normal ranges, and the molecules are linked into centrosymmetric $R_2^2(20)$ dimers by simple C—H···N interactions. Weak intermolecular C—H···π(arene) and π–π interactions, involving the benzene CH groups and the benzene rings, and the pyridine rings, respectively, further stabilize and reinforce the crystal structure.

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 synthesis of unsymmetrical disulfides as flexible ligands, and in their binding modes for the fabrication of different coordination polymer topologies.



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1 and selected geometric parameters are given in Table 1. Yellow crystals of (I) were obtained from the rhodium(I) complex-catalyzed reaction of 5,5′-dinitro-2,2′-dithiodipyridine with 5,5-dithiobis(1-phenyl-1*H*-tetrazole). The molecule consists of a 5-nitropyridine ring and a 1-phenyl-1*H*-tetrazole ring linked by a bridging disulfide group.

A search of the Cambridge Structural Database (CSD, Version 5.28 of May 2007; Allen, 2002) did not find any disulfide compounds with the 1-phenyl-1*H*-tetrazole fragment. The 5-nitropyridine fragment of (I) shows excellent agreement with the bonding geometries of previously reported structures (Brito, Mundaca *et al.*, 2007). The nitro group is rotated by about −12.3 (4)° out the plane of the pyridine ring. In the strongly electronegative 1-phenyltetrazole system, the tetrazole ring is planar, with a mean deviation from the least-squares plane of 0.0036 (17) Å. The dihedral angle between the least-squares planes of the tetrazole and benzene rings is 55.17 (11)°. The tetrazole ring geometry is normal and in agreement with the average values found in 69 entries with the S substituent at C5 for 1,5-disubstituted tetrazoles with alkyl or aryl substituents found in a search of the CSD, as are all other geometric parameters, which fall within the expected ranges.

The gross structure adopted by compound (I) is essentially the same as those reported previously for the precursor products, namely 5,5′-dinitro-2,2′-dithiodipyridine (Brito, Mundaca *et al.*, 2007) and 5,5′-dithiobis(1-phenyl-1*H*-tetrazole) (Brito, Cárdenas *et al.*, 2007). The larger observed differences between (I) and 5,5′-dinitro-2,2′-dithiodipyridine are only in the N—C—S and C—C—S angles [109.64 (18) and 125.8 (2)°, and 120.02 (2) and 116.0 (2)°, respectively]. 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°, the mean S—S bond distances are 2.031 (15) and 2.070 (22) Å, respectively. The corresponding value in the title compound is 2.0427 (10) Å, placing it in the lower quartile for Allen's first set. The N1—C1 bond length is 1.441 (3) Å, which is almost the same as a normal N—C(phenyl) single bond. These facts indicate that conjugation effects between the benzene and tetrazole rings in (I) are negligible (Lyakhov *et al.*, 2006). The C—S bond lengths differ by 0.019 Å and this, coupled with the apparent lack of S—S double-bond character, shows that there is probably no communication between the two ring systems *via* the disulfide bridge, despite having a π donor at one end and a π acceptor at the other. Using a bond length–bond order relationship (Pauling, 1960; Bürgi & Dunitz, 1987), it can be shown that the C—S bonds in compound (I) have partial double-bond character of 12 (1.78 Å) and 20% (1.76 Å),

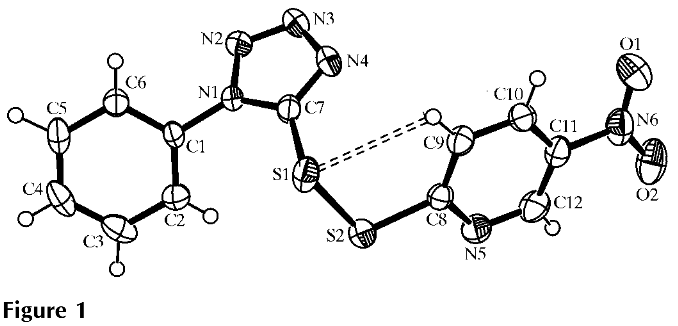


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is indicated by a double-dashed line.

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respectively. The latter value is different from that found in, say, 5,5′-dithiobis(1-phenyl-1*H*-tetrazole), where the sulfide linkage has about 35% double-bond character. The relationship between bond order (n) and bond length (r_n) for sulfur compounds ($r_n = r_l - 0.27\ln n$) has been derived from the following standard (r_l) bond lengths: C—S (single bond, $n = 1$) = 1.81 Å (dimethyl sulfide, ethyl methyl sulfide; Lide, 1993), C—S (double bond, $n = 2$) = 1.61 Å (thioformaldehyde; Lide, 1993) and C—S (triple bond, $n = 3$) = 1.54 Å (carbon monosulfide; Bell *et al.*, 1972).

The molecular conformations are dominated by the near orthogonality of the lone pairs on the two adjacent S atoms (Glidewell *et al.*, 2000). Furthermore, a short intramolecular C9—H9···S1 contact (Table 2) may stabilize the conformation adopted by the molecule in the solid state (Fig. 1). The molecules are linked into centrosymmetric $R_2^2(20)$ dimers centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) by simple C—H···N interactions (Bernstein *et al.*, 1995). Aromatic atom C3 at (x, y, z) acts as a hydrogen-bond donor to atom N5 at ($-x + 1$, $-y + 1$, $-z + 1$) (Fig. 2).

The crystal structure is further stabilized and reinforced by weak intermolecular C—H···π(arene) interactions, involving the benzene C—H groups and the benzene rings (Fig. 3 and Table 2), and by π–π interactions (Fig. 3). The π–π interactions occur between pyridine rings at (x, y, z) and ($-x + 1$, $-y + \frac{1}{2}$, z), with a centroid-to-centroid distance of 3.894 (4) Å and a dihedral angle between the ring planes of 0.02 (1)°; these values are ideal for the development of this type of interaction.

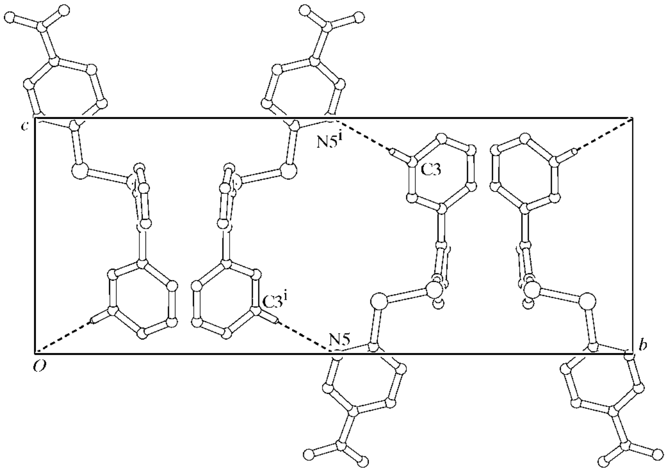

Figure 2
A fragment of the structure of (I), viewed along the *a* axis. Dashed lines show C—H···N interactions. Only H atoms participating in hydrogen bonding are shown. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 1$.]

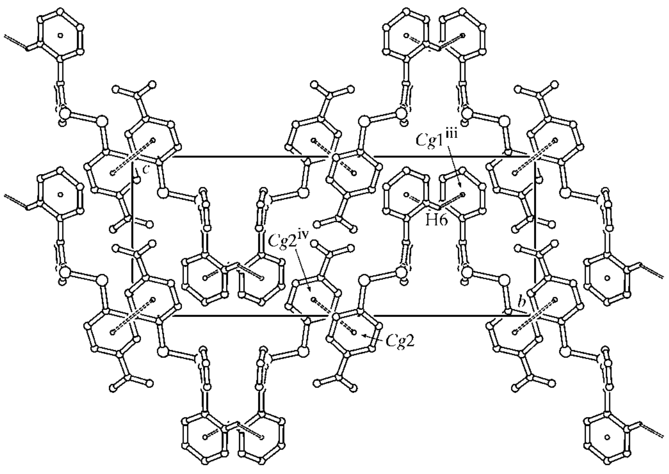

Figure 3
The crystal structure of (I), viewed along the *a* axis. Dashed lines show C—H···*Cg*1 and *Cg*2···*Cg*2 interactions. Only H atoms participating in hydrogen bonding are shown. *Cg*1 and *Cg*2 are the centroids of the rings defined by atoms C1–C6 and N5/C8–C12, respectively. [Symmetry codes: (iii) $x - \frac{1}{2}$, $-y + \frac{3}{2}$, z; (iv) $-x$, $-y + 1$, $-z$.]

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents used were dried and distilled prior to use. The title compound was obtained as yellow block-shaped crystals according to the method described by Tanaka & Ajiki (2004). Into a 20 ml three-necked flask equipped with an overhead stirrer were placed 5,5′-dithiobis(1-phenyl-1*H*-tetrazole) (177.2 mg, 4 mmol) and 4-nitrophenyl disulfide (38.54 mg, 1 mmol) in CH_2Cl_2 (5 ml). Once the components were mixed, bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, $[Rh(cod)_2]BF_4$ (6 mg, 0.03 mmol), was added and the resulting mixture stirred for 3 h at room temperature. The resulting solution was kept at 298 K for 1.5 h under air. The solution was concentrated and purified by silica-gel chromatography (hexane–EtOAc = 20:1 *v*/*v*). Yellow block-shaped crystals of (I) suitable for X-ray analysis were grown from a solution in hexane–EtOAc (1:1 *v*/*v*) at 298 K over a period of a few days in air. Analysis: m.p. 393–394 K; FT–IR (KBr pellet, cm^{-1}): ν(*s*, C—H) 3066, ν(*s*, C—H monosubstitution) 766, ν(*s*, C═C) 1384, ν(*s*, C═C) 1593, ν(*m*, C═N) 1524, ν(*w*, C—S) 740, ν[*s*, N═O of NO_2 (symmetric)] 1345, ν[*s*, N═O of NO_2 (asymmetric)] 1566, ν(*w*, S—S) 555.

Crystal data

$C_{12}H_8N_6O_2S_2$
$M_r = 332.36$
Monoclinic, $P2_1/a$
$a = 7.4161$ (2) Å
$b = 21.6740$ (6) Å
$c = 9.0312$ (3) Å
$\beta = 108.233$ (6)°
$V = 1378.76$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.40$ mm^{-1}
$T = 295$ (2) K
0.22 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.910$, $T_{\max} = 0.943$
9028 measured reflections
3104 independent reflections
2656 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.139$
$S = 1.16$
3104 reflections
231 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

All H atoms were located in a difference map and their positional and isotropic displacement parameters were refined freely [C—H = 0.86 (3)–0.99 (3) Å]. 67 reflections were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction.

Table 1
Selected geometric parameters (Å, °).

S1—C7	1.760 (2)	S2—C8	1.779 (2)
S1—S2	2.0427 (10)	N1—C1	1.441 (3)
C7—S1—S2	102.68 (9)	N1—C7—S1	126.05 (18)
C8—S2—S1	105.70 (9)	N5—C8—S2	109.64 (18)
O1—N6—O2	124.8 (3)	C9—C8—S2	125.8 (2)
N4—C7—S1	125.03 (19)		
C7—S1—S2—C8	76.98 (12)	S1—S2—C8—N5	−175.69 (16)
S2—S1—C7—N4	−79.3 (2)		

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N5^{i}	0.94 (4)	2.61 (4)	3.488 (4)	156 (3)
C9—H9···S1	0.95 (3)	2.80 (3)	3.256 (3)	110.5 (19)
C6—H6···*Cg*1^{ii}	0.89 (3)	2.84 (3)	3.558 (3)	139 (2)

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

Data collection: *COLLECT* (Nonius, 2000); 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3052). Services for accessing these data are described at the back of the journal.

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