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5,5′-Dithiobis(1-phenyl-1*H*-tetrazole)

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.054
wR factor = 0.149
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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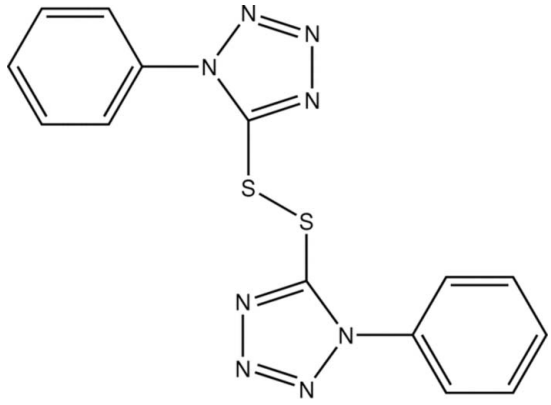
The structure of the title compound, $C_{14}H_{10}N_8S_2$, comprises two 1-phenyl-1*H*-tetrazole-5-thiolate units linked by an S—S disulfide bridge. The C—S—S—C torsion angle is 81.9 (1)°. C—H···N hydrogen bonding, with C···N = 3.413 (4) Å and C—H···N = 147°, link the molecules into supramolecular chains in the crystal structure.

Comment

Organic disulfides are of commercial importance for their anti-wear properties as additives in lubricating oils (Allum & Ford, 1965; Allum & Forbes, 1967), and are also important biologically, being present in molecules such as cystine, ribonuclease and insulin. We report here the structure of the title compound, (I), isolated during an attempt to prepare an unsymmetrical disulfide (Tanaka & Ajiki, 2004).



(I)

The molecular structure of (I) with the atom-numbering scheme is shown in Fig. 1 and selected geometric parameters are given in Table 1. The bond lengths and angles are nearly identical in the two halves of the molecule. As is usual for substituted 1*H*-tetrazoles (Wang *et al.*, 2005), atoms C1 and C9 have a distorted trigonal geometry (Table 1). The C1—S1—S2—C8 torsion angle and S1—S2 bond length are 81.9 (1)° and 2.0128 (9) Å, respectively. These values compare well with those of 80.4 (2)° and 2.055 (3) Å in bis-(2-(2-oxazolin-yl)phenyl)disulfide as one representative example (Kumar *et al.*, 2004). The *p*–π conjugation of the S atoms with the tetrazole rings affects the C—S bond distances (Table 1). The dihedral angles between the phenyl rings and the attached tetrazolyl ring C2–C7/C1–N4 and C9–C14/C8–N8 are 54.4 (9)° and 42.8 (8)°, respectively.

The conformation of (I) is stabilized by one intramolecular hydrogen bond involving atom C14 as donor, C14—H14···S2

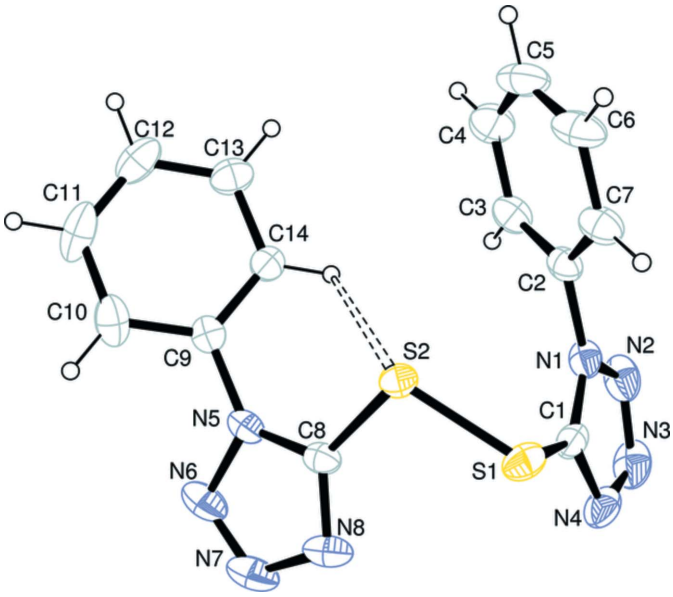


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radius. The dashed line denotes the intramolecular hydrogen bond.

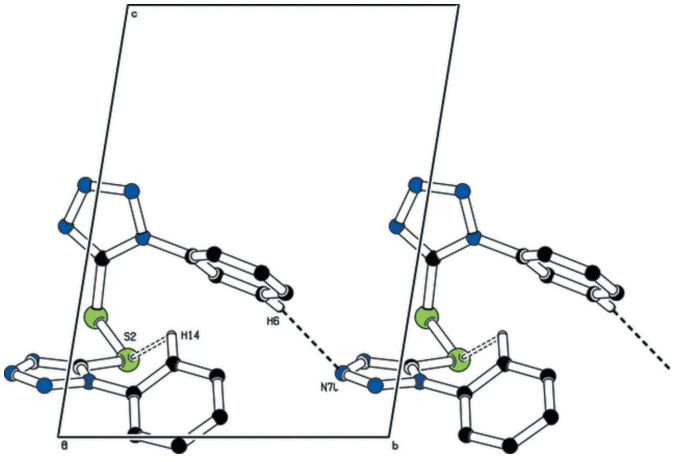


Figure 2
Part of the structure of (I), showing hydrogen-bonding (dashed lines) interactions and the *C*(11) chain. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) $x-1, y+1, z$]

(Fig. 1). Additional interactions (C—H···N and π–π) (Fig. 2) serve to further stabilize the structure. Aromatic atom C6 at (x, y, z) acts as a hydrogen-bond donor to N7 at ($x-1, y+1, z$) (Etter *et al.*, 1990). The π–π stacking involves the tetrazole ring of the 1-phenyl-1*H*-tetrazole group. The ring in the molecule at (x, y, z) stacks above the ring at ($-x+1, -y, -z+1$) across the centre of inversion at ($\frac{1}{2}$, 0, $\frac{1}{2}$), with a distance of 3.507 (2) Å between the ring centroids, a perpendicular distance between the rings of 3.323 (2) Å and a centroid offset of 1.119 (2) Å; these dimensions are ideal for the development of stacking interactions (Fig. 3) (Hunter, 1994).

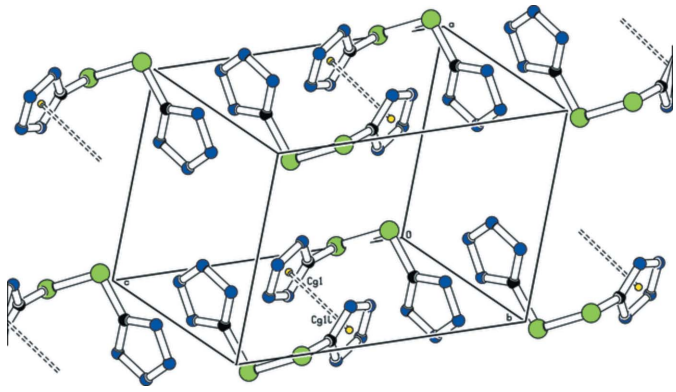


Figure 3
Part of the crystal structure of (I), showing one of the $\pi\cdots\pi$ stacking interactions (dashed lines). For clarity, H atoms and phenyl rings not involved in the motif shown have been omitted. *Cg*1 is the centroid of the five-membered C1/N1/N2/N3/N4 ring. [Symmetry code: (i) $-x+1, -y, -z+1$].

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. The title compound was obtained in an attempt to prepare an unsymmetrical disulfide using 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). After mixing, bis(1,5-cyclooctadiene)rhodium(I) tetrafluoridoborate (6 mg, 0.03 mmol) was added and the reaction mixture was 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). Yellow block-shaped crystals of (I) suitable for X-ray analysis were grown from a hexane/EtOAc solution (1:1 *v*/*v*) at 298 K over a period of a few days. FT–IR (KBr pellet, cm^{-1}): ν (*s*, C—H) 692, ν (*s*, C—H) 760, ν (*m*, C—H) 1107, ν (*s*, C=C) 1384, ν (*s*, C=C) 1497, ν (*m*, C=N) 1594.

Crystal data

$C_{14}H_{10}N_8S_2$
M_r = 354.42
Triclinic, $P\overline{1}$
a = 7.2410 (10) Å
b = 9.2360 (14) Å
c = 11.7760 (19) Å
α = 80.97 (2)°
β = 89.382 (10)°
γ = 74.66 (3)°
V = 749.7 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 298 (2) K
0.42 × 0.23 × 0.12 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.900, T_{max} = 0.952
6734 measured reflections
3524 independent reflections
2979 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.149
S = 1.11
3524 reflections
219 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—S2	2.0128 (9)	N1—C2	1.423 (3)
S1—C1	1.724 (3)	N5—C9	1.424 (3)
S2—C8	1.739 (2)		
C1—S1—S2	102.13 (8)	N4—C1—S1	123.4 (2)
C8—S2—S1	102.83 (8)	N1—C1—S1	127.41 (17)
C1—N1—C2	131.64 (19)	N8—C8—N5	109.6 (2)
C8—N5—C9	131.47 (18)	N8—C8—S2	127.8 (2)
N4—C1—N1	109.1 (2)	N5—C8—S2	122.48 (16)

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···N7^{i}	0.93	2.60	3.413 (4)	147
C14—H14···S2	0.93	2.78	3.202 (2)	108

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

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). 104 unique reflections with sin $\theta/\lambda < 0.6$ and 192 with sin $\theta/\lambda > 0.6$ were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction.

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).

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References

Allum, K. G. & Forbes, E. S. (1967). *J. Inst. Petrol.* **53**, 173–178.
Allum, K. G. & Ford, J. F. (1965). *J. Inst. Petrol.* **51**, 145–161.
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.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hunter, C. A. (1994). *Chem. Soc. Rev.* **23**, 101–109.
Kumar, S., Kandasamy, K., Singh, H. B. & Butcher, R. J. (2004). *New J. Chem.* **28**, 640–645.
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.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Tanaka, K. & Ajiki, K. (2004). *Tetrahedron Lett.* **45**, 5677–5676.
Wang, W., Zhao, B. & Zhang, W.-Q. (2005). *Acta Cryst.* E**61**, o1639–o1640.