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4,4′-Bis(2-pyridyl)-3,3′-bi-1,2,5-thiadiazole

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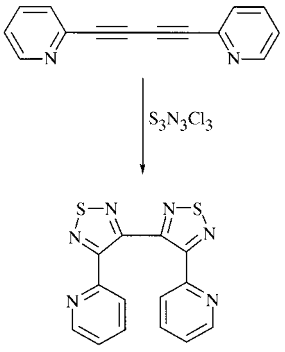
The title compound, $C_{14}H_8N_6S_2$, crystallizes with the planes of the two central 1,2,5-thiadiazole rings orthogonal and with the pyridine rings approximately coplanar with their attached 1,2,5-thiadiazole rings.

Comment

We are currently studying the synthesis and metal complexes of new chelating and bridging heterocyclic ligands that incorporate less commonly encountered heterocyclic rings as donor subunits. For example, we have reported a number of chelating ligands which contain tetrazole (Downard *et al.*, 1995), furoxan (Richardson & Steel, 2000*a*), benzisoxazole (Richardson & Steel, 2000*b*) and benzotriazole (Richardson & Steel, 2001) rings. As part of this work, we have synthesized a number of ligands containing a 1,2,5-thiadiazole ring. Of the several synthetic methods for this ring system, the most general has been the reaction of disulfur dichloride with 1,2-diamines or dioximes (Weinstock *et al.*, 1967). Recently, Rees and co-workers introduced a new efficient method for the synthesis of 1,2,5-thiadiazoles based on reactions of trithiazyl trichloride with alkenes and alkynes (Duan *et al.*, 1996). They have further shown that this reaction is applicable to a range of substrates (Duan *et al.*, 1997; Duan & Rees, 1997). We have utilized this method for the synthesis of the title compound, (I), which was prepared by reaction of $S_3N_3Cl_3$ with 1,4-bis(2-pyridyl)buta-1,3-diyne. In view of our interest in the structures and conformations of biheterocycles (Steel, 1996*a*,*b*) and quaterheterocycles (Honey & Steel, 1991; Phillips & Steel, 1995), we have determined the X-ray crystal structure of (I) at 163 K.



(I)

The ligand crystallizes in the triclinic space group $P\overline{1}$, with one full molecule in the asymmetric unit (Fig. 1). Interestingly, the 1,2,5-thiadiazole rings are approximately orthogonal to each other [84.1 (1)°]. The two halves of the molecule differ in the conformations about the inter-ring bonds. Although both pyridine–thiadiazole bonds have *s-trans* conformations, in one half of the molecule, the thiadiazole (S1–N5) and its attached pyridine ring (N1″–C6″) are coplanar [2.9 (1)°], while for the other half, there exists a slight twist of the pyridine away from the plane of the thiadiazole [17.7 (1)°]. Thus, there is conjugation of the π-systems within each pyridylthiadiazole subunit, but this does not extend over the whole molecule due to the non-planarity of the central bithiadiazole subunit. The bonding geometry of each thiadiazole ring is similar to that found in 3,4-diphenyl-1,2,5-thiadiazole (Mellini & Merlino, 1976).

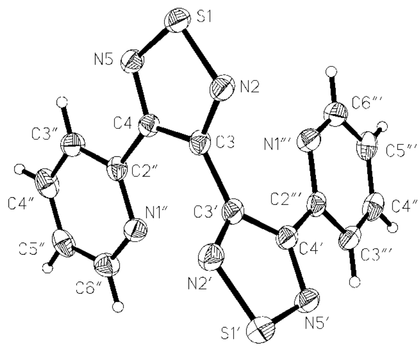


Figure 1
Perspective view and atom labelling of the structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

Inspection of the molecular packing reveals a number of relatively short intermolecular interactions. Firstly, the molecules associate into dimers through a pair of electrostatic interactions between electron-deficient S atoms (S1) and electron-rich N atoms (N5) of two molecules related by a crystallographic centre of inversion [N5···S1* 3.124 (2) Å; * is equivalent position $-x, 1-y, 1-z$]. These dimeric pairs further associate by S···N interactions of the same thiadiazole ring with the other thiadiazole ring of an adjacent molecule displaced one unit cell along the a axis [S1···N2′# 3.302 (2) Å and N2···S1′# 3.331 (2) Å; # is equivalent position $1+x, y, z$]. These interactions (Fig. 2) are all less than the sum of the van der Waals radii of N and S (3.35 Å), and are similar in nature to those previously noted in structurally related molecules (Mellini & Merlino, 1976). In addition to these electrostatic interactions, there are π–π stacking interactions (not shown in Fig. 2) between cofacial pyridine rings (N1‴–C6‴, *e.g.* between molecules at x, y, z and $-x, 2-y, 2-z$) of molecules related by a centre of inversion and separated by 3.41 Å.

This represents the first structure determination of a bi-1,2,5-thiadiazole (Steel, 1996*a*). Metal complexes of this new ligand will be reported elsewhere.

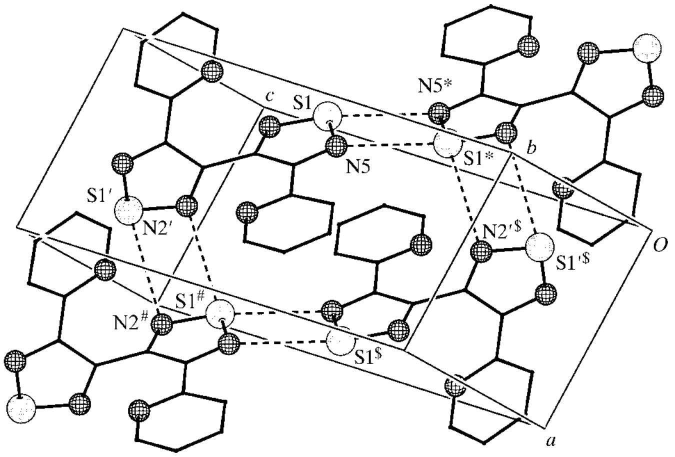


Figure 2
The crystal packing showing the intermolecular S···N interactions. H atoms are not shown. The symbols *, # and \$ represent equivalent positions $-x, 1-y, 1-z$; $1+x, y, z$; and $1-x, 1-y, 1-z$, respectively.

Experimental

The title compound was prepared from 1,4-bis(2-pyridyl)buta-1,3-diyne by reaction with trithiazyl trichloride. Full details will be described elsewhere. Crystals were obtained by slow evaporation of an ethanol solution.

Crystal data

$C_{14}H_8N_6S_2$
$M_r = 324.38$
Triclinic, $P\overline{1}$
$a = 6.330\ (5)$ Å
$b = 9.007\ (7)$ Å
$c = 12.250\ (10)$ Å
$\alpha = 84.427\ (9)°$
$\beta = 85.113\ (9)°$
$\gamma = 79.425\ (9)°$
$V = 681.6\ (9)$ Å^3
$Z = 2$
$D_x = 1.580$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2500 reflections
$\theta = 2.8$–$26.3°$
$\mu = 0.395$ mm^{-1}
$T = 163\ (2)$ K
Irregular fragment, colourless
$0.46 \times 0.34 \times 0.10$ mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.827$, $T_{\max} = 1.000$
8929 measured reflections
2772 independent reflections
2016 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\max} = 26.45°$
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 0.997$
2772 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1157). Services for accessing these data are described at the back of the journal.

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