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2,2′-[1,2-Phenylenebis(methylenethio)]-bis(5-methyl-1,3,4-thiadiazole)

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The title compound (PBT), $C_{14}H_{14}N_4S_4$, possesses C_2 symmetry, with the twofold axis bisecting the central benzene ring. The two terminal 2-(5-methyl-1,3,4-thiodiazolyl)thio groups adopt a *trans* conformation with respect to the benzene moiety, and the dihedral angle between the two thiodiazole planes is 61.3 (2)°, while that between the thiodiazole and benzene planes is 79.4 (5)°.

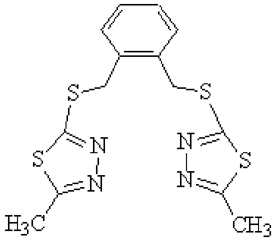
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.078
Data-to-parameter ratio = 14.8

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

Comment

In current coordination and supramolecular chemistry, the rational design of coordination architectures represents one of the most exciting and rapidly developing fields, owing to their potential as functional materials (Braga *et al.*, 1998). The design of ligands is important in adjusting the coordination framework, and the alternation of the coordinating donor may lead to the formation of unique frameworks with tailored properties and functions. Heteroaryl thioether ligands have shown interesting coordination chemistry with metal ions, but they are mainly restricted to pyridine derivatives (Hartshorn *et al.*, 1998), and a small number of examples with other heteroaryl thioether ligands have been reported (Hong *et al.*, 2000; Yang *et al.*, 1997). Herein we report the synthesis and structure of a new ligand, (I) (PBT), which contains two 2-(5-methyl-1,3,4-thiadiazolyl)thio groups separated by an *o*-xylenediyl spacer.



(I)

As shown in Fig. 1, the molecule of PBT possesses C_2 symmetry, with the twofold axis bisecting the central benzene ring. The two terminal 2-(5-methyl-1,3,4-thiodiazolyl)thio groups adopt a *trans* conformation with respect to the benzene moiety, and the dihedral angle between the two thiodiazole planes is 61.3 (2)°. The pseudo-torsion angle of the two C—S bonds (S2—C4···C4*A*—S2*A*) is 139.9 (4)°, forcing the two thiodiazole rings to point in opposite directions and reducing the steric repulsion between them. The dihedral angles between the two terminal groups and the central benzene ring are both 79.4 (5)°.

Because of the π–π conjugation of S2 with the thiodiazole ring, the bond distance C3—S2 [1.746 (2) Å] is obviously

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shorter than C4—S2 [1.825 (2) Å]. A similar effect has been found in 2,2′-[1,4-phenylenebis(methylenethio)]bisthiazole (Zhang *et al.*, 2003).

Experimental

The title compound was synthesized as follows: 5-methyl-2-sulfanyl-1,3,4-thiodiazole (1.32 g, 10 mmol) was added to a stirred solution of KOH (0.56 g, 10 mmol) in ethanol (20 ml). The mixture was warmed to reflux, then 1,2-dibromomethylbenzene (1.32 g, 5 mmol) in tetrahydrofuran (5 ml) was added dropwise and the mixture was refluxed for about 6 h. The precipitate was filtered off and washed with water and ethanol, giving a fine white powder in 80% yield. m.p.: 387–388 K; IR (KBr): 2944 (*m*), 2854 (*w*), 1635 (*w*), 1488 (*s*), 1437 (*vs*), 1379 (*s*), 1365 (*vs*), 1188 (*vs*), 1070 (*vs*), 1038 (*vs*), 789 (*s*), 748 (*m*); ^{1}H NMR (CDCl$_3$): δ 2.72 (*s*, 6H, CH$_3$), 4.70 (*s*, 4H, CH$_2$), 7.35 (*m*, 4H, Ar-H); analysis calculated for $C_{14}H_{14}N_4S_4$: C 45.84, H 3.82, N 15.28%; found: C 45.56, H 3.68, N 14.92%. Colorless single crystals were obtained by recrystallized from chloroform and methanol.

Crystal data

$C_{14}H_{14}N_4S_4$
$M_r = 366.53$
Monoclinic, $C2/c$
$a = 18.100\ (10)$ Å
$b = 9.239\ (5)$ Å
$c = 11.216\ (6)$ Å
$\beta = 114.764\ (8)^\circ$
$V = 1703.3\ (16)$ Å^3
$Z = 4$

$D_x = 1.429$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 774 reflections
$\theta = 2.5$–26.3°
$\mu = 0.56$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996; Blessing, 1995)
$T_{\min} = 0.851$, $T_{\max} = 0.897$
2152 measured reflections

1497 independent reflections
1242 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 25.0^\circ$
$h = -21 \rightarrow 19$
$k = -11 \rightarrow 10$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.078$
$S = 1.08$
1497 reflections
101 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0345P)^2 + 1.2785P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

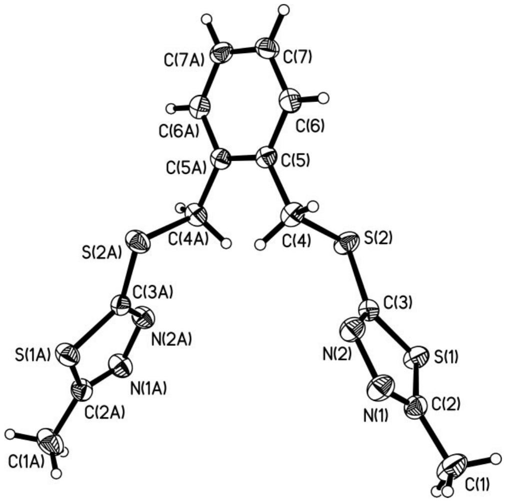

Figure 1
View of the title compound, showing the atom-numbering scheme and displacement elliposids at the 30% probability level.

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