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5,5′-Dimethyl-2,2′-[*p*-phenylenebis(methylenethio)]bis(4,5-dihydrothiazole)

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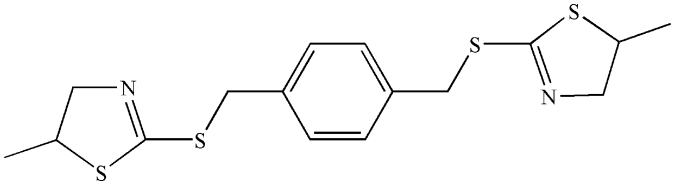
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.050; wR factor = 0.134; data-to-parameter ratio = 15.9.

The title compound, $C_{16}H_{20}N_2S_4$, contains two terminal 5-methyl-4,5-dihydrothiazole rings and a central benzene ring. The molecule lies on an inversion centre. This symmetry imposes a *trans* configuration for the terminal heterocyclic systems with respect to the central benzene ring. The S—C bond lengths are significantly different, depending on the hybridization state of the C atoms.

Related literature

For related literature, see: Constable *et al.* (2002); van den Heuvel *et al.* (1983); Sharma *et al.* (1999); Wang *et al.* (2004, 2005); Yang *et al.* (2000); Zhang *et al.* (2003).



Experimental

Crystal data

$C_{16}H_{20}N_2S_4$
M_r = 368.62
Monoclinic, $P2_1/c$
a = 6.9337 (8) Å
b = 16.133 (2) Å
c = 8.2475 (10) Å
β = 99.519 (6)°
V = 909.89 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 294 (2) K
0.24 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1000 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.886, T_{max} = 0.912
3806 measured reflections
1605 independent reflections
1155 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.135
S = 1.05
1605 reflections
101 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C4	1.764 (4)	S2—C4	1.759 (3)
S1—C2	1.850 (4)	S2—C5	1.822 (4)
N1—C4—S2	127.8 (3)	N1—C4—S1	116.0 (3)

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2122).

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supplementary materials

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5,5'-Dimethyl-2,2'-[*p*-phenylenebis(methylenethio)]bis(4,5-dihydrothiazole)

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Comment

As a type of ditopic ligand, dithioethers can be used as bridging ligands in the construction of coordination polymers with soft metal ions. A series of flexible or rigid chain-linked dithioethers containing N-heterocylcic moieties have been synthesized and investigated (Sharma *et al.*, 1999; Constable *et al.*, 2002). Early studies reported that several tetrazole and imidazole derivatives possess a variety of coordination properties (van den Heuvel *et al.*, 1983; Yang *et al.*, 2000). In order to study the properties of dihydrothiazole derivatives, we have synthesized the title compound, (I), and present here its molecular structure.

The title compound contains two 5-methyl-4,5-dihydrothiazole rings and a central benzene ring. The whole molecule lies on a crystallographic inversion centre [symmetry code: (i) −*x*,-*y* + 1,-*z* + 1] and the terminal (5-methyl-4,5-dihydrothiazole-2-yl)sulfanyl groups thus adopt a *trans* configuration with respect to the central benzene ring. In the thiazole ring, the C4 atom of the C═N bond has a distorted trigonal geometry, with the N1—C4—S2 [127.8 (3)°] and N1—C4—S1 [116.0 (3)°] angles deviating significantly from the ideal values expected for an sp^2 hybridized C atom.

Due to the *p*–π configuration between the S2 atom and the adjacent C═N bond, the S2—C4 bond, 1.759 (3) Å, is significantly shorter than the S2—C5 bond, 1.822 (4) Å. These values compare well with the values of 1.726 (2), 1.720 (8) and 1.800 (3), 1.811 (2)Å reported in the literature (Wang *et al.*, 2004, 2005). The effect is also observed for S1 in the substituted dihydrothiazole ring.

A closely dithiazole structure, 2,2'-[1,4-phenylenebis(methylenethio)]dithiazole, has been published by Zhang *et al.* (2003).

Experimental

A suspension of 1,4-dibromomethylbenzene (5 mmol) in THF (10 ml) was added dropwise to a mixture of 2-mercapto-5-methyl-4,5-dihydrothiazole (11 mmol), KOH (11 mmol) and ethanol (20 ml). The reaction mixture was then stirred for 24 h at room temperature. The precipitate was filtered off, washed with water and recrystallized from ethanol (yield 65%, m.p. 378–379 K). Crystals of (I) suitable for single-crystal X-ray analysis were grown by slow evaporation of a solution in a mixture of chloroform/ethanol (1:1).

Refinement

All H atoms were positioned geometrically and refined using a riding model approximation, with C—H bonds fixed to 0.93 (aromatic CH), 0.96 (methyl CH_3, considered as a rigid group allowed to rotate) 0.97 (methylene CH_2) or 0.98 Å (methine CH). Isotropic displacement parameters for H atoms were fixed as U_{iso} = 1.5U_{eq}(carrier C) for the methyl group and U_{iso} = 1.5U_{eq}(carrier C) otherwise.

Figures

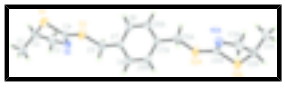


Fig. 1. View of the molecule of (I) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 35% probability level. Symmetry code: (A) $-x$, $-y+1$, $-z+1$.

5,5'-Dimethyl-2,2'-[*p*-phenylenebis(methylenethio)]bis(4,5-dihydrothiazole)

Crystal data

$C_{16}H_{20}N_2S_4$	$F_{000} = 388$
$M_r = 368.62$	$D_x = 1.345$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 378-379 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.9337$ (8) Å	Cell parameters from 1193 reflections
$b = 16.133$ (2) Å	$\theta = 2.5$–24.1°
$c = 8.2475$ (10) Å	$\mu = 0.52$ mm^{-1}
$\beta = 99.519$ (6)°	$T = 294$ (2) K
$V = 909.89$ (19) Å^3	Plate, colourless
$Z = 2$	0.24 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1000 diffractometer	1605 independent reflections
Radiation source: fine-focus sealed tube	1155 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.039$
$T = 294$(2) K	$\theta_{max} = 25.0^\circ$
φ and ω scans	$\theta_{min} = 2.5^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$h = -8 \rightarrow 8$
$T_{min} = 0.886$, $T_{max} = 0.912$	$k = -19 \rightarrow 11$
3806 measured reflections	$l = -9 \rightarrow 7$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.135$	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 0.5874P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
1605 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
101 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.45045 (15)	0.88289 (6)	0.58489 (15)	0.0666 (4)
S2	0.25410 (12)	0.71998 (6)	0.49929 (12)	0.0529 (3)
N1	0.6275 (4)	0.74297 (17)	0.6648 (3)	0.0439 (7)
C1	0.8272 (6)	0.9020 (3)	0.5154 (6)	0.0711 (12)
H1A	0.9653	0.9008	0.5552	0.107*
H1B	0.7913	0.9553	0.4683	0.107*
H1C	0.7945	0.8599	0.4331	0.107*
C2	0.7177 (5)	0.8862 (2)	0.6559 (5)	0.0548 (10)
H2	0.7487	0.9298	0.7387	0.066*
C3	0.7621 (6)	0.8028 (3)	0.7355 (5)	0.0694 (12)
H3A	0.8931	0.7859	0.7229	0.083*
H3B	0.7577	0.8070	0.8521	0.083*
C4	0.4649 (5)	0.7737 (2)	0.5910 (4)	0.0457 (9)
C5	0.3269 (5)	0.6153 (2)	0.5662 (5)	0.0552 (10)
H5A	0.4316	0.5966	0.5104	0.066*
H5B	0.3752	0.6153	0.6835	0.066*
C6	0.1541 (5)	0.4940 (2)	0.4149 (4)	0.0447 (8)
H6	0.2573	0.4895	0.3563	0.054*
C7	0.1553 (5)	0.5568 (2)	0.5287 (4)	0.0409 (8)
C8	−0.0019 (5)	0.5621 (2)	0.6133 (4)	0.0471 (9)
H8	−0.0046	0.6042	0.6900	0.056*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0570 (6)	0.0447 (6)	0.0984 (9)	0.0025 (5)	0.0135 (6)	−0.0024 (5)
S2	0.0413 (5)	0.0431 (5)	0.0681 (7)	−0.0072 (4)	−0.0094 (4)	0.0057 (5)
N1	0.0331 (14)	0.0483 (17)	0.0468 (17)	0.0028 (12)	−0.0042 (13)	0.0158 (13)
C1	0.068 (3)	0.066 (3)	0.084 (3)	−0.019 (2)	0.027 (2)	−0.002 (2)
C2	0.056 (2)	0.058 (2)	0.051 (2)	−0.0226 (18)	0.0062 (18)	−0.0135 (19)
C3	0.058 (2)	0.077 (3)	0.067 (3)	−0.017 (2)	−0.011 (2)	0.013 (2)
C4	0.049 (2)	0.046 (2)	0.043 (2)	−0.0140 (16)	0.0127 (17)	−0.0051 (16)
C5	0.0438 (19)	0.043 (2)	0.074 (3)	−0.0050 (17)	−0.0040 (19)	0.0080 (19)
C6	0.0428 (18)	0.044 (2)	0.049 (2)	0.0019 (15)	0.0137 (16)	0.0023 (17)
C7	0.0390 (17)	0.0343 (18)	0.048 (2)	−0.0033 (14)	0.0018 (16)	0.0075 (15)
C8	0.053 (2)	0.0388 (19)	0.048 (2)	−0.0020 (16)	0.0062 (17)	−0.0091 (16)

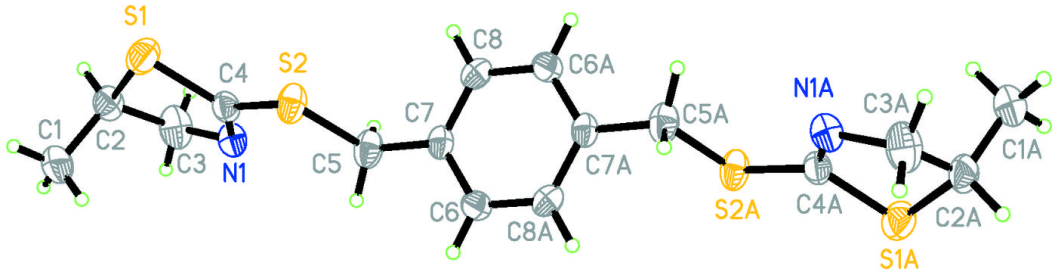
Geometric parameters (Å, °)

S1—C4	1.764 (4)	C3—H3A	0.9700
S1—C2	1.850 (4)	C3—H3B	0.9700
S2—C4	1.759 (3)	C5—C7	1.509 (5)
S2—C5	1.822 (4)	C5—H5A	0.9700

N1—C4	1.289 (4)	C5—H5B	0.9700
N1—C3	1.401 (5)	C6—C7	1.380 (5)
C1—C2	1.509 (5)	C6—C8^{i}	1.382 (5)
C1—H1A	0.9600	C6—H6	0.9300
C1—H1B	0.9600	C7—C8	1.390 (5)
C1—H1C	0.9600	C8—C6^{i}	1.382 (5)
C2—C3	1.505 (5)	C8—H8	0.9300
C2—H2	0.9800		
C4—S1—C2	88.30 (17)	H3A—C3—H3B	108.0
C4—S2—C5	99.09 (17)	N1—C4—S2	127.8 (3)
C4—N1—C3	113.7 (3)	N1—C4—S1	116.0 (3)
C2—C1—H1A	109.5	S2—C4—S1	116.2 (2)
C2—C1—H1B	109.5	C7—C5—S2	110.3 (2)
H1A—C1—H1B	109.5	C7—C5—H5A	109.6
C2—C1—H1C	109.5	S2—C5—H5A	109.6
H1A—C1—H1C	109.5	C7—C5—H5B	109.6
H1B—C1—H1C	109.5	S2—C5—H5B	109.6
C3—C2—C1	113.2 (4)	H5A—C5—H5B	108.1
C3—C2—S1	103.6 (2)	C7—C6—C8^{i}	120.9 (3)
C1—C2—S1	111.5 (3)	C7—C6—H6	119.5
C3—C2—H2	109.5	C8^{i}—C6—H6	119.5
C1—C2—H2	109.5	C6—C7—C8	118.0 (3)
S1—C2—H2	109.5	C6—C7—C5	120.9 (3)
N1—C3—C2	111.1 (3)	C8—C7—C5	121.0 (3)
N1—C3—H3A	109.4	C6^{i}—C8—C7	121.1 (3)
C2—C3—H3A	109.4	C6^{i}—C8—H8	119.5
N1—C3—H3B	109.4	C7—C8—H8	119.5
C2—C3—H3B	109.4		
C4—S1—C2—C3	−21.6 (3)	C2—S1—C4—N1	12.2 (3)
C4—S1—C2—C1	100.4 (3)	C2—S1—C4—S2	−169.1 (2)
C4—N1—C3—C2	−21.6 (5)	C4—S2—C5—C7	170.0 (3)
C1—C2—C3—N1	−92.7 (4)	C8^{i}—C6—C7—C8	−0.4 (5)
S1—C2—C3—N1	28.2 (4)	C8^{i}—C6—C7—C5	176.5 (3)
C3—N1—C4—S2	−175.4 (3)	S2—C5—C7—C6	113.9 (3)
C3—N1—C4—S1	3.2 (4)	S2—C5—C7—C8	−69.3 (4)
C5—S2—C4—N1	7.4 (4)	C6—C7—C8—C6^{i}	0.4 (5)
C5—S2—C4—S1	−171.2 (2)	C5—C7—C8—C6^{i}	−176.5 (3)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Fig. 1


S1
C4
S2
C8
C6A
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C3A
C1
C2
C3
N1
C5
C7
C5A
C1A
C7A
S2A
C4A
C6
C8A
C2A
S1A