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2,2′-[1,4-Phenylenebis(methylenethio)]-dithiazole

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.040
wR factor = 0.086
Data-to-parameter ratio = 16.7

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

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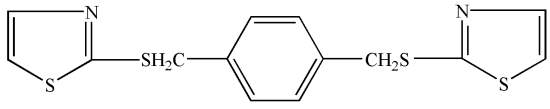
The title compound, $C_{14}H_{12}N_2S_4$, crystallizes in the monoclinic space group $P2_1/c$. The molecule is centrosymmetric; the two thiazole rings are parallel to each other, while the thiazole and the benzene planes are almost perpendicular to each other, forming a dihedral angle of 100.6 (2)°.

Comment

Thiazole and its derivatives have been widely investigated, due to their importance as constituents of many biomolecules, including antibiotics (Chang *et al.*, 1982), vitamins, anti-arthritics, sulphathiazoles, *etc*. (Garbarczyk *et al.*, 1999). In spite of these extensive investigations, there are few studies on the crystal structures of bis(2-thiothiazole)s. In the present paper, we report the crystal structure of a new bisthiazole, 2,2′-[1,4-phenylenebis(methylenethio)]dithiazole, (I)



(I)

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The molecule of (I) is centrosymmetric. The two inversion-related thiazole rings are parallel to each other, while the benzene and thiazole planes are almost perpendicular to each other, forming a dihedral angle of 100.6 (2)°. The distances C1—S2 [1.727 (2) Å] and C3—S2 [1.709 (3) Å], which are slightly longer than the corresponding distances in *N*-methyl-2-thiazolylthiocarboxyamide (NMTA) [1.697 (5) and 1.71 (4) Å; Garbarczyk *et al.*, 1999], are, as expected, between 1.808 Å for a C—S single bond and 1.556 Å for a C═S double bond, while the distances C1—N1 [1.299 (3) Å] and C2—N1 [1.385 (3) Å], which agree well with the corresponding distances of 1.304 (5) and 1.388 (5) Å in NMTA, are inter-

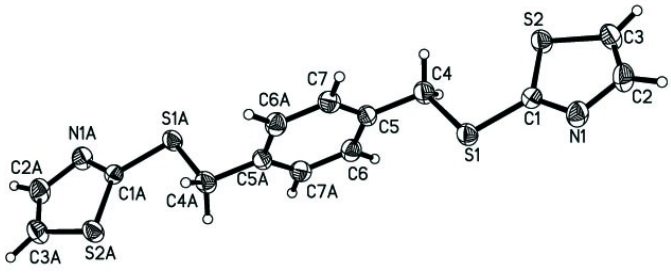

Figure 1
The molecular structure of (I) with atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The H atoms are shown as small spheres of arbitrary radii.

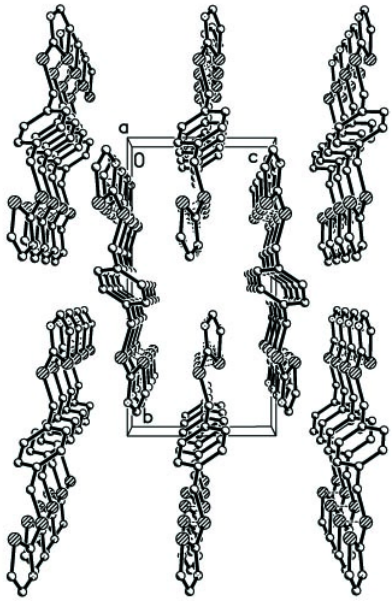

Figure 2
The packing diagram for (I), viewed along the *a* axis.

mediate between 1.47 Å for a C—N single bond and 1.29 Å for a C═N double bond (Boga *et al.*, 1999). The distribution of bond lengths in the thiazole ring suggests a high degree of π-delocalization over the whole thiazole ring. The angles C2—C3—S2 and C1—N1—C2 are 110.1 (2) and 109.0 (2)°, respectively, while the corresponding angles observed in 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazino]thiazole are 111.24 (14) and 109.33 (14)°, respectively (Wouters *et al.*, 2001).

Because of the *p*-π conjugation, the distance C1—S1 [1.743 (3) Å], which is nearly equal to that of the C—S bond [1.7406 (18) Å] in 6-aminopyridine-3-thiol (Sabino *et al.*, 2002), is obviously shorter than that of C4—S1 [1.812 (3) Å]. The exocyclic atoms S1 and C4 are coplanar with their bonded aromatic rings, with displacements of 0.0138 (3) and 0.0238 (2) Å, respectively.

Experimental

2–Thiothiazole was prepared according to the literature method of Harada *et al.* (1999). To a solution containing 2-thiothiazole (0.5 g, 4.3 mmol), KOH (0.97 g, 4.3 mmol) and ethanol (10 ml) at 323–333 K was added, in portions, 1,4-dibromomethylbenene powder (0.57 g, 2.1 mmol) with stirring for 2 h. The reaction mixture was stirred at the same temperature for a further 24 h. Water (8 ml) was then added. The precipitate was filtered off, washed with water and dried at room temperature. Grey crystals (m.p. 382–383 K) were obtained in a yield of 55.9%. Single crystals of (I), suitable for X-ray analysis, were obtained by slow diffusion of cyclohexane into a dichloromethane solution of (I) through an acetone mesosphere. IR (KBr): 3112 (*w*), 3069 (*w*), 1480 (*ms*), 1379 (*s*), 1245 (*ms*), 1054 (*s*), 856 (*ms*) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.42 (4*H*, *s*), 7.22 (2*H*, *s*), 7.32 (4*H*, *s*), 7.70 (2*H*, s) p.p.m.

Crystal data

$C_{14}H_{12}N_2S_4$	D_x = 1.484 Mg m^{-3}
M_r = 336.50	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 567 reflections
a = 6.366 (3) Å	θ = 2.6–26.2°
b = 15.411 (6) Å	μ = 0.62 mm^{-1}
c = 7.679 (3) Å	T = 293 (2) K
β = 91.331 (7)°	Prism, colourless
V = 753.2 (5) Å^3	0.20 × 0.18 × 0.16 mm
Z = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	1518 independent reflections
φ and ω scans	1074 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	R_{int} = 0.031
T_{min} = 0.875, T_{max} = 1.000	θ_{max} = 26.4°
3479 measured reflections	$h = -7 \rightarrow 7$
	$k = -15 \rightarrow 19$
	$l = -9 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.1354P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.086	$\Delta\rho_{max}$ = 0.20 e Å^{-3}
S = 1.04	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
1518 reflections	
91 parameters	
H atoms constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.743 (3)	S2—C1	1.727 (2)
S1—C4	1.812 (3)	N1—C1	1.299 (3)
S2—C3	1.709 (3)	N1—C2	1.385 (3)
C1—S1—C4	102.13 (12)	C1—N1—C2	109.0 (2)
C3—S2—C1	88.87 (13)	N1—C1—S2	115.36 (18)
C2—N1—C1—S1	179.33 (19)	S1—C4—C5—C7	81.2 (3)

All H atoms were positioned geometrically (C—H = 0.96 Å) and refined with riding-model constraints.

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

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