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1,3-Bis(phenylsufanylmethyl)benzene

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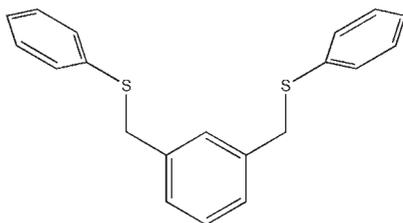
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 Key indicators: single-crystal X-ray study; $T = 228$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.035; wR factor = 0.086; data-to-parameter ratio = 16.4.

The complete molecule of the title compound, $\text{C}_{20}\text{H}_{18}\text{S}_2$, is generated by crystallographic mirror symmetry, with two C atoms lying on the mirror plane. All of the independent atoms are contained within two planes defined by the thiophenyl rings (C_6S) and the central phenyl ring with the methylene bridge; the r.m.s deviations of these planes are 0.012 and 0.025 Å, respectively. The two planes are almost perpendicular to one another at a dihedral angle of 80.24 (10)°. Intermolecular C—H— π interactions are present in the crystal structure.

Related literature

For the use of the title compound as a ligand, see: Bu *et al.* (2002); Romero *et al.* (1996); Loeb & Wisner (1998); Kruithof *et al.* (2008); Bergholdt *et al.* (1998); Kobayashi *et al.* (2000). For related organic molecules, see: Cervantes *et al.* (2006); Sillanpää *et al.* (1994); Arroyo *et al.* (2003).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{18}\text{S}_2$	$V = 1664.1$ (2) Å ³
$M_r = 322.46$	$Z = 4$
Orthorhombic, Cmc_21	Mo $K\alpha$ radiation
$a = 32.072$ (2) Å	$\mu = 0.31$ mm ⁻¹
$b = 7.6053$ (5) Å	$T = 228$ K
$c = 6.8224$ (5) Å	$0.76 \times 0.15 \times 0.10$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	14404 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1689 independent reflections
$T_{\min} = 0.797$, $T_{\max} = 0.970$	1417 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.086$	$\Delta\rho_{\text{max}} = 0.27$ e Å ⁻³
$S = 1.12$	$\Delta\rho_{\text{min}} = -0.31$ e Å ⁻³
1689 reflections	Absolute structure: Flack (1983),
103 parameters	738 Friedel pairs
1 restraint	Flack parameter: 0.05 (12)

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the $\text{C1}-\text{C4}/\text{C3}'/\text{C2}'$ and $\text{C6}-\text{C11}$ rings, respectively.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C1}-\text{H1A}\cdots\text{Cg1}^{\text{i}}$	0.94	2.69	3.57 (5)	155
$\text{C1}-\text{H1A}\cdots\text{Cg1}^{\text{ii}}$	0.94	2.69	3.57 (5)	155
$\text{C7}-\text{H7A}\cdots\text{Cg2}^{\text{iii}}$	0.94	2.85	3.67 (6)	147

Symmetry codes: (i) $-x + 1, -y + 1, z - \frac{1}{2}$ (ii) $x, -y + 1, z - \frac{1}{2}$ (iii) $x, -y + 1, z + \frac{1}{2}$

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: XS in SHELXTL (Sheldrick, 2008); program(s) used to refine structure: XL in SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2007); software used to prepare material for publication: publCIF (McMahon & Westrip, 2008) and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2176).

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1,3-Bis(phenylsufanylmethyl)benzene

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S1. Comment

The title compound, 1,3-bis(phenylthiomethyl)benzene, belongs to a class of transition metal ligands known as SCS-pincer ligands because of their tendency to act as tridentate chelators through one carbon and two sulfur atoms. The plane containing the thiophenyl ring is rotated almost perpendicular to the plane of the central phenyl ring, at an angle of 80.24 (10)°. This is comparable to the para-fluoro (Cervantes *et al.*, 2006) and ortho-ethylester (Sillanpää *et al.*, 1994) derivatives, whose interplanar angles measure 78.13 (10) and 87.66 (10)° respectively. Surprisingly, in the only other structurally characterized derivative, the perfluorinated 1,3-bis(pentafluorophenylthiomethyl)benzene (Arroyo *et al.*, 2003), the rings are nearly co-planar with angles of 8.93 (10) and 10.85 (9)° between the central phenyl and the two independent flanking perfluoro rings. In both the title compound and the para-fluoro derivative, the flanking aryl rings are oriented on the same face of the central ring.

Although the structure of the title compound has not been previously determined, several of its metal complexes are known. Two types of coordination were observed in structurally characterized metal complexes. In the presence of silver perchlorate (Bu *et al.*, 2002) or silver nitrate (Romero *et al.*, 1996), the title compound acts as a bridging ligand through sulfur. In these two complexes, the flanking aryls remain on the same face of the central ring. With Pd (Loeb & Wisner, 1998), Pt (Kruithof *et al.*, 2008) and Te (Bergholdt *et al.*, 1998; Kobayashi *et al.*, 2000) the much more common trihapto-SCS "pincer"-type coordination is observed and the thiophenyl rings rotate to opposite faces of the central phenyl. In all seven examples, the mirror plane present within the free ligand has been broken. The nearly perpendicular orientation of the planes of flanking aryls and the central phenyl (80.24 (10)°) is maintained in each of the Te (Bergholdt *et al.*, 1998; Kobayashi *et al.*, 2000) and Pt (Kruithof *et al.*, 2008) complexes, which have interplanar angles ranging from 77.8 (3) to 89.7 (3)°. In contrast, the interplanar angles in the Ag and Pd complexes cover a much wider range within and across the molecules, measuring 44.1 (6) and 65.5 (6)° in the AgClO₄ based-complex (Bu *et al.*, 2002), 44.5 (3) and 70.4 (2)° for AgNO₃ (Romero *et al.*, 1996), and 40.3 (12) and 88.8 (13)° at one end of the Pd-rotaxane and 41.9 (12) and 89.4 (13)° at the other (Loeb & Wisner, 1998).

S2. Experimental

1,3-Bis((phenylthio)methyl)benzene was synthesized according to the literature method (Romero, *et al.* 1996). To grow crystals, a saturated solution of 1,3-bis((phenylthio)methyl)benzene was prepared in hot pentane. An aliquot of this saturated solution was transferred to a 20 ml vial, which was then tightly capped. The vial was placed in a bath of hot water and allowed to slowly cool to room temperature. Colorless, needle-like crystals of up to 10 mm in length formed over approximately 30 minutes. The solvent was then decanted and the crystals allowed to air dry. Several needles of ca. 1 mm in length were placed in a melting point capillary with an internal diameter 0.5 mm and the melting point was determined to be 84 - 86 °C.

S3. Refinement

Hydrogen atoms were included at geometrically idealized positions with C—H distances of 0.94 Å for aryl H atoms and 0.98 Å for methylene H atoms. The hydrogen atoms were treated as riding on their respective heavy atoms. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 U_{eq} of the parent atom.

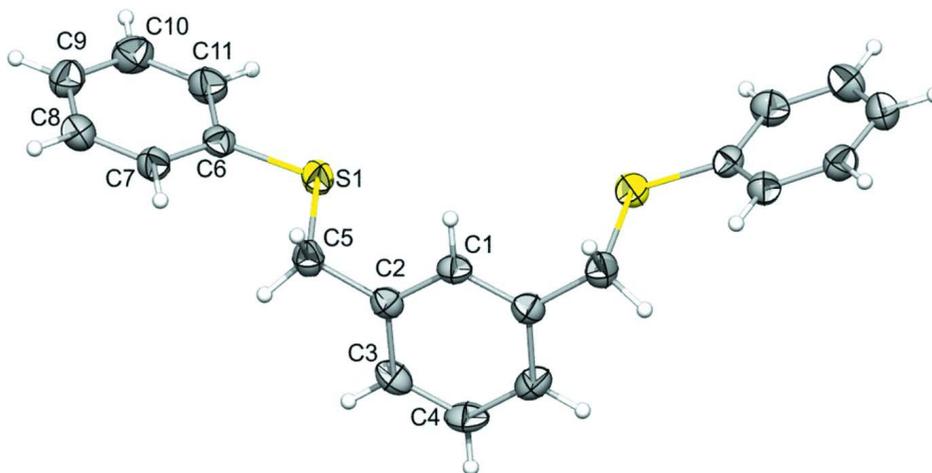


Figure 1

View of the title compound showing full numbering scheme. The displacement ellipsoids are shown at the 50% probability level.

1,3-Bis(phenylsufanylmethyl)benzene

Crystal data

$\text{C}_{20}\text{H}_{18}\text{S}_2$

$M_r = 322.46$

Orthorhombic, $Cmc2_1$

Hall symbol: $C\ 2c\ -2$

$a = 32.072\ (2)\ \text{\AA}$

$b = 7.6053\ (5)\ \text{\AA}$

$c = 6.8224\ (5)\ \text{\AA}$

$V = 1664.1\ (2)\ \text{\AA}^3$

$Z = 4$

$F(000) = 680$

$D_x = 1.287\ \text{Mg m}^{-3}$

Melting point = 357–359 K

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 8194 reflections

$\theta = 2.8\text{--}28.1^\circ$

$\mu = 0.31\ \text{mm}^{-1}$

$T = 228\ \text{K}$

Needle, colourless

$0.76 \times 0.15 \times 0.10\ \text{mm}$

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\text{min}} = 0.797$, $T_{\text{max}} = 0.970$

14404 measured reflections

1689 independent reflections

1417 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 3.3^\circ$

$h = -40 \rightarrow 40$

$k = -9 \rightarrow 9$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.086$

$S = 1.12$

1689 reflections

103 parameters

1 restraint

38 constraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.6358P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983), 736 Friedel
 pairs

Absolute structure parameter: 0.05 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.415866 (15)	0.21909 (7)	0.49099 (13)	0.03480 (17)
C1	0.5000	0.3639 (4)	0.7139 (5)	0.0295 (7)
H1A	0.5000	0.4312	0.5984	0.035*
C2	0.46220 (7)	0.3148 (3)	0.7983 (4)	0.0295 (5)
C3	0.46271 (7)	0.2166 (3)	0.9699 (5)	0.0362 (6)
H3A	0.4374	0.1836	1.0290	0.043*
C4	0.5000	0.1671 (4)	1.0546 (6)	0.0406 (9)
H4A	0.5000	0.0996	1.1700	0.049*
C5	0.42152 (7)	0.3621 (3)	0.7015 (4)	0.0343 (6)
H5A	0.4218	0.4855	0.6601	0.041*
H5B	0.3983	0.3448	0.7928	0.041*
C6	0.36379 (7)	0.2480 (3)	0.4147 (4)	0.0313 (5)
C7	0.33665 (6)	0.3748 (3)	0.4885 (5)	0.0344 (5)
H7A	0.3459	0.4547	0.5843	0.041*
C8	0.29608 (8)	0.3827 (3)	0.4201 (4)	0.0400 (6)
H8A	0.2779	0.4681	0.4710	0.048*
C9	0.28185 (8)	0.2686 (3)	0.2796 (4)	0.0449 (7)
H9A	0.2541	0.2750	0.2353	0.054*
C10	0.30905 (8)	0.1432 (4)	0.2032 (4)	0.0467 (7)
H10A	0.2998	0.0651	0.1058	0.056*
C11	0.34957 (8)	0.1333 (3)	0.2704 (4)	0.0401 (6)
H11A	0.3677	0.0483	0.2183	0.048*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0321 (3)	0.0375 (3)	0.0348 (3)	0.0052 (2)	0.0004 (3)	-0.0071 (4)
C1	0.0353 (17)	0.0270 (15)	0.0264 (19)	0.000	0.000	0.0012 (14)

C2	0.0326 (12)	0.0268 (10)	0.0290 (13)	0.0000 (9)	0.0007 (10)	-0.0049 (11)
C3	0.0406 (12)	0.0326 (10)	0.0356 (15)	-0.0048 (9)	0.0095 (14)	-0.0008 (13)
C4	0.058 (2)	0.0348 (17)	0.029 (2)	0.000	0.000	0.0085 (15)
C5	0.0304 (11)	0.0341 (12)	0.0382 (15)	0.0018 (10)	0.0014 (11)	-0.0071 (11)
C6	0.0316 (12)	0.0328 (11)	0.0295 (13)	-0.0041 (9)	0.0021 (9)	0.0027 (10)
C7	0.0321 (10)	0.0384 (11)	0.0327 (13)	-0.0010 (8)	0.0007 (14)	-0.0038 (15)
C8	0.0355 (13)	0.0476 (14)	0.0369 (15)	0.0035 (11)	0.0043 (11)	-0.0001 (11)
C9	0.0335 (13)	0.0581 (15)	0.0430 (18)	-0.0060 (11)	-0.0051 (12)	0.0049 (15)
C10	0.0478 (16)	0.0509 (16)	0.0413 (18)	-0.0095 (12)	-0.0065 (13)	-0.0095 (13)
C11	0.0446 (14)	0.0375 (13)	0.0381 (16)	0.0002 (11)	0.0010 (12)	-0.0101 (12)

Geometric parameters (Å, °)

S1—C6	1.763 (2)	C5—H5B	0.9800
S1—C5	1.811 (2)	C6—C11	1.392 (3)
C1—C2 ⁱ	1.393 (3)	C6—C7	1.393 (3)
C1—C2	1.393 (3)	C7—C8	1.384 (3)
C1—H1A	0.9400	C7—H7A	0.9400
C2—C3	1.388 (4)	C8—C9	1.371 (4)
C2—C5	1.506 (3)	C8—H8A	0.9400
C3—C4	1.381 (3)	C9—C10	1.394 (4)
C3—H3A	0.9400	C9—H9A	0.9400
C4—C3 ⁱ	1.381 (3)	C10—C11	1.380 (3)
C4—H4A	0.9400	C10—H10A	0.9400
C5—H5A	0.9800	C11—H11A	0.9400
C6—S1—C5	104.72 (11)	C11—C6—C7	119.0 (2)
C2 ⁱ —C1—C2	121.0 (3)	C11—C6—S1	116.16 (18)
C2 ⁱ —C1—H1A	119.5	C7—C6—S1	124.85 (19)
C2—C1—H1A	119.5	C8—C7—C6	119.7 (2)
C3—C2—C1	118.8 (2)	C8—C7—H7A	120.2
C3—C2—C5	120.57 (19)	C6—C7—H7A	120.2
C1—C2—C5	120.5 (2)	C9—C8—C7	121.4 (2)
C4—C3—C2	120.6 (2)	C9—C8—H8A	119.3
C4—C3—H3A	119.7	C7—C8—H8A	119.3
C2—C3—H3A	119.7	C8—C9—C10	119.1 (2)
C3—C4—C3 ⁱ	120.1 (4)	C8—C9—H9A	120.5
C3—C4—H4A	120.0	C10—C9—H9A	120.5
C3 ⁱ —C4—H4A	120.0	C11—C10—C9	120.2 (2)
C2—C5—S1	106.92 (15)	C11—C10—H10A	119.9
C2—C5—H5A	110.3	C9—C10—H10A	119.9
S1—C5—H5A	110.3	C10—C11—C6	120.6 (2)
C2—C5—H5B	110.3	C10—C11—H11A	119.7
S1—C5—H5B	110.3	C6—C11—H11A	119.7
H5A—C5—H5B	108.6		
C2 ⁱ —C1—C2—C3	0.6 (4)	C5—S1—C6—C7	8.5 (2)
C2 ⁱ —C1—C2—C5	-177.45 (19)	C11—C6—C7—C8	1.1 (4)

C1—C2—C3—C4	-0.6 (4)	S1—C6—C7—C8	-178.7 (2)
C5—C2—C3—C4	177.4 (2)	C6—C7—C8—C9	-0.4 (4)
C2—C3—C4—C3 ⁱ	0.7 (5)	C7—C8—C9—C10	-0.5 (4)
C3—C2—C5—S1	-104.0 (2)	C8—C9—C10—C11	0.7 (4)
C1—C2—C5—S1	74.0 (2)	C9—C10—C11—C6	0.0 (4)
C6—S1—C5—C2	168.24 (15)	C7—C6—C11—C10	-0.9 (4)
C5—S1—C6—C11	-171.28 (19)	S1—C6—C11—C10	178.9 (2)

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

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 and Cg2 are the centroids of the C1—C4/C3'/C2' and C6—C11 rings, respectively.

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1A \cdots Cg1 ⁱⁱ	0.94	2.69	3.57 (5)	155
C1—H1A \cdots Cg1 ⁱⁱⁱ	0.94	2.69	3.57 (5)	155
C7—H7A \cdots Cg2 ^{iv}	0.94	2.85	3.67 (6)	147

Symmetry codes: (ii) $-x+1, -y+1, z-1/2$; (iii) $x, -y+1, z-1/2$; (iv) $x, -y+1, z+1/2$.