Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: empirical, ψ-scan
$T_{\min} = 0.95$, $T_{\max} = 1.00$
1185 measured reflections
1121 independent reflections
895 observed reflections $[I > 2\sigma(I)]$
$R_{\text{int}} = 0.010$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 150 reflections intensity variation: decline of −1.20%, linear correction applied

Refinement

Refinement on *F*
$R = 0.044$
$wR = 0.055$
$S = 2.23$
895 reflections
89 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.033$
$\Delta\rho_{\max} = 0.2$ e Å^{-3}
$\Delta\rho_{\min} = -0.3$ e Å^{-3}
Atomic scattering factors from *Xtal*3.0 (Hall & Stewart, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S(1)	0.29308 (6)	0.52931 (6)	0.68847 (8)	0.0487 (3)
O(1)†	0.4890 (5)	0.3466 (3)	0.7885 (4)	0.051 (2)
C(1)	0.4610 (2)	0.7084 (2)	0.6846 (3)	0.0423 (9)
C(2)	0.4254 (3)	0.8178 (3)	0.6224 (4)	0.064 (1)
C(3)	0.4636 (3)	0.9239 (3)	0.6856 (5)	0.087 (2)
C(4)	0.4161 (3)	0.5942 (3)	0.6139 (3)	0.045 (1)
C(5)	0.2946 (3)	0.3770 (3)	0.6275 (4)	0.071 (1)
C(6)	0.3968 (3)	0.3017 (3)	0.6893 (4)	0.071 (1)

† Site occupation 0.5.

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(4)	1.825 (3)	C(1)—C(2)	1.393 (4)
S(1)—C(5)	1.812 (4)	C(1)—C(4)	1.497 (4)
O(1)—C(6)	1.366 (5)	C(2)—C(3)	1.371 (5)
O(1)—C(6$^{\text{i}}$)	1.337 (6)	C(3)—C(3$^{\text{i}}$)	1.368 (7)
C(1)—C(1$^{\text{i}}$)	1.409 (4)	C(5)—C(6)	1.447 (5)
C(4)—S(1)—C(5)	100.6 (2)	C(2)—C(3)—C(3$^{\text{i}}$)	119.9 (3)
C(6)—O(1)—C(6$^{\text{i}}$)	121.8 (4)	S(1)—C(4)—C(1)	110.9 (2)
C(2)—C(1)—C(4)	120.4 (3)	S(1)—C(5)—C(6)	117.8 (2)
C(2)—C(1)—C(1$^{\text{i}}$)	118.4 (3)	O(1)—C(6)—C(5)	120.0 (3)
C(4)—C(1)—C(1$^{\text{i}}$)	121.2 (2)	C(5)—C(6)—O(1$^{\text{i}}$)	119.0 (3)
C(1)—C(2)—C(3)	121.7 (3)		
C(5)—S(1)—C(4)—C(1)	−161.8 (2)	C(1$^{\text{i}}$)—C(1)—C(4)—S(1)	76.5 (3)
C(4)—S(1)—C(5)—C(6)	72.2 (3)	C(1)—C(2)—C(3)—C(3$^{\text{i}}$)	−1.4 (7)
C(6$^{\text{i}}$)—O(1)—C(6)—C(5)	−153.7 (4)	S(1)—C(5)—C(6)—O(1)	−1.0 (6)
C(4)—C(1)—C(2)—C(3)	179.0 (4)	S(1)—C(5)—C(6)—O(1$^{\text{i}}$)	−43.1 (5)
C(1$^{\text{i}}$)—C(1)—C(2)—C(3)	−0.5 (5)	C(5)—C(6)—O(1)—C(6$^{\text{i}}$)	−153.7 (4)
C(2)—C(1)—C(4)—S(1)	−103.0 (3)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed by full-matrix least-squares methods, non-H atoms with anisotropic displacement parameters and H atoms either with isotropic displacement parameters [H(2), H(3), H(4*A*) and H(4*B*)] or included in the calculations at fixed positions (C—H = 0.95 Å). The refinements were carried out with *Xtal*3.0 (Hall & Stewart, 1990). The figure was drawn using *ORTEP*II (Johnson, 1976).

RK is grateful to Suomen Kultuurirahasto for the grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diethyl 2,2′-[1,3-Phenylenebis(methylthio)]dibenzoate

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Abstract

The title molecule, $C_{26}H_{26}O_4S_2$, assumes C_2 symmetry with two C atoms and two H atoms of the cen-

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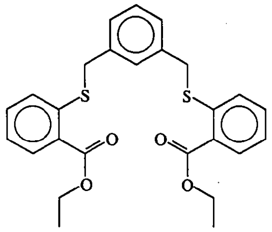
tral phenyl ring located on the twofold axis. The S atoms are synplanar with the benzene moiety, so the observed geometry is suitable for CS_2 coordination. The *o*-(ethoxycarbonyl)phenylthiomethyl moiety is approximately planar and its orientation is almost perpendicular with respect to the central phenyl group.

Comment

Our studies have demonstrated that dithioether macrocycles containing the 1,3-bis(*R*-thiomethyl)benzene (*R* = alkyl or aryl) unit are excellent neutral sensing molecules for silver(I)-selective membrane electrodes (Casabó, Mestres, Escriche, Teixidor & Perez-Jimenez, 1991). Molecular-dynamics calculations confirm that in the series of 2,5,8-trithia[9]benzenophanes only *m*-benzenophane, which contains the 1,3-bis(*R*-thiomethyl)benzene unit, has the necessary features to ensure chelating interactions with the silver(I) metal ion (Lockhart *et al.*, 1992). No difference in the selective behaviour was observed as a function of the length and nature of the aliphatic macrocyclic chain. As part of these studies we are testing the relevance of the cyclic character of these molecules in silver(I) recognition. For this purpose we are synthesizing and characterizing acyclic molecules that include the 1,3-bis(*R*-thiomethyl)benzene unit as a preliminary step to incorporating them in membrane electrodes. Here we report the crystal structure of diethyl 2,2′-[1,3-phenylenebis(methylthio)]dibenzoate (I).



(I)

The title molecule is an example of a ligand that can coordinate tridentately to some metal ions [*e.g.* Pd^{II} and Pt^{II}] through two S atoms and one C atom. This reactivity may best be regarded as a result of electrophilic attack of the metal halide on the C(1) atom of the ligand with elimination of hydrogen halide (Constable, 1984). The intermediate carbanion is stabilized due to the inductive effect of the alkyl substituents in vicinal positions.

The conformation of the title compound in the crystalline state is suitable for CS_2 coordination because, with a value of −23.5 (4)° for the C(1)—C(2)—C(5)—S(1) torsion angle, the orientation of the S(1) atom is synplanar with the C(1)—C(2) bond. The conformation differs from that of 2,6-bis(*p*-nitrophenylthiomethyl)pyridine in which the molecular symmetry is C_1 and the orientation of the other S atom is axial with respect to the central pyridine ring (Sillanpää, Kivekäs, Escriche, Sánchez-Castelló & Teixidor, 1994).

In the title compound, the bulky *o*-(ethoxycarbonyl)-phenylthiomethyl moiety is approximately planar. The C(2)—C(5)—S(1)—C(6) torsion angle is −73.9 (3)° and the orientation of the moiety is almost perpendicular with respect to the central phenyl group. Bond lengths agree with the values reported for (2,6-bis{[(2-methoxycarbonyl)phenyl]thiomethyl}pyridine)dichlorocopper(II) (Teixidor *et al.*, 1991), but the C(13)—C(14) distance is slightly shorter than a normal single-bond length.

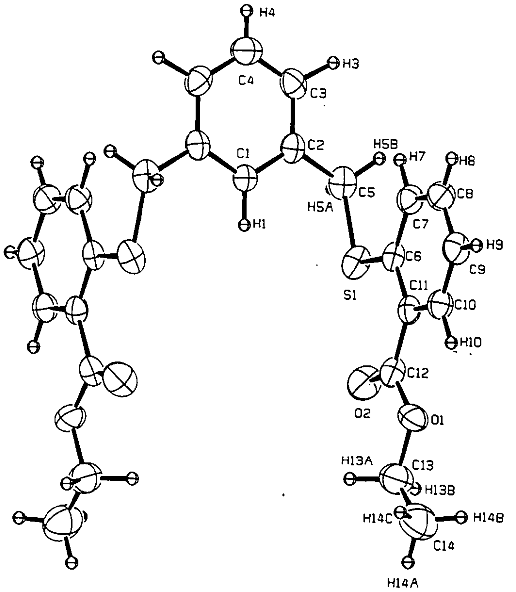


Fig. 1. *ORTEPII* (Johnson, 1976) plot of $C_{26}H_{26}O_4S_2$. Displacement ellipsoids are shown at 30% probability levels except for H atoms which are given arbitrary radii.

Experimental

Dehydrated and deoxygenated ethanol was used in the synthesis. *m*-Dichloroxylene was commercially available (Aldrich) and used as received. Thiosalicyl ethyl ester (7.28 g, 40 mmol) was added to a stirred solution of sodium metal (0.93 g, 40 mmol) in ethanol (40 ml) and the mixture stirred for a further 10 min. The mixture was then added to a solution of *m*-dichloroxylene (3.48 g, 20 mmol) in ethanol (40 ml). After the addition, a white precipitate appeared. The mixture was heated at 303–308 K under reflux and then cooled to room temperature. The precipitate was filtered off, washed with ethanol, vacuum dried and recrystallized from 1,2-dimethoxyethane to afford the title compound as a white crystalline product suitable for X-ray diffraction analysis [yield 6.81 g (67%)].

Crystal data

$C_{26}H_{26}O_4S_2$
$M_r = 466.6$
Monoclinic
$C2/c$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections

$a = 14.502$ (2) Å
$b = 10.904$ (3) Å
$c = 14.503$ (2) Å
$\beta = 90.34$ (1)°
$V = 2293.4$ (7) Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}

$\theta = 13.2$–17.4°
$\mu = 0.251$ mm^{-1}
$T = 296$ K
Cubic
0.35 × 0.35 × 0.25 mm
White

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: empirical, ψ-scan
$T_{\min} = 0.96$, $T_{\max} = 1.00$
2238 measured reflections
2144 independent reflections
1259 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.016$
$\theta_{\max} = 25°$
$h = -17 \rightarrow 0$
$k = -13 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections intensity variation: ±0.5%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.056$
$S = 1.78$
1259 reflections
175 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S(1)	0.66990 (7)	0.3953 (1)	0.68843 (6)	5.41 (5)
O(1)	0.6261 (2)	0.7092 (3)	0.5028 (2)	6.2 (2)
O(2)	0.6503 (2)	0.6365 (3)	0.6430 (2)	7.2 (2)
C(1)	1/2	0.2337 (5)	3/4	4.1 (3)
C(2)	0.5816 (2)	0.1711 (4)	0.7348 (2)	4.3 (2)
C(3)	0.5814 (3)	0.0439 (4)	0.7347 (3)	5.3 (2)
C(4)	1/2	−0.0181 (6)	3/4	6.1 (4)
C(5)	0.6728 (3)	0.2365 (4)	0.7247 (3)	5.4 (2)
C(6)	0.6414 (2)	0.3873 (4)	0.5693 (2)	4.2 (2)
C(7)	0.6333 (3)	0.2755 (4)	0.5242 (3)	4.9 (2)
C(8)	0.6139 (3)	0.2714 (4)	0.4308 (3)	5.5 (2)
C(9)	0.6016 (3)	0.3768 (4)	0.3803 (3)	5.1 (2)
C(10)	0.6088 (3)	0.4875 (4)	0.4231 (3)	4.8 (2)
C(11)	0.6291 (2)	0.4957 (4)	0.5179 (2)	4.2 (2)
C(12)	0.6364 (2)	0.6175 (4)	0.5627 (3)	5.0 (2)
C(13)	0.6316 (4)	0.8302 (5)	0.5456 (4)	7.1 (3)
C(14)	0.6155 (4)	0.9157 (5)	0.4754 (4)	9.4 (4)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(5)	1.810 (5)	C(6)—C(7)	1.388 (5)
S(1)—C(6)	1.776 (3)	C(6)—C(11)	1.408 (5)
O(1)—C(12)	1.332 (5)	C(7)—C(8)	1.384 (5)
O(1)—C(13)	1.461 (5)	C(8)—C(9)	1.374 (6)
O(2)—C(12)	1.198 (4)	C(9)—C(10)	1.362 (5)
C(1)—C(2)	1.386 (4)	C(10)—C(11)	1.407 (5)
C(2)—C(3)	1.386 (5)	C(11)—C(12)	1.483 (5)
C(2)—C(5)	1.510 (5)	C(13)—C(14)	1.399 (7)
C(5)—S(1)—C(6)	103.9 (2)	C(6)—C(7)—C(8)	120.4 (4)
C(12)—O(1)—C(13)	113.3 (3)	C(7)—C(8)—C(9)	121.4 (4)
C(2)—C(1)—C(2$^{\rm i}$)	120.9 (5)	C(8)—C(9)—C(10)	119.3 (4)
C(1)—C(2)—C(3)	119.4 (4)	C(9)—C(10)—C(11)	121.1 (4)
C(1)—C(2)—C(5)	122.1 (4)	C(6)—C(11)—C(10)	119.3 (3)
C(3)—C(2)—C(5)	118.3 (4)	C(6)—C(11)—C(12)	120.8 (3)
C(2)—C(3)—C(4)	119.5 (5)	C(10)—C(11)—C(12)	119.9 (4)
C(3)—C(4)—C(3$^{\rm i}$)	121.3 (6)	O(1)—C(12)—O(2)	121.5 (4)
S(1)—C(5)—C(2)	117.5 (3)	O(1)—C(12)—C(11)	112.3 (4)
S(1)—C(6)—C(7)	121.3 (3)	O(2)—C(12)—C(11)	126.3 (4)
S(1)—C(6)—C(11)	120.1 (3)	O(1)—C(13)—C(14)	106.5 (4)
C(7)—C(6)—C(11)	118.5 (3)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

The structure was solved by direct methods (Gilmore, 1984) and successive Fourier syntheses. Refinement was performed by full-matrix least-squares methods. Non-H atoms were refined with anisotropic displacement parameters and H atoms, except those of the methyl group, with fixed isotropic displacement parameters (1.2 × $B_{\rm eq}$ of the carrying atom). H atoms of the methyl group were included in the calculations in fixed positions (C—H 0.948 Å). The calculations were carried out using *TEXSAN* (Molecular Structure Corporation, 1989) on a VAXstation 3520 computer. The figure was drawn with *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: AB1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,6-Bis(phenylamino)pyridine

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Abstract

The structure of the title compound, $C_{17}H_{15}N_3$, consists of two independent molecules which are

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