

# 9,17-Dioxa-1,3-dithiatetracyclo[18.2.2.2<sup>23,24</sup>.1<sup>25</sup>]-heptacos-5,7,11,13,15-(25),18,20,23,26-nonene

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## Key indicators

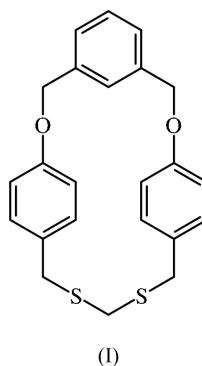
Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
R factor = 0.041  
wR factor = 0.127  
Data-to-parameter ratio = 23.8

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

The title compound,  $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}_2$ , consists of an *m*-xylene moiety symmetrically linked by phenoxymethyl groups, which are bridged by a methanedithiol unit. The two benzene rings at the dithio end of the molecule are almost perpendicular to each other [ $87.1 (1)^\circ$ ]. The crystal packing is stabilized by  $\text{C}-\text{H} \cdots \pi$  and weak  $\pi \cdots \pi$  interactions.

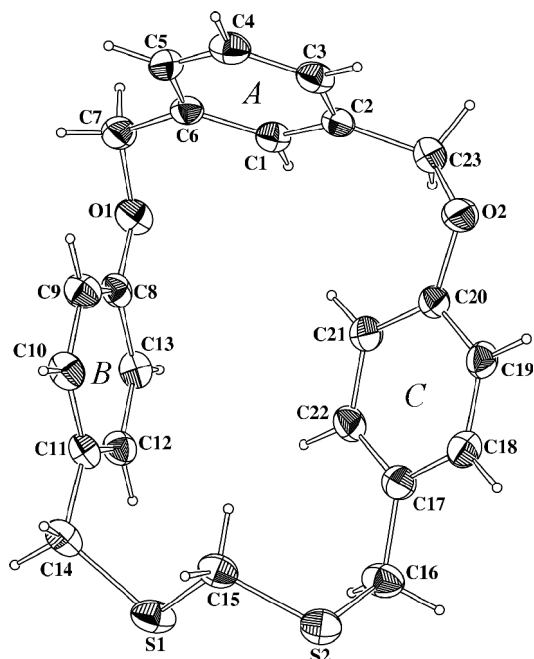
## Comment

Cyclophane receptors are involved in biomimetic catalysis and enhance the pathway to substrate binding (Ngola & Dougherty, 1996) and molecular recognition (Arija *et al.*, 2002). This type of molecule is capable of binding aromatic guest molecules (Brown *et al.*, 1989). Several cyclophane analogues exhibit edge-to-face and face-to-face aromatic interactions (Kim *et al.*, 2002). Cyclophane derivatives containing guest molecules have been synthesized as potential reversal agents of muscle relaxants (Cameron *et al.*, 2002). The structure determination of the title compound, (I), was undertaken as part of our studies of cyclophane derivatives.

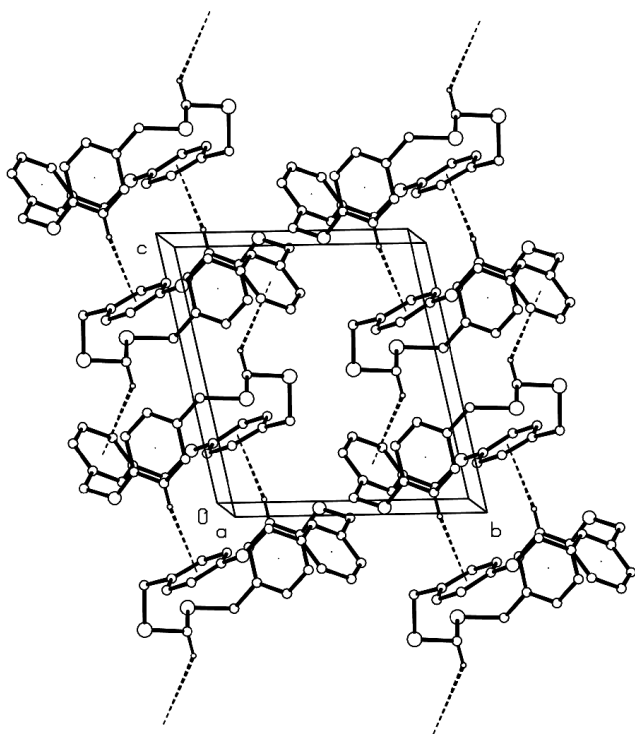


The molecular structure of (I) is shown in Fig. 1. The C—S distances are comparable to the mean reported  $\text{Csp}^3-\text{S}$  value (Allen *et al.*, 1987). The bond angles at S1 and S2 [ $100.7 (1)^\circ$  and  $101.7 (1)^\circ$ ] agree with values reported in a similar structure (Pfisterer & Ziegler, 1983). A short contact between atoms H9 and H7B ( $2.175 \text{ \AA}$ ) results in the widening of the O1—C8—C9 angle [ $125.7 (2)^\circ$ ] from the ideal value of  $120^\circ$ . The orientation of the benzene rings can be defined by torsion angles, such as C6—C7—O1—C8, C2—C23—O2—C20, C11—C14—S1—C15 and C17—C16—S2—C15 (Table 1). Similarly, the angles S1—C15—S2—C16 and S2—C15—S1—C14 describe the conformation of the dithio part of the molecule. Atoms C7 and C23 deviate by  $-0.071 (2)$  and  $-0.0258 (2) \text{ \AA}$ , respectively, from the benzene ring A. Benzene rings A and B are almost perpendicular to each other [ $87.1 (1)^\circ$ ]. The dihedral angles between rings B and C and between rings C and A are  $66.8 (1)^\circ$  and  $71.9 (1)^\circ$ , respectively.

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**Figure 1**  
The molecular structure of title compound, showing 35% probability displacement ellipsoids.



**Figure 2**  
The molecular packing of (I), viewed down the *a* axis.

In the crystal packing, inversion-related molecules are linked *via* C—H $\cdots\pi$  interactions [ $\text{H13}\cdots\text{CgC}^i = 2.65$ ,  $\text{C13}\cdots\text{CgC}^i = 3.571(3) \text{ \AA}$ ,  $\text{C13—H13}\cdots\text{CgC}^i = 171^\circ$ ; symmetry code: (i)  $-x, -y, -z$ ], forming a dimer. Symmetry-related dimers are linked *via* weak C—H $\cdots\pi$  interactions [ $\text{H15B}\cdots\text{CgA}^{ii} = 3.09$ ,  $\text{C15}\cdots\text{CgA}^{ii} = 3.885(1) \text{ \AA}$ ,  $\text{C15—}$

$\text{H15B}\cdots\text{CgA}^{ii} = 141^\circ$ ; symmetry code: (ii)  $-x, -y, 1 - z$ ]. Thus, there is a chain running along the *c* axis. In addition to the C—H $\cdots\pi$  interactions, a weak face-to-face interaction is observed between ring  $\text{CgA}$  at  $(x, y, z)$  and  $\text{CgA}$  at  $(-1 - x, -1 - y, -z)$ , with the centroids separated by  $3.819(3) \text{ \AA}$  ( $\text{CgA}$  and  $\text{CgC}$  represent the centroids of benzene rings A and C, respectively).

## Experimental

A solution of 1,3-bis[4-(bromomethyl)phenoxy]methyl]benzene (100 ml, 1 mmol) and  $\text{CS}_2$  (2 mmol) in dry THF was added at room temperature to a slurry of sodium borohydride (4 mmol) in THF (100 ml) and the resulting solution was stirred for 6 h. The reaction mixture was worked up with aqueous ammonium chloride, extracted with  $\text{CHCl}_3$  and dried over sodium sulfate. The solvent was removed and the crude product was purified by column chromatography [ $\text{SiO}_2$ , ethylacetate-hexane (1:19)] and recrystallized from ethyl acetate.

### Crystal data

$\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}_2$	$Z = 2$
$M_r = 394.53$	$D_x = 1.306 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.995(5) \text{ \AA}$	Cell parameters from 25 reflections
$b = 10.372(7) \text{ \AA}$	$\theta = 1.8\text{--}12.6^\circ$
$c = 10.508(5) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$\alpha = 101.84(5)^\circ$	$T = 293(2) \text{ K}$
$\beta = 91.14(5)^\circ$	Block, colourless
$\gamma = 109.01(5)^\circ$	$0.46 \times 0.29 \times 0.28 \text{ mm}$
$V = 1003.5(10) \text{ \AA}^3$	

### Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 30.0^\circ$
Non-profiled $\omega/2\theta$ scans	$h = -14 \rightarrow 13$
Absorption correction: none	$k = 0 \rightarrow 14$
6133 measured reflections	$l = -14 \rightarrow 14$
5832 independent reflections	3 standard reflections
3032 reflections with $I > 2\sigma(I)$	every 200 reflections
$R_{\text{int}} = 0.023$	intensity decay: 3%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.127$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
5832 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
245 parameters	Extinction correction: <i>SHELXL</i>
H-atom parameters constrained	Extinction coefficient: 0.070(4)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1—C15	1.805(2)	O1—C8	1.370(2)
S1—C14	1.810(3)	O1—C7	1.425(2)
S2—C15	1.786(2)	O2—C20	1.377(2)
S2—C16	1.820(2)	O2—C23	1.435(3)
C15—S1—C14	100.7(1)	C20—O2—C23	118.4(2)
C15—S2—C16	101.7(1)	S2—C15—S1	111.2(1)
C8—O1—C7	118.0(2)		
C6—C7—O1—C8	-72.7(2)	S2—C15—S1—C14	171.8(1)
C11—C14—S1—C15	-77.0(2)	C17—C16—S2—C15	-63.1(2)
S1—C15—S2—C16	-76.3(1)	C2—C23—O2—C20	-80.5(2)

All H atoms were positioned geometrically and allowed to ride on their parent C atoms, with C—H distances in the range  $0.93\text{--}0.97 \text{ \AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{parent C})$ .

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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