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# 1,8,14,20-Tetraoxa-11,23-dithiatricyclo[21.3.0.09,13]hexacos

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# 1,8,14,20-Tetraoxa-11,23-dithiatricyclo[21.3.0.09,13]hexacosa-9,12,21,24-tetraene

## Abstract

Crystals of the title compd. are orthorhombic, space group  $Pbca$ ;  $Z = 4$ . Mols. lie on crystallog. centers of inversion, but have approx.  $C_{2h}$  mol. symmetry. The parallel thiophene rings are almost exactly planar; the overall conformation of the mol. is chair-like. The mols. have voids that could, in principle, accommodate small guest mols., although in the crystal structure access to these voids is blocked by neighboring mols.

## Keywords

13, 9, 12, 24, tetraene, 14, 20, 11, 23, 21, 3, 1, 8, 09, hexacosa, tetraoxa, dithiatricyclo

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# 1,8,14,20-Tetraoxa-11,23-dithia- tricyclo[21.3.0.0<sup>9,13</sup>]hexacosane- 9,12,21,24-tetraene

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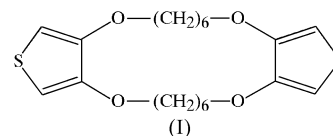
Molecules of the title compound, C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>S<sub>2</sub>, the first compound with a tetraoxacyclohexacosane ring to be structurally characterized, lie on crystallographic centres of inversion, but have approximate C<sub>2h</sub> molecular symmetry. The parallel thiophene rings are almost exactly planar; the overall conformation of the molecule is chair-like. The molecules have voids that could, in principle, accommodate small guest molecules, although in the crystal structure access to these voids is blocked by neighbouring molecules.

## Comment

Since their discovery in 1977 (Shirakawa *et al.*, 1977), conjugated polymers have played an important role in modern science. Among the conjugated polymers studied to date, alkoxy- and dialkoxypolythiophenes (Skompska *et al.*, 2005), and especially ethylenedioxythiophene (EDOT), have proved to be the most interesting among these materials (Groenendal *et al.*, 2003; Ronali *et al.*, 2005). Owing to several distinct advantages, polyethylenedioxythiophene (PEDOT) has rapidly acquired a prominent position among conducting polymers. A unique combination of moderate band gap and low oxidation potential confers on PEDOT an exceptional stability of the oxidized charged state, which furthermore exhibits high conductivity and good optical transparency in the visible spectroscopic region (Jonas & Schrader, 1991). To date, a large family of poly(alkylenedioxythiophenes), and therefore alkylenedioxythiophenes themselves, have been synthesized in order to elucidate the structure–property relationships in these materials (Kumar *et al.*, 1998).

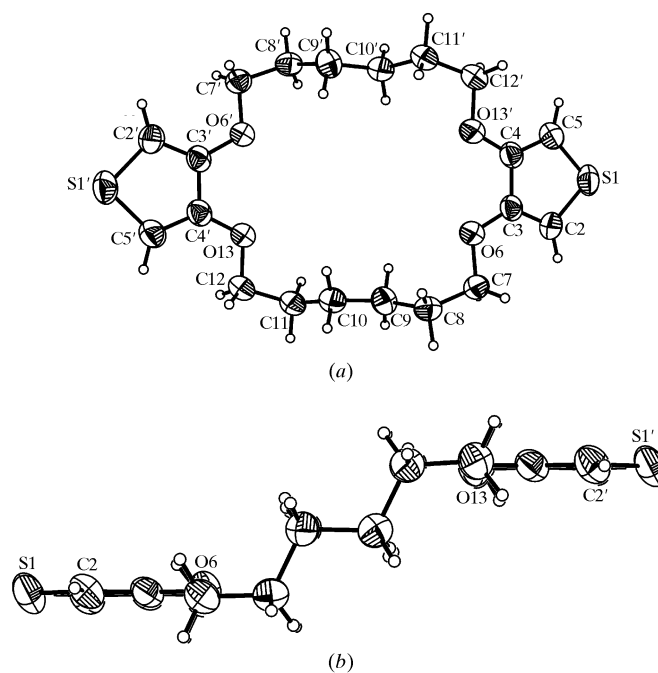
There are only 38 fragments of 3,4-dioxo-substituted thiophenes in the Cambridge Structural Database (CSD, Version 5.27 of November 2005, plus updates to January 2006; Allen,

2002); of these, 30 contain the 3,4-ethylenedioxythienyl group. Only two structures have longer alkoxy chains, *viz.* 3,4-bis(hexadecyloxy)thiophene (CSD refcode ABUQET; Storsberg *et al.*, 2001) and the dithiaporphyrin derivative 2,3,2,13-tetrabutoxy-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (Agarwal *et al.*, 2002). The crystal structure of the title compound, (I), is the first example of a molecule with two thiophene moieties connected by long chains. Surprisingly, it is also the first crystal structure of a molecule that possesses a tetraoxacyclohexacosane ring.



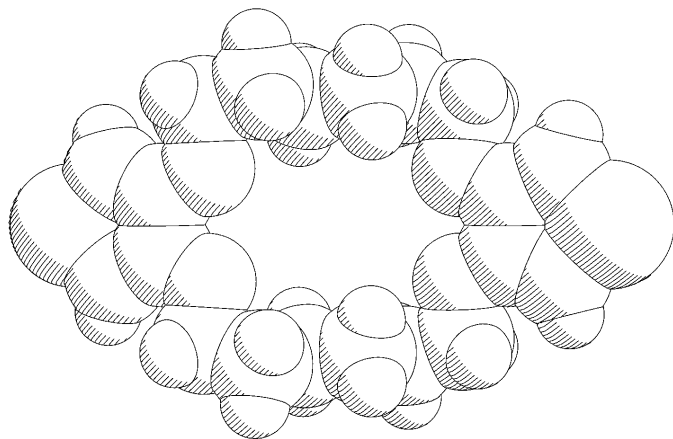
The molecule of (I) is symmetrical (Fig. 1*a*) and lies on a centre of inversion in space group *Pbca*. Moreover, there are two other approximate symmetry elements, namely a twofold axis through the mid-points of the C9–C10 and C9<sup>i</sup>–C10<sup>i</sup> bonds [symmetry code (i)  $-x, 2-y, 1-z$ ], and a mirror plane perpendicular to this axis and containing the S atoms and the mid-points of the C3–C4 and C3<sup>i</sup>–C4<sup>i</sup> bonds. Thus, the overall symmetry of the molecule is closest to C<sub>2h</sub>.

The molecular dimensions are typical (Table 1). The five-membered thiophene ring is planar within experimental error [maximum deviation from the least-squares plane is 0.003 (1) Å for atom C3]. Also, the deviations of the O atoms



**Figure 1**

(*a*) A perspective view of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (*b*) A side view of the molecule of (I), showing the chair-like conformation. Primed atoms are at the symmetry position ( $-x, -y+2, -z+1$ ).



**Figure 2**  
A van der Waals sphere representation of (I).

from this plane are almost negligible [O—C—C—O = 0.2 (3)°]. The conformation of the eight-membered chain can be analyzed in terms of its torsion angles (Table 1) and can be described as *a-sc-a-a-a-sc-a*. This conformation results in an overall chair-like conformation of the molecule (Fig. 1b).

The molecule has a void that, in principle, could accommodate small guest molecules [diagonal O...O distances across the void are 6.702 (3) and 6.754 (3) Å; Fig. 2]. However, in reality, neighbouring molecules completely block access to this void.

Only very weak intermolecular C—H...S interactions can be found in the crystal structure of (I) (H...S distances of ca 3.1 Å and C—H...S angles close to 160°). Therefore, van der Waals forces seem to be responsible for the crystal packing.

## Experimental

The synthesis of the title compound was reported by Czardybon *et al.* (2003). Crystals suitable for X-ray data collection were grown from a methanol solution.

### Crystal data

C<sub>20</sub>H<sub>28</sub>O<sub>4</sub>S<sub>2</sub>  
M<sub>r</sub> = 396.54  
Orthorhombic, *Pbca*  
a = 9.595 (2) Å  
b = 8.267 (2) Å  
c = 26.350 (5) Å  
V = 2090.1 (8) Å<sup>3</sup>  
Z = 4  
D<sub>x</sub> = 1.260 Mg m<sup>-3</sup>

Mo Kα radiation  
Cell parameters from 73 reflections  
θ = 3.3–20.1°  
μ = 0.28 mm<sup>-1</sup>  
T = 295 (2) K  
Block, colourless  
0.6 × 0.4 × 0.3 mm

### Data collection

Kuma KM-4 diffractometer  
ω/2θ scans  
1845 measured reflections  
1845 independent reflections  
1125 reflections with I > 2σ(I)  
θ<sub>max</sub> = 25.1°

h = 0 → 11  
k = 0 → 9  
l = -31 → 30  
2 standard reflections  
every 100 reflections  
intensity decay: 0.7%

**Table 1**  
Selected geometric parameters (Å, °).

S1—C5	1.720 (3)	C4—O13 <sup>i</sup>	1.353 (3)
S1—C2	1.724 (3)	O6—C7	1.435 (3)
C3—O6	1.360 (2)	C12—O13	1.435 (3)
C5—S1—C2	91.79 (11)	O13 <sup>i</sup> —C4—C3	118.34 (17)
C3—C2—S1	111.22 (18)	C5—C4—C3	112.1 (2)
C2—C3—O6	128.9 (2)	C4—C5—S1	111.92 (18)
C2—C3—C4	112.96 (19)	C3—O6—C7	115.95 (16)
O6—C3—C4	118.13 (18)	C4 <sup>i</sup> —O13—C12	116.68 (16)
O13 <sup>i</sup> —C4—C5	129.6 (2)		
C3—O6—C7—C8	179.25 (18)	C9—C10—C11—C12	-163.08 (19)
O6—C7—C8—C9	72.4 (3)	C10—C11—C12—O13	68.5 (3)
C7—C8—C9—C10	-154.3 (2)	C11—C12—O13—C4 <sup>i</sup>	-176.95 (18)
C8—C9—C10—C11	-168.1 (2)		

Symmetry code: (i) -x, -y + 2, -z + 1.

### Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.036  
wR(F<sup>2</sup>) = 0.105  
S = 0.98  
1845 reflections  
175 parameters  
All H-atom parameters refined

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0684P)<sup>2</sup>]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> = 0.001  
Δρ<sub>max</sub> = 0.27 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.21 e Å<sup>-3</sup>  
Extinction correction: SHELXL97  
(Sheldrick, 1997)  
Extinction coefficient: 0.0208 (19)

Data collection: *KM-4 User's Guide* (Kuma, 1991); cell refinement: *KM-4 User's Guide*; data reduction: *KM-4 User's Guide*; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1181). Services for accessing these data are described at the back of the journal.

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