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

Pawel Wagner
University of Wollongong, pawel@uow.edu.au

Maciej Kubicki
Adam Mickiewicz University

Mieczyslaw Lapkowski
Silesian University of Technology

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Abstract
Crystals of the title compd. are orthorhombic, space group Pbca; Z = 4. Mols. lie on crystallog. centers of inversion, but have approx. C2h 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.

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1,8,14,20-Tetraoxa-11,23-dithiacyclo[21.3.0.0^9,13]hexacosa-9,12,21,24-tetraene

Paweł Wagner, a Mieczysław Łapkowski b and Maciej Kubicki* c

a Nanomaterials Research Centre, and MacDiarmid Institute for Advanced Materials and Nanotechnology, Massey University, Private Bag 11 222, Palmerston North, New Zealand, b Institute of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Strzydy 9, 44-100 Gliwice, Poland, and c Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Correspondence e-mail: mkubicki@amu.edu.pl

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Molecules of the title compound, C_{20}H_{28}O_{4}S_{2}, the first compound with a tetraoxacyclohexacosane ring to be structurally characterized, lie on crystallographic centres of inversion, but have approximate \textit{C}_{2h} 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-ethylendioxythiophenyl 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. 1a) and lies on a centre of inversion in space group \textit{Pbca}. Moreover, there are two other approximate symmetry elements, namely a twofold axis through the mid-points of the C9–C10 and C9’–C10’ 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’–C4’ bonds. Thus, the overall symmetry of the molecule is closest to \textit{C}_{2h}.

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

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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 $-x, -y+2, -z+1$.
from this plane are almost negligible \[O - C - C - O = 0.2 \text{ (3)} \]. The conformation of the eight-membered chain can be analyzed in terms of its torsion angles (Table 1) and can be described as \(a-sc-a-a-sc-a\). This conformation results in an overall chair-like conformations of the molecule (Fig. 1b).

The molecule has a void that, in principle, could accommodate small guest molecules [diagonal \(O \cdots O\) 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 \(C \cdots S\) interactions can be found in the crystal structure of (I) (\(H \cdots S\) distances of ca 3.1 Å and \(C - H \cdots S\) 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**

\[C_{20}H_{28}O_{4}S_{2}\]

- Molar mass: 396.54
- Orthorhombic, \(Pbca\)
- \(a = 9.595 \text{ (2)}\) Å
- \(b = 6.827 \text{ (2)}\) Å
- \(c = 26.350 \text{ (5)}\) Å
- \(V = 2090.1 \text{ (8)}\) Å³
- \(Z = 4\)
- \(D_{m} = 1.260 \text{ Mg m}^{-3}\)

**Data collection**

- Mo \(K\alpha\) radiation
- Cell parameters from 73 reflections
- \(\theta = 3.3-20.1°\)
- \(\mu = 0.28 \text{ mm}^{-1}\)
- \(T = 295 \text{ (2)}\) K
- Block, colourless
- \(0.6 \times 0.4 \times 0.3\) mm

**Refinement**

- Refinement on \(F^{2}\)
- \(R[F^{2} > 2\sigma(F^{2})] = 0.036\)
- \(wR(F^{2}) = 0.105\)
- \(S = 0.98\)
- 1845 reflections
- 175 parameters
- All H-atom parameters refined

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

**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.

**References**


