Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1,8,14,20-Tetraoxa-11,23-dithiatricyclo[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, Strzody 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

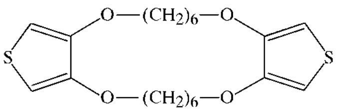
Received 20 January 2006
Accepted 10 February 2006
Online 11 March 2006

Molecules of the title compound, $C_{20}H_{28}O_4S_2$, the first compound with a tetraoxacyclohexacosane ring to be structurally characterized, lie on crystallographic centres of inversion, but have approximate 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).

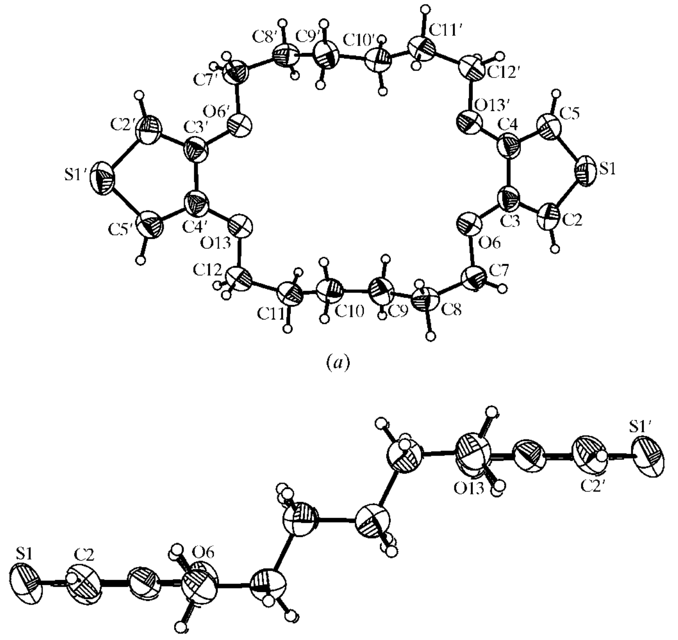
There are only 38 fragments of 3,4-dioxo-substituted thiophenes in the Cambridge Structural Database (CSD, Version 5.27 of November 2005, plus updates to January 2006; Allen, 2002); of these, 30 contain the 3,4-ethylenedioxythienyl group. Only two structures have longer alkyloxy chains, *viz.* 3,4-bis(hexadecyloxy)thiophene (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.



(I)

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^{i}—C10^{i} 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^{i}—C4^{i} bonds. Thus, the overall symmetry of the molecule is closest to 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



(*a*)

(*b*)

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 $(-x, -y+2, -z+1)$.

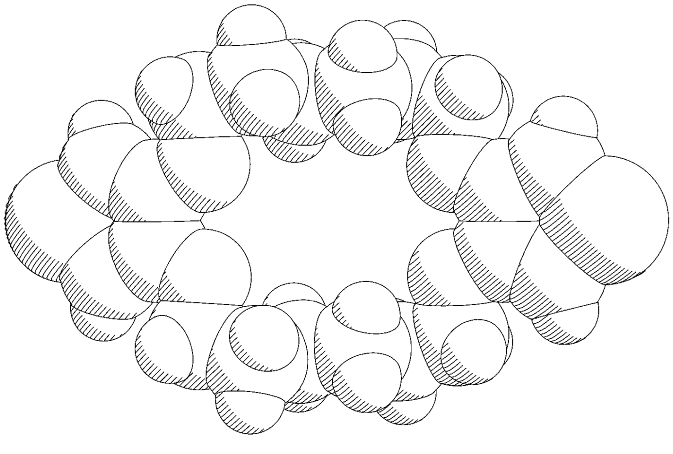


Figure 2
A van der Waals sphere representation of (I).

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. 1*b*).

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

$C_{20}H_{28}O_4S_2$
M_r = 396.54
Orthorhombic, *Pbca*
a = 9.595 (2) Å
b = 8.267 (2) Å
c = 26.350 (5) Å
V = 2090.1 (8) Å^3
Z = 4
D_x = 1.260 Mg m^{-3}

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

Data collection

Kuma KM-4 diffractometer
ω/2*θ* scans
1845 measured reflections
1845 independent reflections
1125 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 25.1°

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

Table 1
Selected geometric parameters (Å, °).

S1—C5	1.720 (3)	C4—O13^i	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^i—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^i—O13—C12	116.68 (16)
O13^i—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^i	−176.95 (18)
C8—C9—C10—C11	−168.1 (2)		

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

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

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 e Å^{-3}
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.

References

Agarwal, N., Mishra, S. P., Kumar, A., Hung, C.-H. & Ravikanth, M. (2002). *Chem. Commun.* pp. 2642–2643.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Czardybon, A., Domagala, W. & Lapkowski, M. (2003). *Synth. Met.* **135–136**, 27–28.
Groenendal, L. B., Zotti, G., Aubert, P. H., Waybright, S. M. & Reynolds, J. R. (2003). *Adv. Mater.* **15**, 855–879.
Jonas, F. & Schrader, L. (1991). *Synth. Met.* **41–43**, 831–836.
Kuma (1991). *KM-4 User's Guide*. Version 5.0. Kuma Diffraction, Wrocław, Poland.
Kumar, A., Welsh, D. M., Morvant, M. C., Piroux, F., Abboud, K. A. & Reynolds, J. R. (1998). *Chem. Mater.* **10**, 896–902.
Ronali, J., Blanchard, P. & Frere, P. (2005). *J. Mater. Chem.* **15**, 1589–1610.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K. & Heeger, A. J. (1977). *J. Chem. Soc. Chem. Commun.* pp. 578–580.
Siemens (1989). *Stereochemical Workstation Operation Manual*. Release 3.4. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Skompska, M., Mieczkowski, J., Holze, R. & Heinze, J. (2005). *J. Electroanal. Chem.* **577**, 9–17.
Storsberg, J., Ritter, H. & Schollmeyer, D. (2001). Contribution from thesis, J. Storsberg, University of Mainz, Germany.

o156 Wagner *et al.* • $C_{20}H_{28}O_4S_2$ *Acta Cryst.* (2006). C**62**, o155–o156