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(E,E,E)-1,3,5-Tris[4-(acetylsulfanyl)-styryl]benzene toluene hemisolvate

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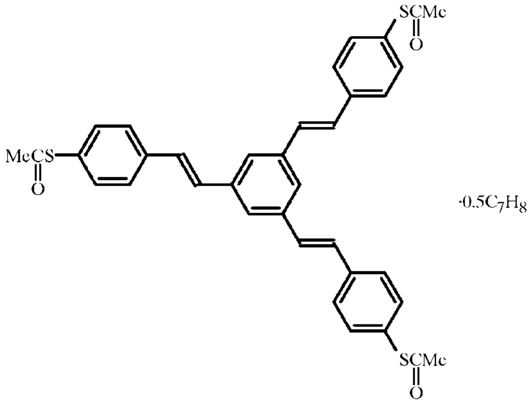
The first crystal structure of a three-terminal sulfur end-capped oligophenylenevinylene, $C_{36}H_{30}O_3S_3 \cdot 0.5C_7H_8$, has been determined at 122 (1) K. The molecular threefold symmetry is not utilized in the crystal structure. It is confirmed that the double bonds have been fully transformed into a *trans* configuration by iodine treatment.

Comment

Sulfur end-capped oligophenylenevinylenes (OPVs) have recently aroused attention since our group has shown that transistors based on one single OPV (Kubatkin *et al.*, 2003) can be made. Despite their potential applications in molecular electronics, only a limited number of sulfur end-capped OPVs have been reported. The title compound and higher analogues are currently being investigated as molecular components in three-terminal electronic devices, either by simply assembling gold clusters at the sulfur terminals (Novak & Feldheim, 2000) or attached between three gold electrodes manufactured by break junction techniques (Tour *et al.*, 1995; Kergueris *et al.*, 1999). Especially regarding the latter system, it is possible that these molecules upon assembly at the electrodes will provide devices possessing so far unknown nanoelectromechanical properties.

Unlike their triple-bonded counterparts phenylene ethynylenes, which can only exist in one geometry, OPVs can adopt several conformations as a result of the possibility of having either a *cis* or *trans* conformation of each double bond. In our recently reported syntheses of sulfur end-capped OPVs (Stuhr-Hansen, 2003; Stuhr-Hansen *et al.*, 2003), all OPVs were prepared all-*trans* by treatment with a catalytic amount of iodine in boiling toluene. By this treatment, eventual *cis* linkages are transformed into the thermodynamically more stable *trans* geometries. In order to determine the structure of the OPVs, a crystal of a representative sulfur end-capped OPV, the title compound, (I), with an appropriate quality for X-ray analysis, was obtained by slow recrystallization from toluene. To our knowledge, this is the first structure determination of a three-terminal sulfur end-capped OPV.



(I)

The structure of (I) shown in Fig. 1 confirms that all double bonds have been converted into the *trans* conformation by the iodine treatment. Furthermore, the possible molecular threefold symmetry is not utilized in the crystal packing. As all three double bonds are found in *trans* conformations with the same bond distances (see Table 1), the lack of molecular symmetry is found in the conformations of the three 4-(acetylsulfanyl)styryl groups. The angles between the planes of the side-chain phenyl groups and the central benzene ring are slightly different, *viz.* 2.25 (9), 9.45 (8) and 5.07 (8)°. Another difference is found in the conformation of the acetylsulfanyl groups, which can be illustrated by the Cn5—Sn—Cn2—Cn1 torsion angles (n = 1, 2 and 3). The torsion angles shown in Table 1 and Fig. 1 illustrate that all three acetylsulfanyl groups are situated on the same side of the

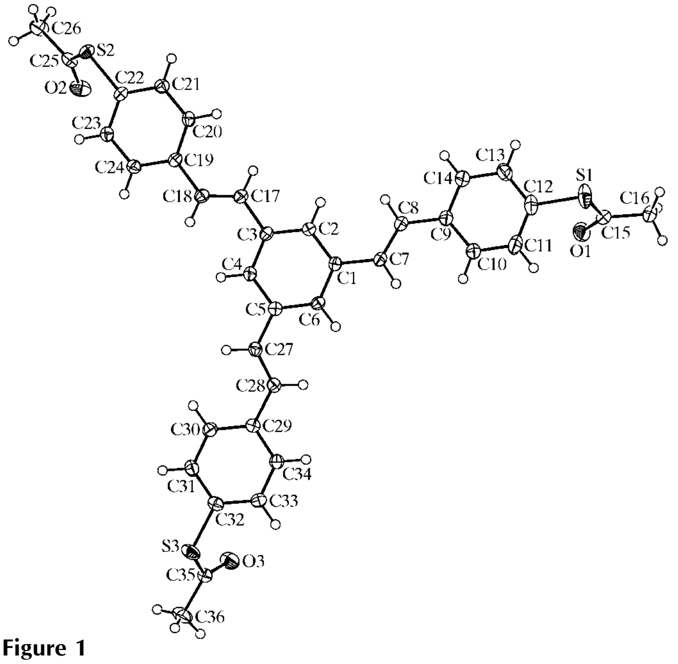


Figure 1
ORTEPII drawing (Johnson, 1976) of (I), including labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres with arbitrary radii.

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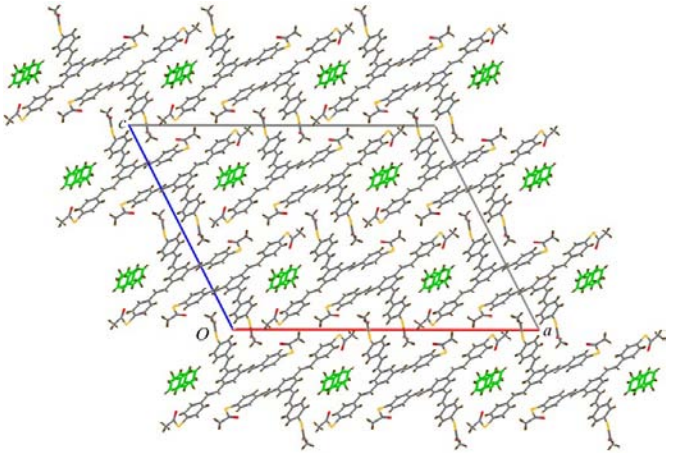

Figure 2
Packing diagram of (I), viewed down the *b* axis, illustrating the alternating layers of aromatic and acetylsulfanyl groups.

molecular plane but are rotated differently. The side group including atom S1 differs from the other two by having a torsion angle of less than 90° and thereby being located on the other side of the plane perpendicular to the phenyl group. Only one bond distance in the acetylsulfanyl group differs, *viz.* S*n*—C*n*5. This difference seems to be related to the variation in the torsion angles just mentioned. The closer the torsion angle is to 90°, the shorter the S*n*—C*n*5 bond distance.

There does not seem to be any appreciable degree of conjugation between the phenyl groups *via* the double bonds, as the $C_{ethenyl}—C_{ph}$ distances are all within 2 s.u. of 1.470 Å, compared with an average double-bond distance of 1.333 (2) Å. These bond lengths (Table 1) are also in perfect agreement with the average styrylbenzene moities extracted from the Cambridge Structural Database (Version 5.26 of November 2004; Allen, 2002), where the complementary average bond lengths are 1.469 and 1.326 Å for single and double bonds, respectively.

The structure consists of alternating layers of sections including the acetylsulfanyl groups (layers centred at $c = 0$ and $c = \frac{1}{2}$) and sections consisting of only the aromatic groups (layers centred at $c = \frac{1}{4}$ and $c = \frac{3}{4}$), as shown in Fig. 2. The three long substituents of the central benzene ring make it difficult to form a dense crystal packing. Instead, channels along the *b* axis in the aromatic layers accommodate toluene molecules in a disordered fashion. The disorder was resolved into two sites related by symmetry ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), with an occupation factor of 0.5. The toluene solvent molecules are involved in intermolecular interactions with the benzene rings of the tristyrylbenzene molecule. The toluene molecule occupying one site is engaged in π–π interactions, as well as acting as a hydrogen-bond donor in a C—H$\cdots\pi$ hydrogen bond, whereas the toluene molecule in the other position acts as a hydrogen-bond acceptor, besides participating in π–π interactions with the tristyrylbenzene molecule. No classical hydrogen-bond donors are available; hence only a few weak bonds that fall within the geometric criteria for C—H$\cdots$O hydrogen bonds suggested by Steiner (1996) are observed. The five hydrogen bonds observed are listed in Table 2.

Experimental

The title compound was synthesized as described by Stuhr-Hansen *et al.* (2003). Crystals suitable for X-ray diffraction analysis were obtained by slow crystallization from hot toluene.

Crystal data

$C_{36}H_{30}O_3S_3 \cdot 0.5C_7H_8$
$M_r = 652.85$
Monoclinic, $C2/c$
$a = 38.419$ (3) Å
$b = 6.8061$ (4) Å
$c = 28.813$ (3) Å
$\beta = 117.115$ (12)°
$V = 6706.1$ (12) Å^3
$Z = 8$

$D_x = 1.293$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 37009 reflections
$\theta = 2.2$–30.0°
$\mu = 0.26$ mm^{-1}
$T = 122$ (1) K
Needle, pale yellow
0.42 × 0.34 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: numerical *via* Gaussian integration (Coppens, 1970)
$T_{min} = 0.91$, $T_{max} = 0.96$
86319 measured reflections

9790 independent reflections
7824 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 30.0°$
$h = -54 \rightarrow 54$
$k = -9 \rightarrow 9$
$l = -40 \rightarrow 40$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.125$
$S = 1.09$
9790 reflections
442 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 9.7732P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C15	1.7834 (19)	C3—C17	1.474 (2)
S2—C25	1.7898 (16)	C17—C18	1.332 (2)
S3—C35	1.7731 (18)	C18—C19	1.467 (2)
C5—C27	1.468 (2)	C1—C7	1.471 (2)
C27—C28	1.335 (2)	C7—C8	1.331 (2)
C28—C29	1.472 (2)	C8—C9	1.467 (2)
C15—S1—C12—C11	67.1 (2)	C35—S3—C32—C31	117.27 (13)
C25—S2—C22—C21	123.26 (13)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C16—H16*A*$\cdots$O3^{i}	0.98	2.52	3.403 (2)	150
C16—H16*B*$\cdots$O2^{ii}	0.98	2.46	3.368 (2)	155
C24—H24$\cdots$O2^{iii}	0.95	2.41	3.356 (2)	173
C26—H26*C*$\cdots$O3^{iv}	0.98	2.40	3.272 (2)	148
C81—H81$\cdots$O1	0.95	2.60	3.181 (5)	120

Symmetry codes: (i) $x + \frac{1}{2}, -y - \frac{7}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{3}{2}, -z + \frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $-x, -y - 1, -z$.

All H atoms were located in a difference Fourier map and then treated as riding atoms, with C—H distances of 0.95 Å for aromatic H atoms and 0.98 Å for methyl H atoms. Isotropic displacement parameters for all H atoms were constrained to $1.2U_{eq}$ of the parent non-H atom ($1.5U_{eq}$ for methyl groups). Disordered toluene molecules were identified in the difference Fourier map. The toluene molecules are related by the symmetry code ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$).

Toluene was introduced with a fixed geometry obtained from the literature (Irngartinger *et al.*, 1999) and initially refined as a rigid body with a fixed occupancy of 0.5. In the final model, the geometrical constraints were removed and the displacement parameters of all non-H atoms were refined. The occupancy factor of toluene did not change upon release and joint refinement.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1855). Services for accessing these data are described at the back of the journal.

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