Flip-type disorder in 3-substituted 2,2':5',2''-terthiophenes

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Abstract
In the crystal structures of four thiophene derivs., (E)-3'-[2-(anthracen-9-yl)ethenyl]-2,2':5',2''-terthiophene, C28H18S3, (E)-3'-[2-(1-pyrenyl)ethenyl]-2,2':5',2''-terthiophene, C30H18S3, (E)-3'-[2-(3,4-dimethoxyphenyl)ethenyl]-2,2':5',2''-terthiophene, C22H18O2S3, and (E,E)-1,4-bis[2-(2,2':5',2''-terthiophen-3'-yl)ethenyl]-2,5-dimethoxybenzene, C36H26O2S6, at least one of the terminal thiophene rings is disordered and the disorder is of the flip type. The terthiophene fragments are far from being coplanar, contrary to terthiophene itself. The central C-C=C-C fragments are almost planar but the bond lengths suggest slight delocalization within this fragment.

Keywords
Flip, type, disorder, substituted, terthiophenes

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Flip-type disorder in 3-substituted 2,2′:5′,2″-terthiophenes

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In the crystal structures of four thiophene derivatives, (E)-3′-[2-(anthracen-9-yl)ethenyl]-2,2′:5′,2″-terthiophene, C 28 H 18 S 3 , (E)-3′-[2-(1-pyrenyl)ethenyl]-2,2′:5′,2″-terthiophene, C 30 H 18 S 3 , (E)-3′-[2-(3,4-dimethoxyphenyl)ethenyl]-2,2′:5′,2″-terthiophene, C 22 H 18 O 2 S 3 , and (E,E)-1,4-bis[2-(2,2′:5′,2″-terthiophen-3′-yl)ethenyl]-2,5-dimethoxybenzene, C 36 H 26 O 2 S 6 , at least one of the terminal thiophene rings is disordered and the disorder is of the flip type. The terthiophene fragments are far from being coplanar, contrary to terthiophene itself. The central C—C=C—C fragments are almost planar but the bond lengths suggest slight delocalization within this fragment. The crystal packing is determined by van der Waals interactions and some weak, relatively short, C—H⋯S and C—H⋯π directional contacts.

Comment

Since their discovery in 1977 (Chiang et al., 1977; Shirakawa et al., 1977), conjugated polymers and oligomers have been investigated extensively for use in applications such as solar cells, actuators, light-emitting diodes and nonlinear optical materials (Skotheim & Reynolds, 2007). Prominent among the conjugated materials studied to date are the oligo- and polythiophenes. These materials have good chemical stability in both their oxidized and reduced states, and a wide variety of functionality can be readily built on to the monomers, whether thiophene, bithiophene or terthiophene (for example, Roncali, 1999; Grant et al., 2005, and references therein).

One of the ways in which the electronic properties of thiophene oligomers and polymers may be tuned is to introduce functionality to the polymer chain, typically in the form of aromatic substituents. Thus, poly(3-arylthiophenes) have improved doping capacity and cyclability compared with polythiophene (Ferraris et al., 1998; Villers et al., 2003), and fusing benzene to thiophene leads to poly(isothianaphthene), the prototypical small band gap polymer (Wudl et al., 1984). In contrast to the planar-fused benzene ring of the isothianaphthene, the 3-aryl substituents are twisted out of the plane of the polymer backbone, reducing their electronic impact as well as disrupting the polymer interchain interactions. The styryl group is an alternative and readily accessible aromatic functionality which should not have these disadvantages and may enhance a planar morphology.

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the molecule with the greater occupancy is represented.

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Attempts to polymerize styrylthiophenes, however, have not been so successful. Electrochemical homopolymerization of 3-styrylthiophene resulted in a nonconductive material, presumably through side-chain polymerization, and other styryl derivatives showed similar behaviour (Smith et al., 1994). However, electrically conductive polymers have been obtained by copolymerization of styryl-substituted thiophenes with 3-methylthiophene (Welzel et al., 1997), and an improvement in the photoconductivity of polythiophene was accomplished on copolymerization of thiophene and 3-(4-nitrostyryl)thiophene (Greenwald et al., 1996). Copolymers of bithiophene and para-substituted (E)-3-styrylthiophenes have also been shown to produce photovoltaic responses in photoelectrochemical cells (Cutler et al., 2001). Whilst these copolymerizations undoubtedly lead to improvement in desirable polymer properties, their irregular and random structure makes it difficult to deconvolute the role of the substituent in these improvements.

An alternative approach to the formation of regioregular styryl-functionalized oligo- and polythiophene is to polymerize styryl-substituted terthiophene monomers, and towards this end we have reported the syntheses of a range of terthiophene functionalized at the 3'-position with styryl groups (for example, Collis et al., 2003; Grant & Officer, 2005). We have demonstrated that the styryl functionality can control oligomer regioregularity and provides advantages in some applications. However, styrylterthiophenes largely form dimers on oxidative polymerization as a result of ‘polaron trapping’ (Clarke et al., 2007).

There are only a few structural determinations of simple terthiophene derivatives; we have therefore determined the X-ray crystal structures of four compounds, viz. (E)-3'-[2-(anthracen-9-yl)ethenyl]-2,2':5',2''-terthiophene, (I), (E)-3'-[2-(1-pyrenyl)ethenyl]-2,2':5',2''-terthiophene, (II), (E,E)-3'-[2-(3,4-dimethoxyphenyl)ethenyl]-2,2':5',2''-terthiophene, (III), and (E,E)-1,4-bis[2-(2,2':5',2''-terthiophen-3'-yl)ethenyl]-2,5-dimethoxybenzene, (IV). In all these structures, the interesting case of a flip disorder of (at least) one of the terminal thiophene rings can be found. The preliminary data of compounds (I)-(III) were reported by Wagner & Officer (2005).

Perspective views of the molecules of (I)-(IV) are shown in Figs. 1-4. In the structure of (III), there are two symmetry-independent molecules (Z' = 2); there are significant differences in the conformations of these two molecules, but the bond lengths and angles are similar [according to the normal probability plot; International Tables for X-ray Crystallography (1969). Vol. IV, pp. 293-309; Abrahams & Keve, 1971].

In all six terthiophene fragments [the molecule of (IV) contains two such fragments, cf. Fig. 4] there is a flip disorder of one of the thiophene rings; in one of the fragments of (IV), two rings are disordered. All the structures were refined successfully with some restraints on the displacement parameters of disordered C atoms. The disorder is connected to two statistically distributed orientations of the thiophene S atom. In practice, that means that there are two molecules in which the thiophene rings are rotated by 180° approximately along the line that bisects the S—C—C angle. These two orientations are not equivalent; the site-occupation factors of the higher-occupancy group refined at 0.71 (1) in (I), 0.76 (1) in (II), 0.66 (1) in (IIIA), 0.76 (1) in (IIIB), 0.56 (1) in (IVA), and 0.54 (1) and 0.67 (1) in (IVB). A disorder of this kind is often observed in the structures of simple thiophene derivatives with one substituent, for example, in (E)-3'-[2-(4-cyanophenyl)ethenyl]-2,2':5',2''-terthiophene (Collis et al., 2003) or in 3-[2-(anthracen-9-yl)ethenyl]thiophene (Wagner et al., 2006).

The terthiophene fragments are far being planar (Table 1), contrary to terthiophene itself (van Bolhus et al., 1989) or its 3-methyl derivatives 3-methyl-2,2':5',2''-terthiophene (Chaloner et al., 1997) and 3,3',4''-trimethyl-2,2':5',2''-terthiophene (Barbarella et al., 1994), in which the dihedral angles between the planes of the rings are not larger than 9°. Two different modes of folding can be recognized.

(i) The terminal rings are twisted in opposite senses with respect to the central ring and, in consequence, the dihedral angles between the planes of the rings are not larger than 9°. Two different modes of folding can be recognized.

(ii) The central ring is twisted in the opposite sense to one of the terminal rings, whereas the other terminal ring is almost parallel to the central one. In consequence, the dihedral angles between the planes of the rings are not larger than 9°.

(iii) The terminal rings are twisted in the same sense with respect to the central ring. In consequence, the dihedral angles between the planes of the rings are not larger than 9°.

Figure 2
A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the molecule with the greater occupancy is represented.

Figure 3
A view of the molecule of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the molecule with the greater occupancy is represented.
The angle between terminal rings is not far from the sum of the angles between the central and the terminal rings [this mode is observed in (I), (II) and (III)].

(ii) The terminal rings are twisted in the same sense with respect to the central ring, and the dihedral angle between the terminal rings is smaller than the angles between the central and terminal rings [(III) and (IV)]. [Fig. 5 shows the comparison of these two modes for the two symmetry-independent molecules of (III).]

The C—C—C—C fragments are almost planar [with a maximum deviation of up to 0.022 (3) Å], but the bond-length patterns suggest that there is only slight delocalization within these systems. For (I) and (II), these C—C—C—C planes are far more twisted with respect to the large aromatic ring planes than with respect to the central thiophene rings; this is probably a manifestation of the tendency towards minimizing the H⋯H steric interactions. For (III) and (IV), the dihedral angles between the appropriate planes are comparable.

The large aromatic fragments in (I) and (II) are twisted significantly with respect to the central thiophene ring [the dihedral angles are 78.80 (8)° for anthracene in (I) and 64.99 (5)° for pyrene in (II)], while the twist of the benzene ring in (III) and (IV) is significantly smaller [up to 10.4 (1)°; Table 1]. These conformations are probably a result of the balance between the steric stress caused by the vicinity of the vinyl and the aromatic H atoms and the tendency towards the flattening of the resonance fragment.

In the crystal structures, the van der Waals forces seem to determine the packing. Some weak specific C—H⋯S and C—H⋯σ directional interactions might also be of some importance (Table 2). In the case of (III), the bifurcated C—H⋯O hydrogen bonds connect the molecules into ‘homomolecular’ ...AA... and ...BB... chains. Interestingly, there are no short contacts between the ring centroids, which shows that the σ⋯π interactions are meaningless in this class of compounds; this might be due to the complicated conformations of the molecules as a whole. The stacking interactions seem to be in conflict with the tendency towards the densest packing.

**Experimental**

The investigated compounds were synthesized in a similar fashion to other styryl terthiophenes (Collis et al., 2001, 2003). Crystals of (I)–(III) were obtained by slow evaporation of ethanol. A crystal of (IV) suitable for analysis was grown by solvent diffusion techniques (tetrahydrofuran/hexane).

**Compound (I)**

**Crystal data**

\[
\begin{align*}
C_{28}H_{18}S_3 & \\
Mr & = 450.60 \\
Triclinic, P & \\
t & = 153 (2) K \\
\theta & = 0.35 \text{ mm}^{-1} \\
T & = 153 (2) K \\
\mu & = 0.35 \text{ mm}^{-1} \\
V & = 1095.51 (17) \text{ Å}^3 \\
Z & = 2 \\
\end{align*}
\]

| \(\gamma\) | 84.837 (6)° |
| \(V\) | 1095.51 (17) Å³ |
| \(\mu\) | 0.35 mm⁻¹ |
| \(T\) | 153 (2) K |
| \(\beta\) | 68.415 (5)° |
| \(\alpha\) | 68.417 (5)° |

**Data collection**

Bruker P4 CCD diffractometer
9448 measured reflections
3831 independent reflections

2736 reflections with \(I > 2\sigma(I)\)

\(R_{int} = 0.064\)
Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.054 \]
\[ wR^2 = 0.140 \]
S = 1.05
3831 reflections

Compound (II)

Crystal data

\( \text{C}_8\text{H}_{12}\text{S}_3 \)
\( M_r = 474.62 \)
Triclinic, \( P \)
\( a = 9.7382 (11) \, \AA \)
\( b = 11.7143 (12) \, \AA \)
\( c = 11.8447 (12) \, \AA \)
\( \alpha = 61.244 (8) ^\circ \)
\( \beta = 78.532 (8) ^\circ \)

Re\`{}nement

3938 independent reflections

Data collection

Buerke P4 CCD diffractometer
9796 measured reflections
3938 independent reflections

Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.043 \]
\[ wR^2 = 0.103 \]
S = 1.03
3938 reflections

Compound (III)

Crystal data

\( \text{C}_{42}\text{H}_{28}\text{O}_2\text{S}_4 \)
\( M_r = 410.54 \)
Monoclinic, \( P_{2_1}/c \)
\( a = 18.934 (1) \, \AA \)
\( b = 27.268 (5) \, \AA \)
\( c = 7.5192 (7) \, \AA \)
\( \beta = 91.84 (1) ^\circ \)

Re\`{}nement

5330 reflections with \( I > 2\sigma(I) \)
\( R_{\text{int}} = 0.035 \)

Data collection

Buerke P4 CCD diffractometer
20681 measured reflections
6812 independent reflections

Refinement

\[ R[F^2 > 2\sigma(F^2)] = 0.044 \]
\[ wR^2 = 0.096 \]
S = 1.08
6812 reflections
505 parameters

Compound (IV)

Crystal data

\( \text{C}_{42}\text{H}_{28}\text{O}_2\text{S}_4 \)
\( M_r = 682.93 \)
Monoclinic, \( P_{2_1}/c \)
\( a = 9.341 (1) \, \AA \)
\( b = 36.688 (3) \, \AA \)
\( c = 10.097 (2) \, \AA \)
\( \beta = 115.36 (1) ^\circ \)

Data collection

Buerke P4 CCD diffractometer
26458 measured reflections
5499 independent reflections

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selected torsion and dihedral angles ((^\circ)).</td>
</tr>
<tr>
<td>(I)</td>
</tr>
<tr>
<td>S1—C2—</td>
</tr>
<tr>
<td>C6—S7</td>
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<tr>
<td>C1—S5</td>
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<td>C2—C3—</td>
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<td>C2/3</td>
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<tr>
<td>C1—C2</td>
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<tr>
<td>C9—S12</td>
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</tbody>
</table>

| Table 2 |
| Weak interaction data (\(\AA\, ^\circ\)). |
| (I) |
| C21—H21 | 2.98 | 3.926 (4) | 171 |
| C25—H25 | 3.02 | 3.885 (3) | 152 |
| C9—H9 | 2.78 | 3.628 (4) | 148 |
| C14—H14 | 2.83 | 3.564 (3) | 135 |
| C17—H17 | 2.89 | 3.576 (3) | 131 |
| (II) |
| C25—H25 | 2.89 | 3.761 (3) | 152 |
| C29—H29 | 2.91 | 3.609 (3) | 132 |
| C14—H14 | 2.85 | 3.75 (2) | 158 |
| C13—H13 | 2.69 | 3.564 (3) | 152 |
| C10—H10 | 2.72 | 3.470 (12) | 136 |
| (III) |
| C27A—H27A | 2.88 | 3.651 (3) | 136 |
| C13A—H13A | 2.57 | 3.443 (3) | 153 |
| C13A—H13A | 2.42 | 3.241 (3) | 145 |
| C13B—H13B | 2.42 | 3.24 (3) | 145 |
| C25A—H25C | 2.86 | 3.749 (3) | 152 |
| C27A—H27B | 2.86 | 3.475 (3) | 122 |
| C28B—H27F | 2.78 | 3.593 (3) | 141 |
| C27B—H27D | 2.71 | 3.516 (3) | 140 |
| (IV) |
| C64—H84 | 2.50 | 3.349 (6) | 149 |
| C13A—H13A | 2.80 | 3.676 (9) | 149 |
| C10A—H10A | 2.89 | 3.567 (5) | 129 |

Symmetry codes: (i) \( x, -y+1, z \); (ii) \( -x, -y+1, -z+1 \); (iii) \( -x, -y, -z+2 \); (iv) \( x, y+1, z \); (v) \( -x+1, -y+1, -z+1 \); (vi) \( x, y+1, z \); (vii) \( -x+1, -y+1, -z+1 \); (viii) \( x, y+1, z \); (ix) \( -x+1, -y+1, -z+1 \); (x) \( x, y+1, z \); (xi) \( x, y+1, z \); (xii) \( x, y+1, z \); (xiii) \( x, y+1, z \); (xiv) \( x, y+1, z \); (xv) \( x, y+1, z \); (xvi) \( x, y+1, z \); (xvii) \( x, y+1, z \); (xviii) \( x, y+1, z \); (xix) \( x, y+1, z \).
H atoms were placed at calculated positions and treated as riding, with isotropic displacement parameters set at 1.2 (1.3 for methyl groups) times the $U_{eq}$ values of the carrier atoms. The disordered parts in (I) were refined without any restraints; in (II)–(IV), the C atoms of the disordered parts were constrained to have the same components of the displacement tensor as the S atoms occupying the same site. This flip disorder is responsible for the relatively large differences in displacement parameters of disordered and nondisordered parts.

For all compounds, data collection: XSCANS (Bruker, 1996); cell refinement: XSCANS; data reduction: XSCANS; 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: DN3048). Services for accessing these data are described at the back of the journal.

References