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

David L. Officer

University of Wollongong, davido@uow.edu.au

Pawel W. Wagner

University of Wollongong, pawel@uow.edu.au

Maciej Kubicki

Adam Mickiewicz university

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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

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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

Paweł Wagner,^a David L. Officer^b and Maciej Kubicki^{c*}

^aNanomaterials Research Centre, and MacDiarmid Institute for Advanced Materials and Nanotechnology, Massey University, Private Bag 11 222, Palmerston North, New Zealand, ^bARC Centre of Excellence for Electromaterials Science, University of Wollongong, Northfield Avenue, Wollongong, NSW 2522, Australia, and

^cDepartment of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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

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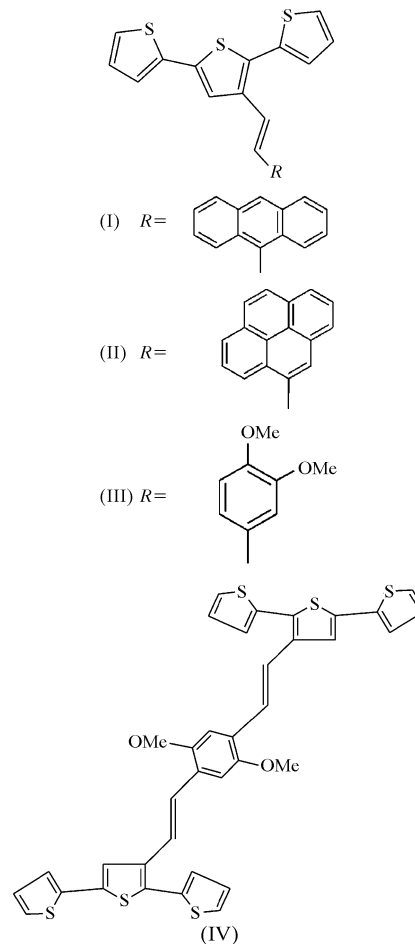
In the crystal structures of four thiophene derivatives, (*E*)-3'-[2-(anthracen-9-yl)ethenyl]-2,2':5',2''-terthiophene, C₂₈H₁₈S₃, (*E*)-3'-[2-(1-pyrenyl)ethenyl]-2,2':5',2''-terthiophene, C₃₀H₁₈S₃, (*E*)-3'-[2-(3,4-dimethoxyphenyl)ethenyl]-2,2':5',2''-terthiophene, C₂₂H₁₈O₂S₃, and (*E,E*)-1,4-bis[2-(2,2':5',2''-terthiophen-3'-yl)-ethenyl]-2,5-dimethoxybenzene, 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. 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.

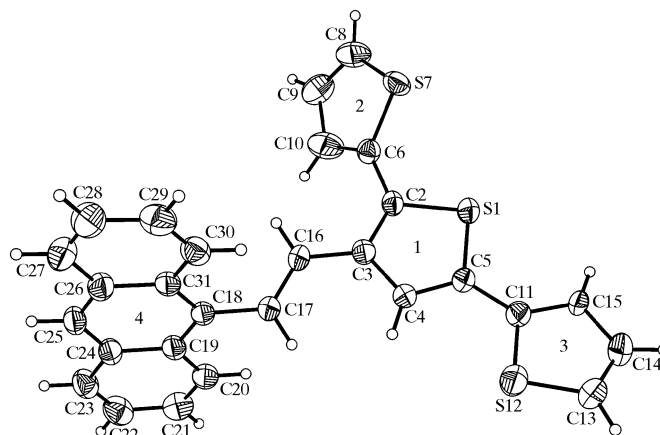


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the molecule with the greater occupancy is represented.

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 polythiophenes is to polymerize styryl-substituted terthiophene monomers, and towards this end we have reported the syntheses of a range of terthiophenes 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*)-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 (III*A*), 0.76 (1) in (III*B*), 0.56 (1) in (IV*A*), and 0.54 (1) and 0.67 (1) in (IV*B*). 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 from 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

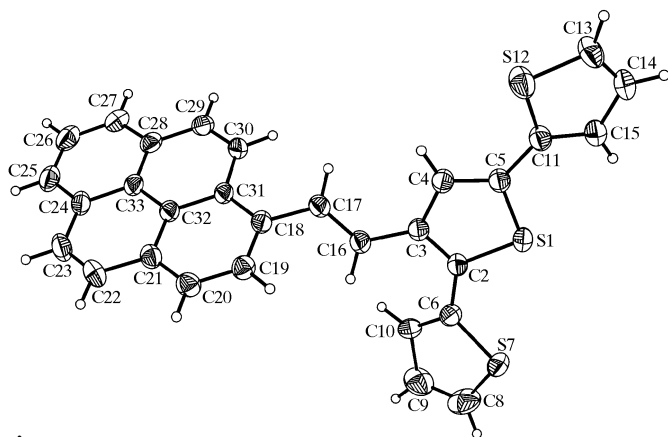


Figure 2

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.

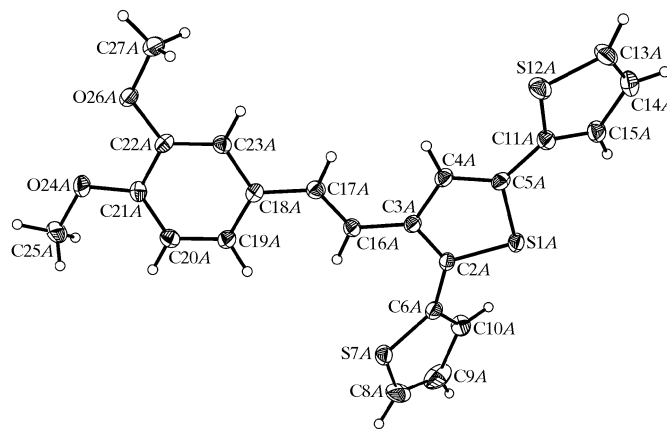
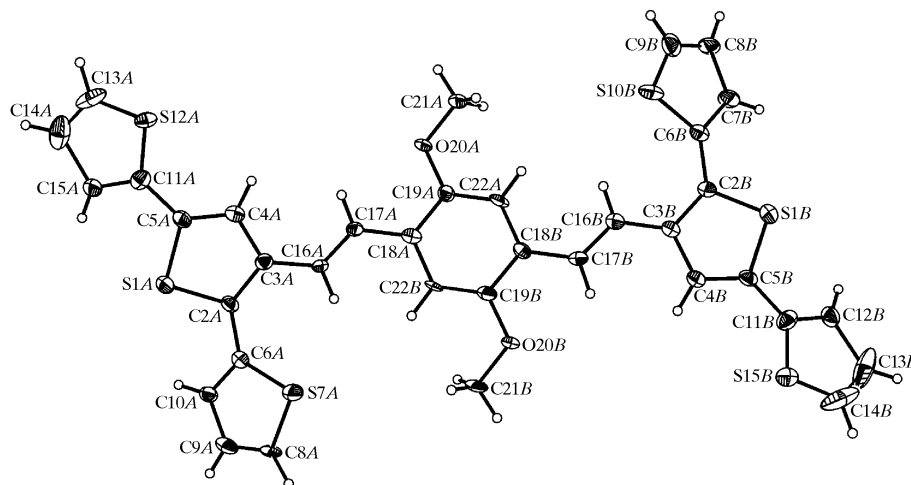
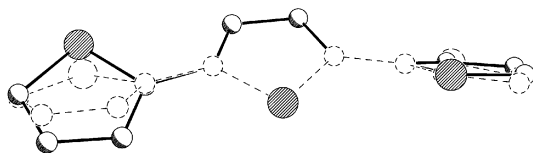


Figure 3

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.


Figure 4

A view of the molecule of (IV), 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 5

A comparison of two different types of twist in the terthiophene fragment (see *Comment*); two symmetry-independent molecules of (III) are shown [(IIIA) with solid lines and (IIIB) with dashed lines] and the central rings were fitted on one another (Siemens, 1989).

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 (IIIB)].

(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 [(IIIA) 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··· π 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’ ...AAA... and ...BBB... chains. Interestingly, there are no short contacts between the ring centroids, which shows that the π – 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

$C_{28}H_{18}S_3$	$\gamma = 84.837 (6)^\circ$
$M_r = 450.60$	$V = 1095.51 (17) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.7668 (8) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.8005 (9) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$c = 12.0272 (10) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\alpha = 68.417 (5)^\circ$	$0.3 \times 0.2 \times 0.1 \text{ mm}$
$\beta = 68.415 (5)^\circ$	

Data collection

Bruker P4 CCD diffractometer	2736 reflections with $I > 2\sigma(I)$
9448 measured reflections	$R_{int} = 0.064$
3831 independent reflections	

Refinement

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

299 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.139$
 $S = 1.09$
 5499 reflections

420 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$\text{C}_{30}\text{H}_{18}\text{S}_3$
 $M_r = 474.62$
 Triclinic, $P\bar{1}$
 $a = 9.7382 \text{ (11) } \text{\AA}$
 $b = 11.7143 \text{ (12) } \text{\AA}$
 $c = 11.8447 \text{ (12) } \text{\AA}$
 $\alpha = 61.244 \text{ (8) }^\circ$
 $\beta = 78.532 \text{ (8) }^\circ$

$\gamma = 72.307 \text{ (7) }^\circ$
 $V = 1126.2 \text{ (2) } \text{\AA}^3$
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.35 \text{ mm}^{-1}$
 $T = 153 \text{ (1) } \text{K}$
 $0.3 \times 0.2 \times 0.1 \text{ mm}$

Data collection

Bruker P4 CCD diffractometer
 9796 measured reflections
 3938 independent reflections

3208 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$

Refinement

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

311 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$

Compound (III)

Crystal data

$\text{C}_{22}\text{H}_{18}\text{O}_2\text{S}_3$
 $M_r = 410.54$
 Monoclinic, $P2_1/c$
 $a = 18.934 \text{ (1) } \text{\AA}$
 $b = 27.268 \text{ (5) } \text{\AA}$
 $c = 7.5192 \text{ (7) } \text{\AA}$
 $\beta = 91.84 \text{ (1) }^\circ$

$V = 3880.4 \text{ (8) } \text{\AA}^3$
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.40 \text{ mm}^{-1}$
 $T = 153 \text{ (1) } \text{K}$
 $0.3 \times 0.2 \times 0.1 \text{ mm}$

Data collection

Bruker P4 CCD diffractometer
 20681 measured reflections
 6812 independent reflections

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

Refinement

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

1 restraint
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$

Compound (IV)

Crystal data

$\text{C}_{36}\text{H}_{26}\text{O}_2\text{S}_6$
 $M_r = 682.93$
 Monoclinic, $P2_1/c$
 $a = 9.341 \text{ (1) } \text{\AA}$
 $b = 36.688 \text{ (3) } \text{\AA}$
 $c = 10.097 \text{ (2) } \text{\AA}$
 $\beta = 115.36 \text{ (1) }^\circ$

$V = 3126.8 \text{ (8) } \text{\AA}^3$
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.47 \text{ mm}^{-1}$
 $T = 150 \text{ (2) } \text{K}$
 $0.3 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Bruker P4 CCD diffractometer
 26458 measured reflections
 5499 independent reflections

3209 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.140$

Table 1

Selected torsion and dihedral angles ($^\circ$).

The second line, if it exists, refers to the less-occupied component and the ring descriptors 1–4 are defined in Fig. 1.

	(I)	(II)	(IIIA)	(IIIB)	(IVA)	(IVB)
S1–C2–C6–S7	−43.1 (4)	30.1 (3)	143.3 (2)	−36.7 (3)	−149.2 (3)	30.8 (5)
S1–C5–C11–S12	166.7 (2)	−163.9 (1)	−155.5 (1)	173.1 (1)	−23.7 (6)	146.7 (5)
C2–C3–C16–C17	167.3 (3)	−161.5 (2)	−176.5 (2)	168.7 (3)	−169.2 (4)	170.9 (5)
C3–C16–C17–C18	176.4 (3)	−176.2 (2)	179.7 (2)	176.6 (2)	175.6 (4)	−176.6 (4)
C16–C17–C18–C19	119.6 (3)	39.6 (3)	6.6 (4)	15.2 (4)	167.0 (4)	−177.9 (4)
1/2	43.2 (4)	30.4 (3)	36.2 (3)	36.4 (2)	28.1 (2)	31.3 (2)
1/3	13.2 (2)	15.5 (1)	26.6 (1)	7.2 (1)	25.4 (1)	30.0 (7)
2/3	53.6 (4)	43.3 (3)	15.2 (4)	43.0 (2)	19.4 (8)	23.6 (4)
1/4	78.8 (1)	65.0 (1)	10.4 (1)	7.3 (1)	7.8 (3)	7.1 (3)

Table 2

Weak interaction data (\AA , $^\circ$).

C_g is the centroid of the appropriate ring (1–4; see Fig. 1); 5 refers to the ring containing atom C22.

(I)				
C21–H21	S1 ⁱ	2.98	3.926 (4)	171
C25–H25	S12 ⁱⁱ	3.02	3.885 (3)	152
C9–H9	C_g4 ⁱⁱⁱ	2.78	3.628 (4)	148
C14–H14	C_g2 ^{iv}	2.83	3.564 (3)	135
C17–H17	C_g5 ⁱⁱ	2.89	3.576 (3)	131
(II)				
C25–H25	S12 ^v	2.89	3.761 (3)	152
C29–H29	S7 ^l	2.91	3.609 (3)	132
C14–H14	S10 ^{vi}	2.85	3.75 (2)	158
C13–H13	C_g4 ^{vi}	2.69	3.564 (3)	152
C10–H10	C_g3 ⁱⁱ	2.72	3.470 (12)	136
(III)				
C27A–H27A	S7B ^{vii}	2.88	3.651 (3)	136
C13A–H13A	O24A ^{viii}	2.57	3.443 (3)	153
C13A–H13A	O26A ^{viii}	2.42	3.241 (3)	145
C13B–H13B	O26B ^{ix}	2.42	3.242 (3)	145
C13B–H13B	O24B ^{ix}	2.59	3.466 (4)	153
C25A–H25C	C_g3A ^x	2.86	3.749 (3)	152
C27A–H27B	C_g2B ^{viii}	2.86	3.475 (3)	122
C25B–H25F	C_g2A ^{xi}	2.78	3.593 (3)	141
C27B–H27D	C_g2B ^{xii}	2.71	3.516 (3)	140
(IV)				
C8A–H8A	O20A ^{xiii}	2.50	3.349 (6)	149
C13A–H13A	S15A ^{xiv}	2.80	3.676 (9)	154
C10A–H10A	C_g2B ^{xii}	2.89	3.567 (5)	129

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x, -y, -z + 2$; (iv) $x, y + 1, z$; (v) $-x - 1, -y + 1, -z + 2$; (vi) $x, y + 1, z - 1$; (vii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (viii) $-x, -y, -z - 1$; (ix) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (x) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (xi) $x, y - 1, z$; (xii) $-x + 1, -y, -z + 1$; (xiii) $x, y, z + 1$; (xiv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

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.

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