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Publication Details

Wagner, P., Officer, D. L. & Kubicki, M. (2006). A flip-disorder in the structure of 3-[2-(anthracen-9-yl)ethenyl]thiophene. *Acta Crystallographica Section E: Structure Reports Online*, 62 (12), o5745-o5747.

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A flip-disorder in the structure of 3-[2-(anthracen-9-yl)ethenyl]thiophene

Abstract

In the crystal structure of the title compound, C₂₀H₁₄S, the thiophene rings are disordered; such a flip-type disorder is typical for simple, monosubstituted thiophene derivatives. Two planar fragments, the thiophene and the anthracene units, are almost perpendicular in order to relieve the H··H steric strains. The crystal packing is determined by van der Waals interactions, π - π stacking between the anthracene fragments, and some weak C—H··S and C—H·· π short directional contacts.

Keywords

3, 2, anthracen, 9, yl, disorder, thiophene, flip, ethenyl, structure

Disciplines

Engineering | Physical Sciences and Mathematics

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A flip-disorder in the structure of 3-[2-(anthracen-9-yl)ethenyl]thiophene

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Key indicators

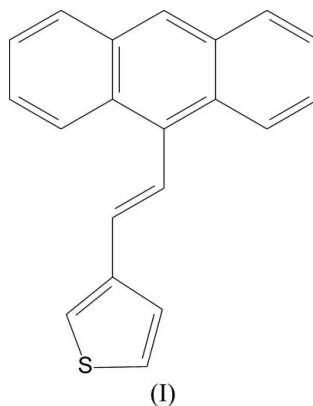
Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.060
wR factor = 0.110
Data-to-parameter ratio = 13.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_{20}\text{H}_{14}\text{S}$, the thiophene rings are disordered; such a flip-type disorder is typical for simple, monosubstituted thiophene derivatives. Two planar fragments, the thiophene and the anthracene units, are almost perpendicular in order to relieve the $\text{H}\cdots\text{H}$ steric strains. The crystal packing is determined by van der Waals interactions, π - π stacking between the anthracene fragments, and some weak $\text{C}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\pi$ short directional contacts.

Received 10 November 2006
Accepted 14 November 2006

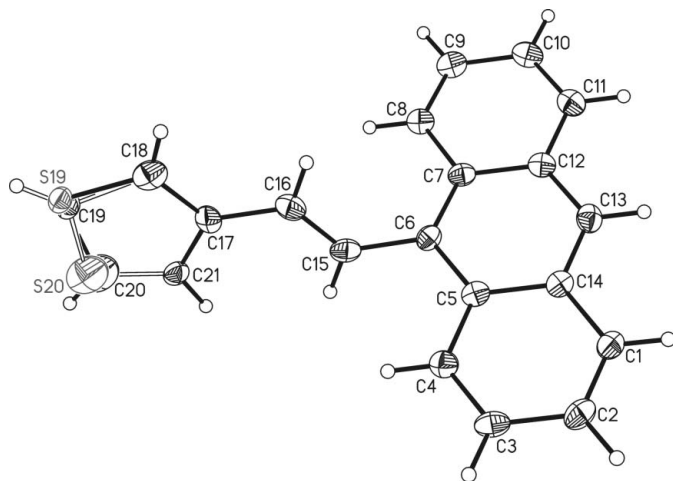
Comment

Since their discovery, conjugated polymers and oligomers (Shirakawa *et al.*, 1977) have been investigated extensively for use in, for example, solar cells or light-emitting diodes. Oligo- and polythiophenes have good chemical stability in both the oxidized and reduced states; in particular, 3-styryl-substituted thiophenes have been studied intensively due to their unique electronic and optical properties (*e.g.* Collis *et al.*, 2003; Grant *et al.*, 2005; Wagner & Officer, 2005).

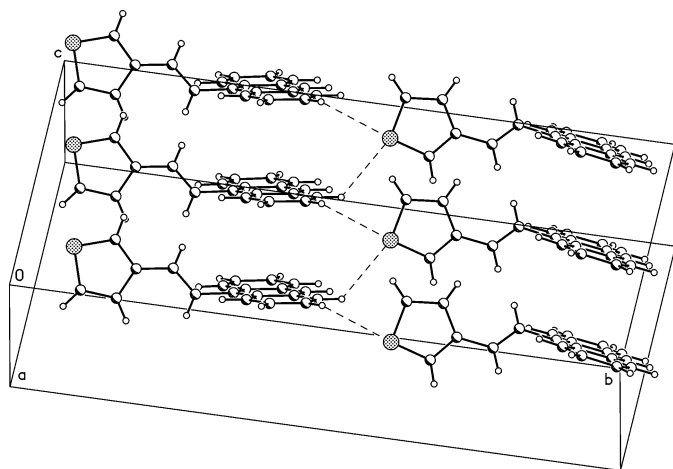


In the crystal structure of (I), a flip-disorder of the thiophene ring is observed (Fig. 1). There are two positions of the thiophene ring, rotated by *ca* 180°. These two orientations are not equivalent; the site-occupation factors refined to 0.689 (3) and 0.311 (3). A disorder of this kind is often observed in the structures of simple thiophene derivatives with one substituent, for example in a family of thiophene-3-carboxamides (Howell *et al.*, 2005) or in 3-thienylacrylonitriles (Sonar *et al.*, 2004, 2005*a,b*).

Both the thiophene and the anthracene units are almost planar; the maximum deviations from the least-squares planes are 0.011 (9) Å for atom C17 from the thiophene ring, and 0.034 (2) Å for atom C8 from the whole anthracene fragment. In the latter, the dihedral angle between the terminal rings is as small as 1.4 (1)°. The dihedral angle between the anthra-

**Figure 1**

The molecular structure of (I) (Siemens, 1989). Displacement ellipsoids are drawn at the 50% probability level. H atoms are depicted as small spheres of arbitrary radii. The minor occupancy component of the thiophene ring is depicted with hollow bonds.

**Figure 2**

The stacking of molecules, showing some of the C—H...S contacts (dashed lines) connecting the stacks.

cene and thiophene planes is $72.6(3)^\circ$. The whole vinylthiophene group is twisted with respect to the naphthalene fragment, as shown by a comparison of torsion angles, for instance $C4A-C5-C11-C12 = 114.7(3)^\circ$ and $C11-C12-C15-C16 = -7.5(4)^\circ$. This conformation is probably a result of the steric stress between vinylic atoms H11 and H12, and naphthalene atoms H4 and H6, respectively. As a result of the twist, these H...H distances are comparable with the H...H distances between the vinylic and the thiophene ring H atoms (the shortest distances are $H4 \cdots H11 = 2.49 \text{ \AA}$ and $H16 \cdots H11 = 2.33 \text{ \AA}$).

In the crystal structure, there are columns of molecules aligned perpendicular to the anthracene rings (approximately along the [101] direction). There is a partial stack between neighboring rings (Fig. 2). The distance between the centroids of these rings is 3.59 \AA ; taking into account the offset, the distance between the planes is around 3.45 \AA , which might

suggest reasonable stacking interactions between the π -electron systems. There are also some weak specific interactions that also can play a role in the crystal structure, namely C—H...S and C—H... π directional contacts (Table 1).

Experimental

The title compound was synthesized according to a literature procedure (Collis *et al.*, 2001) and the details will be published elsewhere.

Crystal data

$C_{20}H_{14}S$	$Z = 4$
$M_r = 286.37$	$D_x = 1.329 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.4991(9) \text{ \AA}$	$\mu = 0.22 \text{ mm}^{-1}$
$b = 23.968(4) \text{ \AA}$	$T = 100(1) \text{ K}$
$c = 10.9768(18) \text{ \AA}$	Block, colorless
$\beta = 98.478(14)^\circ$	$0.3 \times 0.07 \times 0.05 \text{ mm}$
$V = 1431.0(4) \text{ \AA}^3$	

Data collection

Kuma KM-4-CCD four-circle diffractometer	2710 independent reflections
ω scans	1419 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.074$
6934 measured reflections	$\theta_{\text{max}} = 26.0^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.060$	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2710 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
197 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

Cg1 denotes the centroid of the thiophene ring, and Cg4 the centroid of the terminal (C8) ring of the anthracene fragment.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots S13^i$	0.95	3.02	3.742 (6)	134
$C8-H8 \cdots S13^{ii}$	0.95	2.94	3.841 (5)	159
$C2-H2 \cdots S17^{iii}$	0.95	3.11	3.963 (16)	151
$C14-H14 \cdots Cg4^{ii}$	0.95	2.86	3.632	140
$C8-H8 \cdots Cg1^{iv}$	0.95	2.88	3.589	132

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

The flip-type disorder means that in their alternative positions, the different types of atoms (in this case sulfur and carbon) occupy positions that are close to each other, which influences their U^{ij} values. The alternative positions of S and C atoms were constrained to have the same U^{ij} components. H atoms were positioned geometrically (C—H = 0.95 \AA) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; 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*.

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