organic papers

2,5-Bis(2-cyano-2-thienylvinyl)thiophene

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In the crystal structure of the title compound, $C_{18}H_{10}N_2S_3$, the terminal thiophene rings are disordered. This disorder is of a flip-type and has been observed in some other thiophene derivatives. The molecule as a whole is approximately planar; the dihedral angle between the terminal five-membered rings is 6.0 (2)°. The crystal packing is determined by van der Waals interactions, π–π stair-like stacking between the thiophene rings, and some weak C—H···S and C—H···π short directional contacts.

Comment

The first reports on the optical, electronic and photo-electronic properties of poly(*p*-phenylenevinylene) appeared in 1970 (Hörhold & Opfermann, 1970). This compound and its derivatives have attracted attention due to their applications in electroluminescent devices (*e.g.* Mitschke & Bäuerle, 2000). It has been found that the cyano group at a vinyl position may cause a disturbance in the geometry of the molecule (Gill *et al.*, 1997; Leuze *et al.*, 2002) that can result in quenching of the emission (Gordon *et al.*, 2005). In addition, the thiophene equivalent, poly(thienylenevinylene), has been found as an interesting low-band-gap material with a possible application in organic solar cells (*e.g.* Roncali, 1997, 1999). Despite much interest in the topic, the CN derivatives of poly(thienylenevinylene) have not been extensively investigated.

(I)
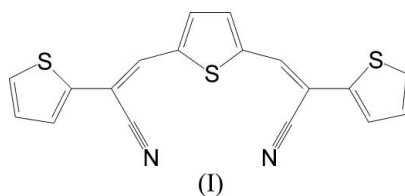
In the structure of the title compound, (I), a flip-disorder of both terminal thiophene rings (*A* and *B*) is observed (Fig. 1). The site-occupancy factors refined to 0.636 (3) and 0.364 (3) for ring *A*, and to 0.814 (3) and 0.186 (3) for ring *B*. A disorder of this kind has been observed in the structures of simple thiophene derivatives, for example, in a family of 3-thienylacrylonitriles (Sonar *et al.*, 2004, 2005*a*,*b*), but it was not reported in the closely related structure of 2,5-bis(2-thienylvinyl)thiophene (Zobel & Ruban, 1978).

The bond-length patterns in the vinyl fragments suggest a slightly larger degree of delocalization in comparison with the previously reported (thiophen-3-yl)(anthracene)ethene (Wagner *et al.*, 2006). All thiophene rings are almost planar and the whole molecule is approximately planar; the largest deviation from the mean plane of all non-H atoms is 0.112 (5) Å. The dihedral angles between the rings are small, the angle between the terminal rings being 6.0 (2)°.

In the crystal structure, there are columns of molecules approximately along the [011] direction. There is a partial stack between neighboring rings; the central ring of one molecule stacks with the terminal rings of the molecules above and below (Fig. 2). The distances between the centroids of these rings are long, 3.78 and 3.91 Å; but taking into account the offset, the distances between the planes are shorter than 3.6 Å, which might suggest at least some stacking between the π-electrons. One can find some weak specific interactions that also may 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 by Knovenagel condensation of thien-2-ylacetonitrile and 2,5-diformylthiophene according to previously described procedures (Ho *et al.*, 1996; Schlick *et al.*, 1998).

Crystal data

$C_{18}H_{10}N_2S_3$	$Z = 8$
$M_r = 350.46$	$D_x = 1.456$ Mg m^{-3}
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 12.379$ (2) Å	$\mu = 0.46$ mm^{-1}
$b = 12.651$ (2) Å	$T = 153$ (2) K
$c = 20.421$ (4) Å	Block, colorless
$V = 3198.1$ (10) Å^3	$0.3 \times 0.1 \times 0.1$ mm

Data collection

Bruker SMART CCD diffractometer	3269 independent reflections
	2672 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.038$
Absorption correction: none	$\theta_{max} = 26.4°$
17718 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 2.6519P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
3269 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
220 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Table 1
C-H···S and C-H···π contact geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C24—H24···S27[i]	0.95	2.94	3.84 (2)	158
C25—H25···S57[ii]	0.95	3.02	3.896 (6)	153
C27—H27···S24[iii]	0.95	3.05	3.880 (8)	147
C55—H55···S24[iv]	0.95	2.88	3.699 (3)	145
C57—H57···S57[v]	0.95	3.00	3.921 (10)	163
C25—H25···Cg3[ii]	0.95	2.69	3.502 (2)	144

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $-x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + 1, -y + 1, -z + 1$. Cg3 denotes the centroid of the S54 thiophene ring.

The two alternative positions for disordered fragments were refined without constraints; the disorder results in differences in displacement parameters and, to some extent, in the geometry. H atoms were constrained to ride on their parent atoms [C–H = 0.95Å; $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine
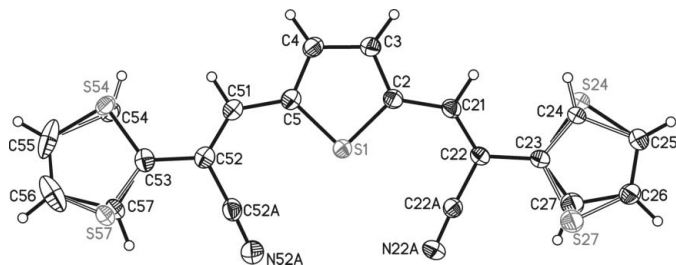
Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as small spheres of arbitrary radii. The bonds within the minor occupancy components of the thiophene rings are depicted with open lines.
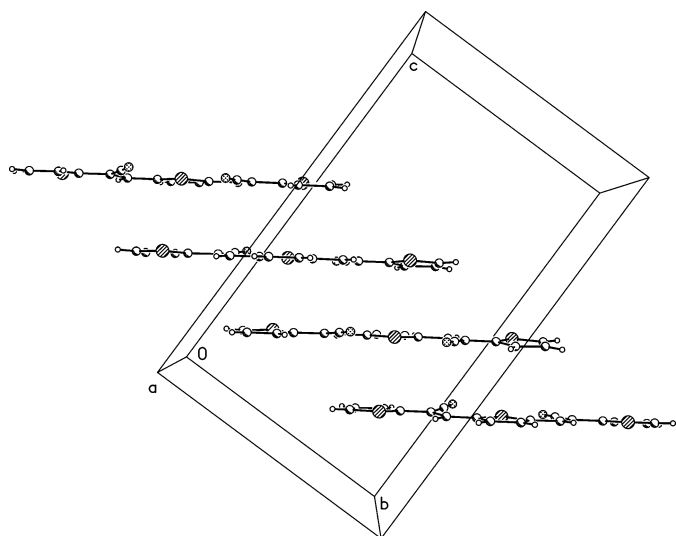
Figure 2
Packing view, showing the stacking of the molecules.

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL97*.

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