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2-(9*H*-Fluoren-9-ylidenemethyl)-thiophene

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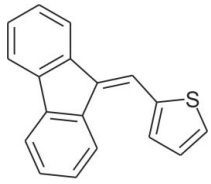
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.034; wR factor = 0.090; data-to-parameter ratio = 16.8.

The title compound, $C_{18}H_{12}S$, contains a thiophene ring which is disordered by rotation of 180° about the linking C—C bond. The site occupancies of the major and minor components of the disordered ring are 0.900 (3) and 0.100 (3), respectively. In one of these disordered components, the molecule is stabilized by an intramolecular C—H···S hydrogen bond. The compound was synthesized in good yield (80%) by a modified phase-transfer-catalysed condensation of fluorene with thiophene-2-carbaldehyde.

Related literature

For a related structure, see: Fave *et al.*, 2004. For related literature, see: Allen (2002); Lukeš *et al.* (2003); Mullen & Wegner (1998).



Experimental

Crystal data

$C_{18}H_{12}S$
M_r = 260.34
Orthorhombic, *Fdd*2
a = 20.757 (4) Å
b = 44.434 (9) Å
c = 5.6260 (11) Å
V = 5189.0 (18) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 100 (2) K
0.57 × 0.13 × 0.08 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (Clark & Reid, 1995)
T_{min} = 0.938, T_{max} = 0.985
11725 measured reflections
3018 independent reflections
1903 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.090
S = 0.99
3018 reflections
180 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 1110 Friedel pairs
Flack parameter: −0.07 (8)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2*A*···S1*A*	0.95	2.55	3.311 (4)	139

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2086).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Fave, C., Hissler, M., Karpati, T., Rault-Berthelot, J., Deborde, V., Toupet, L., Nyulaszi, L. & Reau, R. (2004). *J. Am. Chem. Soc.* **126**, 6058–6059.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Lukeš, V., Végh, D., Hrdlovič, P., Štefko, M., Matuszna, K. & Laurinc, V. (2003). *Synth. Met.* pp. 399–408.
Mullen, K. & Wegner, G. (1998). *Electronic Materials: The Oligomer Approach*. New York: Wiley.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

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2-(9*H*-Fluoren-9-ylidenemethyl)thiophene

Lucia Perašínová, Martin Štefko, Daniel Végh and Jozef Kožíšek

S1. Comment

Our synthetic efforts have been focused on a set of multi-ring monomer systems based on thiophene and fluorene ring system. In this respect, the relationship between the charge transport properties in OFET devices (Mullen & Wegner, 1998) and molecular properties such as redox reversibility and crystal structure have been investigated. As active layers, we used oligomers based on molecules consisting of alternating thiophene and fluorene moieties.

In the title compound (1) the S1—C15 and S1—C18 bond lengths of 1.725 (3) Å and 1.692 (3) Å are in a quite good agreement with similar thiophene compounds in the Cambridge Structural Database (CSD; Version 5.27, 2006 release; Allen, 2002); for example, 2,2′,5,5′-tetrakis(2-Thienyl)-3,4:3′,4′- bis(tetramethylene)-1,1′-biphosphole (Fave *et. al.*, 2004; CDS refcode BERCIL). The thiophene ring is disordered by rotation about the inter-ring C—C bond. There is one intramolecular C–H···S hydrogen bond.

S2. Experimental

8.3 g (0.05 mol) of fluorene and 5.6 g (0.05 mol) of thiophene-2-carbaldehyde were dissolved in 70 ml of toluene. Then 70 ml 40% NaOH and 2.9 g (0.009 mol) $(n\text{-}Bu)_4N^+Br^-$ were added. The resulting heterogenous mixture was vigorously stirred at room temperature for 12 h. After completion of the reaction (TLC control), the water layer was separated, and the organic layer was washed with 100 ml 10% HCl, 300 ml water, 300 ml of brine and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, a dark oil was obtained, which was further dissolved in boiling MeOH, decolorized with Norit, filtered and left to cool to room temperature to obtain 10.4 g (80%) of yellow needles m.p.: 75°C (lit. 73–75°C) (Lukeš *et al.*, 2003). The crude product could be purified by column chromatography using silica gel Merck 60 in toluene as an eluent R_f = 0.71 (toluene).

^{1}H NMR (300 MHz, $CDCl_3$ p.p.m.): δ = 8.11 (d, J=7.79 Hz, 1 H), 7.68 – 7.74 (m, 3 H), 7.60 (s, 1 H), 7.42 – 7.45 (m, 2 H), 7.27 – 7.38 (m, 3 H), 7.12 – 7.23 (m, 2 H).

^{13}C-NMR (75 MHz, $CDCl_3$, p.p.m.) δ = 141.19, 139.48, 139.06, 138.91, 136.51, 136.12, 129.25, 128.72, 128.22, 127.57, 127.32, 126.97, 126.82, 124.34, 120.14, 119.74, 119.58, 118.98.

S3. Refinement

H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C).

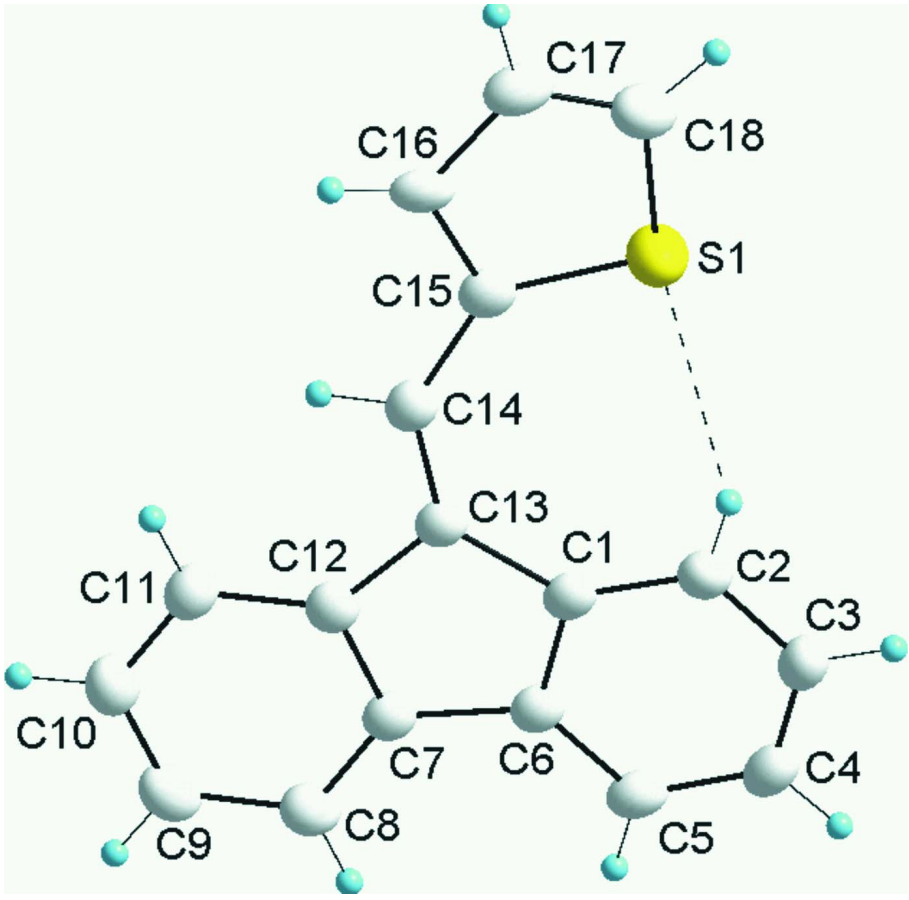

Figure 1

The atomic numbering scheme of 2-(9*H*-fluoren-9-ylidenemethyl)thiophene. Only the major component of the disordered thiophene ring is shown. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen-bond interactions are indicated by dashed lines.

2-(9*H*-Fluoren-9-ylidenemethyl)thiophene

Crystal data

$C_{18}H_{12}S$
$M_r = 260.34$
Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d
$a = 20.757\ (4)$ Å
$b = 44.434\ (9)$ Å
$c = 5.6260\ (11)$ Å
$V = 5189.0\ (18)$ Å^3
$Z = 16$
$F(000) = 2176$
$D_x = 1.333$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4617 reflections
$\theta = 3.7–29.1°$
$\mu = 0.23$ mm^{-1}
$T = 100$ K
Block, yellow
0.57 × 0.13 × 0.08 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Rotation method data acquisition using ω and φ scans
Absorption correction: analytical (Clark & Reid, 1995)
$T_{min} = 0.938$, $T_{max} = 0.985$

11725 measured reflections
3018 independent reflections
1903 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 29.1°$, $\theta_{min} = 3.8°$
$h = -27 \rightarrow 25$
$k = -59 \rightarrow 58$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.090$
$S = 0.99$
3018 reflections
180 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Absolute structure: Flack (1983), 1110 Friedel pairs
Absolute structure parameter: −0.07 (8)

Special details

Experimental. face-indexed (*CrysAlis RED*; Oxford Diffraction, 2006)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.35040 (9)	0.03543 (4)	−0.1480 (3)	0.0504 (5)	
C2	0.40287 (10)	0.01668 (4)	−0.1107 (4)	0.0605 (6)	
H2A	0.4298	0.0194	0.0241	0.073*	
C3	0.41552 (10)	−0.00616 (5)	−0.2727 (4)	0.0656 (6)	
H3A	0.4516	−0.0189	−0.2475	0.079*	
C4	0.37726 (11)	−0.01069 (5)	−0.4680 (4)	0.0640 (6)	
H4A	0.3876	−0.0262	−0.5781	0.077*	
C5	0.32362 (10)	0.00724 (4)	−0.5052 (4)	0.0594 (5)	
H5A	0.2965	0.0040	−0.6387	0.071*	
C6	0.31044 (9)	0.02985 (4)	−0.3442 (3)	0.0490 (5)	
C7	0.25624 (9)	0.05093 (4)	−0.3394 (3)	0.0493 (5)	
C8	0.20399 (10)	0.05396 (5)	−0.4884 (4)	0.0607 (5)	
H8A	0.1994	0.0413	−0.6237	0.073*	
C9	0.15827 (11)	0.07574 (5)	−0.4373 (4)	0.0670 (6)	
H9A	0.1219	0.0780	−0.5380	0.080*	
C10	0.16522 (10)	0.09415 (5)	−0.2405 (4)	0.0658 (6)	
H10A	0.1334	0.1090	−0.2079	0.079*	
C11	0.21746 (10)	0.09134 (5)	−0.0913 (4)	0.0608 (5)	

H11A	0.2221	0.1043	0.0419	0.073*	
C12	0.26339 (9)	0.06932 (4)	−0.1380 (3)	0.0490 (5)	
C13	0.32372 (9)	0.06148 (4)	−0.0145 (3)	0.0490 (5)	
C14	0.34399 (9)	0.07789 (4)	0.1761 (3)	0.0518 (5)	
H14A	0.3125	0.0921	0.2256	0.062*	
C15A	0.40114 (9)	0.07913 (4)	0.3214 (3)	0.0513 (5)	0.900 (3)
C18A	0.50774 (12)	0.07874 (5)	0.5125 (5)	0.0731 (7)	0.900 (3)
H18A	0.5513	0.0759	0.5592	0.088*	0.900 (3)
C17A	0.46607 (12)	0.09565 (5)	0.6332 (4)	0.0670 (6)	0.900 (3)
H17A	0.4767	0.1058	0.7767	0.080*	0.900 (3)
C16A	0.4056 (4)	0.0970 (4)	0.529 (3)	0.0747 (14)	0.900 (3)
H16A	0.3710	0.1087	0.5900	0.090*	0.900 (3)
S1A	0.47511 (8)	0.06280 (3)	0.26734 (16)	0.0755 (3)	0.900 (3)
C15B	0.40114 (9)	0.07913 (4)	0.3214 (3)	0.0513 (5)	0.100 (3)
C17B	0.46607 (12)	0.09565 (5)	0.6332 (4)	0.0670 (6)	0.100 (3)
H17B	0.4781	0.1058	0.7750	0.080*	0.100 (3)
C18B	0.50774 (12)	0.07874 (5)	0.5125 (5)	0.0731 (7)	0.100 (3)
H18B	0.5512	0.0758	0.5602	0.088*	0.100 (3)
C16B	0.481 (3)	0.0659 (10)	0.311 (4)	0.0755 (3)	0.100 (3)
H16B	0.5013	0.0532	0.1960	0.091*	0.100 (3)
S1B	0.3980 (11)	0.0978 (10)	0.532 (7)	0.0747 (14)	0.100 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0532 (11)	0.0451 (11)	0.0528 (11)	−0.0072 (9)	0.0047 (9)	−0.0017 (9)
C2	0.0557 (12)	0.0503 (12)	0.0754 (13)	−0.0021 (10)	−0.0032 (11)	−0.0117 (11)
C3	0.0575 (12)	0.0517 (12)	0.0874 (16)	0.0001 (10)	0.0055 (12)	−0.0126 (12)
C4	0.0699 (14)	0.0503 (13)	0.0717 (13)	−0.0051 (11)	0.0093 (13)	−0.0153 (12)
C5	0.0684 (13)	0.0544 (12)	0.0555 (11)	−0.0128 (10)	0.0014 (11)	−0.0072 (11)
C6	0.0570 (11)	0.0428 (11)	0.0473 (10)	−0.0082 (9)	0.0039 (10)	−0.0004 (9)
C7	0.0542 (11)	0.0438 (11)	0.0500 (11)	−0.0054 (9)	0.0035 (9)	0.0041 (10)
C8	0.0657 (13)	0.0608 (13)	0.0557 (10)	−0.0042 (11)	−0.0049 (12)	0.0017 (11)
C9	0.0649 (14)	0.0688 (15)	0.0673 (15)	−0.0031 (11)	−0.0130 (11)	0.0128 (12)
C10	0.0643 (13)	0.0580 (13)	0.0750 (14)	0.0076 (10)	−0.0009 (12)	0.0077 (13)
C11	0.0671 (13)	0.0519 (12)	0.0634 (12)	0.0033 (10)	0.0028 (12)	−0.0026 (11)
C12	0.0520 (11)	0.0468 (10)	0.0483 (11)	−0.0047 (9)	0.0057 (8)	0.0018 (9)
C13	0.0528 (10)	0.0461 (10)	0.0482 (11)	−0.0072 (9)	0.0042 (9)	0.0000 (9)
C14	0.0555 (11)	0.0487 (11)	0.0513 (11)	−0.0028 (9)	0.0087 (9)	−0.0005 (9)
C15A	0.0598 (12)	0.0461 (11)	0.0480 (11)	−0.0100 (9)	−0.0005 (9)	0.0023 (9)
C18A	0.0757 (15)	0.0666 (15)	0.0771 (14)	−0.0061 (12)	−0.0193 (14)	0.0019 (14)
C17A	0.0865 (16)	0.0614 (14)	0.0531 (12)	−0.0118 (13)	−0.0108 (12)	−0.0052 (12)
C16A	0.082 (3)	0.0744 (16)	0.0680 (12)	−0.022 (2)	−0.005 (2)	0.0022 (11)
S1A	0.0667 (6)	0.0868 (6)	0.0731 (5)	0.0098 (4)	−0.0143 (4)	−0.0252 (5)
C15B	0.0598 (12)	0.0461 (11)	0.0480 (11)	−0.0100 (9)	−0.0005 (9)	0.0023 (9)
C17B	0.0865 (16)	0.0614 (14)	0.0531 (12)	−0.0118 (13)	−0.0108 (12)	−0.0052 (12)
C18B	0.0757 (15)	0.0666 (15)	0.0771 (14)	−0.0061 (12)	−0.0193 (14)	0.0019 (14)
C16B	0.0667 (6)	0.0868 (6)	0.0731 (5)	0.0098 (4)	−0.0143 (4)	−0.0252 (5)

S1B	0.082 (3)	0.0744 (16)	0.0680 (12)	−0.022 (2)	−0.005 (2)	0.0022 (11)

Geometric parameters (Å, º)

C1—C2	1.387 (3)	C10—C11	1.377 (3)
C1—C6	1.403 (3)	C10—H10A	0.9500
C1—C13	1.487 (3)	C11—C12	1.391 (3)
C2—C3	1.389 (3)	C11—H11A	0.9500
C2—H2A	0.9500	C12—C13	1.474 (3)
C3—C4	1.371 (3)	C13—C14	1.363 (3)
C3—H3A	0.9500	C14—C15A	1.442 (3)
C4—C5	1.385 (3)	C14—H14A	0.9500
C4—H4A	0.9500	C15A—C16A	1.416 (19)
C5—C6	1.380 (3)	C15A—S1A	1.725 (3)
C5—H5A	0.9500	C18A—C17A	1.332 (3)
C6—C7	1.464 (3)	C18A—S1A	1.692 (3)
C7—C8	1.377 (3)	C18A—H18A	0.9500
C7—C12	1.405 (3)	C17A—C16A	1.388 (3)
C8—C9	1.386 (3)	C17A—H17A	0.9500
C8—H8A	0.9500	C16A—H16A	0.9500
C9—C10	1.384 (3)	C16B—H16B	0.9500
C9—H9A	0.9500		
C2—C1—C6	118.53 (18)	C11—C10—H10A	119.5
C2—C1—C13	133.10 (18)	C9—C10—H10A	119.5
C6—C1—C13	108.35 (17)	C10—C11—C12	119.2 (2)
C1—C2—C3	119.2 (2)	C10—C11—H11A	120.4
C1—C2—H2A	120.4	C12—C11—H11A	120.4
C3—C2—H2A	120.4	C11—C12—C7	119.26 (19)
C4—C3—C2	121.6 (2)	C11—C12—C13	131.25 (18)
C4—C3—H3A	119.2	C7—C12—C13	109.45 (17)
C2—C3—H3A	119.2	C14—C13—C12	120.45 (17)
C3—C4—C5	120.2 (2)	C14—C13—C1	134.33 (19)
C3—C4—H4A	119.9	C12—C13—C1	105.19 (16)
C5—C4—H4A	119.9	C13—C14—C15A	136.09 (18)
C6—C5—C4	118.6 (2)	C13—C14—H14A	112.0
C6—C5—H5A	120.7	C15A—C14—H14A	112.0
C4—C5—H5A	120.7	C16A—C15A—C14	122.8 (4)
C5—C6—C1	121.84 (18)	C16A—C15A—S1A	108.9 (4)
C5—C6—C7	129.06 (17)	C14—C15A—S1A	128.03 (14)
C1—C6—C7	109.09 (16)	C17A—C18A—S1A	113.1 (2)
C8—C7—C12	121.16 (18)	C17A—C18A—H18A	123.5
C8—C7—C6	131.03 (19)	S1A—C18A—H18A	123.5
C12—C7—C6	107.78 (17)	C18A—C17A—C16A	113.4 (9)
C7—C8—C9	118.8 (2)	C18A—C17A—H17A	123.3
C7—C8—H8A	120.6	C16A—C17A—H17A	123.3
C9—C8—H8A	120.6	C17A—C16A—C15A	112.5 (12)
C10—C9—C8	120.5 (2)	C17A—C16A—H16A	123.8

C10—C9—H9A	119.8	C15A—C16A—H16A	123.8
C8—C9—H9A	119.8	C18A—S1A—C15A	92.08 (13)
C11—C10—C9	121.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···S1*A*	0.95	2.55	3.311 (4)	139