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Diethyl 2,5-bis[(*E*)-thiophen-2-ylmethyleneamino]-thiophene-3,4-dicarboxylate

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.114
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the molecule of the highly conjugated title compound, $C_{20}H_{18}N_2O_4S_3$, the thiophene rings are in an antiparallel arrangement and both azomethine bonds adopt the thermo-dynamically stable E isomeric form. The mean planes of the terminal thiophene rings are twisted by 9.04 (4) and 25.07 (6)° from the mean plane of the azomethine groups and the central thiophene ring.

Comment

Conjugated thiophenes have received much attention because they are ideal for functional devices (Rupprecht, 1999). Azomethines are suitable replacements for conjugated thiophenes because they can be simply synthesized. We successfully used a stable diaminothiophene, (I), to obtain new conjugated thiophenoazomethines, (II) and (III) (see scheme). The crystal structure of the title compound, (III), is presented here.
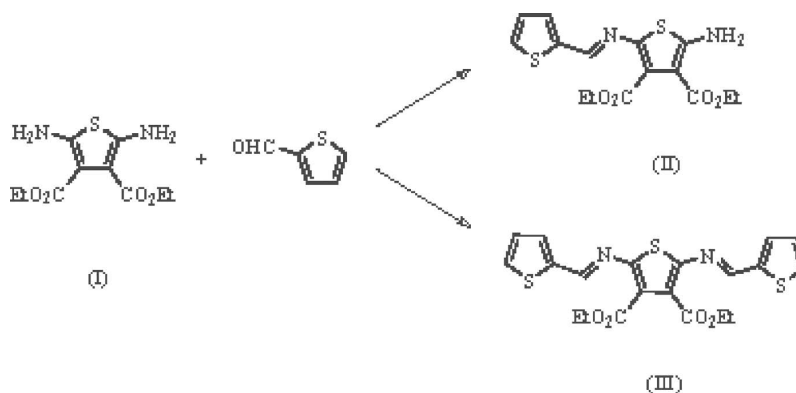

The molecular structure of (III) is shown in Fig. 1. The three essentially planar thiophene rings are rotated such that adjacent pairs are antiparallel. Both terminal thiophene rings are twisted from the mean plane that passes through the central thiophene and the azomethine bonds by 9.04 (4) and 25.07 (6) Å for the thiophene rings containing S3 and S2, respectively and the near coplanarity is illustrated in Fig. 2. For compound (II), this angle is 7.25 (11) Å (Skene *et al.*, 2006). This is in contrast to the mean plane angle for homoaryl azomethines, which is considerably larger (65°; Bürgi & Dunitz, 1969). In (III), the mean planes of the two ester groups are also twisted by 37.0 (2) and 64.88 (13) Å from the mean plane of the central thiophene ring. These angles are greater than in (I), where the values are 26.16 (8) and 28.87 (9)°.

The central thiophene ring has S—C bonds that are *ca* 0.039 Å longer than in the two terminal thiophene rings
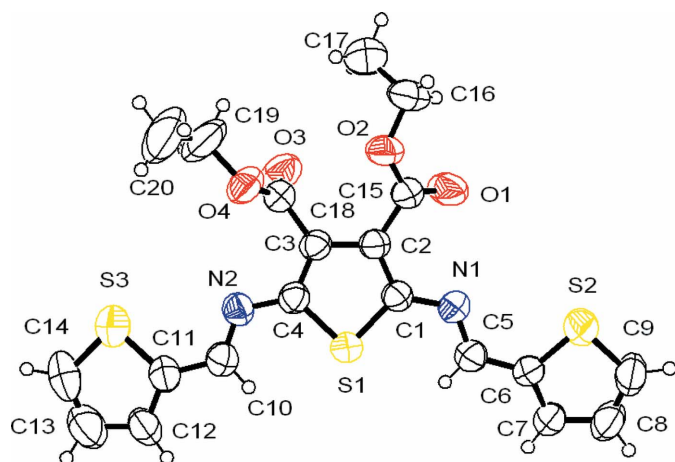
Figure 1
The molecular structure of (III), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.
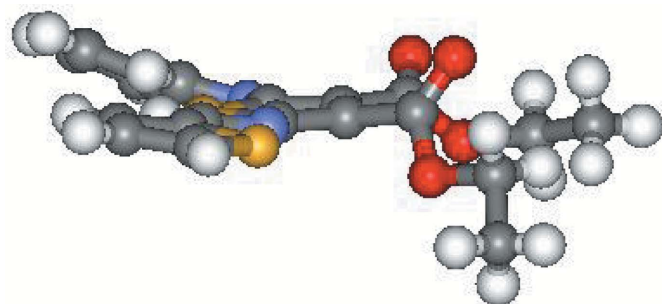
Figure 2
The molecule of compound (III) viewed approximately parallel to the plane of the thiophene rings.

(Table 1). The C1—C2 bond of the central thiophene ring is also *ca* 0.018 Å shorter than the corresponding C12—C13 and C7—C8 bonds. The longer bonds are consistent with the values in (I). However, the N1—C1 and N2—C4 bond distances in (III) are longer than the reported values for the corresponding bonds in (I) of 1.348 (2) and 1.350 (3) Å (Bourgeaux *et al.*, 2006). The azomethine bond distances of N2—C10 and N1—C5 are statistically the same as in (II). These bonds are *ca* 0.042 Å shorter than in the thiopheno–vinylene analog (Ruban & Zobel, 1975; Zobel & Ruban, 1978).

Compound (III) possesses three weak intramolecular interactions (see Table 2). These interactions may be in part responsible for the antiparallel arrangement of the thiophene rings. In the crystal structure, pairs of molecules are related to each other *via* a twofold axis along *b*. S1 and S2 are located above the center of the corresponding thiophene ring of its neighboring molecule. Each pair is related *via* an inversion center to the next pair. Stacking of the S1-containing thiophene ring with the S3-containing thiophene ring of the inverted molecule occurs in such a way that C1 and C11 are positioned above the center of the stacked rings. The crystal structure also confirms that the thermodynamically preferred *E* isomer is formed for both azomethine bonds.

Experimental

Compound (III) was obtained according to our previously reported method (Skene & Trefz, 2004). Single crystals of (III) were obtained by slow evaporation of an ethanol and dichloromethane solution (10:1) of (III).

Crystal data

$C_{20}H_{18}N_2O_4S_3$	$Z = 8$
$M_r = 446.54$	$D_x = 1.364$ Mg m^{-3}
Orthorhombic, $Pbcn$	Cu $K\alpha$ radiation
$a = 17.039$ (5) Å	$\mu = 3.36$ mm^{-1}
$b = 18.642$ (8) Å	$T = 293$ (2) K
$c = 13.690$ (4) Å	Block, red
$V = 4349$ (3) Å^3	$0.44 \times 0.35 \times 0.14$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	4130 independent reflections
ω scans	1716 reflections with $I > 2\sigma(I)$
Absorption correction: Gaussian from crystal shape (reference?)	$R_{int} = 0.091$
	$\theta_{max} = 70.0°$
	4 standard reflections
$T_{min} = 0.160$, $T_{max} = 0.650$	frequency: 60 min
32236 measured reflections	intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.114$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
$S = 0.73$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
4130 reflections	Extinction correction: *SHELXL97*
265 parameters	Extinction coefficient: 0.00082 (4)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.734 (3)	N2—C10	1.266 (4)
S1—C4	1.742 (3)	N2—C4	1.380 (3)
S2—C9	1.695 (4)	C1—C2	1.369 (4)
S2—C6	1.702 (3)	C5—C6	1.439 (4)
S3—C14	1.692 (4)	C7—C8	1.406 (4)
S3—C11	1.707 (3)	C10—C11	1.445 (4)
N1—C5	1.278 (3)	C12—C13	1.397 (5)
N1—C1	1.397 (3)		
C5—N1—C1—C2	−163.1 (3)	N1—C5—C6—S2	5.1 (5)
C10—N2—C4—S1	−5.1 (5)	C4—N2—C10—C11	179.5 (3)
C1—N1—C5—C6	−179.6 (3)	N2—C10—C11—S3	−2.1 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C5—H5$\cdots$S1	0.93	2.59	3.024 (3)	109
C10—H10$\cdots$S1	0.93	2.58	3.038 (4)	111
C16—H16$B\cdots$O1	0.97	2.28	2.689 (5)	104

H atoms were paced in calculated positions (C—H = 0.93-0.97 Å) and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local program;

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program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (Marris, 2004).

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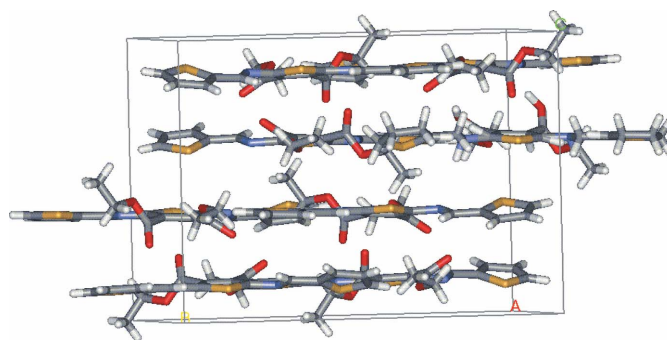
Figure 3
Part of the crystal structure of (III).

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