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(*E*)-Diethyl 2-amino-5-(2-thienylmethyleneamino)thiophene-3,4-dicarboxylate

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Key indicators

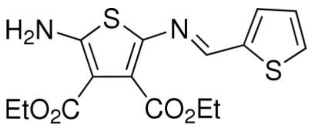
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.098
Data-to-parameter ratio = 14.6

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

The highly conjugated title compound, $C_{15}H_{16}N_2O_4S_2$, exhibits an extended planar configuration. This unusual behavior is the result of the azomethine that adopts the *E* configuration concomitant with the antiparallel orientation of the thiophene units. The nitrogen-containing double bond is also *ca* 0.04 Å shorter than its carbon analogue.

Comment

Recently, conjugated polymers have received much attention because of the many new possibilities that exist for devices combining unique optical, electrical and mechanical properties (MacDiarmid, 2001). A few such applications of conjugated polymers involve organic light emitting diodes (OLEDs) and molecular wires to be used in flexible light displays and/or low power consumption products (Brabec *et al.*, 2001; Rupprecht, 1999). Because of the many interesting properties they possess, these materials have been heavily investigated both in terms of their synthesis and for their various electrical and optical properties. As attractive as these compounds are for their physical properties, the main synthetic methods used are, however, not straightforward (Kraft *et al.*, 1998; Leclerc, 2001; Lavastre *et al.*, 2002). These normally entail challenging and tedious purifications to isolate the desired compounds, which are often compounded with low to moderate yields (Kraft *et al.*, 1998; Leclerc, 2001). Owing to our synthetic success of light harvesting materials using azomethine (–C=N–) linkages (Skene & Dufresne, 2004), we applied this simple method to synthesize novel conjugated thiopheno azomethines that are isoelectronic to their carbon analogues (Wang *et al.*, 1996; Yang & Jenekhe, 1995, 1991). During our studies, we isolated the title conjugated azomethine, (I), as a deep-orange solid, which easily crystallized from ethanol. The crystal data reported here illustrate the unique azomethine crystal properties that arise with the use of a thiophene unit.



(I)

The molecular structure of (I) is shown in Fig. 1. Both aryl rings are slightly twisted out of the mean plane of the azomethine unit. In the case of homoaryl units, the planes described by the two aromatics units are twisted by 65° (Bürgi & Dunitz, 1969; Manecke *et al.*, 1972). The angle can decrease to 32.6 (8)° by linking a thiophene unit to the azomethine bond (Skene & Dufresne, 2006). In (I), connecting two thio-

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phene units to the azomethine further reduces the mean plane angle to 7.25 (11)°; this near-coplanarity is illustrated in Fig. 2. Even though the N═C bond is isoelectronic with the C═C bond, the bond distances for the azomethine are shorter than those for its carbon analogue. For example, the distances corresponding to C5—C6, C5—N2, and N2—C4 for the carbon analogue of (I) are 1.457 (7), 1.326 (10) and 1.453 (9) Å, respectively (Ruban & Zobel, 1975; Zobel & Ruban, 1978). These are longer than the corresponding values for (I) that are reported in Table 1.

The ^{1}H NMR spectrum confirms that only one isomer for (I) is formed, although the absolute assignment of the isolated isomer to either the *E* or the *Z* configuration is not possible. The crystal structure of (I) clearly shows that the thermodynamically favored *E* isomer is formed.

Experimental

Compound (I) was obtained according to our previously reported method (Skene & Trefz, 2004). Single crystals of (I) were formed upon evaporating the flash chromatography solvent under reduced pressure.

Crystal data

$C_{15}H_{16}N_2O_4S_2$
$M_r = 352.42$
Monoclinic, $P2_1/n$
$a = 9.428$ (4) Å
$b = 14.907$ (6) Å
$c = 11.671$ (4) Å
$\beta = 99.28$ (3)°
$V = 1618.8$ (11) Å^3
$Z = 4$
$D_x = 1.446$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 3.18$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.64 × 0.30 × 0.22 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: Gaussian (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.220$, $T_{\max} = 0.580$
32753 measured reflections
3071 independent reflections
2255 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\max} = 70.0°$
5 standard reflections
frequency: 60 min
intensity decay: 1.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.098$
$S = 0.92$
3071 reflections
211 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0045 (3)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.349 (3)	N2—C5	1.283 (3)
N2—C4	1.381 (3)	C5—C6	1.426 (3)
C5—N2—C4—S1	−0.9 (3)	C4—N2—C5—C6	179.13 (18)
C1—S1—C4—C3	0.65 (16)	N2—C5—C6—C7	−174.6 (2)

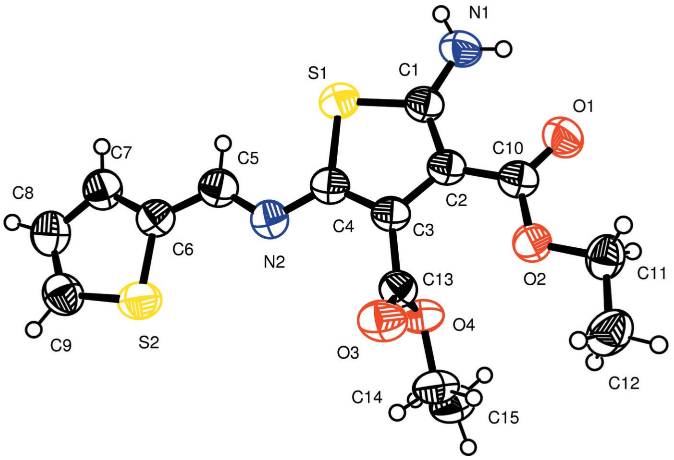

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

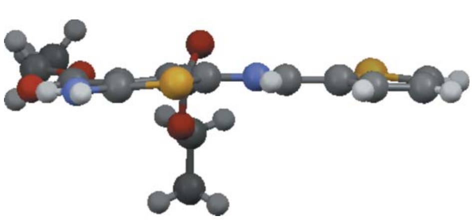

Figure 2
Schematic representation of compound (I), viewed parallel to the plane of the thiophene rings.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.86	2.20	2.778 (3)	124
N1—H1*A*···O1$^{\rm i}$	0.86	2.22	2.880 (3)	134

Symmetry code: (i) $-x, -y+1, -z+1$.

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and the torsion angle refined to fit the electron density [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C)]. Other H atoms were placed in calculated positions with C—H = 0.93 (aromatic) or 0.97 Å (methylene), and N—H = 0.86 Å, and refined in riding mode with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

Data collection: *UdMX* (Marris, 2004); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: *UdMX*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX*.

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