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# Hydrogen-bonded network of diethyl 2,5-diaminothiophene-3,4-dicarboxylate

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**Key indicators**

Single-crystal X-ray study
$T$ = 220 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.042
$wR$ factor = 0.125
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.



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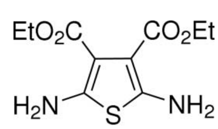
The crystal structure of the title compound, $C_{10}H_{14}N_2O_4S$, has a supramolecular network involving both inter- and intramolecular hydrogen bonding. The thiophene core of the molecule adopts a planar geometry.

## Comment

Thiophenes have attracted much attention in the areas of organic synthesis and materials science alike. This interest is in part due to their pharmaceutical properties, which include anti-ulcer and antiviral/antitumor properties (Stephens *et al.*, 2001), along with other biological activities, including human leukocyte elastases (Guetschow *et al.*, 1999), allosteric enhancers (Lütjens *et al.*, 2003) and non-peptide antagonists (Sasaki *et al.*, 2003), to name but a few. Not only do thiophenes possess desired pharmaceutical properties, they also exhibit desirable properties for functional materials, including organic light-emitting diodes (Perepichka *et al.*, 2005) and field-effect transistors (MacDiarmid, 2001). We are interested in amino thiophenes such as the title compound, (I), because they are useful precursors in the synthesis of conjugated functional materials *via* Schiff bases (Skene, 2004; Skene & Trefz, 2004*a*,*b*; Dufresne & Skene, 2005*a*,*b*,*c*,*d*; Bourgeaux & Skene, 2005; Skene *et al.*, 2006). During synthetic optimization studies, we isolated compound (I) as yellow crystals.




(I)

The salient features of the tetrasubstituted compound (I) are the planar geometry of the thiophene ring and the two ethyl ester groups twisted away from this plane (Fig. 1, Table 1). The mean planes of the two esters make angles of 26.16 (8) and 28.87 (9)° with the thiophene mean plane. The N—C bond distances of the amine are in good agreement with those in the literature, *e.g.* 1.349 (3) (Skene *et al.*, 2006), 1.345 (3) (Çoruh *et al.*, 2005) and 1.354 (5) Å (Çoruh *et al.*, 2003).

The strong amine donor group undergoes multiple hydrogen bonding. Two such bonds are intramolecular (Table 2, entries 1 and 4). There are also two intermolecular hydrogen bonds which occur between the complementary donor and acceptor pairs (Table 2, entries 3 and 4). Two units of (I) self-associate to form a planar antiparallel dimer-like coordination (Fig. 2). The remaining donor site coordinates with the carbonyl ester in an out-of-plane fashion. The combined effect of the intermolecular hydrogen bonds is a

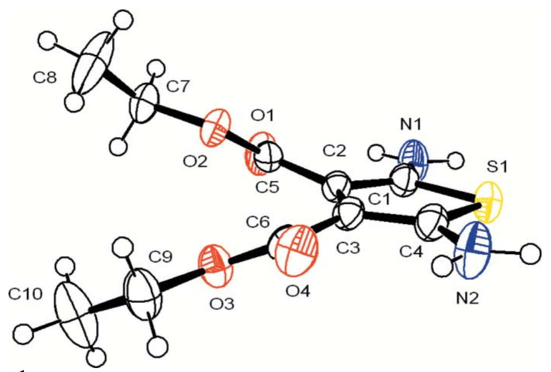



**Figure 1**
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

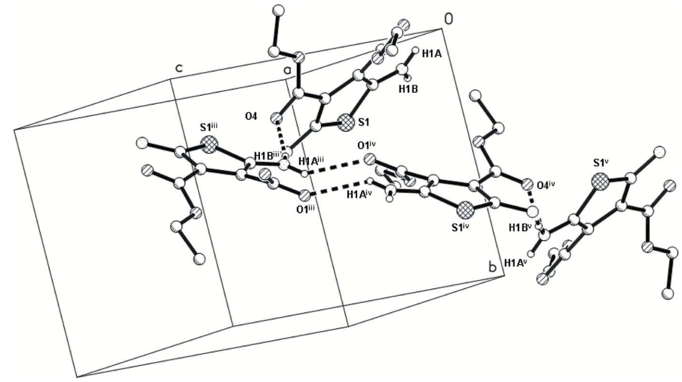



**Figure 2**
A view of the hydrogen-bonding interactions in (I), shown as dashed lines. Atoms C7$^{iii}$ and C8$^{iii}$ have been omitted for clarity. [Symmetry codes: (iii) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $-x, 1 - y, -z$.]

supramolecular zigzag network along the *c* axis (Fig. 3), which is responsible for the crystallinity of (I) (Wuest, 2005).

## Experimental

Compound (I) was obtained according to our previously reported method (Bourgeaux & Skene, 2005, and references therein). Crystals suitable for X-ray analysis were obtained upon slow evaporation of a solution of the freshly synthesized material dissolved in ethyl acetate.

*Crystal data*

$C_{10}H_{14}N_2O_4S$
$M_r = 258.29$
Monoclinic, $P2_1/c$
$a = 9.5306$ (3) Å
$b = 8.8206$ (3) Å
$c = 15.5518$ (5) Å
$\beta = 105.9630$ (10)°
$V = 1256.96$ (7) Å$^3$
$Z = 4$
$D_x = 1.365$ Mg m$^{-3}$
Cu $K\alpha$ radiation
$\mu = 2.37$ mm$^{-1}$
$T = 220$ (2) K
Block, colorless
0.32 × 0.28 × 0.15 mm

*Data collection*

Bruker SMART 6000 diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.405$, $T_{max} = 0.702$
16465 measured reflections
2270 independent reflections
2032 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 68.3°$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.126$
$S = 1.07$
2270 reflections
156 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 0.1856P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.30$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—C4 | 1.7434 (19) | C1—C2 | 1.381 (2) |
| S1—C1 | 1.7519 (17) | C2—C5 | 1.457 (2) |
| O4—C6 | 1.230 (2) | C2—C3 | 1.459 (2) |
| N1—C1 | 1.348 (2) | C3—C4 | 1.378 (2) |
| N2—C4 | 1.350 (2) | | |
| C3—C2—C5—O2 | 20.2 (2) | C2—C3—C6—O3 | 19.8 (2) |

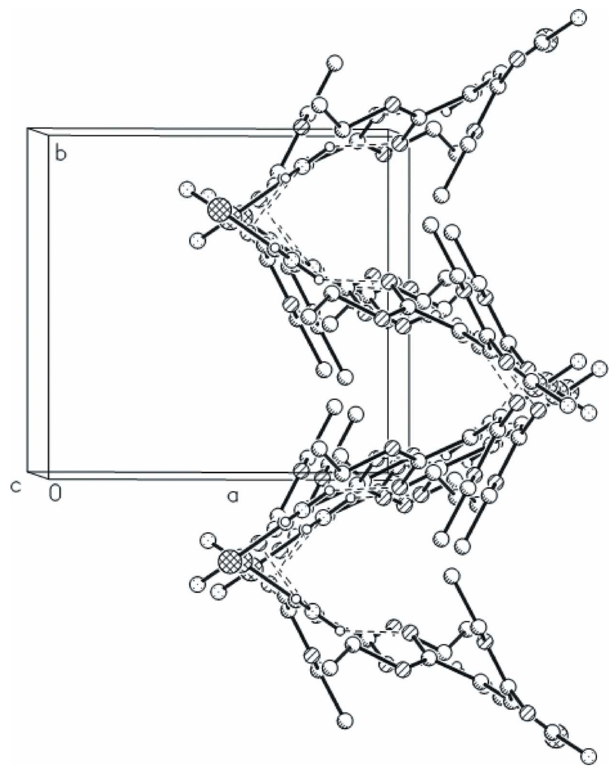



**Figure 3**
The zigzag supramolecular-like network of (I). Dashed lines indicate hydrogen bonds.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O1 | 0.87 | 2.26 | 2.827 (2) | 123 |
| N1—H1*A*···O1$^{i}$ | 0.87 | 2.31 | 3.002 (2) | 137 |
| N1—H1*B*···O4$^{ii}$ | 0.87 | 2.09 | 2.907 (2) | 157 |
| N2—H2*A*···O4 | 0.87 | 2.17 | 2.753 (2) | 124 |

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

H atoms were positioned geometrically and treated as riding [C—H = 0.97–0.98 Å, N—H = 0.87 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$].

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Farrugia, 1997) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *UdMX* (Maris, 2004).

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