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Ethyl 3-amino-6-phenyl-4-tolylthieno[2,3-*b*]pyridine-2-carboxylate

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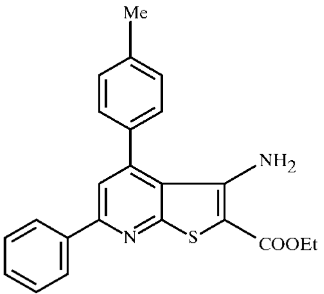
In the title compound, $C_{23}H_{20}N_2O_2S$, the central thienopyridine ring system is essentially planar, the dihedral angle between the planes of the two rings being 0.3 (2)°. The terminal ethyl carboxylate group is twisted by 26.7 (3)° away from the central ring system. A short intramolecular hydrogen bond involving the amino N atom and the carbonyl O atom [N···O = 2.806 (4) Å] forms a pseudo-six-membered ring. Significant intermolecular C—H···N, C—H···O and C—H···π interactions contribute strongly to the stability of the structure, along with weak π–π-stacking interactions.

Comment

Thienopyridines are bicyclic heterocycles in which a thiophene ring is fused to a pyridine ring. Being isoesters of classical quinolines (Friedrichsen, 1984), these compounds show a wide range of pharmaceutical activities, such as antihypertensive, antimicrobial (Gills *et al.*, 1980) and antiulcer (Briel, 1998) properties. In a continuation of our recent studies of the 2-pyridine class of compounds carried out to investigate the influence of different substituents on the structural parameters of the molecule (Patel *et al.*, 2002), we report here the crystal and molecular structure of a fused system of a π-deficient pyridine ring and a π-rich thiophene ring, *viz.* the title compound, (I).



(I)

Fig. 1 shows the molecular structure of (I). The molecular dimensions of the thienopyridine ring system are normal, except for a slight deviation observed in the endocyclic angle at C1 of the pyridine ring; the C2—C1—N1 angle is enlarged to 126.7 (3)° (Kvick & Noordik, 1977). The C1—N1—C5 angle of 116.3 (2)° is as expected for a non-protonated ring system, being smaller than 120° (Ghosh & Simonsen, 1993). The C—S bonds [1.739 (3) and 1.742 (3) Å] of the thiophene ring are long compared with the values observed in both free thiophene, measured using electron diffraction (1.714 Å; Bonham & Momany, 1963), and thieno[2,3-*c*]pyridine [1.728 (1) and 1.731 (1) Å; Nerenz *et al.*, 1997]. The corresponding values in the non-fused system 2-(2-thienyl)pyridine (Ghosh & Simonsen, 1993) are 1.712 (3) and 1.723 (3) Å to the substituted and non-substituted C atoms, respectively. The C—S—C angle of 90.1 (2)° in (I) is comparable with that observed in thieno[2,3-*c*]pyridine, but is slightly less than that observed in free thiophene [92.2 (2)°]. In general, the molecular dimensions of the fused-ring system of (I) agree well with the corresponding values in other similar compounds (Nerenz *et al.*, 1997).

The O—Csp^2 bond of the terminal ester group in (I) [1.360 (4) Å] is longer than the normal value but agrees well with the values found in other compounds containing this molecular fragment (Csöregh & Palm, 1977). The unusual C22—C23 bond distance [1.401 (7) Å] can probably be attributed to unresolved disorder of the methyl terminus, as indicated by the unusual displacement parameters for atoms C22 and C23.

The C20—C21—O2—C22 torsion angle of 175.5 (4)° describes the *trans* configuration of the molecule about the C21—O2 bond. The central thienopyridine ring system is planar, the dihedral angle between these ring planes being 0.3 (2)°. Both phenyl rings are planar within themselves, with maximum deviations of 0.0035 and 0.0054 Å for atoms C16 and C15, respectively, from their respective mean planes. However, the participation of two atoms (C10 and C11) of the phenyl ring at C3 in strong intermolecular interactions with the NH_2 group at C19 (see below) rotates the ring markedly [by 69.9 (1)° out of the central ring system], whereas in the absence of any such interactions, the phenyl ring at C5 is almost coplanar with the central ring system [dihedral angle 5.2 (2)°].

The terminal ester group is twisted substantially out of the central ring system [dihedral angle 26.7 (3)°]. The carbonyl moiety is coplanar with the thiophene ring and has a *cis* orientation, characterized by a C19—C20—C21—O1 torsion angle of 1.1 (6)°, thereby placing the amino atom N2 in a strong intramolecular contact with carbonyl atom O1 [N2—H2*A*···O1; see Table 2] and forming a pseudo-six-membered ring.

A network of intermolecular C—H···N and C—H···O interactions (Spek, 1997; Fig. 2), as well as C—H···π and π–π interactions, provide strong packing in the structure of (I). Phenyl ring atoms C10 and C11 are hydrogen bonded to atom

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N1 of two different symmetry-related molecules at ($x + 1, y, z$) and ($1 - x, 1 - y, 1 - z$), respectively (Table 2). Carbonyl atom O1 of one molecule acts as an acceptor in another hydrogen-bond interaction with phenyl atom C18 in a symmetry-related molecule at ($1 - x, y - \frac{1}{2}, \frac{1}{2} - z$) (Table 2). In addition, methyl atom C12 is involved in two separate C—H$\cdots\pi$ interactions, with C12$\cdots$*Cg*1 = 4.070 (4) Å, H12*A*$\cdots$*Cg*1 = 3.1 Å and C12—H12*A*$\cdots$*Cg*1 = 163°, and C12$\cdots$*Cg*2 = 4.001 (5) Å, H12*B*$\cdots$*Cg*2 = 3.1 Å and C12—H12*B*$\cdots$*Cg*2 = 133°, where *Cg*1 is the centre of gravity of the pyridine ring of the molecule at ($1 + x, y, z$) and *Cg*2 is the centre of gravity of the phenyl ring of the molecule at ($2 - x, 1 - y, z$). A comparatively weak π–π interaction between the thiophene ring and a symmetry-related pyridine ring at ($1 - x, -y, 2 - z$), with their centroids separated by 3.721 (2) Å, is also observed in the structure of (I).

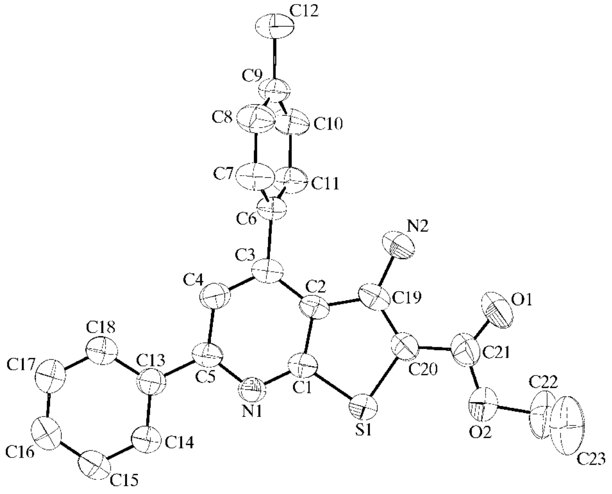

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

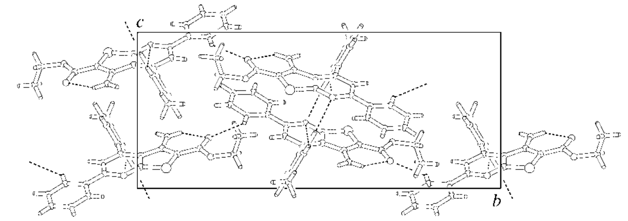

Figure 2
The molecular packing of (I), viewed in the *bc* plane, with the C—H$\cdots$O and C—H$\cdots$N interactions shown as dashed lines.

Experimental

The title compound was synthesized according to the method of Shah (2000); details of the synthesis will be published elsewhere. Plate-like single crystals of (I) were grown from a solution in ethyl acetate by slow evaporation.

Crystal data

$C_{23}H_{20}N_2O_2S$
M_r = 388.47
Monoclinic, $P2_1/c$
a = 9.200 (3) Å
b = 22.465 (5) Å
c = 9.708 (3) Å
β = 94.06 (3)°
V = 2001.4 (10) Å^3
Z = 4
D_x = 1.289 Mg m^{-3}
D_m = 1.289 Mg m^{-3}
D_m measured by flotation in aqueous potassium iodide
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 25–35°
μ = 0.18 mm^{-1}
T = 293 (2) K
Plate, light yellow
0.2 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
3513 measured reflections
3513 independent reflections
1922 reflections with $I > 2\sigma(I)$
θ_{max} = 24.9°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 11$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.156
S = 0.98
3504 reflections
253 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2]$ where $P = (F_c^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.739 (3)	O2—C21	1.360 (4)
S1—C20	1.742 (3)	O2—C22	1.450 (5)
N1—C1	1.335 (4)	C2—C1	1.413 (4)
N1—C5	1.346 (4)	O1—C21	1.215 (4)
N2—C19	1.362 (4)	C22—C23	1.401 (7)
C1—S1—C20	90.07 (15)	O1—C21—O2	123.7 (4)
C1—N1—C5	116.3 (2)	O1—C21—C20	125.2 (4)
C21—O2—C22	118.0 (3)	O2—C21—C20	111.1 (3)
N1—C1—C2	126.7 (3)	C23—C22—O2	112.6 (5)
C22—O2—C21—C20	175.5 (4)	S1—C20—C21—O1	−176.4 (3)
C19—C20—C21—O1	1.1 (6)	C21—O2—C22—C23	93.7 (6)

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N2—H2*A*$\cdots$O1	0.86	2.20	2.806 (4)	128
C10—H10$\cdots$N1^{iii}	0.93	2.62	3.488 (4)	155
C11—H11$\cdots$N1^{i}	0.93	2.55	3.453 (4)	164
C14—H14$\cdots$N1	0.93	2.45	2.787 (4)	101
C18—H18$\cdots$O1^{ii}	0.93	2.59	3.253 (5)	129

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

H atoms were treated as riding, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.86 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1192). Services for accessing these data are described at the back of the journal.

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