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Ethyl 2-amino-6-methyl-4,5,6,7-tetrahydrothieno-[2,3-*c*]pyridine-3-carboxylate monohydrate

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.056
wR factor = 0.137
Data-to-parameter ratio = 14.7

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

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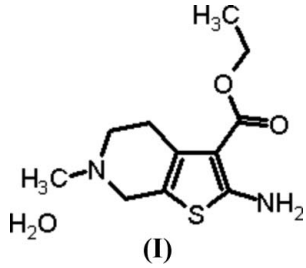
The title compound, $C_{11}H_{16}N_2O_2S\cdot H_2O$, is stabilized by a number of inter- and intramolecular O—H···O, O—H···N, N—H···O and C—H···O hydrogen bonds. Delocalization in the thiophene system is indicated by the C—S bond distances.

Comment

The bicyclic tetrahydropyridinothiophenes are an important class of hetrocycles which are known for their wide range of biological activities (Sebnis *et al.*, 1999). The title compound, (I), was amongst many compounds which were screened for their antimicrobial and anti-inflammatory activities (Mohan & Saravanan, 2003). Schiff bases (Csaszar & Morvay, 1983; Lakshmi *et al.*, 1985; Cohen *et al.*, 1977) and their thiophene derivatives (El-Maghraby *et al.*, 1984; Dzhurayev *et al.*, 1992; Gewald *et al.*, 1966) possess antibacterial, antitubercular and antifungal activities. The structure of (I) (Fig. 1) was determined with a view to establishing the orientation of the vicinally substituted amino and ester functions in the solid state.



(I)

The C—N bond distance in 2-aminothiophenes has been used as a measure of the conjugation across bicyclic thiophenes (Chandra Kumar *et al.*, 2005). The C2—N2 bond distance of 1.342 (3) Å in (I) supports this proposition. Furthermore, the difference between C2—C3 [1.389 (3) Å] and C7—C8 [1.349 (3) Å] shows the compound to have a slightly reduced double-bond character for the C2—C3 bond.

The bicyclic system exhibits a non-planar structure, particularly at the ring junction. The ester function has the ethyl group (C10—C11) and the thiophene ring in an *S–trans* arrangement across the O2—C9 bond. The N—CH_3 group also shows a significant deviation from the molecular plane.

The water molecules form O—H···N and O—H···O hydrogen bonds with the ring N atom and the carboxyl O atom of the ester, and N—H···O and C—H···O hydrogen bonds with the amino group and the H atom on C6. Intramolecular interactions are of two types. The first, between the carbonyl O atom and the amino group. The second is due to the non-

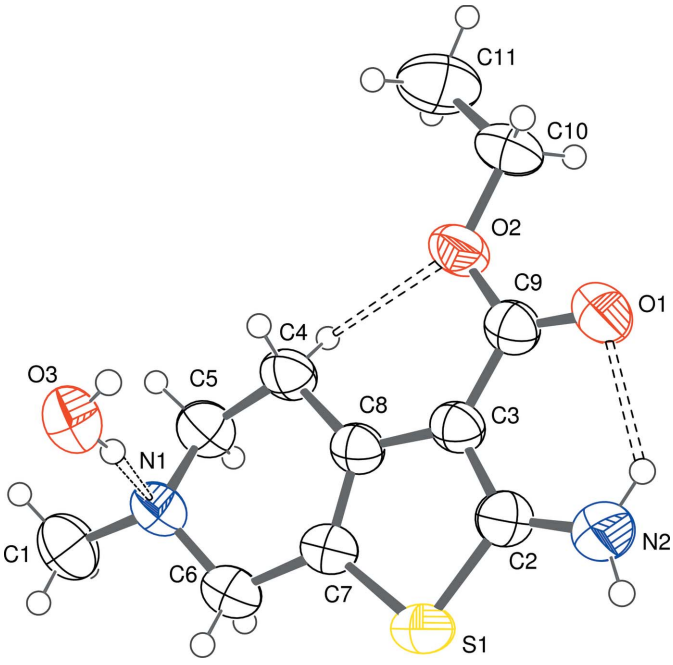


Figure 1
A view of the title compound (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

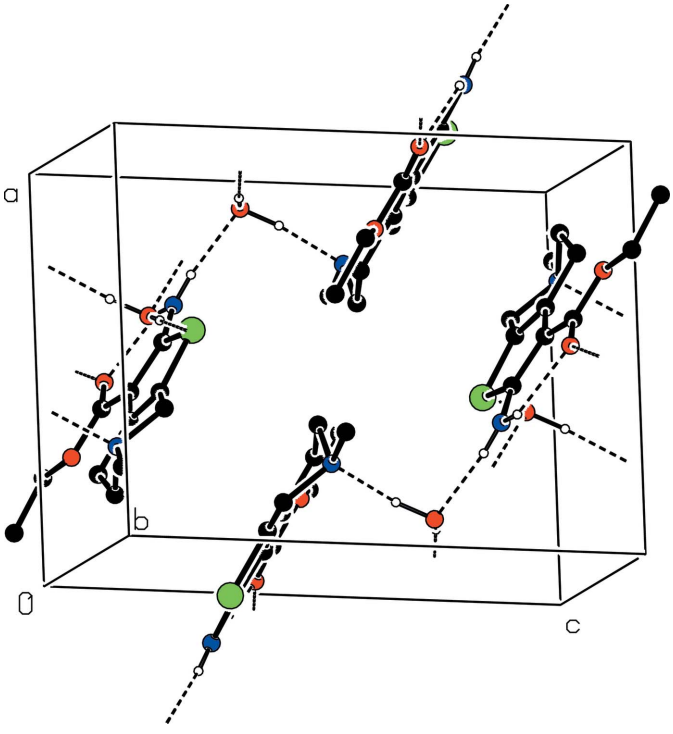


Figure 2
A packing diagram for (I). Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bonding have been omitted.

planar nature of the tetrahydropyridine skeleton, which results in an interaction between C4—H and atom O2 of the ester group (Fig. 2).

Experimental

To a mixture of *N*-methylpiperidin-4-one (4.1 ml), ethyl cyanoacetate (4.5 ml) and elemental sulfur (1.2 g) in ethanol (20 ml) was added diethylamine (4 ml) with stirring at a temperature between 318 and 323 K until the sulfur dissolved. Stirring was continued until the product precipitated. The reaction mixture was cooled to room temperature and kept overnight in a refrigerator. The precipitate was filtered off and recrystallized from ethanol to give the title compound, (I) (m.p. 378 K). The source of hydrate water could be the diethylamine and ethanol reagents used for the synthesis.

Crystal data

$C_{11}H_{16}N_2O_2S\cdot H_2O$
$M_r = 258.34$
Monoclinic, $P2_1/n$
$a = 9.670$ (2) Å
$b = 11.514$ (3) Å
$c = 12.219$ (3) Å
$\beta = 93.074$ (4)°
$V = 1358.4$ (6) Å^3
$Z = 4$
$D_x = 1.263$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.24$ mm^{-1}
$T = 291$ (2) K
Block, colourless
0.31 × 0.28 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.930$, $T_{max} = 0.955$
9867 measured reflections
2526 independent reflections
2115 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.137$
$S = 1.19$
2526 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 0.1443P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N2—C2	1.342 (3)	C7—C8	1.349 (3)
C2—C3	1.389 (3)		
C9—C3—C8	128.39 (19)	O2—C9—C3	113.53 (19)
O1—C9—C3	124.6 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.84 (3)	2.02 (3)	2.846 (3)	171 (3)
N2—H2B···O1	0.88 (2)	2.10 (3)	2.741 (3)	130 (2)
C4—H4A···O2	0.97 (2)	2.52 (3)	2.858 (2)	100 (4)
O3—H3A···N1	1.00 (4)	1.80 (4)	2.790 (3)	170 (3)
O3—H3B···O1^{ii}	0.71 (3)	2.17 (3)	2.874 (3)	176 (2)

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

Carbon-bound H atoms were placed in idealized positions, with C—H = 0.93–0.97 Å, and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl H. A rotating-group model was used for the methyl groups. The positions of H atoms on N2 (amine) and O3 (hydrate) were located in a difference fourier map and refined isotropically.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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