Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 3-amino-4*H*-thieno[2,3-*b*]pyridine-2-carboxylate

Ren-lin Zheng, Wen-qin Zhang, Luo-Ting Yu, Sheng-Yong Yang and Li Yang*

State Key Laboratory of Biotherapy and Cancer Center, West China Hospital, West China Medical School, Sichuan University, Chengdu 610041, People's Republic of China
Correspondence e-mail: yangli@scu.edu.cn

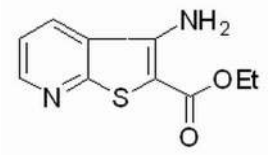
Received 20 November 2008; accepted 27 November 2008

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.003 Å; R factor = 0.040; wR factor = 0.118; data-to-parameter ratio = 12.9.

The molecule of the title compound, $C_{10}H_{10}N_2O_2S$, is essentially planar, except for the ethyl group, which is twisted away from the carboxyl plane by −90.5 (3)°. In the crystal structure, molecules are linked into a zigzag sheet propagating along the b axis by intermolecular N—H···O and N—H···N hydrogen bonds.

Related literature

For general background, see: Litvinov *et al.* (2005).



Experimental

Crystal data

$C_{10}H_{10}N_2O_2S$
M_r = 222.26
Monoclinic, $P2_1/c$
a = 6.657 (4) Å
b = 13.891 (4) Å
c = 10.902 (4) Å
β = 91.64 (4)°
V = 1007.8 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 292 (2) K
0.60 × 0.46 × 0.42 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: spherical (Dwiggins, 1975)
T_{min} = 0.840, T_{max} = 0.884
1978 measured reflections
1864 independent reflections
1515 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
3 standard reflections
every 150 reflections
intensity decay: 0.6%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.118
S = 1.14
1864 reflections
145 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N2···O2	0.84 (2)	2.26 (2)	2.848 (3)	127 (2)
N2—H1N2···O2^{i}	0.84 (2)	2.38 (3)	3.067 (3)	139 (2)
N2—H2N2···N1^{ii}	0.81 (3)	2.38 (3)	3.118 (3)	152 (3)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *DIFRAC* (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2735).

References

Dwiggins, C. W. (1975). *Acta Cryst.* A**31**, 146–148.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gabe, E. J. & White, P. S. (1993). *DIFRAC*. American Crystallographic Association Meeting, Pittsburgh, Abstract PA 104.
Litvinov, V. P., Dotsenko, V. V. & Krivokolysko, S. G. (2005). *Russ. Chem. Bull.* **54**, 864–904.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2009). E**65**, o9 [doi:10.1107/S1600536808039974]

Ethyl 3-amino-4*H*-thieno[2,3-*b*]pyridine-2-carboxylate

Ren-lin Zheng, Wen-qin Zhang, Luo-Ting Yu, Sheng-Yong Yang and Li Yang

S1. Comment

Thieno[2,3-*b*]pyridine derivatives are of great importance owing to their wide biological properties (Litvinov *et al.*,2005). The title compound is one of the key intermediates in our synthetic investigations of antitumor drugs. We report here its crystal structure.

The thieno[2,3-*b*]pyridine ring system of the title molecule (Fig.1) is essentially planar. The amino group and the carbonyl group are nearly coplanar with the heterocyclic ring system. The ethyl group is twisted perpendicular to the remaining part of the molecule [C8—O1—C9—C10 = -90.5 (3)°].

In the crystal structure, the molecules are linked into a zigzag sheet propagating along the *b* axis by intermolecular N—H···O and N—H···N hydrogen bonds (Fig. 2).

S2. Experimental

A mixture of 2-chloro-3-cyanopyridine (3.3 g, 0.023 mol), ethyl 2-mercaptoacetate (3.62 g, 0.03 mol), sodium carbonate (2.65 g, 0.025 mol) and anhydrous ethanol (12.0 ml) was heated for 4.5 h under reflux. The reaction mixture was cooled to ambient temperature and added to water (150 ml). The resultant precipitate was stirred for 45 min and then filtered. The filter cake was washed with two portions of water (25 ml) and dried to yield the title compound as a yellow solid (5.032 g, 95.1% yield). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a tetrahydrofuran solution.

S3. Refinement

H atoms of the amino group were located in a difference map and refined freely. The reminaing H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined using a riding model, with U_{iso}(H) = 1.2–1.5U_{eq}(C).

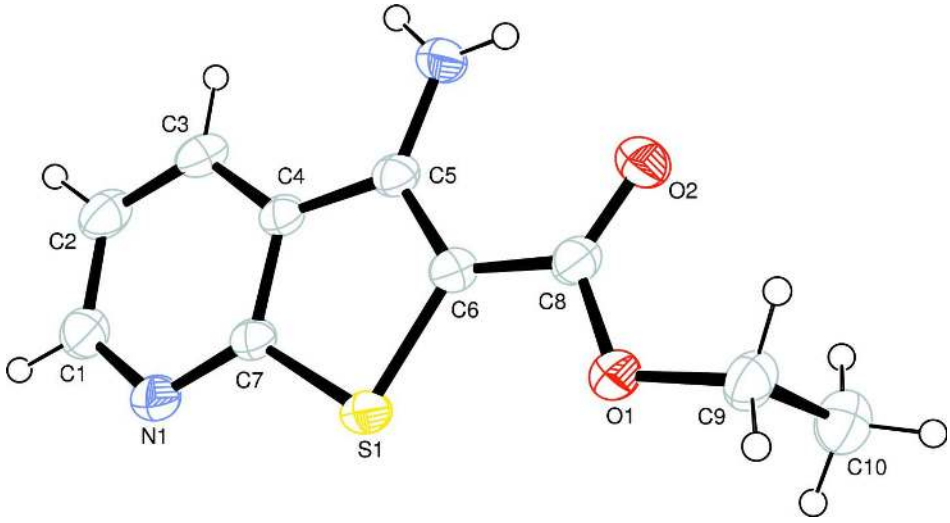


Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

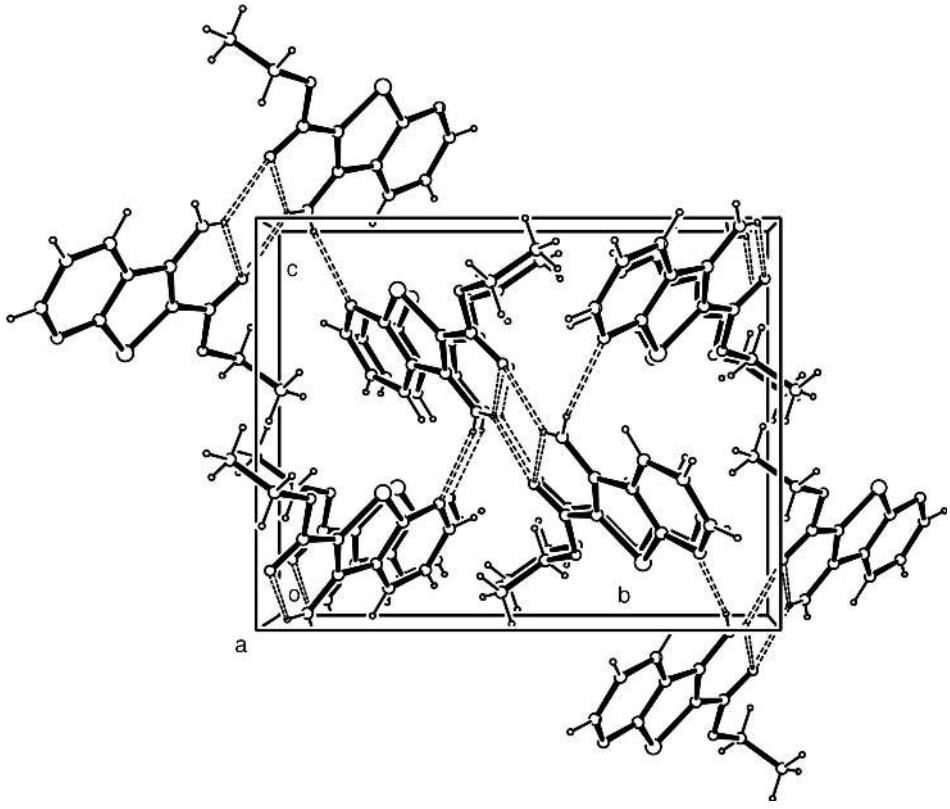


Figure 2

A packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed open lines.

Ethyl 3-amino-4*H*-thieno[2,3-*b*]pyridine-2-carboxylate

Crystal data

$C_{10}H_{10}N_2O_2S$
$M_r = 222.26$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 6.657$ (4) Å
$b = 13.891$ (4) Å
$c = 10.902$ (4) Å
$\beta = 91.64$ (4)°
$V = 1007.8$ (8) Å^3
$Z = 4$
$F(000) = 464$
$D_x = 1.465$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 4.3$–$5.7°$
$\mu = 0.30$ mm^{-1}
$T = 292$ K
Block, colourless
0.60 × 0.46 × 0.42 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: for a sphere (Dwiggins, 1975)
$T_{min} = 0.840$, $T_{max} = 0.884$
1978 measured reflections
1864 independent reflections
1515 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.4°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -6 \rightarrow 13$
3 standard reflections every 150 reflections
intensity decay: 0.6%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.118$
$S = 1.14$
1864 reflections
145 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.4962P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.20405 (9)	0.73591 (5)	0.16994 (5)	0.0405 (2)
O1	−0.1351 (2)	0.60921 (12)	0.17935 (15)	0.0442 (4)
O2	−0.0551 (3)	0.52930 (13)	0.35384 (16)	0.0487 (5)

N1	0.5470 (3)	0.83735 (15)	0.20206 (18)	0.0416 (5)
N2	0.3157 (4)	0.58481 (17)	0.46991 (19)	0.0429 (5)
H1N2	0.215 (4)	0.5502 (18)	0.481 (2)	0.032 (7)*
H2N2	0.407 (4)	0.593 (2)	0.519 (3)	0.049 (8)*
C1	0.7139 (4)	0.8539 (2)	0.2686 (2)	0.0461 (6)
H1	0.8010	0.9013	0.2419	0.055*
C2	0.7661 (4)	0.8045 (2)	0.3756 (2)	0.0468 (6)
H2	0.8851	0.8192	0.4184	0.056*
C3	0.6422 (4)	0.73450 (18)	0.4178 (2)	0.0394 (6)
H3	0.6751	0.7009	0.4894	0.047*
C4	0.4659 (3)	0.71448 (16)	0.35153 (19)	0.0326 (5)
C5	0.3088 (3)	0.64550 (16)	0.3736 (2)	0.0333 (5)
C6	0.1607 (3)	0.64942 (17)	0.2830 (2)	0.0348 (5)
C7	0.4275 (3)	0.76841 (17)	0.2448 (2)	0.0344 (5)
C8	−0.0161 (4)	0.59041 (17)	0.2784 (2)	0.0363 (5)
C9	−0.3115 (4)	0.5493 (2)	0.1610 (2)	0.0457 (6)
H9A	−0.4178	0.5864	0.1209	0.055*
H9B	−0.3587	0.5280	0.2398	0.055*
C10	−0.2633 (4)	0.4637 (2)	0.0840 (3)	0.0527 (7)
H10A	−0.2104	0.4849	0.0076	0.079*
H10B	−0.3832	0.4268	0.0684	0.079*
H10C	−0.1653	0.4245	0.1267	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0453 (4)	0.0474 (4)	0.0286 (3)	−0.0085 (3)	−0.0057 (2)	0.0056 (2)
O1	0.0454 (10)	0.0502 (10)	0.0366 (9)	−0.0120 (8)	−0.0092 (7)	0.0033 (8)
O2	0.0504 (11)	0.0543 (11)	0.0411 (10)	−0.0142 (8)	−0.0030 (8)	0.0107 (8)
N1	0.0478 (12)	0.0464 (12)	0.0307 (10)	−0.0095 (9)	0.0028 (9)	0.0007 (9)
N2	0.0456 (13)	0.0488 (13)	0.0338 (11)	−0.0089 (11)	−0.0060 (10)	0.0094 (9)
C1	0.0465 (14)	0.0514 (16)	0.0404 (14)	−0.0145 (12)	0.0050 (11)	−0.0037 (12)
C2	0.0390 (14)	0.0640 (17)	0.0372 (13)	−0.0085 (12)	−0.0022 (10)	−0.0084 (12)
C3	0.0399 (13)	0.0513 (14)	0.0268 (11)	−0.0002 (11)	−0.0007 (9)	−0.0036 (10)
C4	0.0371 (12)	0.0358 (12)	0.0250 (11)	−0.0001 (9)	0.0024 (9)	−0.0048 (9)
C5	0.0380 (12)	0.0364 (12)	0.0258 (11)	0.0013 (9)	0.0024 (9)	−0.0026 (9)
C6	0.0396 (13)	0.0372 (12)	0.0277 (11)	−0.0029 (10)	−0.0002 (9)	0.0008 (9)
C7	0.0404 (13)	0.0387 (12)	0.0242 (10)	−0.0020 (10)	0.0024 (9)	−0.0039 (9)
C8	0.0396 (13)	0.0390 (13)	0.0303 (12)	−0.0014 (10)	−0.0012 (10)	−0.0023 (10)
C9	0.0386 (14)	0.0545 (16)	0.0435 (14)	−0.0059 (11)	−0.0068 (11)	−0.0061 (12)
C10	0.0517 (16)	0.0523 (16)	0.0540 (16)	−0.0050 (13)	0.0001 (13)	−0.0078 (13)

Geometric parameters (Å, º)

S1—C7	1.736 (3)	C2—H2	0.93
S1—C6	1.752 (2)	C3—C4	1.389 (3)
O1—C8	1.347 (3)	C3—H3	0.93
O1—C9	1.448 (3)	C4—C7	1.401 (3)

O2—C8	1.215 (3)	C4—C5	1.444 (3)
N1—C1	1.330 (3)	C5—C6	1.376 (3)
N1—C7	1.337 (3)	C6—C8	1.434 (3)
N2—C5	1.346 (3)	C9—C10	1.495 (4)
N2—H1N2	0.84 (2)	C9—H9A	0.97
N2—H2N2	0.81 (3)	C9—H9B	0.97
C1—C2	1.389 (4)	C10—H10A	0.96
C1—H1	0.93	C10—H10B	0.96
C2—C3	1.364 (4)	C10—H10C	0.96

C7—S1—C6	90.20 (11)	C5—C6—C8	125.0 (2)
C8—O1—C9	117.08 (19)	C5—C6—S1	113.77 (17)
C1—N1—C7	115.4 (2)	C8—C6—S1	121.27 (17)
C5—N2—H1N2	117.9 (17)	N1—C7—C4	125.2 (2)
C5—N2—H2N2	116 (2)	N1—C7—S1	122.16 (18)
H1N2—N2—H2N2	125 (3)	C4—C7—S1	112.63 (17)
N1—C1—C2	123.9 (2)	O2—C8—O1	123.1 (2)
N1—C1—H1	118.0	O2—C8—C6	124.5 (2)
C2—C1—H1	118.0	O1—C8—C6	112.4 (2)
C3—C2—C1	119.8 (2)	O1—C9—C10	110.4 (2)
C3—C2—H2	120.1	O1—C9—H9A	109.6
C1—C2—H2	120.1	C10—C9—H9A	109.6
C2—C3—C4	118.5 (2)	O1—C9—H9B	109.6
C2—C3—H3	120.7	C10—C9—H9B	109.6
C4—C3—H3	120.7	H9A—C9—H9B	108.1
C3—C4—C7	117.1 (2)	C9—C10—H10A	109.5
C3—C4—C5	130.7 (2)	C9—C10—H10B	109.5
C7—C4—C5	112.2 (2)	H10A—C10—H10B	109.5
N2—C5—C6	126.3 (2)	C9—C10—H10C	109.5
N2—C5—C4	122.5 (2)	H10A—C10—H10C	109.5
C6—C5—C4	111.2 (2)	H10B—C10—H10C	109.5

C7—N1—C1—C2	0.0 (4)	C1—N1—C7—C4	0.0 (4)
N1—C1—C2—C3	−0.1 (4)	C1—N1—C7—S1	−179.49 (18)
C1—C2—C3—C4	0.1 (4)	C3—C4—C7—N1	0.0 (4)
C2—C3—C4—C7	0.0 (3)	C5—C4—C7—N1	179.9 (2)
C2—C3—C4—C5	−180.0 (2)	C3—C4—C7—S1	179.53 (17)
C3—C4—C5—N2	−1.1 (4)	C5—C4—C7—S1	−0.5 (2)
C7—C4—C5—N2	178.9 (2)	C6—S1—C7—N1	179.8 (2)
C3—C4—C5—C6	−179.5 (2)	C6—S1—C7—C4	0.22 (18)
C7—C4—C5—C6	0.6 (3)	C9—O1—C8—O2	−3.2 (3)
N2—C5—C6—C8	1.9 (4)	C9—O1—C8—C6	176.0 (2)
C4—C5—C6—C8	−179.8 (2)	C5—C6—C8—O2	−0.6 (4)
N2—C5—C6—S1	−178.65 (19)	S1—C6—C8—O2	−179.94 (19)
C4—C5—C6—S1	−0.4 (3)	C5—C6—C8—O1	−179.8 (2)
C7—S1—C6—C5	0.12 (19)	S1—C6—C8—O1	0.9 (3)
C7—S1—C6—C8	179.6 (2)	C8—O1—C9—C10	−90.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*2···O2	0.84 (2)	2.26 (2)	2.848 (3)	127 (2)
N2—H1*N*2···O2^{i}	0.84 (2)	2.38 (3)	3.067 (3)	139 (2)
N2—H2*N*2···N1^{ii}	0.81 (3)	2.38 (3)	3.118 (3)	152 (3)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*, −*y*+3/2, *z*+1/2.