organic compounds

7-Azathieno[2,3-c]cinnoline

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The title compound (systematic name: pyrido[4,3-e]thieno-[2,3-c]pyridazine), $C_9H_5N_3S$, consists of three fused heterocyclic rings. The molecule is planar and the N=N bond length of 1.302 (2) Å is in good agreement with values observed in similar compounds. The molecules show π–π stacking interactions, forming molecular stacks along the b axis with interplanar distances of 3.39 (2) and 3.49 (2) Å. The C—H groups of the thiophene ring are involved in C—H···N interactions, joining molecules into two-dimensional sheets parallel to (0$\bar{1}$1).

Related literature

For related literature, see: Barton et al. (1985); Hansen et al. (2007); Holt & Fiksdahl (2006); Hökelek et al. (1990, 1991a,b); Stockmann & Fiksdahl (2007); van der Meer et al. (1972).
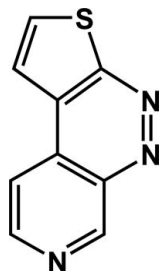
Experimental

Crystal data

C9H5N3S
M_r = 187.22
Triclinic, $P\bar{1}$
a = 6.8340 (18) Å
b = 7.656 (2) Å
c = 8.847 (2) Å
α = 104.172 (3)°
β = 101.376 (4)°

γ = 107.042 (5)°
V = 410.63 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 293 (2) K
0.40 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan [ABSCALC in OSCAIL (McArdle & Daly, 1999; North et al., 1968)]
T_{min} = 0.882, T_{max} = 0.935

2646 measured reflections
2387 independent reflections
1805 reflections with $I > 2\sigma(I)$
R_{int} = 0.008
3 standard reflections frequency: 120 min intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.132
S = 1.09
2387 reflections

138 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···N3^i	0.943 (19)	2.441 (18)	3.352 (3)	159.1 (18)
C2—H2···N1^{ii}	0.89 (2)	2.52 (2)	3.360 (2)	158 (2)

Symmetry codes: (i) $x - 1, y - 1, z - 1$; (ii) $x - 1, y, z$.

Data collection: CAD-4-PC Software (Enraf–Nonius, 1992); cell refinement: CELDIM in CAD-4-PC Software; data reduction: XCAD (McArdle & Higgins, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEX (McArdle, 1995) and ORTEPIII (Burnett & Johnson, 1996); software used to prepare material for publication: OSCAIL (McArdle, 1993).

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supplementary materials

7-Azathieno[2,3-*c*]cinnoline

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Comment

The crystal structure of the title compound was solved as part of a study of new tris-heterocyclic compounds with potential biological activity (Stockmann & Fiksdahl, 2007). Thieno[*c*]cinnolines (Barton *et al.*, 1985) have been described in the literature and the crystal structure of benzo[*c*]cinnoline (9,10-diazaphenanthrene) has been solved (van der Meer *et al.*, 1972). A view of the title molecule with the atomic numbering scheme is presented in Fig. 1. The bond lengths are within the normal range of such bonds and also in accordance with the regio-isomer 7-azathieno[3,2-*c*]cinnoline (Hansen *et al.*, 2007) and other benzo[*c*]cinnoline derivatives (Hökelek *et al.*, 1990, 1991*a,b*). The mean N=N distance for seven similar structures is 1.293 (10) Å, ranging from 1.283 (4) to 1.306 (2) Å. The C6—C7 bonds are always significantly shorter than the C7—C8 bonds. Mean C6—C7 bond is 1.364 (10) Å while the mean C7—C8 bond is 1.409 (10) Å. Also the angles show the same systematic differences. The mean C8—C9—C3 angle and the mean C4—C8—C9 angle are 117.8(2.) and 116.1(1.9)°, respectively, while the mean N2—C4—C8 angle is 122.3(2.0)° (see van der Meer, 1972 and references cited therein). The C—H groups of the thiophene ring are involved in intermolecular C—H⋯N interactions.

Experimental

7-Azathieno[2,3-*c*]cinnoline was prepared by intramolecular diazo coupling of the diazonium ion intermediate, made by NOBF$_4$ diazotization (Holt & Fiksdahl, 2006) of the 3-amino-4-(thiophen-3-yl)pyridine precursor. Single crystals were grown by crystallization from ethyl acetate (Stockmann & Fiksdahl, 2007).

Refinement

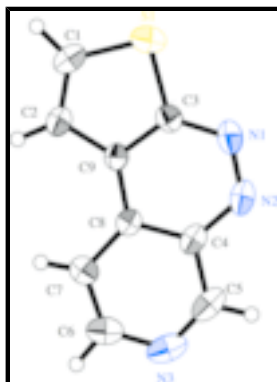All H atoms were found from a difference map and were refined with isotropic displacement parameters.

Figures

Fig. 1. A view of the title molecule with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

supplementary materials

pyrido[4,3-*e*]thieno[2,3-*c*]pyridazine

Crystal data

$C_9H_5N_3S$	$Z = 2$
$M_r = 187.22$	$F_{000} = 192$
Triclinic, $P\overline{1}$	$D_x = 1.514$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 6.8340$ (18) Å	Cell parameters from 25 reflections
$b = 7.656$ (2) Å	$\theta = 12–18^\circ$
$c = 8.847$ (2) Å	$\mu = 0.34$ mm^{-1}
$\alpha = 104.172$ (3)$^\circ$	$T = 293$ (2) K
$\beta = 101.376$ (4)$^\circ$	Prism, colourless
$\gamma = 107.042$ (5)$^\circ$	$0.40 \times 0.30 \times 0.20$ mm
$V = 410.63$ (18) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.008$
Radiation source: fine-focus sealed tube	$\theta_{max} = 29.9^\circ$
Monochromator: graphite	$\theta_{min} = 2.5^\circ$
$T = 298(2)$ K	$h = 0\rightarrow9$
$\omega/2\theta$ scans	$k = -10\rightarrow10$
Absorption correction: ψ scan [ABSCALC in OSCAIL (McArdle & Daly, 1999; North *et al.*, 1968)]	$l = -12\rightarrow12$
$T_{min} = 0.882$, $T_{max} = 0.935$	3 standard reflections
2646 measured reflections	every 120 min
2387 independent reflections	intensity decay: 1%
1805 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	All H-atom parameters refined
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.041P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.016$
2387 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
138 parameters	$\Delta\rho_{min} = -0.28$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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.

Least-squares planes (*x*,*y*,*z* in crystal coordinates) and deviations from them (* indicates atom used to define plane)

− 0.8879 (0.0025) *x* + 6.8684 (0.0030) *y* − 5.7312 (0.0029) *z* = 1.8667 (0.0014)

* 0.0357 (0.0008) S1 * −0.0053 (0.0012) N1 * −0.0173 (0.0012) N2 * 0.0186 (0.0014) N3 * 0.0049 (0.0013) C1 * −0.0149 (0.0013) C2 * 0.0030 (0.0013) C3 * −0.0112 (0.0013) C4 * 0.0111 (0.0015) C5 * 0.0122 (0.0014) C6 * −0.0038 (0.0013) C7 * −0.0169 (0.0012) C8 * −0.0161 (0.0012) C9

Rms deviation of fitted atoms = 0.0156

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 $F^2 > 2\text{sigma}(F^2)$ 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	0.31663 (8)	0.41015 (6)	0.11053 (5)	0.05756 (17)
N2	0.78580 (19)	0.7761 (2)	0.48565 (19)	0.0527 (3)
N1	0.6832 (2)	0.6459 (2)	0.34347 (19)	0.0516 (3)
N3	0.7020 (3)	1.0644 (2)	0.83784 (19)	0.0640 (4)
H2	0.009 (3)	0.557 (3)	0.340 (3)	0.064 (6)*
H5	0.937 (4)	1.042 (3)	0.766 (3)	0.071 (6)*
H6	0.419 (4)	1.059 (4)	0.871 (3)	0.083 (7)*
H7	0.203 (4)	0.833 (4)	0.648 (3)	0.084 (7)*
H1	−0.045 (3)	0.332 (3)	0.077 (2)	0.057 (5)*
C1	0.0860 (3)	0.4135 (2)	0.1556 (2)	0.0521 (4)
C2	0.1168 (2)	0.5381 (2)	0.30372 (18)	0.0440 (3)
C3	0.4669 (2)	0.5808 (2)	0.29745 (17)	0.0400 (3)
C4	0.6725 (2)	0.8437 (2)	0.58315 (18)	0.0421 (3)
C5	0.7900 (3)	0.9894 (3)	0.7357 (2)	0.0584 (4)
C6	0.4846 (3)	1.0005 (3)	0.7961 (2)	0.0576 (4)
C7	0.3532 (3)	0.8628 (2)	0.65419 (18)	0.0449 (3)
C8	0.44728 (19)	0.77948 (18)	0.54209 (15)	0.0349 (3)
C9	0.33770 (19)	0.63693 (18)	0.38810 (15)	0.0342 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0703 (3)	0.0558 (3)	0.0418 (2)	0.0245 (2)	0.01587 (18)	0.00583 (17)
N2	0.0308 (6)	0.0565 (8)	0.0718 (9)	0.0165 (5)	0.0131 (6)	0.0227 (7)

N1	0.0395 (6)	0.0590 (8)	0.0648 (8)	0.0245 (6)	0.0224 (6)	0.0205 (7)
N3	0.0738 (10)	0.0452 (7)	0.0484 (8)	0.0114 (7)	−0.0071 (7)	0.0048 (6)
C1	0.0461 (8)	0.0480 (8)	0.0460 (8)	0.0091 (6)	−0.0026 (6)	0.0096 (6)
C2	0.0311 (6)	0.0470 (7)	0.0487 (8)	0.0118 (5)	0.0057 (5)	0.0139 (6)
C3	0.0390 (6)	0.0418 (7)	0.0426 (7)	0.0178 (5)	0.0136 (5)	0.0139 (5)
C4	0.0314 (6)	0.0393 (7)	0.0492 (7)	0.0090 (5)	0.0024 (5)	0.0151 (6)
C5	0.0450 (8)	0.0463 (8)	0.0611 (10)	0.0050 (7)	−0.0090 (7)	0.0116 (7)
C6	0.0773 (12)	0.0485 (8)	0.0421 (8)	0.0242 (8)	0.0131 (8)	0.0076 (6)
C7	0.0481 (8)	0.0444 (7)	0.0426 (7)	0.0177 (6)	0.0157 (6)	0.0115 (6)
C8	0.0315 (6)	0.0347 (6)	0.0373 (6)	0.0115 (5)	0.0077 (5)	0.0119 (5)
C9	0.0291 (5)	0.0368 (6)	0.0367 (6)	0.0126 (5)	0.0083 (4)	0.0121 (5)

Geometric parameters (Å, °)

S1—C1	1.7058 (19)	C2—H2	0.89 (2)
S1—C3	1.7267 (17)	C3—C9	1.3929 (18)
N2—N1	1.302 (2)	C4—C8	1.4114 (18)
N2—C4	1.375 (2)	C4—C5	1.421 (2)
N1—C3	1.3534 (19)	C5—H5	0.92 (2)
N3—C5	1.293 (3)	C6—C7	1.359 (2)
N3—C6	1.361 (3)	C6—H6	0.97 (2)
C1—C2	1.354 (2)	C7—C8	1.4089 (19)
C1—H1	0.95 (2)	C7—H7	0.97 (3)
C2—C9	1.4205 (18)	C8—C9	1.4136 (18)
C1—S1—C3	90.68 (7)	N3—C5—C4	123.69 (16)
N1—N2—C4	119.47 (12)	N3—C5—H5	115.1 (15)
N2—N1—C3	118.30 (13)	C4—C5—H5	121.2 (15)
C5—N3—C6	117.91 (15)	C7—C6—N3	124.48 (17)
C2—C1—S1	114.11 (12)	C7—C6—H6	117.7 (15)
C2—C1—H1	127.8 (12)	N3—C6—H6	117.8 (15)
S1—C1—H1	118.1 (12)	C6—C7—C8	118.13 (16)
C1—C2—C9	111.69 (14)	C6—C7—H7	112.6 (15)
C1—C2—H2	122.8 (14)	C8—C7—H7	129.3 (15)
C9—C2—H2	125.4 (14)	C7—C8—C4	118.27 (13)
N1—C3—C9	126.65 (14)	C7—C8—C9	126.32 (12)
N1—C3—S1	121.77 (11)	C4—C8—C9	115.40 (12)
C9—C3—S1	111.58 (11)	C3—C9—C8	115.56 (12)
N2—C4—C8	124.60 (13)	C3—C9—C2	111.93 (13)
N2—C4—C5	117.89 (14)	C8—C9—C2	132.50 (12)
C8—C4—C5	117.51 (15)		
C4—N2—N1—C3	−0.5 (2)	C6—C7—C8—C9	−179.09 (14)
C3—S1—C1—C2	0.64 (13)	N2—C4—C8—C7	−179.74 (13)
S1—C1—C2—C9	−0.48 (18)	C5—C4—C8—C7	−0.2 (2)
N2—N1—C3—C9	−0.8 (2)	N2—C4—C8—C9	−0.6 (2)
N2—N1—C3—S1	179.35 (11)	C5—C4—C8—C9	178.96 (13)
C1—S1—C3—N1	179.21 (14)	N1—C3—C9—C8	1.4 (2)
C1—S1—C3—C9	−0.63 (11)	S1—C3—C9—C8	−178.80 (9)
N1—N2—C4—C8	1.2 (2)	N1—C3—C9—C2	−179.35 (14)
N1—N2—C4—C5	−178.37 (15)	S1—C3—C9—C2	0.49 (15)

C6—N3—C5—C4	−0.4 (3)	C7—C8—C9—C3	178.46 (13)
N2—C4—C5—N3	−179.99 (16)	C4—C8—C9—C3	−0.58 (18)
C8—C4—C5—N3	0.4 (3)	C7—C8—C9—C2	−0.6 (2)
C5—N3—C6—C7	0.1 (3)	C4—C8—C9—C2	−179.69 (14)
N3—C6—C7—C8	0.1 (3)	C1—C2—C9—C3	−0.02 (18)
C6—C7—C8—C4	−0.1 (2)	C1—C2—C9—C8	179.12 (14)

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$N3[i]	0.943 (19)	2.441 (18)	3.352 (3)	159.1 (18)
C2—H2$\cdots$N1[ii]	0.89 (2)	2.52 (2)	3.360 (2)	158 (2)

Symmetry codes: (i) $x-1$, $y-1$, $z-1$; (ii) $x-1$, y, z.

Fig. 1