organic compounds

N'-[1-(2-Thienyl)ethylidene]pyridine-2-carbohydrazide

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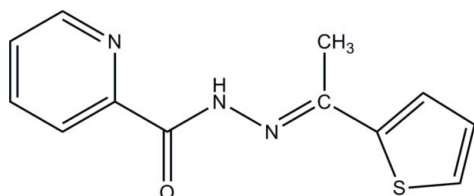Correspondence e-mail: jmdou@lcu.edu.cn

The title compound, $C_{12}H_{11}N_3OS$, was synthesized by the
reaction of 2-pyridinecarbonylhydrazide with 2-acetylthio-
phene in ethanol. In the molecule, the dihedral angle between
the pyridine and thiophene rings is 24.4 (3)°. In the crystal
structure, zigzag chains are formed along the b axis by weak
intermolecular C—H⋯N interactions. These chains are, in
turn, further assembled into a two-dimensional supra-
molecular structure through weak intermolecular C—H⋯O
and N—H⋯O hydrogen bonds.

Related literature

For the crystal structures of metal complexes with related
aroylhydrazone derivatives, see: Matthews *et al.* (1999);
Bernhardt *et al.* (2006). For bond lengths in molecules related
to the title compound, see: Allen *et al.* (1987); Pan & Yang
(2005).

Experimental

Crystal data

$C_{12}H_{11}N_3OS$
$M_r = 245.30$
Monoclinic, $P2_1/c$
$a = 12.162$ (2) Å
$b = 9.8259$ (16) Å
$c = 10.2461$ (17) Å
$\beta = 104.857$ (2)°

$V = 1183.5$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.26$ mm^{-1}
$T = 298$ (2) K
$0.56 \times 0.50 \times 0.22$ mm

Data collection

Siemens SMART CCD
 area-detector diffractometer
Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.868$, $T_{max} = 0.945$

5755 measured reflections
2088 independent reflections
1531 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.154$
$S = 1.01$
2088 reflections
154 parameters

1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7A⋯O1^i	0.96	2.50	3.250 (7)	135
N1—H1⋯O1^i	0.86	2.69	3.337 (6)	133
C11—H11⋯N2^{ii}	0.93	2.60	3.306 (8)	133

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT*
(Siemens, 1996); data reduction: *SAINT*; program(s) used to solve
structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine
structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics:
SHELXTL (Sheldrick, 1997*b*); software used to prepare material for
publication: *SHELXTL*.

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supplementary materials

N'-[1-(2-Thienyl)ethylidene]pyridine-2-carbohydrazide

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Comment

In recent years, much attention has been devoted to multinuclear complex systems with aroylhydrazone ligands due to their interesting structural and magnetic properties (Matthews *et al.*, 1999; Bernhardt *et al.* 2006). Investigation of the crystal structures of aroylhydrazone ligands may provide useful information concerning their coordination potential. In the present study, we report the synthesis and structure of the title compound.

The molecular structure of the title compound is shown in Fig. 1. The X-ray single-crystal analysis reveals that the compound is non-planar and the dihedral angle between the two aromatic rings is 24.4 (3)°. The molecule displays a *trans* configuration with respect to the C—N double bond. All bond lengths show normal values (Allen *et al.*, 1987; Pan *et al.*, 2005). The C8—N2 bond length of 1.285 (7)Å conforms to the value for a double bond. Bond lengths C1—O1 and C1—N2 are 1.215 (6)Å and 1.335 (7) Å, respectively, indicating that the molecule exists in the keto form.

Atoms C11 of the thiophene group in one molecule and atoms N2 of the hydrazide group in adjacent molecule act as acceptor and donor to form the C—H⋯N weak interactions (Table 2). The occurrence of C—H⋯N weak interactions results in the formation of infinite zigzag chains along [010]. The chains are further assembled into a two-dimensional supramolecular structure through intermolecular C—H⋯O weak interactions and N—H⋯O hydrogen bonds (Fig. 2).

Experimental

Pyridine-2-carboxylic acid hydrazide (1.37 g, 10 mmol) was dissolved in anhydrous ethanol (30 ml), and 2-acetylthiophene (1.26 g, 10 mmol) was added. The reaction mixture was refluxed for 6 h to give a clear yellow solution. Light-yellow crystals suitable for X-ray diffraction were obtained at the bottom of the vessel after standing at room temperature in air for 8 d (yield 83%, m.p. 443–444 K). Analysis calculated for $C_{12}H_{11}N_3O_S$: C 58.76, H 4.52, N 17.13%; found: C 58.74, H 4.58, N 17.10%.

Refinement

All H atoms were placed geometrically and treated as riding on their parent atoms with C—H 0.96 Å (methyl) [$U_{iso}(H) = 1.5U_{eq}(C)$] and N—H 0.86 C—H 0.93 Å [$U_{iso}(H) = 1.2U_{eq}(C, N)$].
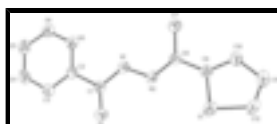
Figures

Fig. 1. The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.
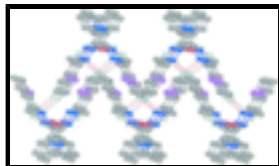
Fig. 2. The packing of the title compound. Hydrogen bonds are shown as dashed lines.

N'-[1-(2-Thienyl)ethylidene]pyridine-2-carbohydrazide

Crystal data

$C_{12}H_{11}N_3OS$	$F_{000} = 512$
$M_r = 245.30$	$D_x = 1.377$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2156 reflections
$a = 12.162$ (2) Å	$\theta = 2.7–26.2°$
$b = 9.8259$ (16) Å	$\mu = 0.26$ mm^{-1}
$c = 10.2461$ (17) Å	$T = 298$ (2) K
$\beta = 104.857$ (2)°	Block, light-yellow
$V = 1183.5$ (4) Å^3	$0.56 \times 0.50 \times 0.22$ mm
$Z = 4$	

Data collection

Siemens SMART CCD area-detector diffractometer	2088 independent reflections
Radiation source: fine-focus sealed tube	1531 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.025$
$T = 298(2)$ K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -13 \rightarrow 14$
$T_{min} = 0.868$, $T_{max} = 0.945$	$k = -11 \rightarrow 6$
5755 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.154$	$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2 + 0.601P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2088 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
1 restraint	Extinction correction: none

Primary atom site location: structure-invariant direct
methods

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
N1	0.1445 (4)	0.8579 (5)	0.0924 (5)	0.0484 (12)
H1	0.1133	0.8729	0.0084	0.058*
N2	0.2426 (4)	0.9265 (4)	0.1575 (4)	0.0447 (11)
N3	−0.0534 (4)	0.7579 (5)	−0.0438 (4)	0.0482 (12)
O1	0.1393 (3)	0.7400 (4)	0.2790 (4)	0.0579 (12)
S1	0.43434 (14)	1.0654 (2)	0.33637 (15)	0.0677 (7)
C1	0.0987 (4)	0.7684 (6)	0.1611 (5)	0.0431 (13)
C2	−0.0087 (4)	0.7049 (5)	0.0788 (5)	0.0416 (12)
C3	−0.0575 (5)	0.5980 (6)	0.1313 (6)	0.0512 (15)
H3	−0.0241	0.5642	0.2171	0.061*
C4	−0.1572 (5)	0.5424 (7)	0.0530 (6)	0.0585 (16)
H4	−0.1922	0.4701	0.0850	0.070*
C5	−0.2034 (5)	0.5957 (7)	−0.0723 (6)	0.0595 (17)
H5	−0.2705	0.5604	−0.1269	0.071*
C6	−0.1494 (5)	0.7020 (7)	−0.1162 (6)	0.0568 (16)
H6	−0.1817	0.7372	−0.2017	0.068*
C7	0.2513 (5)	1.0330 (7)	−0.0622 (6)	0.0583 (16)
H7A	0.1828	0.9830	−0.1004	0.087*
H7B	0.3093	1.0058	−0.1051	0.087*
H7C	0.2368	1.1286	−0.0761	0.087*
C8	0.2906 (4)	1.0040 (5)	0.0875 (5)	0.0414 (12)
C9	0.3943 (4)	1.0717 (5)	0.1632 (5)	0.0426 (13)
C10	0.4717 (5)	1.1431 (7)	0.1159 (6)	0.0607 (17)
H10	0.4650	1.1585	0.0247	0.073*
C11	0.5637 (5)	1.1916 (7)	0.2204 (7)	0.0663 (18)
H11	0.6242	1.2413	0.2049	0.080*
C12	0.5543 (5)	1.1585 (7)	0.3430 (7)	0.0596 (17)
H12	0.6068	1.1831	0.4227	0.071*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.040 (2)	0.055 (3)	0.044 (2)	−0.009 (2)	−0.0010 (19)	0.006 (2)
N2	0.035 (2)	0.048 (3)	0.046 (3)	−0.004 (2)	0.0006 (19)	0.003 (2)
N3	0.041 (3)	0.054 (3)	0.047 (3)	−0.004 (2)	0.007 (2)	0.000 (2)
O1	0.052 (2)	0.070 (3)	0.046 (2)	−0.008 (2)	0.0029 (18)	0.010 (2)
S1	0.0572 (11)	0.0936 (14)	0.0457 (10)	−0.0204 (9)	0.0013 (7)	−0.0024 (8)
C1	0.037 (3)	0.045 (3)	0.046 (3)	0.003 (2)	0.008 (2)	0.001 (2)
C2	0.039 (3)	0.042 (3)	0.045 (3)	0.002 (2)	0.012 (2)	−0.002 (2)
C3	0.048 (3)	0.057 (4)	0.049 (3)	−0.003 (3)	0.013 (3)	0.003 (3)
C4	0.054 (4)	0.062 (4)	0.062 (4)	−0.016 (3)	0.021 (3)	−0.002 (3)
C5	0.048 (3)	0.073 (4)	0.056 (4)	−0.018 (3)	0.011 (3)	−0.013 (3)
C6	0.050 (3)	0.068 (4)	0.048 (3)	−0.004 (3)	0.004 (3)	−0.002 (3)
C7	0.061 (4)	0.064 (4)	0.044 (3)	−0.010 (3)	0.003 (3)	−0.001 (3)
C8	0.040 (3)	0.040 (3)	0.041 (3)	0.002 (2)	0.005 (2)	0.001 (2)
C9	0.041 (3)	0.038 (3)	0.046 (3)	0.001 (2)	0.006 (2)	0.001 (2)
C10	0.060 (4)	0.063 (4)	0.057 (4)	−0.018 (3)	0.012 (3)	0.002 (3)
C11	0.054 (4)	0.062 (4)	0.081 (5)	−0.019 (3)	0.014 (3)	−0.010 (4)
C12	0.043 (3)	0.066 (4)	0.062 (4)	−0.007 (3)	−0.001 (3)	−0.015 (3)

Geometric parameters (Å, °)

N1—C1	1.335 (7)	C5—C6	1.370 (9)
N1—N2	1.384 (6)	C5—H5	0.9300
N1—H1	0.8600	C6—H6	0.9300
N2—C8	1.285 (7)	C7—C8	1.512 (7)
N3—C6	1.331 (7)	C7—H7A	0.9600
N3—C2	1.339 (7)	C7—H7B	0.9600
O1—C1	1.215 (6)	C7—H7C	0.9600
S1—C12	1.709 (6)	C8—C9	1.460 (7)
S1—C9	1.716 (6)	C9—C10	1.359 (8)
C1—C2	1.497 (7)	C10—C11	1.419 (9)
C2—C3	1.382 (8)	C10—H10	0.9300
C3—C4	1.384 (8)	C11—C12	1.330 (9)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.367 (9)	C12—H12	0.9300
C4—H4	0.9300		
C1—N1—N2	119.5 (4)	C5—C6—H6	118.1
C1—N1—H1	120.2	C8—C7—H7A	109.5
N2—N1—H1	120.2	C8—C7—H7B	109.5
C8—N2—N1	118.6 (4)	H7A—C7—H7B	109.5
C6—N3—C2	116.7 (5)	C8—C7—H7C	109.5
C12—S1—C9	92.0 (3)	H7A—C7—H7C	109.5
O1—C1—N1	123.9 (5)	H7B—C7—H7C	109.5
O1—C1—C2	122.6 (5)	N2—C8—C9	115.3 (5)
N1—C1—C2	113.6 (5)	N2—C8—C7	127.4 (5)

N3—C2—C3	123.3 (5)	C9—C8—C7	117.4 (5)
N3—C2—C1	116.9 (5)	C10—C9—C8	128.9 (5)
C3—C2—C1	119.8 (5)	C10—C9—S1	110.4 (4)
C2—C3—C4	118.3 (6)	C8—C9—S1	120.7 (4)
C2—C3—H3	120.8	C9—C10—C11	112.9 (6)
C4—C3—H3	120.8	C9—C10—H10	123.5
C5—C4—C3	118.8 (6)	C11—C10—H10	123.5
C5—C4—H4	120.6	C12—C11—C10	112.8 (6)
C3—C4—H4	120.6	C12—C11—H11	123.6
C4—C5—C6	119.0 (6)	C10—C11—H11	123.6
C4—C5—H5	120.5	C11—C12—S1	111.9 (5)
C6—C5—H5	120.5	C11—C12—H12	124.1
N3—C6—C5	123.9 (6)	S1—C12—H12	124.1
N3—C6—H6	118.1		

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C7—H7A$\cdots$O1[i]	0.96	2.50	3.250 (7)	135
N1—H1$\cdots$O1[i]	0.86	2.69	3.337 (6)	133
C11—H11$\cdots$N2[ii]	0.93	2.60	3.306 (8)	133

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

Fig. 1

Fig. 2