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N′-[(*E*)-(4-Bromo-2-thienyl)methylene]-isonicotinohydrazide

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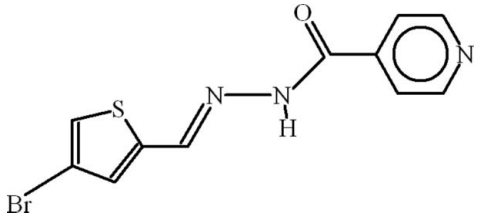
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.044; wR factor = 0.113; data-to-parameter ratio = 18.0.

In title compound, $C_{11}H_8BrN_3OS$, the dihedral angle between the two aromatic rings is 27.61 (14)° and the Br atom is disordered over two sites with an occupancy ratio of 0.804 (2):0.196 (2). In the crystal, the molecules are linked by N—H···O, C—H···O and C—H···N interactions, resulting in chains.

Related literature

For related structures, see: Jing *et al.* (2007); Shafiq *et al.* (2009); Wang *et al.* (2007). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{11}H_8BrN_3OS$
M_r = 310.17
Orthorhombic, *Fdd*2
a = 14.3507 (6) Å
b = 48.732 (2) Å
c = 7.2115 (3) Å
V = 5043.3 (4) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 3.41 mm^{-1}
T = 296 K
0.26 × 0.14 × 0.12 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.567, T_{max} = 0.666
12209 measured reflections
2837 independent reflections
1954 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 1.04
2837 reflections
158 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Absolute structure: Flack (1983), 1205 Friedal Pairs
Flack parameter: −0.002 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.86	2.08	2.920 (4)	165
C7—H7···O1^{i}	0.93	2.52	3.318 (5)	144
C11—H11···N1^{ii}	0.93	2.60	3.277 (7)	130

Symmetry codes: (i) $x-\frac{1}{4}, -y+\frac{1}{4}, z-\frac{1}{4}$; (ii) $x+\frac{3}{4}, -y+\frac{1}{4}, z-\frac{1}{4}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5101).

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supporting information

Acta Cryst. (2009). E**65**, o2496 [doi:10.1107/S160053680903709X]

N′-[(*E*)-(4-Bromo-2-thienyl)methylene]isonicotinohydrazide

Zahid Shafiq, Muhammad Yaqub, M. Nawaz Tahir, Abid Hussain and M. Saeed Iqbal

S1. Comment

In continuation of synthesizing various derivatives of 4-bromothiophene-2-carbaldehyde (Shafiq *et al.*, 2009), the title compound (I, Fig. 1), has been prepared. The metal complexes of (I) have been prepared and the biological studies of all the compounds are in progress.

The crystal structure of (II) *N*′-((thiophen-3-yl)methylene)isonicotinohydrazide (Jing *et al.*, 2007) and (III) (*E*)-*N*′-((5-methylthiophen-2-yl)methylene)isonicotinohydrazide (Wang *et al.*, 2007) have been published. The title compound (I) differs from both due to substitution moiety of bromo.

We have recently reported the crystal structure of (IV) *N*′-[(*E*)-(4-bromothiophen-2-yl)methylidene]benzohydrazide (Shafiq *et al.*, 2009). Due to change of benzene ring (IV) with the pyridine (I) ring, the crystal structure has been substantially changed. The title compound crystalizes with single molecule, whereas in (IV) there are two molecules along with fractional quantity of water. In (I), the dihedral angle between two aromatic rings A (C1—C3/N1/C4/C5) and B (C8—C11/S1) is 27.61 (14)°. The molecules of present compound are stabilized in the form of polymeric chains extending along the diagonal of crystallographic *ac*-plane. The list of strong H-bondings is given in Table 1. Due to the heterocyclic rings, the Br-Atom is disordered over two sites with occupancy ratio of 0.804:0.196. There exist $R_2^1(6)$ ring motif (Bernstein *et al.*, 1995) due to intermolecular H-bonding of type C—H···O and N—H···O (Fig. 2).

S2. Experimental

To a hot stirred solution of isoniazid (1.37 g, 0.01 mol) in ethanol (15 ml) was added 4-bromothiophene-2-carbaldehyde (1.91 g, 0.01 mol). The resultant mixture was then heated under reflux. After an hour precipitates were formed. The reaction mixture was further heated about 30 min for the completion of the reaction which was monitored through TLC. Then it was allowed to cool to room temperature, filtered and washed with hot ethanol. The crude material was recrystallized in (1:3 *v*/*v*) 1,4-dioxan:ethanol, to afford light yellow needles of (I).

S3. Refinement

A large Fourier difference peak close to the Br-atom and higher values of its thermal parameters indicated the presence of disorder. The two parts of Br-atom were refined with equal ainisotropic displacement parameters (EADP). All other efforts like *DFIX* were utilized but the C10—Br1B bond could not be shortened.

The H-atoms were positioned geometrically with N—H = 0.86, C—H = 0.93 Å for aromatic like H atoms and constrained to ride on their parent atoms, with U_{iso}(H) = xUeq(C, N), where x = 1.2 for all H atoms.

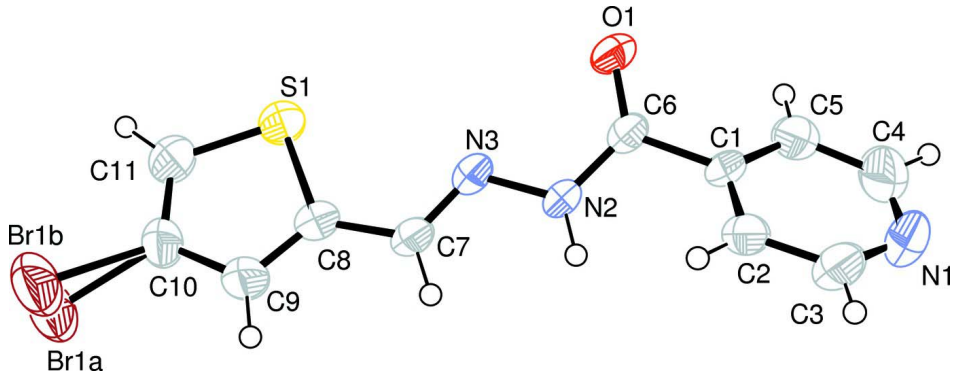

Figure 1

View of (I) with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radius.

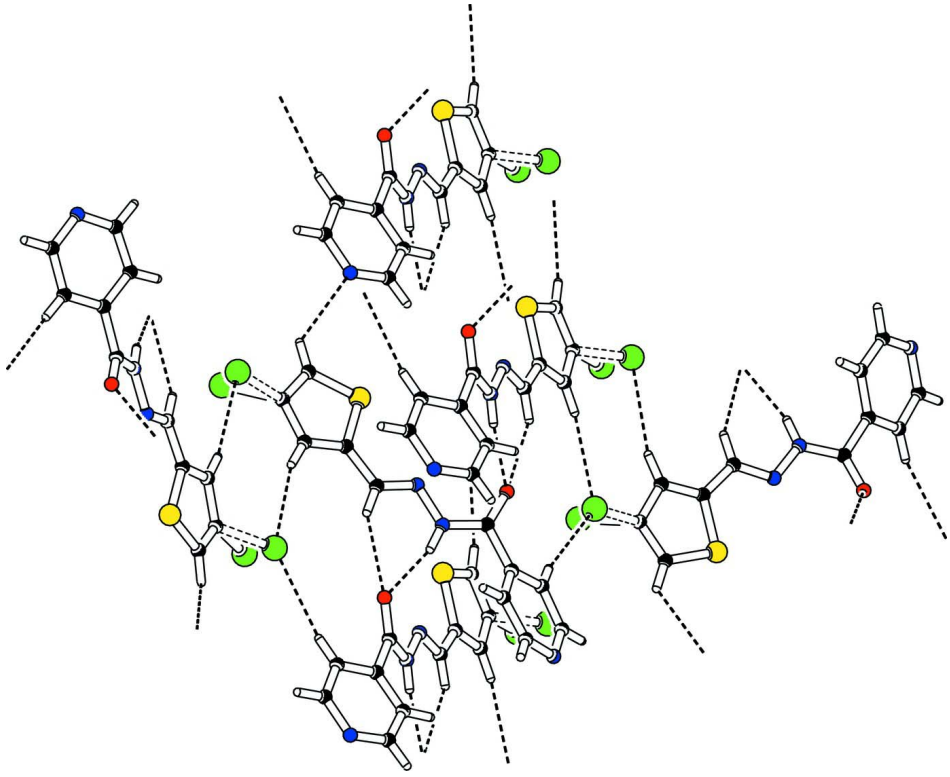

Figure 2

The partial packing of (I) which shows that molecules form polymeric chains with ring motifs due to H-bondings.

N′-[(*E*)-(4-Bromo-2-thienyl)methylene]isonicotinohydrazide

Crystal data

$C_{11}H_8BrN_3OS$
$M_r = 310.17$
Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d
$a = 14.3507\ (6)$ Å
$b = 48.732\ (2)$ Å
$c = 7.2115\ (3)$ Å
$V = 5043.3\ (4)$ Å^3
$Z = 16$
$F(000) = 2464$
$D_x = 1.634$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2837 reflections
θ = 3.0–27.9°
μ = 3.41 mm^{-1}
T = 296 K
Cut needle, light yellow
0.26 × 0.14 × 0.12 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.50 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.567, T_{max} = 0.666
12209 measured reflections
2837 independent reflections
1954 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.9°, θ_{min} = 3.0°
h = −18→18
k = −64→63
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.113
S = 1.04
2837 reflections
158 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 9.3783P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Absolute structure: Flack (1983), 1205 Friedal Pairs
Absolute structure parameter: −0.002 (13)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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}	Occ. (<1)
Br1A	0.42406 (6)	0.25903 (2)	−0.16312 (17)	0.0946 (5)	0.804 (2)
Br1B	0.4270 (3)	0.26462 (9)	−0.0262 (10)	0.0946 (5)	0.196 (2)
S1	0.44553 (8)	0.17467 (2)	0.0252 (2)	0.0549 (4)	
O1	0.27773 (19)	0.09307 (6)	0.2899 (5)	0.0505 (10)	
N1	−0.0545 (3)	0.06098 (14)	0.3270 (10)	0.099 (3)	
N2	0.1935 (2)	0.12740 (7)	0.1634 (5)	0.0406 (11)	
N3	0.2717 (2)	0.14261 (7)	0.1259 (5)	0.0424 (11)	
C1	0.1129 (3)	0.08803 (8)	0.2787 (6)	0.0418 (14)	
C2	0.0333 (3)	0.10184 (10)	0.3343 (7)	0.0527 (16)	
C3	−0.0467 (3)	0.08712 (15)	0.3572 (10)	0.080 (3)	
C4	0.0234 (5)	0.04764 (13)	0.2750 (10)	0.092 (3)	
C5	0.1084 (4)	0.06041 (10)	0.2517 (8)	0.0620 (19)	

C6	0.2039 (3)	0.10290 (8)	0.2448 (6)	0.0382 (14)
C7	0.2561 (3)	0.16678 (9)	0.0670 (7)	0.0460 (16)
C8	0.3315 (3)	0.18499 (9)	0.0213 (7)	0.0470 (14)
C9	0.3246 (3)	0.21142 (11)	−0.0287 (9)	0.068 (2)
C10	0.4113 (3)	0.22347 (9)	−0.0687 (9)	0.0643 (19)
C11	0.4832 (3)	0.20625 (11)	−0.0432 (9)	0.0653 (18)
H2	0.13903	0.13346	0.13520	0.0485*
H2A	0.03442	0.12066	0.35548	0.0632*
H3	−0.09935	0.09650	0.39733	0.0962*
H4	0.01970	0.02885	0.25376	0.1106*
H5	0.16110	0.05044	0.21847	0.0746*
H7	0.19500	0.17278	0.05327	0.0554*
H9	0.26831	0.22080	−0.03612	0.0813*
H11	0.54538	0.21094	−0.06045	0.0783*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1A	0.0709 (4)	0.0603 (5)	0.1526 (14)	−0.0081 (3)	0.0142 (7)	0.0410 (7)
Br1B	0.0709 (4)	0.0603 (5)	0.1526 (14)	−0.0081 (3)	0.0142 (7)	0.0410 (7)
S1	0.0358 (5)	0.0516 (7)	0.0773 (9)	0.0035 (5)	−0.0020 (6)	0.0081 (6)
O1	0.0291 (14)	0.0495 (17)	0.073 (2)	0.0004 (12)	−0.0118 (16)	0.0034 (17)
N1	0.056 (3)	0.111 (5)	0.130 (5)	−0.041 (3)	−0.031 (3)	0.053 (4)
N2	0.0250 (16)	0.0437 (19)	0.053 (2)	−0.0055 (14)	−0.0080 (15)	0.0056 (16)
N3	0.0281 (16)	0.049 (2)	0.050 (2)	−0.0061 (15)	−0.0043 (15)	0.0029 (16)
C1	0.0315 (19)	0.048 (2)	0.046 (3)	−0.0076 (17)	−0.0167 (19)	0.007 (2)
C2	0.037 (2)	0.062 (3)	0.059 (3)	0.0025 (19)	−0.002 (2)	0.022 (2)
C3	0.039 (3)	0.108 (5)	0.094 (5)	−0.011 (3)	−0.012 (3)	0.042 (4)
C4	0.091 (5)	0.068 (4)	0.118 (6)	−0.032 (3)	−0.041 (4)	0.030 (4)
C5	0.062 (3)	0.046 (3)	0.078 (4)	−0.007 (2)	−0.026 (3)	0.012 (3)
C6	0.0276 (19)	0.043 (2)	0.044 (3)	−0.0029 (16)	−0.0040 (17)	−0.0027 (19)
C7	0.029 (2)	0.056 (3)	0.053 (3)	−0.0051 (18)	−0.0089 (19)	0.011 (2)
C8	0.034 (2)	0.049 (2)	0.058 (3)	0.0006 (17)	−0.008 (2)	0.006 (2)
C9	0.039 (2)	0.057 (3)	0.107 (5)	0.002 (2)	−0.008 (3)	0.026 (3)
C10	0.045 (3)	0.046 (3)	0.102 (4)	−0.007 (2)	−0.001 (3)	0.017 (3)
C11	0.035 (2)	0.063 (3)	0.098 (4)	−0.003 (2)	0.000 (3)	0.015 (3)

Geometric parameters (Å, º)

Br1A—C10	1.871 (5)	C2—C3	1.364 (7)
Br1B—C10	2.041 (6)	C4—C5	1.380 (9)
S1—C8	1.712 (4)	C7—C8	1.438 (6)
S1—C11	1.704 (5)	C8—C9	1.341 (7)
O1—C6	1.207 (5)	C9—C10	1.406 (6)
N1—C3	1.297 (10)	C10—C11	1.343 (6)
N1—C4	1.347 (9)	C2—H2A	0.9300
N2—N3	1.372 (4)	C3—H3	0.9300
N2—C6	1.339 (5)	C4—H4	0.9300

N3—C7	1.272 (6)	C5—H5	0.9300
N2—H2	0.8600	C7—H7	0.9300
C1—C2	1.385 (6)	C9—H9	0.9300
C1—C5	1.362 (6)	C11—H11	0.9300
C1—C6	1.513 (6)		

C8—S1—C11	91.9 (2)	Br1A—C10—C11	123.6 (4)
C3—N1—C4	116.7 (5)	Br1B—C10—C9	118.5 (4)
N3—N2—C6	118.5 (3)	C9—C10—C11	113.0 (4)
N2—N3—C7	115.0 (3)	Br1B—C10—C11	120.6 (4)
C6—N2—H2	121.00	Br1A—C10—C9	123.3 (4)
N3—N2—H2	121.00	S1—C11—C10	111.1 (3)
C2—C1—C6	121.7 (4)	C1—C2—H2A	121.00
C5—C1—C6	119.4 (4)	C3—C2—H2A	121.00
C2—C1—C5	118.9 (4)	N1—C3—H3	118.00
C1—C2—C3	118.3 (5)	C2—C3—H3	118.00
N1—C3—C2	124.7 (5)	N1—C4—H4	118.00
N1—C4—C5	123.4 (6)	C5—C4—H4	118.00
C1—C5—C4	118.1 (5)	C1—C5—H5	121.00
N2—C6—C1	113.7 (3)	C4—C5—H5	121.00
O1—C6—C1	121.6 (4)	N3—C7—H7	120.00
O1—C6—N2	124.7 (4)	C8—C7—H7	119.00
N3—C7—C8	121.0 (4)	C8—C9—H9	123.00
C7—C8—C9	126.8 (4)	C10—C9—H9	123.00
S1—C8—C7	122.3 (3)	S1—C11—H11	124.00
S1—C8—C9	110.9 (3)	C10—C11—H11	124.00
C8—C9—C10	113.0 (4)		

C11—S1—C8—C7	179.5 (5)	C2—C1—C6—N2	−38.5 (6)
C11—S1—C8—C9	−0.5 (5)	C5—C1—C6—O1	−39.9 (7)
C8—S1—C11—C10	−0.5 (5)	C5—C1—C6—N2	140.6 (5)
C4—N1—C3—C2	2.2 (11)	C1—C2—C3—N1	−1.5 (10)
C3—N1—C4—C5	−0.6 (11)	N1—C4—C5—C1	−1.6 (10)
C6—N2—N3—C7	−172.8 (4)	N3—C7—C8—S1	5.3 (7)
N3—N2—C6—O1	0.6 (6)	N3—C7—C8—C9	−174.7 (5)
N3—N2—C6—C1	−179.9 (3)	S1—C8—C9—C10	1.4 (7)
N2—N3—C7—C8	−179.7 (4)	C7—C8—C9—C10	−178.6 (5)
C5—C1—C2—C3	−0.9 (8)	C8—C9—C10—Br1A	174.2 (4)
C6—C1—C2—C3	178.3 (5)	C8—C9—C10—C11	−1.9 (8)
C2—C1—C5—C4	2.2 (8)	Br1A—C10—C11—S1	−174.6 (3)
C6—C1—C5—C4	−176.9 (5)	C9—C10—C11—S1	1.4 (7)
C2—C1—C6—O1	141.0 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.86	2.08	2.920 (4)	165

C7—H7···O1[i]	0.93	2.52	3.318 (5)	144
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