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N-[(E)-Thiophen-2-ylmethylidene]-1,3-benzothiazol-2-amine

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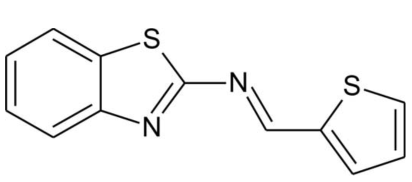
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.033; wR factor = 0.085; data-to-parameter ratio = 53.6.

In the title thiophene-derived Schiff base compound, $C_{12}H_8N_2S_2$, the thiophene ring is slighty rotated from the benzothiazole group mean plane, giving a dihedral angle of 12.87 (6)°. The largest displacement of an atom in the molecule from the nine-atom mean plane defined by the non-H atoms of the benzothiazole ring system is 0.572 (1) Å, exhibited by the C atom at the 3-position of the thiophene ring. In the crystal, weak C—H···S hydrogen bonds involving the thiophene group S atom and the 4-position thiophene C—H group of a symmetry-related molecule lead to an infinite one-dimensional chain colinear with the c axis. The structure is further stabilized by π–π interactions; the distance between the thiazole ring centroid and the centroid of an adjacent benzene ring is 3.686 (1) Å. The crystal studied was an inversion twin with the ratio of components 0.73 (3):0.27 (3).

Related literature

For the synthesis and crystal structure of 2-aminobenzothiazole, see: Ding *et al.* (2009). For crystal structures containing 2-aminobenzothiazole derivatives, see: Garcia-Hernandez *et al.* (2006). For inhibitory properties against human cancer cell lines and general antitumor properties of benzothiazole derivatives, see: Racane *et al.* (2001); O'Brien *et al.* (2003). For antibacterial, antifungal, antitumor and antiviral activites of benzthiazoles, see: Yadav & Malipatil (2011); Singh & Seghal (1988); Pattan *et al.* (2005).



Experimental

Crystal data

$C_{12}H_8N_2S_2$
M_r = 244.32
Monoclinic, Pc
a = 10.7244 (5) Å
b = 4.6021 (2) Å
c = 11.1280 (5) Å
β = 100.367 (2)°
V = 540.25 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 100 K
0.45 × 0.20 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.625, T_{max} = 0.749
14476 measured reflections
7768 independent reflections
7126 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 1.04
7768 reflections
145 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Absolute structure: Flack (1983), 2974 Friedel pairs
Flack parameter: 0.27 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···S2^{i}	0.95	2.92	3.517 (1)	122 (1)

Symmetry code: (i) $x, -y-1, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5495).

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supplementary materials

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N-[(*E*)-Thiophen-2-ylmethylidene]-1,3-benzothiazol-2-amine

Irvin N. Booysen, Muhammed B. Ismail and Matthew P. Akerman

Comment

Benzothiazoles are naturally occurring molecules which consist of a 5-membered 1,3-thiazole ring fused to a benzene ring. Their derivatives are abundantly distributed in nature and have been shown to have very interesting pharmacological activity, particularly antibacterial, antifungal, antitumor and antiviral properties (Yadav & Malipatil, 2011; Singh & Seghal, 1988; Pattan *et al.*, 2005). The heterocyclic scaffold is readily substituted at the 2-position of the thiazole ring, allowing for derivatization.

The thiophene ring of the title compound (I) is not in the same plane as the 1,3-benzothiazole moiety, with a dihedral angle of 13.6 (1)° relative to the benzthiazole ring. This out-of-plane rotation of the thiophene results in the carbon atom in the 3-position of the thiophene ring (C10) sitting 0.572 (1) Å from the 9-atom mean plane defined by all non-hydrogen atoms of the benzthiazole ring system. The C8—N2 bond distance of 1.290 (1) Å and the C7—N2—C8 bond angle of 118.12 (7)° emphasize the sp^2 hybridization of the imino nitrogen atom (refer to Figure 1 for the atom numbering scheme). An *(E)*-configuration about the imine bond is observed for this Schiff base moiety.

The structure exhibits both hydrogen bonding and $\pi\cdots\pi$ interactions. The distance between the centroid of the benzene ring and the centroid of the thiazole ring of an adjacent molecule is 3.686 (1) Å. In addition to the $\pi\cdots\pi$ interactions there are non-classical hydrogen bonds between the thiophene sulfur atom, S2, and the thiophene hydrogen atom H11 of an adjacent molecule. This hydrogen bond links the molecules into infinite, one-dimensional hydrogen-bonded chains, which are co-linear with the *c*-axis. The adjacent, hydrogen-bonded molecules are not both in the same plane, the 24-atom mean planes of two adjacent molecules make an angle of 75.9 (1)° to each other. Although the hydrogen bonds are not likely very strong as they are only marginally shorter than the sum of the van der Waals radii (0.066 Å), these intermolecular interactions can stabilize the lattice.

Experimental

A mixture of 2-aminobenzothiazole (1.27 g; 8.45 mmol) and thiophene-2-carbaldehyde (0.92 ml; 10.2 mmol) in methanol (50 ml) was heated to reflux for 24 h. The resulting orange solution was allowed to cool to room temperature and concentrated by rotary evaporation under reduced pressure. Dry toluene (45 ml) was added to the solution and heated to reflux with a Dean and Stark apparatus for an additional 24 h. Upon cooling the title compound was isolated as brown, needle-shaped crystals.

Refinement

The positions of all C-bonded hydrogen atoms were calculated using the standard riding model of *SHELXL97* (Sheldrick, 2008) with C—H(aromatic) distances of 0.93 Å and $U_{iso} = 1.2U_{eq}(C)$.

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

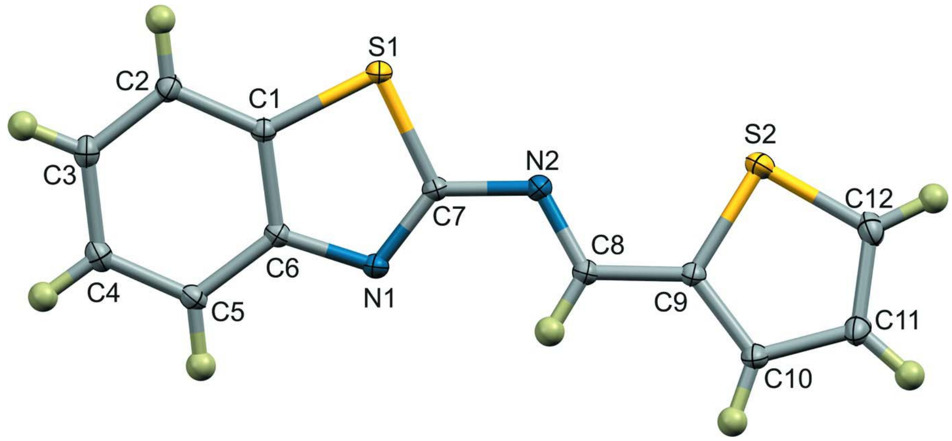

Figure 1

A thermal ellipsoid plot of (I). Ellipsoids are rendered at the 50% probability level.

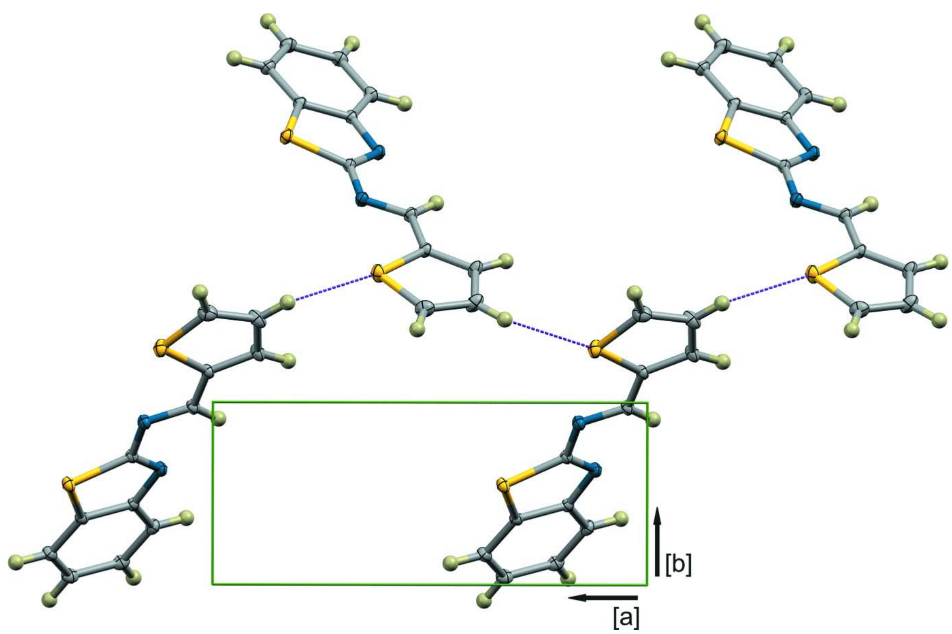

Figure 2

The one-dimensional, hydrogen-bonded chains of (I). Viewed along the *a*-axis. Hydrogen bonds are shown as dotted lines.

N-[(E)-Thiophen-2-ylmethylidene]-1,3-benzothiazol-2-amine

Crystal data

$C_{12}H_8N_2S_2$
M_r = 244.32
Monoclinic, *Pc*
Hall symbol: P -2yc
a = 10.7244 (5) Å
b = 4.6021 (2) Å
c = 11.1280 (5) Å
β = 100.367 (2)°
V = 540.25 (4) Å^3
Z = 2
F(000) = 252
D_x = 1.502 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 7126 reflections
θ = 1.9–46.7°
μ = 0.46 mm^{-1}
T = 100 K
Neelde, yellow
0.45 × 0.20 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
T_{min} = 0.625, T_{max} = 0.749
14476 measured reflections
7768 independent reflections
7126 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 46.7°, θ_{min} = 2.0°
$h = -21\rightarrow21$
$k = -9\rightarrow9$
$l = -21\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.085
S = 1.04
7768 reflections
145 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
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 0.0113P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}
Absolute structure: Flack (1983), 2974 Friedel pairs
Flack parameter: 0.27 (3)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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	0.784499 (18)	0.45575 (5)	0.332022 (16)	0.01350 (4)
S2	0.443816 (19)	−0.29395 (6)	0.120085 (18)	0.01726 (4)
N1	0.84951 (6)	0.36879 (17)	0.11966 (6)	0.01280 (9)

N2	0.66346 (7)	0.11200 (17)	0.15758 (6)	0.01375 (10)
C4	1.11614 (8)	0.8815 (2)	0.21064 (8)	0.01636 (12)
H4	1.1852	0.9670	0.1808	0.020*
C5	1.03822 (8)	0.68618 (19)	0.13798 (7)	0.01428 (11)
H5	1.0537	0.6364	0.0591	0.017*
C6	0.93578 (7)	0.56279 (17)	0.18281 (7)	0.01178 (10)
C7	0.76580 (7)	0.29951 (17)	0.18671 (7)	0.01226 (10)
C8	0.63195 (8)	0.02760 (18)	0.04564 (7)	0.01376 (11)
H8	0.6783	0.0935	−0.0142	0.017*
C9	0.52640 (7)	−0.16652 (18)	0.01185 (7)	0.01283 (10)
C10	0.47648 (8)	−0.2709 (2)	−0.10331 (8)	0.01632 (12)
H10	0.5091	−0.2242	−0.1749	0.020*
C11	0.37091 (9)	−0.4557 (2)	−0.10202 (9)	0.01923 (14)
H11	0.3248	−0.5476	−0.1727	0.023*
C3	1.09458 (8)	0.9554 (2)	0.32807 (9)	0.01656 (12)
H3	1.1494	1.0901	0.3761	0.020*
C2	0.99466 (8)	0.83477 (19)	0.37474 (7)	0.01491 (11)
H2	0.9803	0.8841	0.4540	0.018*
C1	0.91594 (7)	0.63843 (17)	0.30119 (7)	0.01210 (10)
C12	0.34282 (9)	−0.4870 (2)	0.01255 (10)	0.01891 (14)
H12	0.2750	−0.6026	0.0303	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01409 (7)	0.01617 (8)	0.01111 (6)	−0.00243 (6)	0.00462 (5)	−0.00251 (6)
S2	0.01686 (8)	0.02164 (9)	0.01432 (7)	−0.00281 (7)	0.00559 (6)	0.00148 (6)
N1	0.0128 (2)	0.0148 (2)	0.0111 (2)	−0.00094 (18)	0.00313 (16)	−0.00076 (18)
N2	0.0137 (2)	0.0151 (3)	0.0127 (2)	−0.00233 (19)	0.00298 (17)	−0.00149 (18)
C4	0.0137 (3)	0.0163 (3)	0.0195 (3)	−0.0015 (2)	0.0040 (2)	0.0025 (2)
C5	0.0129 (2)	0.0164 (3)	0.0143 (2)	−0.0002 (2)	0.0044 (2)	0.0016 (2)
C6	0.0117 (2)	0.0121 (3)	0.0117 (2)	0.00034 (18)	0.00274 (18)	0.00046 (18)
C7	0.0132 (2)	0.0131 (3)	0.0107 (2)	−0.0009 (2)	0.00263 (18)	−0.00112 (19)
C8	0.0142 (3)	0.0150 (3)	0.0125 (2)	−0.0025 (2)	0.0037 (2)	−0.0016 (2)
C9	0.0126 (2)	0.0142 (3)	0.0122 (2)	−0.0008 (2)	0.00370 (19)	−0.00131 (19)
C10	0.0152 (3)	0.0208 (3)	0.0138 (3)	−0.0033 (2)	0.0047 (2)	−0.0044 (2)
C11	0.0140 (3)	0.0229 (4)	0.0211 (3)	−0.0032 (3)	0.0041 (2)	−0.0073 (3)
C3	0.0140 (3)	0.0156 (3)	0.0195 (3)	−0.0028 (2)	0.0012 (2)	−0.0005 (2)
C2	0.0147 (3)	0.0147 (3)	0.0151 (3)	−0.0013 (2)	0.0020 (2)	−0.0022 (2)
C1	0.0119 (2)	0.0123 (3)	0.0122 (2)	−0.00014 (19)	0.00249 (18)	−0.00036 (19)
C12	0.0143 (3)	0.0185 (3)	0.0249 (4)	−0.0031 (2)	0.0062 (3)	−0.0015 (3)

Geometric parameters (Å, º)

S1—C1	1.7279 (8)	C6—C1	1.4152 (10)
S1—C7	1.7480 (7)	C8—C9	1.4379 (11)
S2—C12	1.7111 (10)	C8—H8	0.9500
S2—C9	1.7213 (8)	C9—C10	1.3830 (11)
N1—C7	1.3058 (10)	C10—C11	1.4183 (13)
N1—C6	1.3831 (10)	C10—H10	0.9500

N2—C8	1.2904 (10)	C11—C12	1.3694 (15)
N2—C7	1.3879 (10)	C11—H11	0.9500
C4—C5	1.3844 (12)	C3—C2	1.3880 (12)
C4—C3	1.4091 (13)	C3—H3	0.9500
C4—H4	0.9500	C2—C1	1.3966 (11)
C5—C6	1.4055 (11)	C2—H2	0.9500
C5—H5	0.9500	C12—H12	0.9500
C1—S1—C7	88.76 (4)	C10—C9—S2	111.59 (6)
C12—S2—C9	91.61 (4)	C8—C9—S2	120.57 (6)
C7—N1—C6	109.46 (6)	C9—C10—C11	112.06 (8)
C8—N2—C7	118.12 (7)	C9—C10—H10	124.0
C5—C4—C3	121.06 (8)	C11—C10—H10	124.0
C5—C4—H4	119.5	C12—C11—C10	112.47 (8)
C3—C4—H4	119.5	C12—C11—H11	123.8
C4—C5—C6	118.89 (7)	C10—C11—H11	123.8
C4—C5—H5	120.6	C2—C3—C4	121.13 (8)
C6—C5—H5	120.6	C2—C3—H3	119.4
N1—C6—C5	125.08 (7)	C4—C3—H3	119.4
N1—C6—C1	115.64 (7)	C3—C2—C1	117.74 (8)
C5—C6—C1	119.28 (7)	C3—C2—H2	121.1
N1—C7—N2	127.91 (7)	C1—C2—H2	121.1
N1—C7—S1	116.87 (6)	C2—C1—C6	121.90 (7)
N2—C7—S1	115.22 (6)	C2—C1—S1	128.84 (6)
N2—C8—C9	119.77 (7)	C6—C1—S1	109.26 (6)
N2—C8—H8	120.1	C11—C12—S2	112.27 (7)
C9—C8—H8	120.1	C11—C12—H12	123.9
C10—C9—C8	127.83 (7)	S2—C12—H12	123.9
C3—C4—C5—C6	0.46 (13)	C8—C9—C10—C11	−179.24 (9)
C7—N1—C6—C5	−179.28 (8)	S2—C9—C10—C11	−0.19 (11)
C7—N1—C6—C1	0.46 (10)	C9—C10—C11—C12	0.20 (13)
C4—C5—C6—N1	178.98 (8)	C5—C4—C3—C2	0.04 (14)
C4—C5—C6—C1	−0.76 (12)	C4—C3—C2—C1	−0.22 (13)
C6—N1—C7—N2	179.97 (8)	C3—C2—C1—C6	−0.10 (12)
C6—N1—C7—S1	−1.01 (9)	C3—C2—C1—S1	−179.40 (7)
C8—N2—C7—N1	−12.23 (13)	N1—C6—C1—C2	−179.17 (7)
C8—N2—C7—S1	168.73 (7)	C5—C6—C1—C2	0.60 (12)
C1—S1—C7—N1	1.00 (7)	N1—C6—C1—S1	0.26 (9)
C1—S1—C7—N2	−179.84 (6)	C5—C6—C1—S1	−179.98 (6)
C7—N2—C8—C9	−179.96 (7)	C7—S1—C1—C2	178.73 (8)
N2—C8—C9—C10	177.50 (9)	C7—S1—C1—C6	−0.64 (6)
N2—C8—C9—S2	−1.47 (12)	C10—C11—C12—S2	−0.12 (12)
C12—S2—C9—C10	0.10 (8)	C9—S2—C12—C11	0.01 (8)
C12—S2—C9—C8	179.23 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C11—H11···S2^{i}	0.95	2.92	3.517 (1)	122 (1)

Symmetry code: (i) x, $-y-1$, $z-1/2$.