

Hapipah M. Ali,^a Siti Nadiah Abdul Halim,^a Nordin Hj. Lajis,^b Wan Jefri Basirun,^a Sharifuddin M. Zain^a and Seik Weng Ng^{a*}

^aDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, and ^bLaboratory of Natural Products, Institute of Bioscience, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in main residue
 R factor = 0.053
 wR factor = 0.151
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

5-Bromo-1*H*-indole-3-carbaldehyde 2-thienoyl-hydrazone

In the title molecule, $\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{OS}$, the indole moiety is twisted by $36.0(2)^\circ$ with respect to the disordered thienyl group and the nitrogen-bound H atoms interact with the amide O atoms of symmetry-related molecules, resulting in an $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonded layer structure.

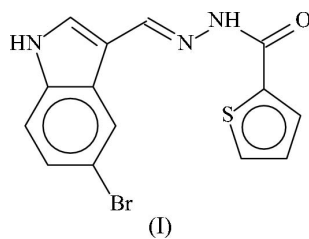
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Comment

Indole-3-carbaldehyde, which possesses an aldehydic unit, is not commonly used in the synthesis of Schiff bases; the Cambridge Structural Database (Version 5.26; Allen, 2002) lists only one example, that of the isonicotinoylhydrazone derivative (Tai *et al.*, 2003). In that crystal structure, the substituents on the amide C–N bond, which possesses double-bond character, are on opposite sides. The molecules are stabilized by hydrogen bonds that also involve the solvent molecule. In the present thienoylhydrazine derivative, (I), of bromoindole-3-carbaldehyde, the substituents are located on the same side of this bond so that the molecule (Fig. 1) experiences crowding between the indole system and the thienyl ring. The molecule is not planar as the indole and thienyl moieties are twisted by $36.0(2)^\circ$. Crowding probably accounts for the disorder in the thienyl ring, over two orientations.



Geometry-optimization calculations at the molecule at *AM1* level with Hyperchem (Hypercube Inc., 2000) suggest that this conformation is more stable than the conformation adopted by indole-3-carboxaldehyde isonicotinoylhydrazone (Tai *et al.*, 2003) by some 5 kcal mol^{-1} . Furthermore, as the potential-energy surface is relatively flat, the thienyl ring can oscillate by as much as 50° , a theoretical finding that may also account for the observed disorder. In the crystal structure, molecules are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form a layer structure (Table 1).

Experimental

Thienoylhydrazide (0.50 g, 3.52 mmol) was dissolved in an ethanol–acetic acid mixture (pH = 4.5). A solution of 5-bromoindole-3-carbaldehyde (0.30 g, 1.34 mmol) in the same mixed solvent was added;

the resulting yellow solution was heated under reflux for 2 h. The product that was isolated from the cooled solution was recrystallized from ethyl acetate.

Crystal data

$C_{14}H_{10}BrN_3OS$
 $M_r = 348.22$
 Orthorhombic, *Pbca*
 $a = 7.3437$ (4) Å
 $b = 17.944$ (1) Å
 $c = 21.340$ (1) Å
 $V = 2812.1$ (3) Å³
 $Z = 8$
 $D_x = 1.645$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4416 reflections
 $\theta = 2.3$ – 27.1°
 $\mu = 3.07$ mm⁻¹
 $T = 295$ (2) K
 Block, yellow
 $0.48 \times 0.42 \times 0.40$ mm

Data collection

Bruker SMART area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{\min} = 0.178$, $T_{\max} = 0.293$
 15764 measured reflections

3073 independent reflections
 2135 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\text{max}} = 27.1^\circ$
 $h = -9 \rightarrow 5$
 $k = -22 \rightarrow 22$
 $l = -25 \rightarrow 27$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.151$
 $S = 1.01$
 3073 reflections
 194 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 8.173P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.62$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1n\cdots O1^i$	0.86	2.16	2.921 (5)	147
$N3-H3n\cdots O1^{ii}$	0.86	2.09	2.927 (4)	165

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

H atoms were placed in calculated positions ($C-H = 0.93$ Å and $N-H = 0.86$ Å) and were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(H)$ set at $1.2U_{\text{eq}}(C,N)$. The final difference Fourier map had a large peak and a deep hole, both about 1 Å from Br1. The thienyl ring is disordered over two positions, the occupancies refining to a 0.81 (1):0.19 (1) ratio. The minor component is rotated by 180° around the C4–C5 bond as the two components share a common C4 atom. Pairs of bond distances in the two components were restrained to be within 0.01 Å of each other, and the displacement parameters of their corresponding atoms were

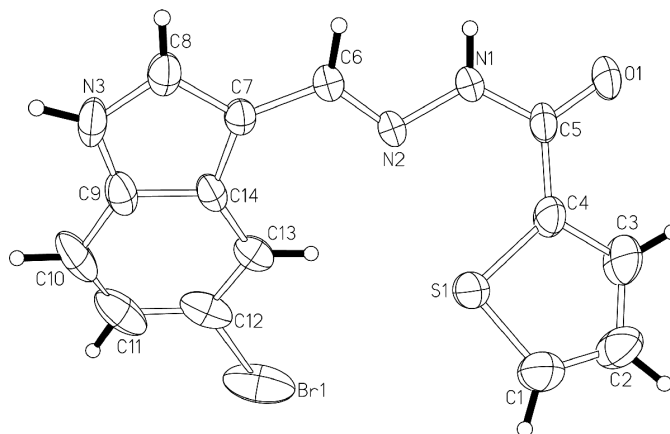


Figure 1

ORTEPII plot (Johnson, 1976) of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The minor disorder component is not shown.

constrained to be equal. The ring was restrained to be approximately planar. Some of the atoms of the benzene ring had somewhat elongated ellipsoids but the disorder, if any, could not be satisfactorily modeled. All C atoms were restrained to be approximately isotropic.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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