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3-(2-Thienylmethyl)-4,4′-bi-1*H*-1,2,4-triazol-5(4*H*)-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.087
wR factor = 0.284
Data-to-parameter ratio = 17.8

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

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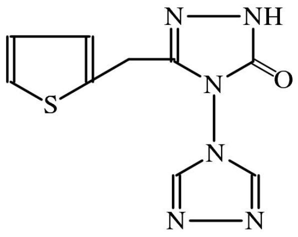
The title compound, $C_9H_8N_6OS$, crystallizes with two molecules in the asymmetric unit. In the crystal structure, intermolecular N—H···N hydrogen bonds form a three-dimensional network.

Comment

The considerable biological importance of azoles and triazoles has stimulated much work on these heterocycles and there are a variety of methods available for the synthesis of 1,2,4-triazol-5-one (Ray & Hank, 1990; Mullican *et al.*, 1993). 1,2,4-Triazole, 1,2,4-triazol-5-one and imidazole are the hetero-rings of choice and are essential structural features of many of the potent azole fungicides (Narayana *et al.*, 1993). It is also known that the triazole ring has been used instead of imidazole, which is found in the structure of some antagonist, anti-ulcer and antifungal drugs (Menozzi *et al.*, 2001). In a continuing search for pharmacologically active 1,2,4-triazole and 1,2,4-triazol-5-one compounds, it has been found that most azole fungicides have been developed for diseases of cereal crops; examples include fluconazole (Ichikawa *et al.*, 2001), ravuconazole (Ueda, 2003) and posaconazole (Kim *et al.*, 2003). Furthermore, in many compounds, the thiophene unit is associated with high anticancer and antifungal activity (Smith *et al.*, 2001; Nakib *et al.*, 1994).



(I)

The title compound, (I), crystallizes with two molecules (*a* and *b*) in the asymmetric unit. An *ORTEP*-3 (Farrugia, 1997) view and a packing diagram are shown in Figs. 1 and 2, respectively. The geometrical parameters of both triazole rings are in very good agreement with literature values (Çoruh *et al.*, 2003; Zhu *et al.*, 2000). The bond lengths and angles in the thienyl ring of molecule *b* are normal (Sommerer *et al.*, 1998). However, the geometry of the thienyl ring in molecule *a* is unusual, with C6*a*=C7*a* = 1.551 (5) Å; this may be due to unresolved disorder.

In the crystal structure, intermolecular N—H···N hydrogen bonds (Table 1) form a three-dimensional network.

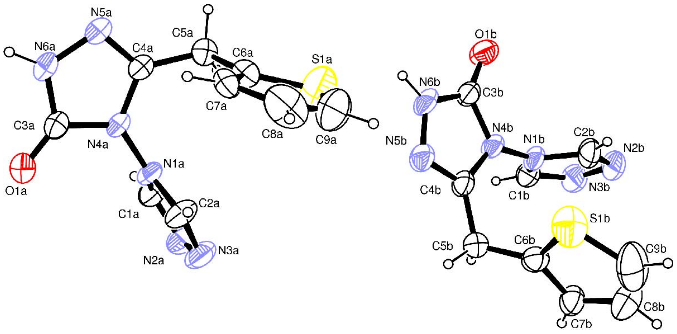


Figure 1
A view of the asymmetric unit of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids.

Experimental

Two synthetic routes were employed. 2-Thienylethyl acetate ethoxycarbonylhydrazone (2.563 g, 0.001 mol) or 2-thienylethyl acetate *tert*-butoxycarbonylhydrazone (2.843 g, 0.001 mol) was heated with 4-amino-4*H*-1,2,4-triazole (0.841 g, 0.001 mol) at 423–438 K for 2 h and then cooled. The solid product was recrystallized from methanol to give the pure title compound [yield: 1.685 g (67.86%) from the ethoxycarbonylhydrazone and 2.042 g (71.82%) from the *tert*-butoxycarbonylhydrazone; m.p. 493–494 K].

Crystal data

$C_9H_8N_6OS$
$M_r = 248.27$
Monoclinic, $P2_1/n$
$a = 15.8942$ (13) Å
$b = 6.9666$ (3) Å
$c = 20.2673$ (17) Å
$\beta = 102.634$ (6)°
$V = 2189.8$ (3) Å^3
$Z = 8$

$D_x = 1.506$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4150 reflections
$\theta = 1.5$–28.3°
$\mu = 0.29$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.25 × 0.20 × 0.15 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min} = 0.804$, $T_{\max} = 0.935$
13 819 measured reflections

5396 independent reflections
2911 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 28.3°$
$h = -35 \rightarrow 35$
$k = -5 \rightarrow 5$
$l = 22 \rightarrow -22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.087$
$wR(F^2) = 0.284$
$S = 1.02$
5396 reflections
304 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1827P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.28$ e Å^{-3}
$\Delta\rho_{\min} = -1.04$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N6*b*—H6*b*···N3*a*$^{\rm i}$	0.86	2.05	2.881 (4)	163
N6*a*—H6*a*···N2*b*$^{\rm ii}$	0.86	2.00	2.849 (4)	170
N6*a*—H6*a*···N3*b*$^{\rm ii}$	0.86	2.64	3.400 (5)	148

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

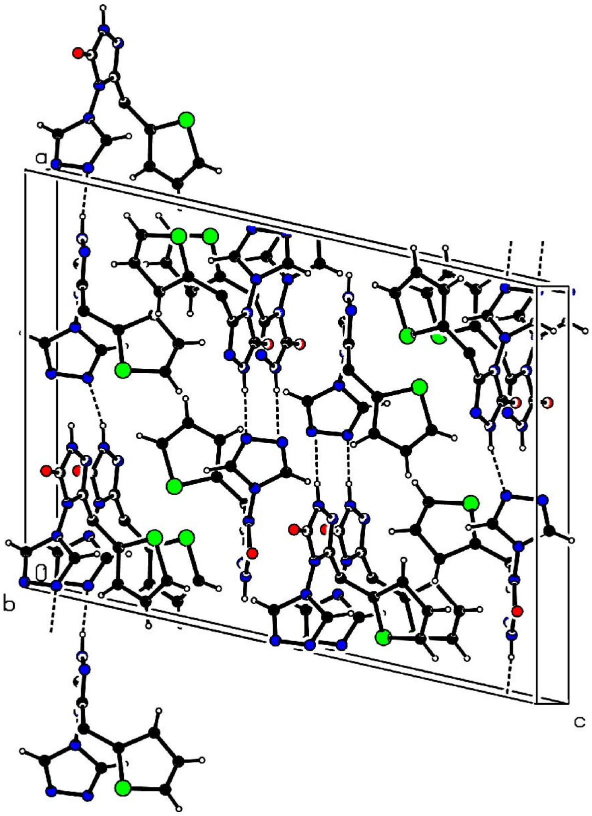


Figure 2
A packing diagram of the title compound. Broken lines indicate hydrogen bonds.

All H atoms were positioned geometrically and treated using a riding model, with Csp^2—H = 0.93 Å, Csp^3—H = 0.97 Å and N—H = 0.86 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N). The highest peak and deepest hole in the final difference Fourier map are located 0.04 Å from C7*a* and 0.4 Å from S1*a*, respectively; these, together with the unusual displacement parameters of C7*a* and S1*a* and the unusual bond lengths, indicate probable disorder of the ring over two orientations, but this has not been resolved. The crystals are unstable at room temperature and gradually decompose.

Data collection: *X-AREA* (Stoe, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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