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1-(Benzoylmethyl)-4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)-3-(2-thienylmethyl)-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) = 0.009 Å
R factor = 0.085
wR factor = 0.249
Data-to-parameter ratio = 21.0

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

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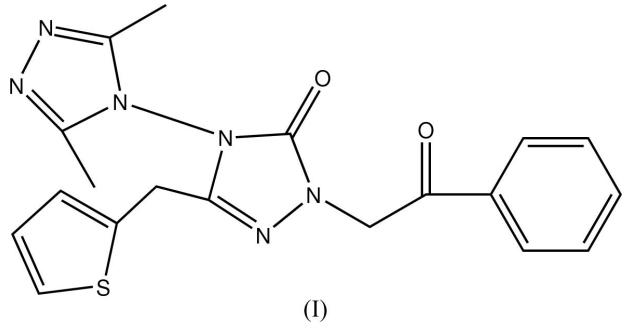
In the title compound, $C_{19}H_{18}N_6O_2S$, none of the five- and six-membered rings are coplanar with the triazolone ring. Intramolecular C—H···N and intermolecular C—H···N and C—H···O hydrogen bonds, together with some C—H···π interactions, help to stabilize the structure.

Comment

Triazole compounds have afforded many effective antifungal drugs in current clinical use. Particular attention has been paid to 1,2,4-triazole derivatives because of their generally broad antifungal spectrum and low toxicity. Triazole agents, for example, fluconazol (Richardson *et al.*, 1985), itraconazol (Donald & Leger, 2004), voriconazol (Dickinson *et al.*, 1996), posaconazol (Saksena *et al.*, 1996) and ravuconazol (Hata *et al.*, 1996) are active fungicides that are currently undergoing clinical trials. In addition to their antifungal properties, 1,2,4-triazole derivatives have broad-spectrum biological effects, such as insecticidal (Tsuda *et al.*, 2004), herbicidal (Chai *et al.*, 2003), anticonvulsant (Er-Rahimini & Mornet, 1992), anti-tumour (Nakib *et al.*, 1994) and plant growth regulatory activities (Jenkins *et al.*, 1989). Disubstituted 1,2,4-triazole derivatives have also been reported to show activity against tuberculosis (İkizler *et al.*, 1998).



(I)

In a previous paper, we reported the synthesis and biological activity of new 1,2,4-triazol-5-one derivatives, in which different substituents were bound to N1 (Demirbaş *et al.*, 2004). We and others (Çoruh, Ustabaş *et al.*, 2003; Zhu *et al.*, 2000; Li *et al.*, 2004) have also reported spectroscopic and structural data for some bis-1,2,4-triazole-5-ones and structures of 1,2,4-triazole systems with substituents in various positions on the triazole framework. These include 1-acetyl-4-(*p*-chlorobenzylidenamino)-3-methyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (Çoruh, Kahveci, Şaşmaz, Ağar & Kim, 2003), 1-acetyl-3-(*p*-chlorobenzyl)-4-(*p*-chlorobenzylidenamino)-4,5-

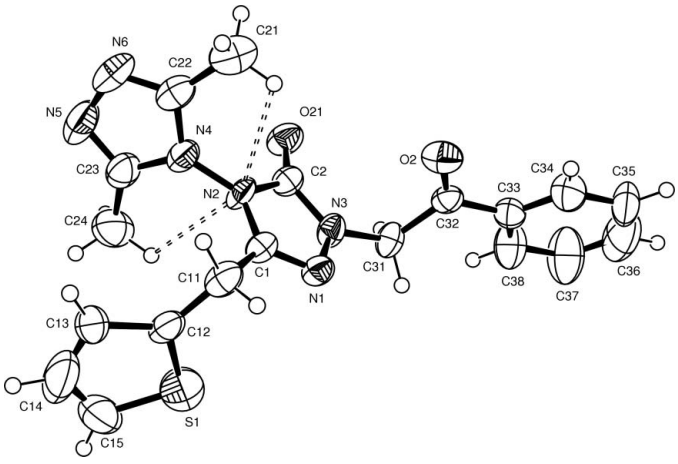


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are drawn as double dashed lines.

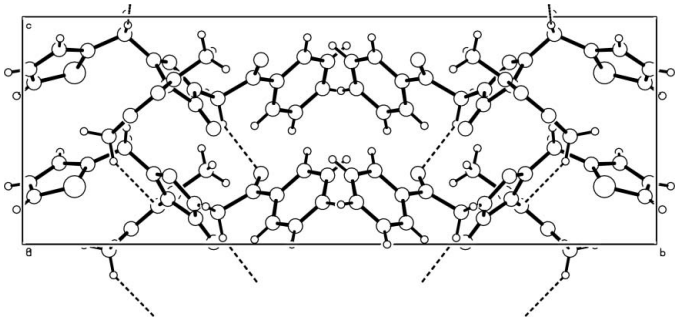


Figure 2
A packing diagram of (I), illustrating the intermolecular hydrogen bonding network. The view direction is parallel to the *a* axis. Hydrogen bonds are drawn as dashed lines.

dihydro-1*H*-1,2,4-triazol-5-one (Ocak *et al.*, 2003) and 1-acetyl-4-(*p*-chlorobenzylidenamino)-3-ethyl-4,5-dihydro-1*H*-1,2,4-triazol-5-one (Çoruh, Kahveci, Şaşmaz, Ağar, Kim & Erdönmez, 2003). We report here the preparation and structure of 1-(benzoylmethyl)-4-(3,5-dimethyl-4*H*-1,2,4-triazol-4-yl)-3-(2-thienylmethyl)-1*H*-1,2,4-triazol-5(4*H*)-one, (I) (Fig. 1), in order to examine structure–activity relationships in a triazole with a thiophene substituent.

Compound (I) contains four planar rings (Fig. 1), namely two triazole rings [N1/C1/N2/C2/N3 (*A*) and N4/C23/N5/N6/C22 (*B*)], a benzene ring (*C*) and a thiophene ring (*D*). The maximum deviations for rings *A*, *B*, *C* and *D* from their individual planes are 0.020 Å for C2, 0.007 Å for C23, 0.011 Å for C34 and 0.010 Å for C12, respectively. The dihedral angles between rings *A*/*B*, *A*/*C*, *A*/*D*, *B*/*C*, *B*/*D* and *C*/*D* are 85,45(16), 78.81 (18), 77.90 (17), 34.2 (2), 28.8 (2) and 23.4 (2) Å, respectively. A non-planar orientation of two substituted triazole rings has been observed previously (Ocak *et al.*, 2003; Zhu *et al.*, 2000; Bruno *et al.*, 2003; Yılmaz *et al.*, 2004, 2005). However, 1,2,4-triazole derivatives with two N-linked triazole rings have been observed to be planar (Çoruh, Kahveci, Şaşmaz, Ağar & Kim, 2003; Çoruh, Kahveci, Şaşmaz, Ağar, Kim & Erdönmez, 2003). The slightly different orientations of the 1,2,4-triazole rings may be due to stacking interactions.

Bond distances, angles and torsion angle data for (I) (Table 1) show good agreement with those reported previously (Allen, 2002; Yılmaz *et al.*, 2005; Ocak *et al.*, 2003; Wen *et al.*, 2005; Çoruh, Kahveci, Şaşmaz, Ağar & Kim, 2003; Çoruh, Kahveci, Şaşmaz, Ağar, Kim & Erdönmez, 2003). The shorter C1—N1, N5—C23 and N6—C22 bonds confirm their expected double-bond character.

Two weak non-classical C—H···N intramolecular interactions may contribute to the relative orientations of the two triazole rings. The structure is stabilized by C—H···N and C—H···O intermolecular interactions, forming infinite chains parallel to the *a* axis (Fig. 2), together with some C—H···π interactions (Table 2).

Experimental

4-(3,5-Dimethyl-4*H*-1,2,4-triazol-4-yl)-3-(2-thienylmethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (0.001 mol) was refluxed with sodium metal (0.001 mol) in absolute ethanol (50 ml) for 1 h. 2-Bromoacetophenone (0.001 mol) was added and the solution refluxed for 8 h. Compound (I) precipitated on cooling and was recrystallized from benzene–petroleum ether (1:2) (yield 60%; m.p. 381–382 K). IR (cm^{-1}): 1658 (C═O benzophenone), 1746 (C═O triazole), 1597 (C═N), 711(thiophene), 758 (phenyl); ^{1}H NMR: δ 4.06 (2H, *s*, CH_2 thiophene), 5.23 (2H, *s*, CH_2), 7.11–7.30 (3H, ABC system), 7.46–7.86 (5H, *m*, phenyl), 8.10 (2H, *s*, 2 × CH triazole); ^{13}C NMR: δ 26.49 (CH_2 thiophene), 52.29 (NCH_2), 126.33, 127.27, 127,74 (CH thiophene), 133.91 (C thiophene), 128.18, 129.07, 134.47 (CH phenyl), 133.87 (C phenyl), 143.45 (C═N), 151.02 (C═N), 152.17 (C═O triazole), 191.07 (C═O).

Crystal data

$C_{19}H_{18}N_6O_2S$
M_r = 394.45
Orthorhombic, $Pca2_1$
a = 9.8596 (10) Å
b = 23.584 (2) Å
c = 8.4499 (8) Å
V = 1964.8 (3) Å^3
Z = 4
D_x = 1.333 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2375 reflections
θ = 2.0–28.0°
μ = 0.19 mm^{-1}
T = 293 (2) K
Prism, colourless
0.40 × 0.34 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
11 257 measured reflections
4305 independent reflections
2374 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 28.0°
$h = -12 \rightarrow 11$
$k = -29 \rightarrow 30$
$l = -10 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.085
$wR(F^2)$ = 0.249
S = 1.08
4305 reflections
205 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1325P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.049
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}
Absolute structure: Flack (1983), 1821 Friedel pairs
Flack parameter = 0.0 (3)

Table 1
Selected geometric parameters (Å, °).

C21—C22	1.470 (8)	N3—C2	1.360 (6)
C24—C23	1.467 (9)	N3—C31	1.447 (6)
S1—C15	1.666 (6)	O2—C32	1.199 (6)
S1—C12	1.672 (8)	N4—C23	1.366 (7)
N1—C1	1.303 (6)	N4—C22	1.377 (6)
N1—N3	1.379 (6)	C1—C11	1.470 (7)
O21—C2	1.212 (6)	N5—C23	1.296 (7)
N2—C1	1.368 (6)	N5—N6	1.403 (8)
N2—N4	1.383 (5)	C22—N6	1.287 (7)
N2—C2	1.395 (6)		
C1—N1—N3	106.2 (4)	O21—C2—N3	131.7 (5)
C1—N2—N4	126.7 (4)	O21—C2—N2	127.5 (4)
C1—N2—C2	111.2 (4)	N3—C2—N2	100.7 (4)
N4—N2—C2	122.1 (4)	C23—N5—N6	107.5 (5)
C2—N3—N1	113.3 (4)	N6—C22—N4	108.9 (5)
C2—N3—C31	126.4 (4)	N6—C22—C21	128.3 (5)
N1—N3—C31	120.2 (4)	N4—C22—C21	122.7 (5)
C23—N4—C22	106.2 (4)	N3—C31—C32	112.1 (4)
C23—N4—N2	126.6 (4)	N3—C31—H31*A*	109.2
C22—N4—N2	127.1 (4)	C22—N6—N5	108.1 (5)
N1—C1—N2	108.5 (4)	N5—C23—N4	109.2 (5)
N1—C1—C11	123.7 (4)	N5—C23—C24	127.0 (6)
N2—C1—C11	127.8 (4)		
N1—C1—C11—C12	−97.4 (6)	N1—N3—C31—C32	−91.7 (5)
N2—C1—C11—C12	80.7 (6)	C21—C22—N6—N5	174.7 (6)
C2—N3—C31—C32	83.7 (6)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C21—H21*A*···N2	0.96	2.59	3.014 (6)	107
C24—H24*A*···N2	0.96	2.60	3.012 (6)	106
C24—H24*B*···N6^{i}	0.96	2.60	3.424 (6)	143
C31—H31*A*···O2^{ii}	0.97	2.40	3.284 (3)	150
C11—H11*A*···N5^{iii}	0.97	2.32	3.286 (6)	175
C21—H21*B*···*Cg*1^{iii}	0.96	2.65	3.439 (5)	140
C21—H21*C*···*Cg*2^{iv}	0.96	3.34	4.262 (5)	162
C24—H24*C*···*Cg*3	0.96	3.19	3.640 (5)	110
C24—H24*A*···*Cg*3	0.96	3.30	3.640 (5)	103

Symmetry codes: (i) $-\frac{1}{2}-x, y, z-\frac{1}{2}$; (ii) $\frac{1}{2}-x, y, z-\frac{1}{2}$; (iii) $-\frac{1}{2}-x, y, \frac{1}{2}+z$; (iv) $x-1, y, z$. *Cg*1, *Cg*2 and *Cg*3 are the centroids of rings *B*, *C* and *D* respectively.

All H atoms in (I) were placed in calculated positions and refined using a riding model; C—H = 0.93 Å (aromatic) with U_{iso}(H) = 1.2U_{eq}(C), and C—H = 0.96 (methyl) and 0.97 Å (methylene) with U_{iso}(H) = 1.5U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995), *PLATON* (Spek, 1997) and *WinGX* (Farrugia, 1999).

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