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4-(2-Fluorobenzylideneamino)-3-(1,2,4-triazol-4-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Key indicators

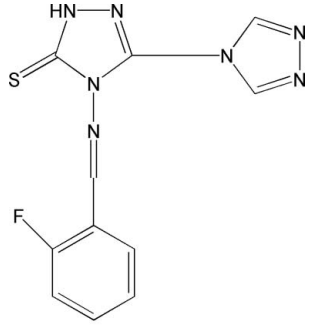
Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.099
Data-to-parameter ratio = 14.6

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

In the title compound, $C_{12}H_{10}FN_7S$, the dihedral angles made by the plane of the thione-substituted triazole ring with the planes of the other triazole ring and the benzene ring are 74.55 (2) and 11.50 (3)°, respectively. The structure shows a number of N—H···N intermolecular hydrogen-bonding interactions, and weak C—H···S intra- and intermolecular interactions.

Comment

Amine- and thione-substituted triazoles have been studied as anti-inflammatory and antimicrobial agents (Eweiss *et al.*,1986; Awad *et al.*, 1991). In addition, 1,2,4-triazoles display a broad range of biological activity, finding application as antitumour, antibacterial, antifungal and antiviral agents (Holla *et al.*, 1996; Jantova *et al.*, 1998). In this paper, we report the structure of the title compound (I) (Fig. 1).



(I)

In the molecule of (I), the bond lengths and angles are generally normal in the benzene and triazole rings (Ji *et al.*, 2002). The molecule exists in the thione tautomeric form, with an S=C distance of 1.6710 (19) Å, which indicates substantial double-bond character (Escobar-Valderrama *et al.*, 1989). Atoms S1 and N1 lie in the plane of the thione-substituted triazole ring (*P*1). The dihedral angles made by *P*1 with the planes of the other triazole ring and the benzene ring are 74.55 (2) and 11.50 (3)°, respectively. Atoms N1, N2, C6 and C7 are coplanar (plane *P*2). The dihedral angles formed by plane *P*1 and the C7–C12 ring with *P*2 are 16.75 (3) and 7.91 (3)°, respectively.

The structure of (I) shows a number of N—H···N intermolecular hydrogen-bonding interactions and weak C—H···S intra- and intermolecular interactions (Table 2).

Experimental

1,2,4-Triazol-4-ylacetic acid was prepared by refluxing a mixture of triazole (6.9 g, 0.1 mol) and chloroacetic acid (9.5 g, 0.1 mol) in H_2O

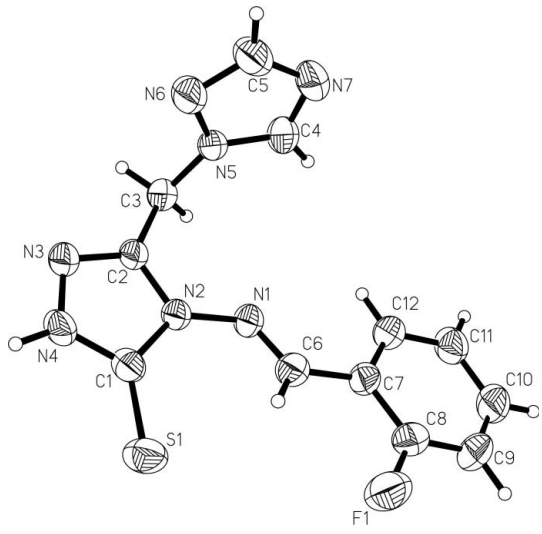


Figure 1
The structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

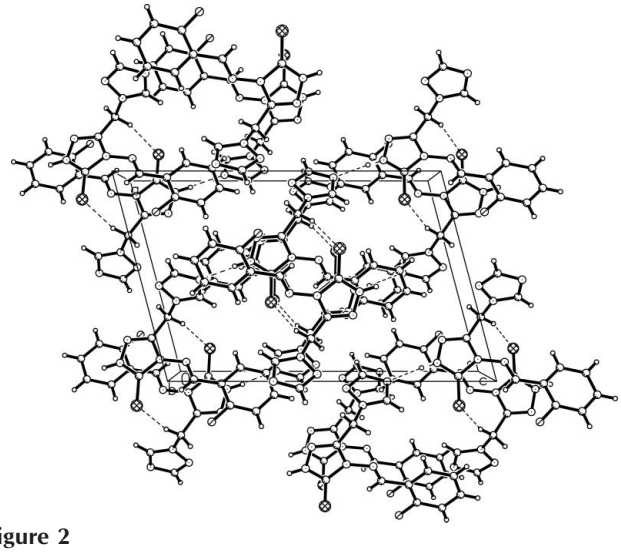


Figure 2
A packing diagram for (I), viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

(30 ml) for 4 h. 4-Amino-5-(1,2,4-triazol-4-ylmethyl)-2,4-dihydro-1,2,4-triazol-3-thione was prepared by refluxing a mixture of thiocarbohydrazide (10 g, 0.094 mol) and 1,2,4-triazol-4-ylacetic acid (12.7, 0.1 mol) in acetone (50 ml) for 5–6 h. Within 1 h of refluxing, a cream-coloured solid began to separate from the solution. After the period of reflux, the remaining liquid was allowed to stand overnight at room temperature. The solid that crystallized was filtered, washed with diethyl ether and recrystallized from an equimolar solution of dioxane and water. Cream-coloured crystals of 4-amino-5-(1,2,4-triazol-4-ylmethyl)-2,4-dihydro-1,2,4-triazol-3-thione were isolated in 71% yield. The final product, 4-(2-fluorobenzylideneamino)-3-(1,2,4-triazol-4-ylmethyl)-1*H*-1,2,4-triazole-5(4*H*)-thione, was prepared by refluxing an equimolar mixture of 2-fluorobenzaldehyde and 4-amino-5-(1,2,4-triazol-4-ylmethyl)-2,4-dihydro-1,2,4-triazol-3-thione in ethanol for 2–3 h. The solution was concentrated and allowed to stand overnight at room temperature, during which time colourless crystals of (I) formed. The product was recrystallized from ethanol (m.p. 461–462 K). Spectroscopic analysis: ^{1}H NMR (600 MHz, acetone-d$_6$, δ, p.p.m.): 7.0–8.02 (6H, *m*, Ar), 8.1 (1H, *s*, N=CH), 4.99 (2H, *s*, N—CH$_2$), 3.0 (1H, *s*, SH). Analysis, calculated for $C_{12}H_{10}FN_7S$: C 47.52, H 3.32, N 32.33%; found: C 47.38, H 3.28, N 32.58%.

Crystal data

$C_{12}H_{10}FN_7S$
M_r = 303.34
Monoclinic, $P2_1/n$
a = 11.0071 (17) Å
b = 7.9150 (12) Å
c = 16.645 (3) Å
β = 104.823 (3)°
V = 1401.9 (4) Å^3
Z = 4
D_x = 1.437 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2541 reflections
θ = 2.6–26.1°
μ = 0.25 mm^{-1}
T = 294 (2) K
Block, colourless
0.36 × 0.22 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.937, T_{max} = 0.952
7625 measured reflections
2842 independent reflections
1990 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 26.4°
$h = -13 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.03
2842 reflections
194 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.34P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.6710 (19)	C2—C3	1.488 (2)
N1—C6	1.270 (2)	C6—C7	1.461 (2)
N1—N2	1.3999 (18)	C8—F1	1.362 (2)
N5—C3	1.451 (2)		
C6—N1—N2	117.98 (15)	N4—C1—S1	126.52 (14)
C2—N2—N1	119.01 (13)	N2—C1—S1	131.32 (14)
C1—N2—N1	132.57 (14)	N1—C6—C7	119.92 (17)
C4—N5—C3	129.57 (16)	C8—C7—C6	119.79 (18)
N6—N5—C3	121.11 (14)	C12—C7—C6	123.43 (17)
C4—N5—C3—C2	114.2 (2)	N3—C2—C3—N5	109.6 (2)
N6—N5—C3—C2	−68.9 (2)	N2—C2—C3—N5	−71.2 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N7^{i}	0.87 (2)	1.98 (2)	2.846 (2)	173 (2)
C3—H3A···S1^{ii}	0.97	2.78	3.703 (2)	159
C6—H6···S1	0.93	2.52	3.225 (2)	133

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

The H atom attached to atom N4 was located in a difference map and freely refined. All other H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

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