

6-(2,4-Difluorophenyl)-3-(3-methylphenyl)-
7H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazineGuang-Qi Xiang, Li-Xue Zhang,
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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.079
 wR factor = 0.195
Data-to-parameter ratio = 12.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_{17}\text{H}_{12}\text{F}_2\text{N}_4\text{S}$, the five-membered triazole ring and two benzene rings are planar, while the six-membered thiadiazole ring is slightly distorted, with a mean deviation of 0.234 \AA . Both the ring S and adjacent non-bridgehead C atom deviate significantly [$0.320(2)$ and $0.370(2)\text{ \AA}$] from the thiadiazole plane. In the crystal structure, four different kinds of intra- and intermolecular C—H \cdots N hydrogen-bonding interactions are observed, leading to the formation of a one-dimensional zigzag chain along the crystallographic b axis.

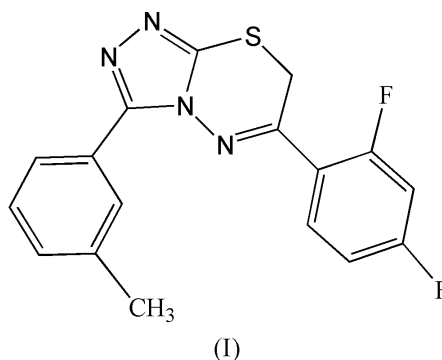
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Comment

1,2,4-Triazoles fused with six-membered ring systems are found to possess diverse applications in the fields of medicine, agriculture and industry. The commonly known systems are triazoles fused with pyridine, pyridazine, pyrimidine, pyrazines and triazines. A literature survey reveals that there are not many examples of triazoles fused with thiadiazines. Moreover, a large number of triazolothiazines have been shown to exhibit antimicrobial (Feng *et al.*, 1992) and diuretic (Mohan & Anjaneyulu, 1987) properties and act as photographic couplers (Holla *et al.*, 2001). On the other hand, much attention has been paid to partially fluorinated heterocyclic compounds, because of their unique chemical, physical and biological properties (Shaaban & Fuchigami, 2002). The development of efficient methods for selective fluorination of heterocycles is, therefore, of much importance. In this paper, we report the synthesis and crystal structure of the title compound, (I).



In (I), the five-membered triazole ring (atoms N2, N3, N4, C9 and C10) and the benzene rings (C1, C2, C3, C4, C5 and C6 of the difluorobenzene ring, and C11, C12, C13, C14, C15 and C16 of the methylbenzene ring) are essentially planar, with mean deviations of 0.002 , 0.003 and 0.007 \AA , respectively, while the six-membered thiadiazole ring, composed of atoms

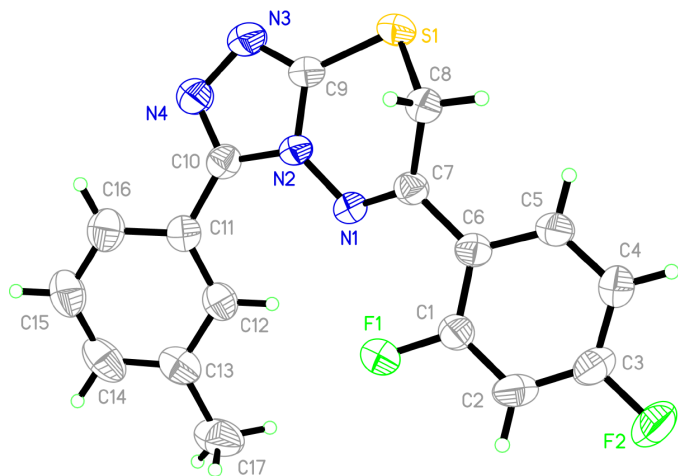


Figure 1

The molecular structure of (I) with the atom numbering, showing displacement ellipsoids at the 50% probability level.

N1, N2, C7, C8, C9 and S1, is slightly distorted, with a mean deviation of 0.234 Å (Fig. 1). Owing to the greater bulk of the 3-methylphenyl and 2,4-difluorophenyl rings, both C8 and S1 deviate significantly [0.370 (2) and 0.320 (2) Å] from the thiadiazole plane. Both the S—C (with mean distance 1.775 Å) and C—N bond lengths are in line with this observation in related complexes (Sert *et al.*, 2003; Zou *et al.*, 2004). The C and N atoms are involved in the conjugated form of the five-membered triazole ring, because the C—N bond lengths, in the range 1.290 (5)–1.374 (5) Å, are longer than a typical double C=N bond [*ca* 1.269 (2) Å], but shorter than a C—N single bond [*ca* 1.443 (4) Å] (Jin *et al.*, 2004) (Table 1). The dihedral angle between the thiadiazole ring and the 2,4-difluorobenzene ring is 26.47 (9)°, which is larger than that between the two benzene rings [12.57 (17)°]; the thiadiazole ring and the triazole ring of (I) subtend a dihedral angle of 12.43 (12)°.

In the crystal structure, the title compound forms four different kinds of intra- and intermolecular C—H···N hydrogen bonds, with C···N distances in the range 3.032 (5)–3.394 (5) Å; these hydrogen-bonding interactions lead to the formation of a one-dimensional zigzag chain along the crystallographic *b* axis (Fig. 2).

Experimental

The key intermediate 4-amino-5-mercapto-3-(3-methylphenyl)-1,2,4-triazole was prepared from 3-methylbenzoic acid hydrazide, whose starting material was 3-methylbenzoic acid, following the literature method of Zhang *et al.* (1990). To a solution of 4-amino-5-mercapto-3-(3-methylphenyl)-1,2,4-triazole (0.01 mol) in absolute ethanol was added 2-bromo-4'-methylacetophenone (0.01 mol). The mixture was refluxed for 7 h. The solid obtained on cooling was filtered, washed with cold water, dried and recrystallized from ethanol to give crystals of the title compound. IR (KBr): 2917, 2845 (CH₂), 1597 (C=N), 1540, 1497, 1482, 1447 (C=N, C=C), 1274 (N—N=C), 1102 (C—F), 851, 787, 708 (di- and trisubstituted benzene), 700 (C—S—C) cm⁻¹. ¹H NMR (chloroform-*d*): δ 7.76–7.92 (*m*, 3H, Ar-H), 7.30–7.53 (*m*, 4H, Ar-H), 4.35 (*s*, 2H, SCH₂), 2.38 (*s*, 3H, CH₃). MS *m/z*(%): 344

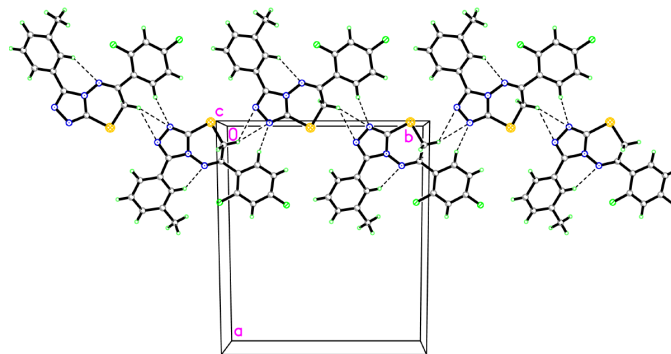


Figure 2

Part of the crystal structure, showing the infinite hydrogen-bonding network of (I) running along the *b* axis. Hydrogen bonds are indicated by dashed lines.

(*M*⁺ + 2, 4.59), 342 (*M*⁺, 72.29), 229 (3.13), 206 (12.14), 153 (21.99), 145 (20.76), 139 (100), 119 (42.59), 118 (33.33), 117 (53.46), 116 (26.97), 91 (15.54), 90 (22.93), 89 (22.13), 58 (95.41), 51 (11.74), 39 (13.56). Elemental analysis for C₁₇H₁₂F₂N₄S: C 59.23, H 3.76, N 16.02%; calculated: C 59.58, H 3.51, N 16.36%; *m.p.* 432–434 K.

Crystal data

C₁₇H₁₂F₂N₄S
M_r = 342.37
 Monoclinic, *P*2₁/*c*
a = 15.4067 (15) Å
b = 13.3329 (13) Å
c = 7.7173 (7) Å
 β = 103.117 (2)°
V = 1543.9 (3) Å³
Z = 4

D_x = 1.473 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1797 reflections
 θ = 2.4–24.7°
 μ = 0.24 mm⁻¹
T = 298 (2) K
 Block, colorless
 0.38 × 0.16 × 0.14 mm

Data collection

Bruker SMART APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
T_{min} = 0.915, *T_{max}* = 0.963
 8055 measured reflections

2783 independent reflections
 2414 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{\max} = 25.2°
h = −15 → 18
k = −13 → 15
l = −9 → 8

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.080
wR(*F*²) = 0.195
S = 1.29
 2783 reflections
 218 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2 + 0.5857P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e \AA}^{-3}$

Table 1
 Selected bond lengths (Å).

S1—C9	1.743 (4)	N2—C10	1.374 (5)
S1—C8	1.807 (4)	N3—C9	1.290 (5)
N1—C7	1.285 (4)	N3—N4	1.395 (5)
N1—N2	1.395 (4)	N4—C10	1.306 (5)
N2—C9	1.369 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5 \cdots N3 ⁱ	0.93	2.49	3.364 (5)	157
C8—H8A \cdots N3 ⁱ	0.97	2.47	3.394 (5)	159
C8—H8A \cdots N4 ⁱ	0.97	2.62	3.312 (5)	129
C12—H12 \cdots N1	0.93	2.42	3.032 (5)	123

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $Csp^2-H = 0.93 \text{ \AA}$ with $U_{iso} = 1.2U_{eq}(C)$, $Csp^3-H = 0.96$ or 0.97 \AA with $U_{iso} = 1.5U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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References

- Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Feng, X. M., Chen, R. & Yang, W. D. (1992). *Chem. J. Chin. Univ.* **13**, 187–194.
- Holla, B. S., Akberali, P. M. & Shivananda, M. K. (2001). *Farmaco*, **56**, 919–927.
- Jin, Z. M., Li, L., Li, M. C., Hu, M. L. & Shen, L. (2004). *Acta Cryst.* **C60**, o642–o643.
- Mohan, J. & Anjaneyulu, G. S. R. (1987). *Pol. J. Chem.* **61**, 547–551.
- Shaaban, M. R. & Fuchigami, T. (2002). *Tetrahedron Lett.* **43**, 273–276.
- Sert, S., Ercag, A., Senturk, O. S., Sterenberg, B. T., Udachin, K. A., Ozdemir, U. & Sarikahya, F. U. (2003). *Polyhedron*, **22**, 1689–1693.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Release 97-2. University of Göttingen, Germany.
- Zhang, L. X., Zhang, Z. Y. & Zeng, F. L. (1990). *Chem. J. Chin. Univ.* **11**, 148–151.
- Zou, K. H., Cai, X. Q., Chen, J. X., Zhang, L. X., Zhang, A. J. & Hu, M. L. (2004). *Acta Cryst.* **E60**, o1736–o1738.