

Li-Xue Zhang,* Jian-Yu Jin,
San-Nu Zhou, Hong-Ping Xiao
and An-Jiang Zhang

Department of Chemistry and Materials Science,
Wenzhou Normal College, Wenzhou 325027,
People's Republic of China

Correspondence e-mail:
zhanglixuelz@yahoo.com.cn

Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.036
 wR factor = 0.093
Data-to-parameter ratio = 12.7

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

3-(4-Chlorophenyl)-6-(2,4-difluorophenyl)- 7H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazine

The title compound, $\text{C}_{16}\text{H}_9\text{ClF}_2\text{N}_4\text{S}$, was prepared by the reaction of 4-amino-5-mercapto-3-chlorophenyl-1,2,4-triazole and 2-bromo-2',4'-fluoroacetophenone. The six-membered thiadiazine ring is distorted from planarity, with an r.m.s. deviation of 0.201 \AA . All C and N atoms of the triazole ring are conjugated.

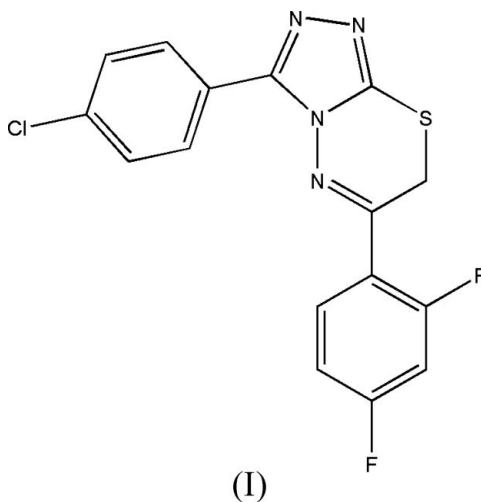
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Comment

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 considerable importance. Here we report the synthesis and crystal structure of the title compound, (I).



The molecular structure of the title compound, (I), is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The five-membered triazole ring (N2–N4 and C9, C10) and the benzene rings (C1–C6 and C11–C16) are essentially planar, while the six-membered thiadiazine ring,

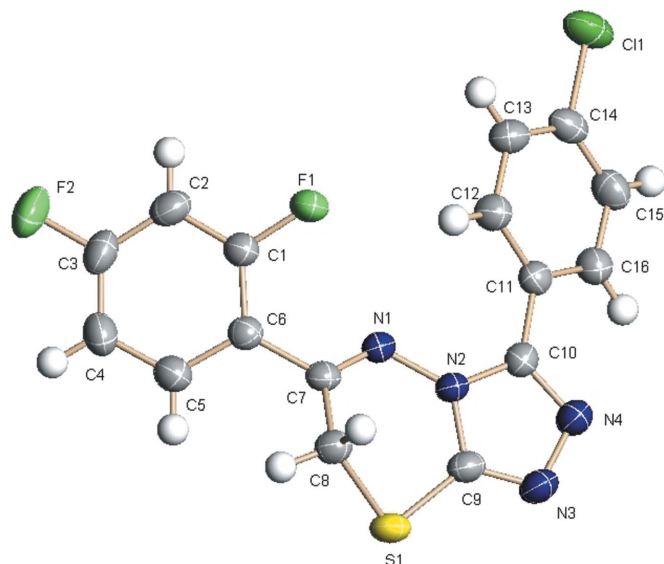


Figure 1

The molecular structure of compound (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

(N1, N2, C7, C8, C9 and S1), is distorted from planarity, with an r.m.s deviation of 0.201 Å (Fig. 1). Atoms C8 and S1 deviate by $-0.401(2)$ and $0.323(1)$ Å, respectively, from the thiadiazine mean plane. The thiadiazine ring exists in a chair form. Both the S—C (mean distance 1.774 Å) and C—N bond lengths are comparable to those in related compounds (Sert *et al.*, 2003; Xiang *et al.*, 2004). All C and N atoms of the triazole ring are conjugated and the bond lengths are normal (Allen *et al.*, 1987; Jin *et al.*, 2004; Table 1). The dihedral angle between the N2—N4/C9, C10 and C11—C16 rings is $24.1(1)^\circ$ and that between the C1—C6 and C11—C16 rings is $135.3(2)^\circ$. The two benzene rings are located on the same side of the triazole ring, resembling the two front claws of a crab.

Experimental

4-Amino-3-(4-chlorophenyl)-5-mercapto-1,2,4-triazole was prepared from 4-chlorobenzoic acid hydrazide (prepared from 4-chlorobenzoic acid), following the literature method of Zhang *et al.* (1990). To a solution of 4-amino-5-mercapto-3-(4-chlorophenyl)-1,2,4-triazole (0.001 mol) in absolute ethanol was added 2-bromo-2',4'-difluoroacetophenone (0.001 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 compound (I). The purified product was dissolved in 95% ethanol and kept at room temperature for 5 d when colourless single crystals of (I) were formed (m.p. 454–455 K).

Crystal data

$C_{16}H_9ClF_2N_4S$
 $M_r = 362.78$
 Monoclinic, $P2_1/c$
 $a = 11.892(2)$ Å
 $b = 12.962(1)$ Å
 $c = 10.430(1)$ Å
 $\beta = 108.80(1)^\circ$
 $V = 1522.0(3)$ Å³
 $Z = 4$

$D_x = 1.583$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4232 reflections
 $\theta = 2.4$ – 25.2°
 $\mu = 0.42$ mm⁻¹
 $T = 298(2)$ K
 Block, colorless
 $0.43 \times 0.31 \times 0.25$ mm

Data collection

Bruker APEX area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.842$, $T_{\max} = 0.903$
 7940 measured reflections

2754 independent reflections
 2519 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 25.3^\circ$
 $h = -6 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.093$
 $S = 1.07$
 2754 reflections
 217 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.561P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C9	1.7328 (19)	N2—C10	1.373 (2)
S1—C8	1.8145 (18)	N3—C9	1.299 (2)
N1—C7	1.280 (2)	N3—N4	1.396 (2)
N1—N2	1.3920 (19)	N4—C10	1.307 (2)
N2—C9	1.369 (2)	C7—C8	1.506 (2)
C9—S1—C8	95.05 (8)	C9—N3—N4	106.90 (14)
C7—N1—N2	116.04 (14)	C10—N4—N3	108.03 (15)
C9—N2—C10	105.21 (14)	N3—C9—S1	128.46 (14)
C9—N2—N1	128.31 (14)	N2—C9—S1	120.78 (13)
C10—N2—N1	124.64 (14)	C7—N1—N2—C9	27.0 (2)
C7—N1—N2—C9	−170.73 (16)	C10—N2—C9—S1	−173.74 (13)
C9—N3—N4—C10	−0.3 (2)	N1—N2—C9—S1	−8.8 (3)
N2—N1—C7—C6	179.64 (14)	C8—S1—C9—N3	159.37 (19)
N2—N1—C7—C8	2.6 (2)	C8—S1—C9—N2	−26.34 (16)
N1—C7—C8—S1	−42.4 (2)	N3—N4—C10—N2	1.2 (2)
C6—C7—C8—S1	140.60 (14)	N3—N4—C10—C11	−179.61 (17)
C9—S1—C8—C7	47.06 (15)	C9—N2—C10—N4	−1.7 (2)
N4—N3—C9—N2	−0.8 (2)	N1—N2—C10—N4	−167.28 (16)
N4—N3—C9—S1	173.99 (15)	N1—N2—C10—C11	13.6 (3)
C10—N2—C9—N3	1.5 (2)		

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

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 (Bruker, 2002); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

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