organic compounds

3-(2-Furyl)-6-(4-methylphenyl)-7H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazine and its 6-phenyl analogue

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In the title compounds, $C_{15}H_{12}N_4OS$, (I), and $C_{14}H_{10}N_4OS$, (II), the thiadiazine ring adopts a skew-boat conformation, while the triazole and furyl rings are essentially planar. The phenyl group is twisted by 33.5 (2) and 47.9 (1)° out of the triazole-ring plane in (I) and (II), respectively.

Comment

The prevalence of resistant infections has decreased the applicability of existing chemotherapeutic and chemopreventive antimicrobial agents and stimulated the search for new compounds. The 1,2,4-triazole nucleus and the nitrogen-bridged heterocycles derived from it have recently been incorporated into a variety of compounds with antibacterial (Holla & Kalluraya, 1988), antifungal (Prasad *et al.*, 1989) and antiparasitic (El-Dawy *et al.*, 1983) properties. In a previous work, we reported on the synthesis and antimicrobial effects of novel 6-aryl-3-(2-furyl)-7H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazines (Ergenç *et al.*, 1996). To further investigate this bicyclic system and establish its structure unambiguously, single-crystal X-ray diffraction studies were carried out on 6-phenyl- and 6-(4-methylphenyl)-3-(2-furyl)-7H-1,2,4-triazolo[3,4-b][1,3,4]thiadiazine, *i.e.* (II) and (I), respectively.

(I) R = Me
(II) R = H
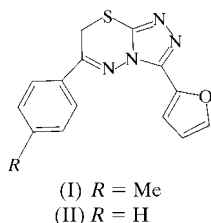
The title compounds (Figs. 1 and 2) consist of a fused triazolo–thiadiazine system, one furyl ring and one phenyl ring. The four rings do not share a common plane. As expected, the 1,2,4-triazole and furyl rings in both compounds are planar, which can be attributed to a wide range of electron delocalization [maximum deviations of 0.007 (2) and −0.003 (3) Å for C4 and C8, respectively, in (I), and of −0.006 (2) and
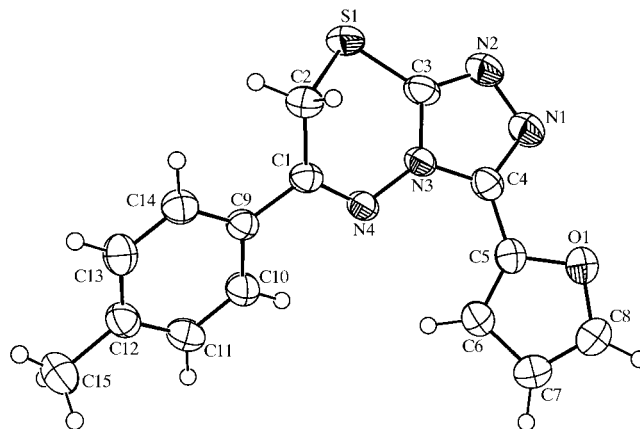

Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

0.003 (3) Å for N3 and C7 in (II)]. The thiadiazine ring fused to the triazole ring deviates from planarity. The puckering parameters (Cremer & Pople, 1975) are Q = 0.587 (2) and 0.616 (2) Å, θ = 65.8 (2) and 66.7 (2)°, and φ = 34.2 (2) and 34.6 (2)° for (I) and (II), respectively. So the thiadiazine moiety assumes a skew-boat conformation in both compounds. The phenyl ring is essentially planar and twisted out of the plane of the triazole ring; the dihedral angle between these planes is 33.5 (2)° in (I) and 47.9 (1)° in (II). The dihedral angles between the triazole and furyl rings are 16.2 (2) and 10.8 (1)° in (I) and (II), respectively.

The bond lengths and angles in both compounds are very similar and within expected ranges. The N1—C4 and N2—C3 bond distances [average values 1.311 (3) and 1.304 (3) Å, respectively] are in a good agreement with those found for structures containing the 1,2,4-triazole ring (Özbey *et al.*, 1999; Wang *et al.*, 1998). In both compounds, the presence of the electron-donating furyl group in the 3-position of the triazole ring leads to an elongation of the N1—N2 bond length to
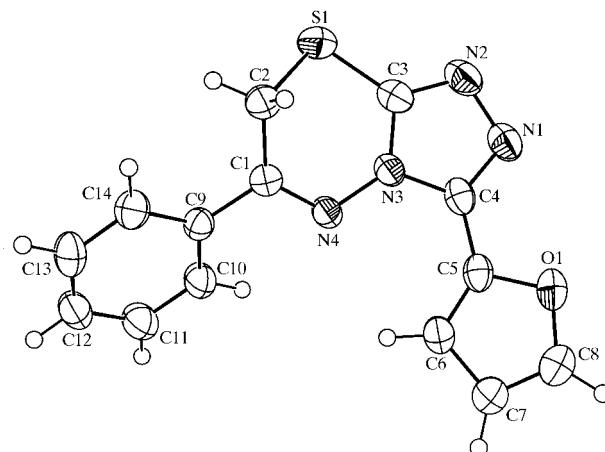

Figure 2
*ORTEP*II (Johnson, 1976) drawing of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

1.402 (3) Å (average value). This bond is 1.371 (2) Å in 5-amino-3-trifluoromethyl-1H-1,2,4-triazole (Borbulevych *et al.*, 1998), in which an electron-withdrawing group is bound to the 3-position of the triazole ring. The difference between the S1—C2 bond distance [average value 1.814 (3) Å] and the S1—C3 bond distance [average value 1.733 (3) Å] can be attributed to the different hybridization of the Csp^3 and Csp^2 atoms (Argay *et al.*, 1977, 1980).

Since (I) is the 4-methyl derivative of (II), the identical space groups and the similarity of the lattice parameters suggest some degree of isostructurality, as shown by the descriptors Δ(pc) = 3.6% and Π = 0.034 (Kálmán *et al.*, 1991, 1993). In terms of the predictions given by Kitaigorodskii (1961), it is unique that a relatively small molecule such as (I) (M_r = 296.35) retains similar close packing to that of (II) enlarged by the bulky methyl group (5% of the molecular weight). This, of course, accounts for the low index of isostructurality; I_i(20) = 52% calculated by the algorithm of Kálmán (Kálmán, Argay *et al.*, 1991; Kálmán, Párkányi & Argay, 1993). To avoid the ambivalence raised by the choice of a common origin for oblique (monoclinic) unit cells, the isostructuralities of (I) and (II) were calculated by the novel volumetric method developed by Fábián (1999) and reported in detail by Fábián & Kálmán (1999). The volumetric index of isostructurality amounts to 72% for the whole unit cell, with four molecules indicating significant packing similarity of the related structures.

In both compounds, the N4 atom of the thiadiazine moiety is involved in an intramolecular hydrogen-bond interaction (Tables 2 and 4). In compound (I), there is also one inter-molecular interaction (Table 2). These bonds, together with normal van der Waals interactions, are responsible for the packing in the crystal.

Experimental

Both compounds were synthesized as described by Ergenç *et al.* (1996) and recrystallized from C_2H_5OH.

Compound (I)

Crystal data

$C_{15}H_{12}N_4OS$	D_x = 1.43 Mg m^{-3}
M_r = 296.35	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
a = 9.342 (1) Å	reflections
b = 9.106 (1) Å	θ = 9.99–18.16°
c = 16.208 (1) Å	μ = 0.239 mm^{-1}
β = 92.58 (1)°	T = 295 K
V = 1377.4 (2) Å^3	Prismatic, yellow
Z = 4	0.64 × 0.40 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffract-ometer	R_{int} = 0.011
$\omega/2\theta$ scans	θ_{max} = 26.3°
Absorption correction: empirical *via* ψ scans (Fair, 1990)	h = −11 → 0
	k = −11 → 0
	l = −20 → 20
T_{min} = 0.940, T_{max} = 1.000	3 standard reflections
3072 measured reflections	frequency: 120 min
2705 independent reflections	intensity decay: 0.8%
1890 reflections with $I > 2\sigma(I)$	

Compound (II)

Crystal data

$C_{14}H_{10}N_4OS$	D_x = 1.49 Mg m^{-3}
M_r = 282.33	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
a = 8.799 (2) Å	reflections
b = 9.302 (1) Å	θ = 9.84–18.19°
c = 15.5437 (1) Å	μ = 0.257 mm^{-1}
β = 97.40 (1)°	T = 295 K
V = 1261.6 (2) Å^3	Prismatic, yellow
Z = 4	0.60 × 0.42 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffract-ometer	R_{int} = 0.018
$\omega/2\theta$ scans	θ_{max} = 26.3°
Absorption correction: empirical *via* ψ scans (Fair, 1990)	h = −10 → 0
	k = −11 → 0
	l = −19 → 19
T_{min} = 0.932, T_{max} = 1.00	3 standard reflections
2893 measured reflections	frequency: 120 min
2546 independent reflections	intensity decay: 0.6%
1986 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F	H-atom parameters constrained
R = 0.038	$w = 1/[\sigma(F^2) + (0.02F)^2 + 1]$
wR = 0.043	$(\Delta/\sigma)_{max} < 0.001$
S = 0.70	$\Delta\rho_{max}$ = 0.25 e Å^{-3}
1890 reflections	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
190 parameters	

Table 1
Selected geometric parameters (Å, °) for (I).

S1—C2	1.813 (3)	N3—N4	1.388 (2)
S1—C3	1.732 (3)	N3—C3	1.367 (3)
O1—C5	1.361 (3)	N3—C4	1.371 (3)
O1—C8	1.364 (3)	N4—C1	1.293 (3)
N1—N2	1.400 (3)	C1—C2	1.505 (3)
N1—C4	1.310 (3)	C1—C9	1.475 (3)
N2—C3	1.301 (3)		
C2—S1—C3	94.0 (1)	S1—C3—N2	129.4 (2)
C5—O1—C8	106.1 (2)	S1—C3—N3	119.7 (2)
N2—N1—C4	107.6 (2)	N2—C3—N3	110.8 (2)
N1—N2—C3	106.8 (2)	N1—C4—N3	109.7 (2)
N4—N3—C3	129.2 (2)	N1—C4—C5	126.5 (2)
N4—N3—C4	125.0 (2)	N3—C4—C5	123.6 (2)
C3—N3—C4	105.0 (2)	O1—C5—C4	114.8 (2)
N3—N4—C1	115.7 (2)	O1—C5—C6	110.0 (2)
N4—C1—C2	122.7 (2)	C4—C5—C6	135.1 (2)
N4—C1—C9	116.2 (2)	C5—C6—C7	106.7 (2)
C2—C1—C9	121.0 (2)	C6—C7—C8	106.5 (2)
S1—C2—C1	111.9 (2)	O1—C8—C7	110.7 (3)

Table 2
Hydrogen-bonding or short-contact geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$N4	0.95	2.60	3.063 (3)	110
C2—H22$\cdots$N2^i	0.97	2.62	3.286 (3)	126

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

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Table 3
Selected geometric parameters (Å, °) for (II).

S1—C2	1.815 (2)	N3—N4	1.389 (2)
S1—C3	1.733 (2)	N3—C3	1.369 (2)
O1—C5	1.364 (2)	N3—C4	1.374 (2)
O1—C8	1.365 (3)	N4—C1	1.296 (3)
N1—N2	1.403 (3)	C1—C2	1.506 (3)
N1—C4	1.311 (2)	C1—C9	1.477 (2)
N2—C3	1.306 (3)		
C2—S1—C3	94.1 (1)	S1—C3—N2	130.1 (2)
C5—O1—C8	106.1 (2)	S1—C3—N3	119.3 (1)
N2—N1—C4	107.8 (2)	N2—C3—N3	110.6 (2)
N1—N2—C3	106.8 (2)	N1—C4—N3	109.6 (2)
N4—N3—C3	128.6 (2)	N1—C4—C5	127.6 (2)
N4—N3—C4	125.1 (2)	N3—C4—C5	122.7 (2)
C3—N3—C4	105.2 (2)	O1—C5—C4	115.9 (2)
N3—N4—C1	115.4 (1)	O1—C5—C6	109.5 (2)
N4—C1—C2	122.8 (2)	C4—C5—C6	134.5 (2)
N4—C1—C9	115.6 (2)	C5—C6—C7	107.3 (2)
C2—C1—C9	121.5 (2)	C6—C7—C8	106.1 (2)
S1—C2—C1	110.4 (1)	O1—C8—C7	111.0 (2)

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *MolEN*; program(s) used to refine structure: *MolEN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN* and *PLATON* (Spek, 1990).

Table 4
Hydrogen-bonding or short-contact geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$N4	0.95	2.53	3.018 (3)	112

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1344). Services for accessing these data are described at the back of the journal.

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