$C_{14}H_{13}IO_3$

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7-Methyl-3-(2-methylphenyl)-1,2,4-triazolo-[3,4-b][1,3]benzothiazole, (I), and 7-methyl-3-(4-methylphenyl)-1,2,4-triazolo[3,4-b]-[1,3]benzothiazole, (II)

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Abstract

The two title compounds, both $C_{16}H_{13}N_3S$, were synthesized by photolysis of 4-(2-bromo-4-methylphenyl)-5-(2-methylphenyl)-1,2,4-triazole-3-thione and 4-(2-bromo-4-methylphenyl)-5-(4-methylphenyl)-1,2,4-triazole-3-thione, respectively. Both molecules consist of a 7-

methyl-1,2,4-triazolo[3,4-b][1,3]benzothiazole moiety linked to a methyl-substituted phenyl ring. The interplanar angle between the triazole–benzothiazole fused fragment and the phenyl ring is 66.8 (1)° in (I) and 35.4 (1)° in (II). The structures of both compounds are stabilized by weak C—H···N-type interactions.

Comment

The benzothiazole moiety possesses many useful pharmacological properties, such as acting as antitumour (Shi et al., 1996), antifungal (Kü et al., 1997), antimicrobial (Kü et al., 1995), antineoplastic (Alarcón et al., 1998) and anti-inflammatory (Dannhardt et al., 1997) agents. Condensed [1,2,4]triazoles are also medicinally important compounds (Francis & Gelotte, 1988; Kottke et al., 1983). Substituted 1,2,4-triazolo[3,4-b]-benzothiazoles have been prepared from the respective triazole-3-thiones by a photochemical method. In order to confirm the identity of the compounds and to study the stereochemistry and the structure–activity relationships, a detailed crystallographic study has been carried out and the results are presented here.

In the following discussion, the values given without brackets are for (I), and those within square brackets are for (II). Figs. 1 and 2 show the ORTEP (Johnson, 1965) drawings of the two molecules in the same relative orientation. The structure consists of methylbenzothia-

(I)   (II)
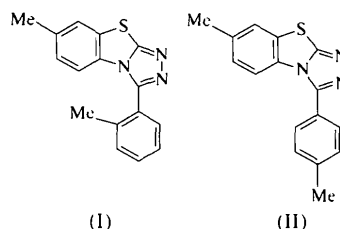
zole–triazole fused fragments linked to a methylphenyl group. The N—N, C—N and S—C bond distances in the fused fragment system are comparable with those found in related structures (Ruiwu et al., 1997; Palmer & Parsons, 1996). The S1—C7 distance of 1.728 (3) [1.736 (3) Å], and the C7—N1 and C7—N2 distances of 1.367 (3) [1.370 (3) Å] and 1.307 (4) [1.302 (3) Å], respectively, clearly show the resonance of the thiourea system (Valle et al., 1970). The C7—S1—C1 angle of 89.3 (1) [89.4 (1)°] suggests that the S atom uses only p-orbitals to form bonds with C1 and C7. In order to maintain the planar conformation of the thiazole ring, the other bond angles, namely, C7—N1—C6, N1—C6—C1, C6—C1—S1 and S1—C7—N1, are in the range 110.1 (2)–114.4 (2)° [109.6 (2)–114.1 (2)°], which is less than the ideal 120° for sp^2 orbital hybridizations of C and N atoms and greater than the ideal 108° required for a regular planar pentagon. These results agree with a similar structure found in 2-amino-6-fluorobenzothiazole (Jai-Nhuknan et al., 1997). The

benzothiazole-1,2,4-triazole fragment is planar, with a maximum deviation of 0.045 (3) for N2 in (I) and 0.064 (2) Å for N1 in (II).
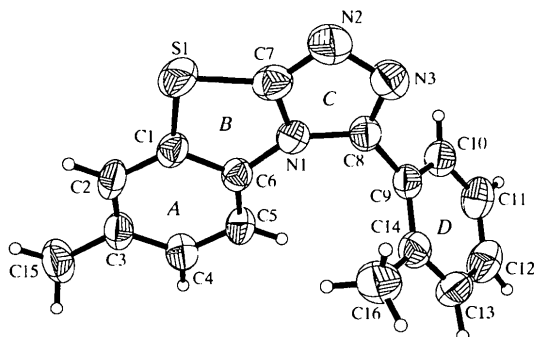

Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.
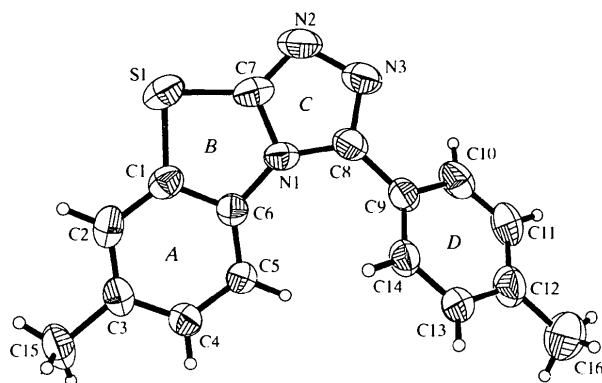

Fig. 2. The molecular structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

The central fused ring systems of (I) and (II) have a high degree of similarity, as shown by the close agreement between the corresponding bond distances and bond and torsion angles. In contrast, the substituted phenyl ring deviates from this plane by an angle of 66.8 (1) in (I) and 35.4 (1)° in (II) and adopts an equatorial orientation. The endocyclic bond angles are larger than normal bond angle values. The geometry of the basic [3,4-*b*]benzothiazole ring, which is aromatic and therefore planar, is well known from crystallographic data. The dihedral angles between the rings are *A*/*B* 0.5 (1) [3.0 (1)°], *A*/*C* 2.3 (1) [4.8 (1)°] and *B*/*C* 1.8 (1)° [3.1 (1)°]. The structures are stabilized by van der Waals interactions and by two weak C—H···N-type interactions (Tables 2 and 4).

Experimental

Compound (I) was obtained from the photolysis of 4-(2-bromo-4-methylphenyl)-5-(2-methylphenyl)-1,2,4-triazole-

3-thione on irradiation in a Rayonet Applied Photophysics reactor for 24 h in absolute methanol (Jayanthi *et al.*, 1997); m.p. 393–395 K. The compound was recrystallized from an ethyl acetate and petroleum ether mixture (1:6) by slow evaporation. Compound (II) was obtained from the photolysis of 4-(2-bromo-4-methylphenyl)-5-(4-methylphenyl)-1,2,4-triazole-3-thione in a Rayonet Applied Photophysics reactor for 18 h in absolute methanol (Jayanthi *et al.*, 1997); m.p. 455–459 K. The compound was recrystallized from an ethyl acetate and petroleum ether mixture (1:6) by slow evaporation.

Compound (I)

Crystal data

$C_{16}H_{13}N_3S$	Mo $K\alpha$ radiation
$M_r = 279.35$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 3498
$P2_1/n$	reflections
$a = 9.7934 (2)$ Å	$\theta = 1.52–33.24°$
$b = 9.5005 (1)$ Å	$\mu = 0.225$ mm^{-1}
$c = 15.2958 (1)$ Å	$T = 293 (2)$ K
$\beta = 102.297 (1)°$	Block
$V = 1390.50 (3)$ Å^3	$0.40 \times 0.22 \times 0.16$ mm
$Z = 4$	Colourless
$D_x = 1.334$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens SMART CCD area-detector diffractometer	3175 independent reflections
	1751 reflections with
ω scans	$I > 2\sigma(I)$
Absorption correction:	$R_{int} = 0.054$
empirical *via SADABS*	$\theta_{max} = 27.50°$
(Sheldrick, 1996)	$h = -12 \rightarrow 12$
$T_{min} = 0.914$, $T_{max} = 0.965$	$k = 0 \rightarrow 12$
8672 measured reflections	$l = 0 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.163$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.959$	$\Delta\rho_{max} = 0.306$ e Å^{-3}
3175 reflections	$\Delta\rho_{min} = -0.292$ e Å^{-3}
209 parameters	Extinction correction: none
H atoms treated by a	Scattering factors from
mixture of independent	*International Tables for*
and constrained refinement	*Crystallography* (Vol. C)

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

S1—C7	1.728 (3)	N2—C7	1.307 (4)
S1—C1	1.763 (3)	N2—N3	1.402 (3)
N1—C7	1.367 (3)	N3—C8	1.313 (3)
N1—C8	1.377 (3)	C3—C15	1.505 (4)
N1—C6	1.411 (3)	C14—C16	1.507 (4)
C7—S1—C1	89.3 (1)	N2—C7—S1	135.7 (2)
C8—N1—C6	140.4 (2)		
C7—N2—N3—C8	0.2 (3)	C6—N1—C7—S1	2.4 (3)
C7—S1—C1—C6	0.86 (19)	C1—S1—C7—N1	-1.8 (2)
S1—C1—C6—N1	0.3 (2)	N2—N3—C8—N1	0.3 (3)
N3—N2—C7—N1	-0.6 (3)	C7—N1—C8—N3	-0.7 (3)
C8—N1—C7—N2	0.8 (3)		

Table 2. *Hydrogen-bonding and short-contact geometry*
$(\mathring{A}, °)$ *for (I)*

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···N3^i	0.87 (3)	2.69 (3)	3.530 (4)	161 (2)
C11—H11···N2^{ii}	0.96 (3)	2.68 (3)	3.518 (4)	147 (3)

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

Compound (II)

Crystal data

$C_{16}H_{13}N_3S$
$M_r = 279.35$
Orthorhombic
$Pca2_1$
$a = 24.4820$ (12) Å
$b = 7.5509$ (4) Å
$c = 7.5060$ (4) Å
$V = 1387.57$ (12) Å^3
$Z = 4$
$D_x = 1.337$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5360
  reflections
$\theta = 1.35–33.20°$
$\mu = 0.226$ mm^{-1}
$T = 293$ (2) K
Rectangular block
$0.52 \times 0.38 \times 0.24$ mm
Yellow

Data collection

Siemens SMART CCD area-
  detector diffractometer
ω scans
Absorption correction:
  empirical *via SADABS*
  (Sheldrick, 1996)
  $T_{min} = 0.882$, $T_{max} = 0.962$
8674 measured reflections

3057 independent reflections
2435 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 27.50°$
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 9$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.125$
$S = 1.016$
3057 reflections
209 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0727P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.370$ e Å^{-3}
$\Delta\rho_{min} = -0.329$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Table 3. *Selected geometric parameters $(\mathring{A}, °)$ for (II)*

S1—C7	1.736 (3)	N2—C7	1.302 (3)
S1—C1	1.754 (3)	N2—N3	1.394 (3)
N1—C7	1.370 (3)	N3—C8	1.323 (3)
N1—C8	1.378 (3)	C3—C15	1.509 (4)
N1—C6	1.422 (3)	C12—C16	1.513 (4)
C7—S1—C1	89.4 (1)	N2—C7—S1	134.3 (2)
C8—N1—C6	141.6 (2)		
C7—N2—N3—C8	-0.6 (4)	C8—N1—C7—N2	0.0 (3)
C7—S1—C1—C6	-0.4 (2)	C6—N1—C7—S1	5.0 (3)
S1—C1—C6—N1	3.1 (3)	C1—S1—C7—N1	-2.6 (2)
C7—N1—C6—C1	-5.1 (3)	N2—N3—C8—N1	0.6 (3)
N3—N2—C7—N1	0.4 (4)	C7—N1—C8—N3	-0.4 (3)

Table 4. *Hydrogen-bonding and short-contact geometry*
$(\mathring{A}, °)$ *for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···N2^i	0.91 (3)	2.81 (3)	3.577 (4)	143 (2)
C13—H13···N3^{ii}	0.88 (3)	2.69 (3)	3.451 (4)	145 (3)

Symmetry codes: (i) $\frac{3}{2} - x, 1 + y, \frac{1}{2} + z$; (ii) $x, 1 + y, z$.

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was $-35°$. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections, and was found to be negligible.

The H atoms of the C15 and C16 methyl groups were fixed geometrically and refined using a constrained model. The other H atoms were refined independently in both compounds.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structures: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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5-(2-Chlorophenyl)-4-phenyl-3,4-dihydro-2H-1,2,4-triazole-3-thione

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Abstract

The title compound, $C_{14}H_{10}ClN_3S$, was prepared by the reaction of benzhydrazide and 2-chlorophenyl isothiocyanate. The triazole ring is planar to within 0.003 (2) Å. The dihedral angles between the phenyl rings and the 1,2,4-triazole ring are 59.2 (1) and 58.9 (1)°. The dihedral angle between the two phenyl rings is 63.7 (1)°. The molecules are linked by N—H···S hydrogen bonds.

Comment

Bridging systems based on the 1,2,4-triazole ring are interesting owing to their similarity to the 1,3-imidazole bridging found in the Cu–Zn protein superoxide dismutase (Feiters, 1990). Condensed 1,2,4-triazoles are biologically important compounds (Kottke et al., 1983; Francis et al., 1988). The ability of triazoles to form a bridge between metal ions makes these complexes particularly important for magnetochemistry applications (Groenneveld et al., 1982). The 1,2,4-triazole ring systems are typical planar 6π-electron partially aromatic systems. They possess an extensive chemistry (Temple, 1981; Benson, 1967). 1,2,4-Triazole and its derivatives are starting materials for the synthesis of many heterocycles (Desenko, 1995). Thiosemicarbazones and related compounds with S—C—N linkages display a wide range of biological activities. Metal complexes of these compounds have been synthesized in order to gauge their activity compared with that of the free ligand and to determine the coordination behaviour of the ligand towards the metal (Offiong, 1995; West et

al., 1993). Apart from its extensive chemical significance, the 1,2,4-triazole nucleus is also found to be associated with diverse medicinal properties, such as analgesic, anti-asthmatic, diuretic, antifungal and anti-inflammatory activities (Mohamed et al., 1993). Knowledge of the molecular structure of these compounds is important for understanding their reactivity under condensation reaction conditions. Therefore, the crystal structure analysis of the title compound, (I), was undertaken.
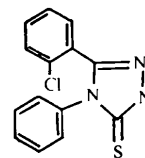
(I)

The structure of (I) (Fig. 1) consists of one 1,2,4-triazole-3-thione moiety with two benzene rings substituted at N1 (ring A) and C2 (ring B). The C=S bond length [1.6781 (18) Å] agrees with literature values (Allen et al., 1987; Sen et al., 1996). The triazole ring is planar and the maximum deviation observed is −0.003 (2) Å for atom N3. The S atom is also located in the plane. The C14—Cl1 bond length [1.734 (2) Å] conforms with those found in 3,5-bis(2-pyridyl)-4-p-chlorophenyl-4H-1,2,4-triazole (Wang et al., 1998). The Cl atom deviates by 0.127 (1) Å from the mean plane of the phenyl ring B. The average bond lengths and angles in ring A are 1.380 (3) Å and 120.0 (2)°; similarly, the average bond lengths and angles in ring B are 1.381 (3) Å and 120.0 (2)°. The orientation of the 1,2,4-triazole ring with respect to the two phenyl rings is given by the torsion angles C2—N1—C3—C8 = −125.3 (2), C1—N1—C3—C4 = −117.6 (2), N2—C2—C9—C14 = −120.4 (2) and N1—C2—C9—C10 = −120.3 (2)°. The
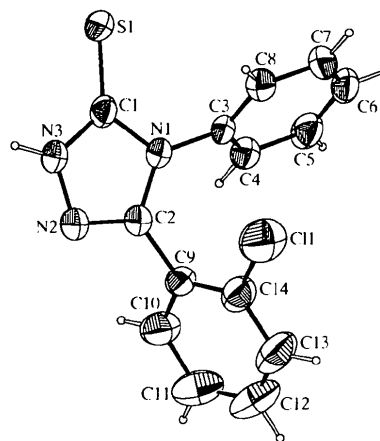

Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of an arbitrary radius.