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3-Cyclopropyl-1,2,4-triazolo[3,4-*b*]benzothiazole monohydrate†

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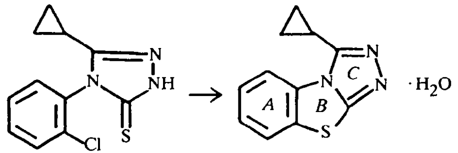
Abstract

The title structure, $C_{11}H_9N_3S{\cdot}H_2O$, contains two crystallographically independent molecules, each consisting of a 1,2,4-triazolo[3,4-*b*]benzothiazole-fused ring fragment substituted with a cyclopropyl ring, and a water molecule. The geometry of both molecules differs slightly. Both molecules are planar within 0.041 and 0.03 Å. The dihedral angle between triazole and the cyclopropyl ring is 60.0 (1) and 61.7 (1)° for molecules *A* and *B*, respectively, and the cyclopropyl ring is inclined at an angle of 2.0 (1) and 1.2 (1)° to the benzothiazole moiety for molecules *A* and *B*, respectively. The packing of the molecules is stabilized by O—H···N-type hydrogen bonds.

Comment

The triazole part of the title compound is used as an antimicrobial (Habib *et al.*, 1997), potential antiviral (Ergen *et al.*, 1996), anti-HIV-1 (Invidiata *et al.*, 1996), antifungal, antimycobacterial and anticonvulsant (Gülerman *et al.*, 1997) agent. It is also a highly potent eosinophilia inhibitor (Naito *et al.*, 1996) and is used as a fungicide (Crofton, 1996) and a herbicide (Tada *et al.*, 1995). Some of the 1,2,4-triazolo[3,4-*b*] derivatives have been evaluated for their antibacterial activity against both Gram-positive and Gram-negative bacteria (Bs *et al.*, 1996). Benzothiazoles are extremely important heterocycles from an industrial, agricultural, biological and pharmaceutical point of view. Benzothiazoles are used as antineoplastic agents and show antinociceptive, anti-inflammatory and antitumour activities (Bradshaw *et al.*, 1998; Dögruer *et al.*, 1998). The fused benzothiazole–triazole fragment may have useful medicinal properties. Some Schiff bases derived from thiazole and benzothiazoles (Dash *et al.*, 1980) and several derivatives of the styryl–benzothiazoles have shown biological activity (Cox *et al.*, 1982).

In view of the above biological activities associated with the benzothiazole and triazole moieties, we focused our interest on the structure determination of 1,2,4-triazolo[3,4-*b*]benzothiazole, incorporating both the units. Substituted 1,2,4-triazolo[3,4-*b*]benzothiazoles were prepared from the respective triazole-3-thiones by photochemical methods. In order to confirm the identity and to study the stereochemistry, a single-crystal X-ray structure determination was carried out. It was found that the asymmetric unit of the title compound, (I), consists of two crystallographically unique but structurally similar molecules, along with two water molecules.



(I)

In both molecules (Fig. 1), the average C—N, C—S and C—C distances (1.370, 1.730 and 1.390 Å, respectively) for the benzothiazole are similar to those found in a related structure (Muir *et al.*, 1987; Ruiwu *et al.*, 1997). It should be mentioned that the large size of the S atom compared with the N atom results in a reduction of the average C—S—C angle [89.24 (7)°] compared with the C—N—C angle [114.74 (12)°] and the other internal angles [111.64° (N—C—C, C—C—S)] within the thiazole ring. This suggests that the S atom might be using unhybridized *p* orbitals for bonding (Muir *et al.*, 1987; Cox *et al.*, 1997). In the triazole rings in both molecules, the average N—C distances [1.313 (2) Å] agree well with those found in 3,5-bis(2-pyridyl)-4-*p*-chlorophenyl-4*H*-1,2,4-triazole (Wang *et al.*, 1998). The average N—N distance [1.411 (2) Å] is slightly greater than the literature value (Cromer & Storm, 1991).

Both the benzene and thiazole rings in the benzothiazole moiety are essentially planar, with no atom deviating from the plane by more than 0.027 (2) Å (C7*A*) in molecule *A* and 0.026 (2) Å in molecule *B*. The orientation of the cyclopropyl ring is explained by the torsion angles N1*A*—C8*A*—C9*A*—C10*A* of 154.57 (17) and N3*A*—C8*A*—C9*A*—C11*A* of −95.2 (2)° in molecule *A*, and N1*B*—C8*B*—C9*B*—C10*B* of −159.59 (17) and N3*B*—C8*B*—C9*B*—C11*B* of 89.5 (2)° in molecule *B*.

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† DCB contribution No. 886.

The cyclopropyl ring adopts an equatorial orientation and makes angles of 60.0 (1) (molecule *A*) and 61.7 (1)° (molecule *B*) with the triazole moiety. The dihedral angles between the best plane of rings *A*, *B* and *C* are: *A*/*B* 1.2 (1), *B*/*C* 1.3 (1) and *C*/*A* 2.5 (1)° for molecule *A*; *A*/*B* 0.5 (1), *B*/*C* 1.7 (1) and *C*/*A* 2.3 (1)° for molecule *B*. Due to the fusion of the benzothiazole and triazole moieties, the ring-junction endocyclic bond angles are slightly greater than normal values. O—H···N hydrogen bonds formed between the organic molecules and the water molecules stabilize the system in the solid-state conformation. A view showing the water-mediated hydrogen bonds of the molecule is shown in Fig. 2.

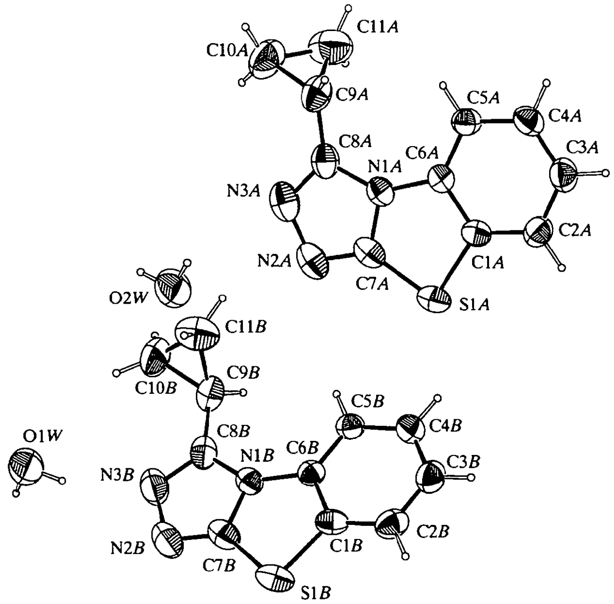

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

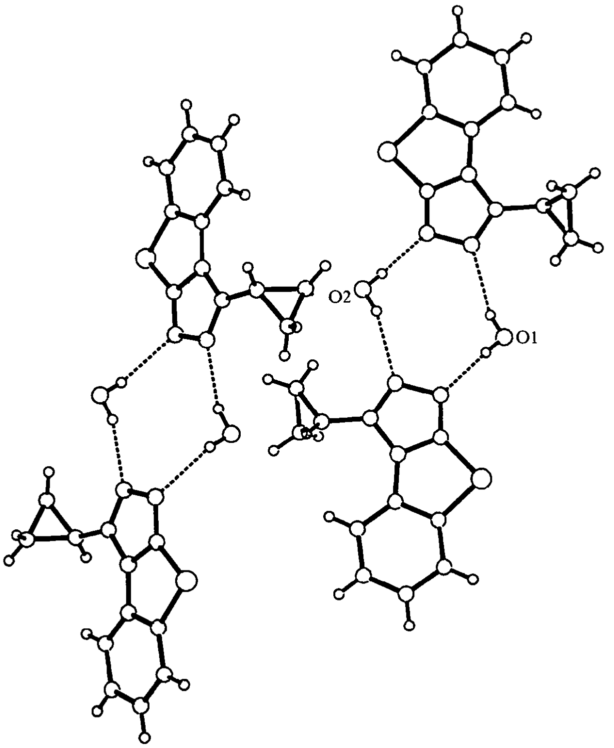

Fig. 2. A view of (I) showing the water-mediated hydrogen bonds.

Experimental

The title compound, (I), was obtained from the photolysis of 4-(2-chlorophenyl)-5-cyclopropyl-1,2,4-triazole-3-thione (0.61 g, 2.43 mmol) in absolute methanol (180 ml). It was irradiated for 1 h in a thin-file reactor (equipped with one lamp) at 245 nm. A slow stream of nitrogen gas was passed through the solution during the course of the reaction. After completion of the reaction, the solvent was removed and the residue, on chromatographic purification using an ethyl acetate/petroleum ether mixture (1:6), afforded compound (I). A single crystal was grown by slow evaporation from absolute methanol (Jayanthi & Ramakrishnan, 1998).

Crystal data

$C_{11}H_9N_3S{\cdot}H_2O$
$M_r = 233.29$
Triclinic
$P\bar{1}$
$a = 7.5453\ (3)$ Å
$b = 12.0114\ (5)$ Å
$c = 13.5984\ (5)$ Å
$\alpha = 109.342\ (1)°$
$\beta = 99.980\ (1)°$
$\gamma = 98.593\ (1)°$
$V = 1116.54\ (8)$ Å^3
$Z = 4$
$D_x = 1.388$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6711 reflections
$\theta = 1.45$–$33.18°$
$\mu = 0.271$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.68 × 0.64 × 0.44 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.77$, $T_{\max} = 0.93$
6711 measured reflections
4458 independent reflections

3903 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 26.50°$
$h = -9 \rightarrow 7$
$k = -15 \rightarrow 14$
$l = -16 \rightarrow 17$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.103$
$S = 1.05$
4458 reflections
305 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.2685P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1*A*—C7*A*	1.7421 (17)	S1*B*—C7*B*	1.7404 (18)
S1*A*—C1*A*	1.7651 (15)	S1*B*—C1*B*	1.7672 (16)
N1*A*—C7*A*	1.369 (2)	N1*B*—C7*B*	1.3711 (19)
N1*A*—C8*A*	1.3779 (19)	N1*B*—C8*B*	1.3778 (19)
N1*A*—C6*A*	1.4076 (18)	N1*B*—C6*B*	1.4098 (18)
N2*A*—C7*A*	1.308 (2)	N2*B*—C7*B*	1.306 (2)
N2*A*—N3*A*	1.412 (2)	N2*B*—N3*B*	1.410 (2)
N3*A*—C8*A*	1.317 (2)	N3*B*—C8*B*	1.318 (2)
C8*A*—C9*A*	1.469 (2)	C8*B*—C9*B*	1.466 (2)
C9*A*—C10*A*	1.489 (2)	C9*B*—C10*B*	1.478 (2)
C9*A*—C11*A*	1.487 (3)	C9*B*—C11*B*	1.483 (3)
C7*A*—S1*A*—C1*A*	89.22 (7)	C7*B*—S1*B*—C1*B*	89.26 (7)
C7*A*—N1*A*—C8*A*	105.51 (13)	C7*B*—N1*B*—C8*B*	105.48 (13)
C7*A*—N1*A*—C6*A*	114.83 (12)	C8*B*—N1*B*—C6*B*	139.87 (13)
C8*A*—N1*A*—C6*A*	139.63 (13)	C7*B*—N2*B*—N3*B*	105.44 (13)
C7*A*—N2*A*—N3*A*	105.30 (14)	C2*B*—C1*B*—S1*B*	126.40 (12)
C5*A*—C6*A*—N1*A*	128.64 (13)	C5*B*—C6*B*—N1*B*	128.66 (13)
N2*A*—C7*A*—S1*A*	135.70 (13)	N2*B*—C7*B*—S1*B*	135.63 (13)
N3*A*—C8*A*—C9*A*	127.96 (15)	N3*B*—C8*B*—C9*B*	127.05 (15)
N1*A*—C8*A*—C9*A*	123.53 (14)	N1*B*—C8*B*—C9*B*	124.49 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H2O1···N3*B*	0.88 (4)	2.16 (4)	3.011 (3)	163 (3)
O2*W*—H2O2···N3*A*^{i}	0.85 (4)	2.26 (4)	3.067 (3)	157 (3)
O2*W*—H1O2···N2*A*^{ii}	0.84 (3)	2.14 (3)	2.980 (2)	177 (3)
O1*W*—H1O1···N2*B*^{iii}	0.80 (3)	2.22 (3)	3.006 (2)	167 (3)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, -y, -z$.

H atoms on O1*W* and O2*W* were located by difference Fourier synthesis, while others were placed in calculated positions using a riding model.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1448). Services for accessing these data are described at the back of the journal.

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Tetraethylammonium (*N*,*N*-diethyldithiocarbamato-*S*,*S*′)tetraiodotellurate(IV)

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Abstract

The title compound, $[(C_2H_5)_4N][TeI_4L]$ (L is diethyldithiocarbamate, $C_5H_{10}NS_2$) or $C_8H_{20}N^+\cdot C_5H_{10}I_4NS_2Te^-$, was prepared by the addition of tetraethylammonium

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