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Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.050
 wR factor = 0.107
Data-to-parameter ratio = 14.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

2-[[4-(3-Mesityl-3-methylcyclobutyl)thiazol-2-yl]-hydrazono]-1,2-diphenylethanol ethanol solvate

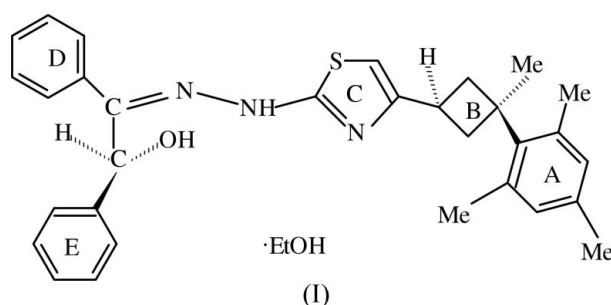
In the title compound, $\text{C}_{31}\text{H}_{33}\text{N}_3\text{OS}\cdot\text{C}_2\text{H}_6\text{O}$, the dihedral angle between the least-squares planes of the thiazole and mesityl rings is $77.3(1)^\circ$. There are intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and intermolecular $\text{O}-\text{H}\cdots\text{N/O}$ and $\text{C}-\text{H}\cdots\text{O}$ interactions.

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Comment

Various hydrazone compounds possess strong bactericidal, herbicidal, insecticidal and fungicidal properties (Sahni *et al.*, 1977). In addition, hydrazones have analytical applications (Jensen & Pflaum, 1967). Hydrazones have been widely studied as chelating ligands for the spectrophotometric and fluorimetric determination of trace metal ions (Katyal & Dutt, 1975; Galiano-Roth & Collum, 1988). Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic activities (Williams, 1972), and the sulfur-containing Schiff bases are particularly effective. Benzothiazolium groups have been used in organic dyes as either electron-withdrawing or electron-donating substituents, depending on whether the N atom is cationic or not (Zollinger, 1991). Various thiazole derivatives show herbicidal, anti-inflammatory, antimicrobial and antiparasite activity (Koparr *et al.*, 2004; Ahmedzade *et al.*, 2003) and also liquid crystal properties (Coghi *et al.*, 1976). In this paper, we report the structure of the title compound, (I).



A view of the asymmetric unit of (I) is shown in Fig. 1, and selected geometric parameters are given in Table 1. The central $\text{NH}-\text{N}=\text{C}-\text{C}$ fragment is strictly planar. The molecule adopts a *Z* geometry about the azomethine $\text{C}=\text{N}$ double bond, the $\text{N}2-\text{N}3=\text{C}18-\text{C}19$ torsion angle being $1.3(5)^\circ$. The *Z* configuration allows the formation of an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond (Table 2). The angles between mesityl ring *A*, thiazole ring *C* and benzene rings *D* and *E* are $A/C = 77.3(1)^\circ$, $C/D = 20.2(2)^\circ$ and $D/E = 85.8(1)^\circ$. The steric interaction between the substituent groups on the cyclobutane ring causes significant deformation

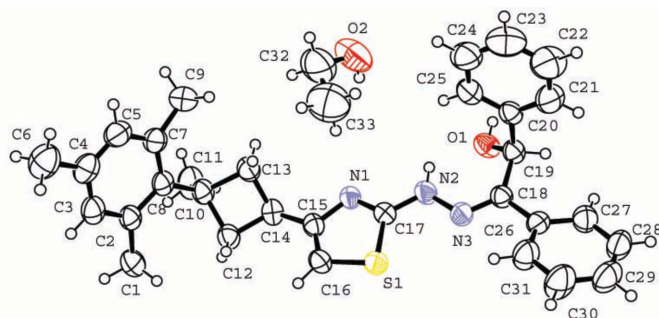


Figure 1
The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

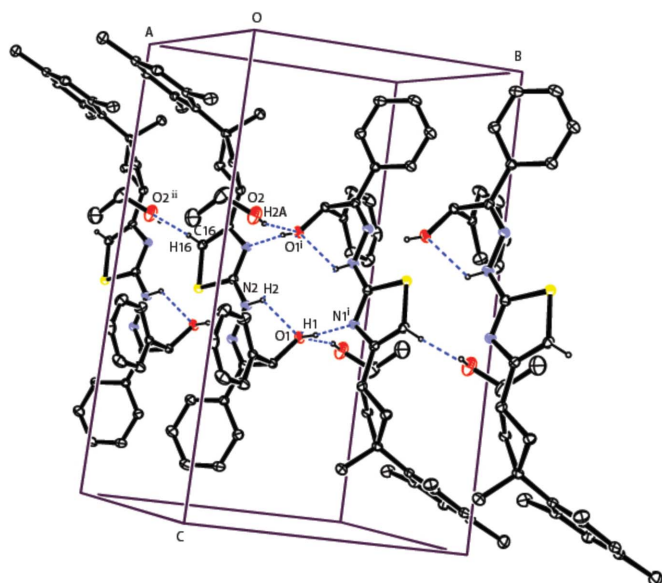


Figure 2
The crystal structure of (I). H atoms have been omitted, except for those involved in hydrogen bonds (dashed lines). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.]

of the ring from planarity. In the cyclobutane ring *B*, the C12/C14/C13 plane makes an angle of $27.9(3)^\circ$ with the C12/C10/C13 plane. Similar puckering of a cyclobutane ring has been reported previously [23.5° (Swenson *et al.*, 1997) and $29.03(13)^\circ$ (Yüksektepe *et al.*, 2004)].

In the crystal structure, molecules related by an inversion centre are connected by $O1-H1 \cdots N1^i$ [symmetry code: (i) $1 - x, 1 - y, 1 - z$] hydrogen bonds, forming dimers (Fig. 2). These dimers are interlinked by $O2-H2A \cdots O1^i$ and $C16-H16 \cdots O2^{ii}$ [symmetry code: (ii) $1 + x, y, z$] hydrogen bonds involving the ethanol solvent molecule. There is also a $C-H \cdots \pi$ interaction between ring *A* and atom H22(C22) of ring *E*, the distance between H22 and the centroid *Cg1* of ring *E* being 2.90 \AA [symmetry code: $1 - x, -y, 1 - z$], and the $C22-H22 \cdots Cg1$ angle being 136° .

Experimental

Compound (I) was synthesized by the following procedure. To a solution of benzoin (2.1224 g, 10 mmol) in ethanol (50 ml), thio-

semicarbazide (0.9113 g, 10 mmol) was added in portions. Subsequently, a solution of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl)-cyclobutane (2.6479 g, 10 mmol) in absolute ethanol (20 ml) was added. After the addition of the α -haloketone, the temperature was raised to $323\text{--}328 \text{ K}$ and kept at this temperature for 2 h. The solution was then cooled to room temperature and made alkaline with an aqueous solution of NH_3 (5%), and the dirty-yellow precipitate which formed was separated by suction, washed several times with aqueous NH_3 solution and dried in air. Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution (yield 69%, m.p. 417 K). Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3468 (O—H), 3254 (N—H), 1609 (C=N carbazone), 1586 (C=N thiazole), 682 (C—S—C thiazole); $^1\text{H NMR}$ ($\text{CDCl}_3, \delta, \text{p.p.m.}$): 1.53 (s, 3H, $-\text{CH}_3$ on cyclobutane), 2.14 (s, 1H, $-\text{NH}-$), 2.17 (s, 1H, $-\text{OH}$), 2.21 (s, 9H, $-\text{CH}_3$ on mesitylene), $2.44\text{--}2.59$ (m, 4H, $-\text{CH}_2-$ on cyclobutane), 3.34 (q, $J = 9.1 \text{ Hz}$, 1H, $>\text{C}-\text{H}$ on cyclobutane), 6.12 (s, 1H, $=\text{CH}-\text{S}$), 6.25 (s, 1H, $-\text{H}$ on benzoin), 6.74 (s, 2H, aromatics on mesitylene), $7.25\text{--}7.42$ (m, 8H, aromatics), 7.69 (dd, $J = 2.2 \text{ Hz}$, 2H, aromatics).

Crystal data

$\text{C}_{31}\text{H}_{33}\text{N}_3\text{OS}\cdot\text{C}_2\text{H}_6\text{O}$

$M_r = 541.76$

Triclinic, $P\bar{1}$

$a = 9.0997(11) \text{ \AA}$

$b = 9.9104(14) \text{ \AA}$

$c = 17.540(2) \text{ \AA}$

$\alpha = 92.876(10)^\circ$

$\beta = 100.365(10)^\circ$

$\gamma = 105.410(10)^\circ$

$V = 1492.0(3) \text{ \AA}^3$

$Z = 2$

$D_x = 1.206 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\mu = 0.14 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Prism, colourless

$0.32 \times 0.22 \times 0.16 \text{ mm}$

Data collection

Stoe IPDS 2 diffractometer

ω scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\text{min}} = 0.955, T_{\text{max}} = 0.986$

13616 measured reflections

5247 independent reflections

2724 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.107$

$S = 0.87$

5247 reflections

358 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.015$

$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

| | | | |
|---------------|------------|---------------|-----------|
| S1—C17 | 1.716 (3) | N2—N3 | 1.363 (3) |
| S1—C16 | 1.730 (3) | N2—C17 | 1.364 (3) |
| N1—C17 | 1.306 (3) | N3—C18 | 1.279 (3) |
| N1—C15 | 1.385 (3) | | |
| C17—S1—C16 | 88.17 (14) | C18—N3—N2 | 120.6 (2) |
| C17—N1—C15 | 109.9 (2) | N3—C18—C26 | 114.5 (2) |
| N3—N2—C17 | 117.2 (2) | N3—C18—C19 | 126.6 (2) |
| C17—N2—N3—C18 | 179.4 (3) | N2—N3—C18—C19 | 1.3 (5) |
| N3—N2—C17—S1 | 5.8 (4) | N3—C18—C19—O1 | −35.3 (4) |
| N2—N3—C18—C26 | 176.6 (2) | | |

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

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1...N1 ⁱ | 0.84 | 1.84 | 2.674 (3) | 172 |
| O2—H2A...O1 ⁱ | 0.82 | 2.12 | 2.913 (4) | 163 |
| N2—H2...O1 | 0.86 | 2.06 | 2.642 (3) | 126 |
| C16—H16...O2 ⁱⁱ | 0.93 | 2.49 | 3.412 (4) | 177 |

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

The hydroxy H atoms were located in a difference map. The other H atoms were placed in idealized positions, with C—H = 0.93–0.98 Å and N—H = 0.86 Å. All H atoms were then treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$, or $1.5U_{\text{eq}}(\text{C}, \text{O})$ for methyl and hydroxy groups.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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