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4-Bromo-2-{[4-(3-mesityl-3-methylcyclobutyl)thiazol-2-yl]hydrazonomethyl}phenol, with N—H···N, C—H···π and π–π interactions

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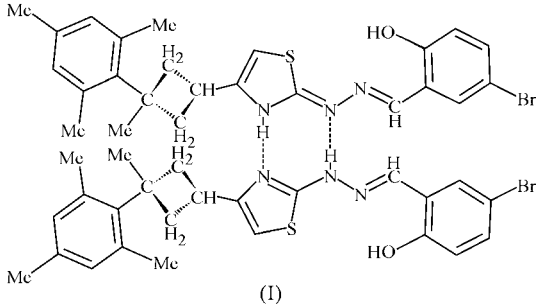
The title compound, $C_{24}H_{26}BrN_3OS$, crystallizes in the triclinic space group $P\overline{1}$, with two independent molecules in the asymmetric unit. The molecules adopt an *E* geometry about the azomethine C=N double bond. The structure is stabilized as dimers by N—H···N hydrogen bonding. C—H···π and π–π interactions are also effective in the crystal packing.

Comment

Hydrazine is a highly reactive base and reducing agent. Its primary uses are as a high-energy rocket propellant, as a reactant in military fuel cells, in nickel plating, in the polymerization of urethane, for removal of halogens from wastewater, as an oxygen scavenger in boiler feed water to inhibit corrosion and in photographic development (Von Burg & Stout, 1991). Hydrazine was historically used experimentally as a therapeutic agent in the treatment of tuberculosis, sickle cell anemia and non-specific chronic illnesses (Von Burg & Stout, 1991; Gold, 1987). Moreover, hydrazones are frequently more efficient than oximes in this reaction, since the greater molecular weight of hydrazones causes a lower solubility in most solvents, and they can, therefore, often be more easily isolated and recrystallized. 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).



The title compound, (I), crystallizes in the triclinic space group $P\overline{1}$, with two independent molecules in the asymmetric unit. A view of the asymmetric unit with the atom-labeling scheme is shown in Fig. 1. The structure of (I) was initially identified by NMR and IR spectroscopy. The crystal structure determination of (I) was carried out in order to compare the double-bond geometry of this compound with those found in related compounds containing the thiazole moiety, such as 2-({4-[3-methyl-3-(2,4,6-trimethylphenyl)cyclobutyl]-3*H*-thiazol-2-ylidene}hydrazonomethyl)benzene-1,4-diol ethanol solvate (Yüksektepe *et al.*, 2005), (II), and to obtain more detailed information on the structural conformation of the molecule, which may be of value in structure–activity analysis.

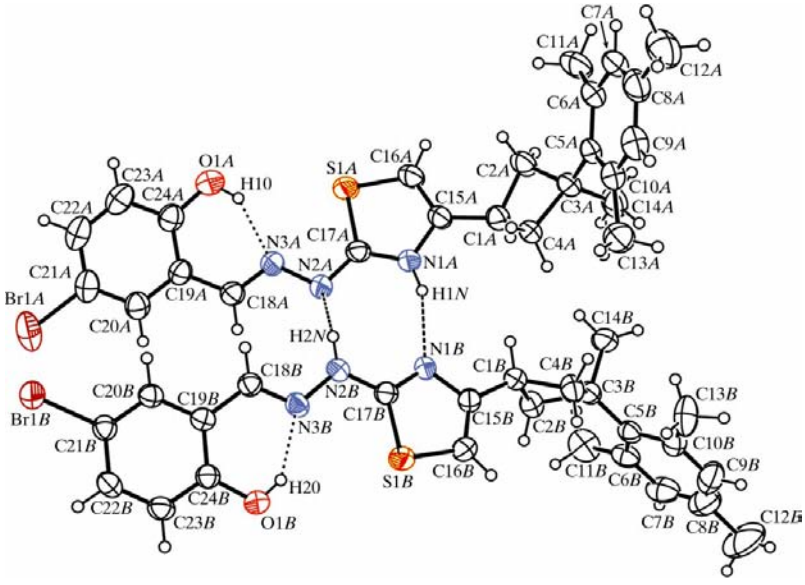


Figure 1
View of the dimer formed in the crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level and the atom-numbering scheme is given. Hydrogen bonds are shown as dashed lines.

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The molecules of (I) adopt an *E* geometry about the azomethine C═N double bond, with an N2—N3═C18—C19 torsion angle of 175.5 (3)° in molecule *A* and 177.7 (2)° in molecule *B* (Fig. 1). The skeleton of the molecules (except for the mesityl and methylcyclobutane moieties) deviates significantly from planarity. The r.m.s. deviations from the planes passing through all non-H atoms for the 3-bromo, 5-hydroxybenzene, thiazole and hydrazine moieties are 0.1492 (for molecule *A*) and 0.1072 Å (for molecule *B*). The dihedral angles between the 3-bromo-5-hydroxybenzene plane *A* (C19–C24), the thiazole plane *B* (N1/C15/C16/S1/C17) and the mesityl plane *C* (C5–C10) are 17.47 (11) and 13.21 (9)° (*A*/*B*), 13.00 (15) and 5.36 (18)° (*A*/*C*), and 4.75 (14) and 8.09 (15)° (*B*/*C*), respectively, for molecules *A* and *B*. In the thiazole ring, the S1—C16 and S1—C17 bond lengths (Table 1) are shorter than the accepted value for an S—Csp^2 single bond (1.76 Å; Allen, 1984).

In the cyclobutane ring, the C4/C1/C2 plane forms dihedral angles of 26.57 (3)° (molecule *A*) and 29.55 (2)° (molecule *B*) with the C2/C3/C4 plane. Literature values for the puckering of the cyclobutane ring are 23.5 (Swenson *et al.*, 1997), 29.03 (13) (Yüksektepe *et al.*, 2004) and 26.8 (2)° for (II). These values are comparable to the reported values for (I).

An interesting feature was found in the crystal packing. While electron delocalization occurs along the hydrazine moiety in molecule *A* and in (II), the H atom is transferred to atom N2*B* of the hydrazine group from atom N1*B* of the thiazole moiety in molecule *B*. In consequence of this H-atom migration, the independent molecules in the asymmetric unit are linked by strong N—H···N hydrogen bonds into a dimer in the $R_2^2(8)$ formation (Bernstein *et al.*, 1995) (Figs. 2 and 3, and Table 2). A similar dimeric assembly has not been reported before for related structures. The C17*A*—N1*A* and C15*A*—N1*A* bonds [1.339 (4) and 1.394 (4) Å, respectively] are longer than the corresponding bonds of molecule *B* [1.318 (4) and 1.387 (4) Å]. The N2*B*—C17*B* bond [1.348 (4) Å] is also longer than the N2*A*—C17*A* bond [1.327 (4) Å]. Intramolecular O—H···N hydrogen bonds are also effective in the crystal packing (Table 2, and Figs. 2 and 3).

Of greater interest are the intermolecular π–ring interactions with the mesityl plane and methyl group (C12*A*—H12*C*···*Cg*1; *Cg*1 is the centroid of the C5*A*–C10*A* ring), which stabilize the molecules in the crystal. This C—H···π interaction links the above-mentioned dimers again in a dimeric form, thus forming tetramers (Fig. 2 and Table 2). Additionally, π–π interactions between the 3-bromo-5-hydroxybenzene rings of molecule *B* (*Cg*2 is the centroid of the C19*B*–C24*B* ring) is also effective in the molecular packing in the crystal structure [the distance between centroids is 3.814 (2) Å and the perpendicular distance is 3.41 Å; Fig. 3]. Propagation of the C—H···π and π–π interactions by inversion thus links the $R_2^2(8)$ dimers into a chain of these rings parallel to the [011] direction.

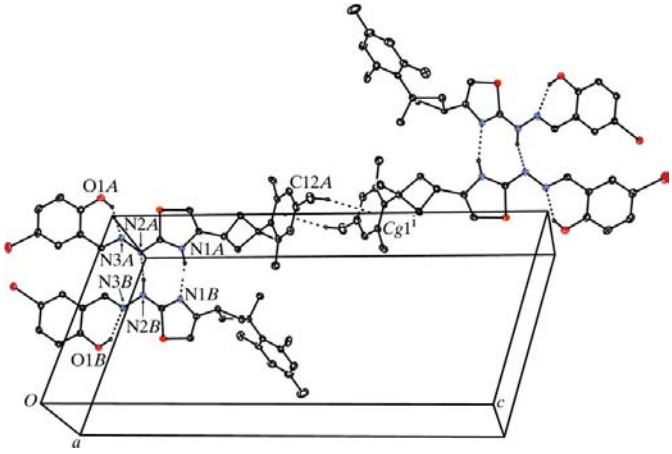

Figure 2
A partial packing diagram for (I), showing the N—H···N and C—H···π interactions as broken lines. *Cg*1 is the centroid of the C5*A*–C10*A* ring. H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (i) $-x, -y+2, -z+1$.]

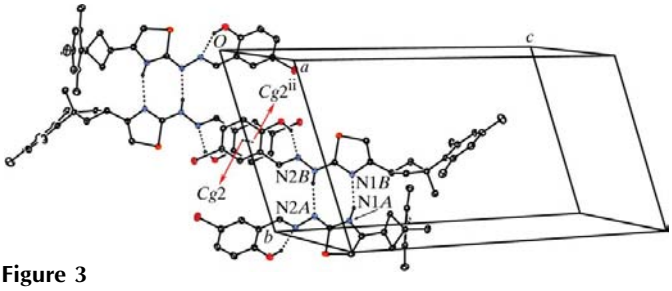

Figure 3
A partial packing diagram for (I), showing the N—H···N and π–π interactions as broken lines. *Cg*2 is the centroid of the C19*B*–C24*B* ring. H atoms not involved in hydrogen bonding have been omitted. [Symmetry code: (ii) $-x, -y+1, -z$.]

Experimental

To an alcoholic suspension of 1-(5-bromo-2-hydroxybenzylidene)-thiosemicarbazide (1.3707 g, 5 mmol), a solution of 3-(2-chloro-1-oxoethyl)-1-mesityl-1-methylcyclobutane (1.3225 g, 5 mmol) in absolute ethanol (20 ml) was added dropwise at *ca* 323–328 K with continuous stirring. After the addition of the α-haloketone, the temperature was kept at 323–328 K for a further 2 h. The solution was cooled to room temperature and then made alkaline with an aqueous solution of NH_3 (5%); a light-yellow precipitate separated. The precipitate was filtered off, washed with an aqueous NH_3 solution several times and dried in air. Single crystals suitable for crystal structure determination were obtained by slow evaporation of an ethanol solution (yield 87%, m.p. 503 K). IR (cm^{-1}): 3285 ν(O—H), 1165 ν(C—O), 1625 ν(C═N thiazole), 1600 ν(C═N azomethine), 3131 ν(N—H), 655 ν(C—S—C thiazole). ^{1}H NMR ($CDCl_3$): δ 1.49 (*s*, 3H, –CH_3 on cyclobutane), 2.14 (*s*, 6H, *o*-CH_3), 2.39 (*s*, 3H, *p*-CH_3), 2.54 (*m*, 4H, –CH_2– cyclobutane), 3.31 (*q*, 1H, >CH– cyclobutane), 5.96 (*s*, 1H, thiazole), 6.7–7.4 (*m*, 5H, aromatic), 8.02 (*s*, 1H, azomethine).

Crystal data

$C_{24}H_{26}BrN_3OS$
M_r = 484.45
Triclinic, $P\overline{1}$
a = 8.3589 (5) Å
b = 11.9903 (7) Å
c = 24.1438 (14) Å
α = 75.507 (5)°
β = 86.063 (5)°
γ = 77.418 (5)°
V = 2286.3 (2) Å^3
Z = 4
D_x = 1.407 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24578 reflections
θ = 1.7–27.2°
μ = 1.91 mm^{-1}
T = 293 (2) K
Plate, light-yellow
0.40 × 0.31 × 0.07 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.396, T_{max} = 0.877
27215 measured reflections
8041 independent reflections
5444 reflections with $I > 2\sigma(I)$
R_{int} = 0.074
θ_{max} = 25.0°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.099
S = 0.99
8041 reflections
547 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

	Molecule *A*	Molecule *B*
S1—C16	1.717 (4)	1.730 (3)
S1—C17	1.729 (3)	1.730 (3)
N1—C17	1.339 (4)	1.318 (4)
N1—C15	1.394 (4)	1.387 (4)
N2—C17	1.327 (4)	1.348 (4)
N2—N3	1.386 (3)	1.381 (3)
N3—C18	1.281 (4)	1.277 (4)
C15—C16	1.331 (4)	1.337 (4)
C18—C19	1.446 (4)	1.458 (4)
C16—S1—C17	89.19 (15)	88.49 (15)
C16—C15—N1	111.9 (3)	114.6 (3)
C17—N2—N3—C18	172.3 (3)	−179.3 (3)

The H atoms on atoms N1*A* and N2*B* were located at the end of the refinement in a Fourier difference synthesis. Once located, they were refined as riding (N—H = 0.86 Å). All other H atoms were placed in calculated positions and refined as riding, with C—H distances in the range 0.93–0.98 Å and O—H distances of 0.82 Å. The U_{iso}(H) values were set at 1.2 or 1.5 times U_{eq} of the parent atom.

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

*Cg*1 is the centroid of the C5*A*–C10*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1N···N1*B*	0.86	2.17	2.979 (3)	158
O1*A*—H1O···N3*A*	0.82	1.89	2.613 (3)	146
N2*B*—H2N···N2*A*	0.86	2.21	2.880 (4)	134
O1*B*—H2O···N3*B*	0.82	1.91	2.635 (3)	146
C12*A*—H12*C*···*Cg*1^{i}	0.96	2.74	3.627 (3)	154

Symmetry code: (i) $-x, -y+2, -z+1$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); 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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1259). Services for accessing these data are described at the back of the journal.

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