Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-(1*H*-1,3-Benzimidazol-2-ylsulfanyl)-1-(4-methylphenyl)ethanone semicarbazone

N. Kiruthiga,[a] S. Athimoolam,[a]* S. Saravanan,[b] S. Muthusubramanian[b] and S. Natarajan[a]

[a]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India, and [b]Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: xrdsopmku@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.071
wR factor = 0.211
Data-to-parameter ratio = 16.2

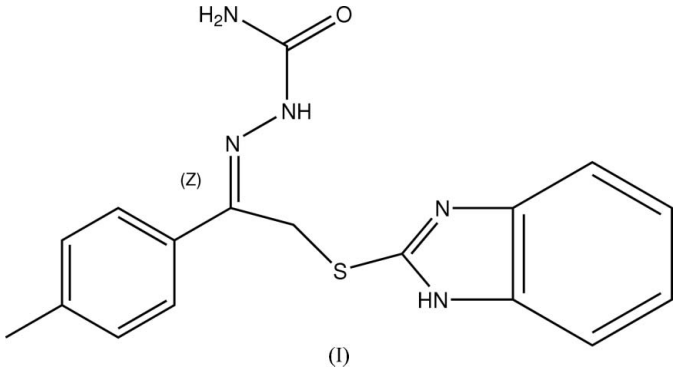
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 3 August 2006
Accepted 10 August 2006

The title compound, $C_{17}H_{17}N_5OS$, adopts the configurations *Z* around the imine C=N bond and *E* around the C(O)—NH bond. The configurations are stabilized by two intramolecular N—H···N hydrogen bonds. In the crystal structure, molecules are linked together by N—H···O hydrogen bonds, forming a three-dimensional network.

Comment

Semicarbazones and thiosemicarbazones are important groups of ligands very often used in complexing different metal atoms with effective biological activities (Palenik & Wester, 1978). Such compounds exhibit well known pharmacological activities, such as selective inhibition of the herpes virus and inhibition of the human immunodeficiency virus (HIV) (Teitz *et al.*, 1994). These pharmacological activities also include antitumour and antileukaemic properties (Agarwal *et al.*, 1972), antibacterial and antiviral activities (Chattopadhyay *et al.*, 1987), infertility properties (Nagarajan *et al.*, 1984), and anticancer (Ali & Livingstone, 1974) and antimalarial activities (Klayman *et al.*, 1979). The carcinostatic activities of thiosemicarbazone are confirmed in the metal coordination complexes (Liu *et al.*, 1995; Lukevics *et al.*, 1996) and it is observed that semicarbazone complexes also exhibit nonlinear optical (NLO) properties (Tian *et al.*, 1999). The heterocyclic unit present in the compound is also known for its importance as several benzimidazole derivatives are popular antiulcer agents and proton pump inhibitors (Balant, 2003).



(I)

The title compound, (I), adopts a *Z* configuration around the N3=C4 bond and *E* configuration around the C1—N2 bond (Fig. 1), and two intramolecular N—H···N hydrogen bonds (Table 2) are formed. Similar types of intramolecular hydrogen bonds are observed in isatin 3-semicarbazone and 1-methylisatin 3-semicarbazone (Pelosi *et al.*, 2005). An analysis of the Cambridge Structural Database (Version 5.27 of 2006;

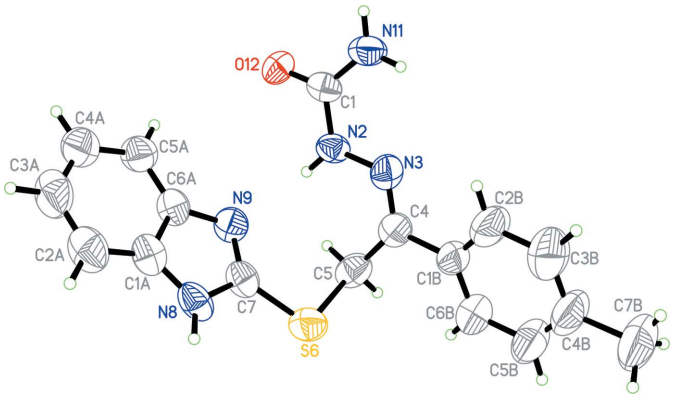


Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

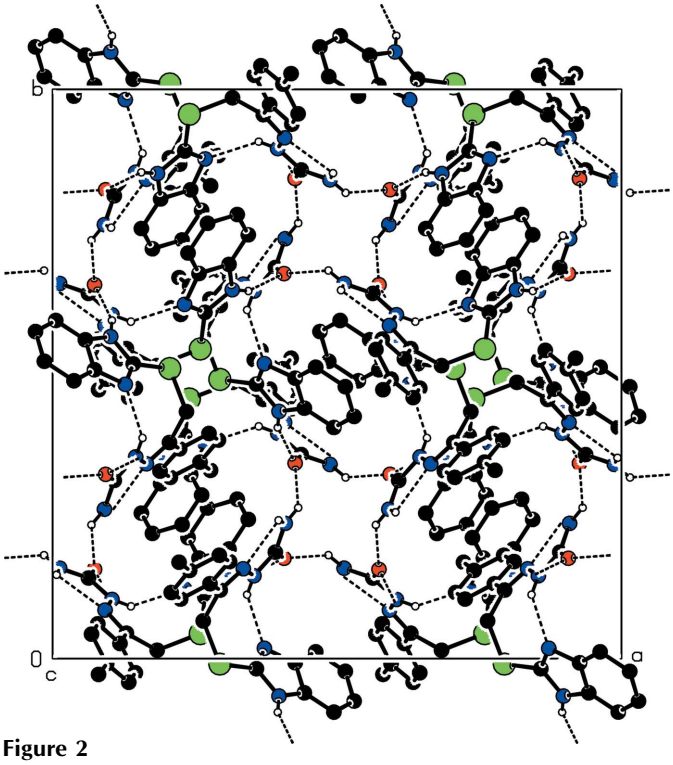


Figure 2
Packing diagram of the molecules viewed down the *c* axis. H atoms have been omitted unless these are involved in hydrogen bonds (dashed lines).

Allen, 2002) showed that, in metal coordination complexes, the carbonyl O atom and the imine N atom are involved in coordination with the metal. Hence, the configuration of the O=C—N—N fragment is *cis*. However, the free semicarbazone group prefers the *trans* configuration as observed in (I). The dihedral angle between the methylphenyl and benzoimidazole ring systems is 87.2 (2)°. Fig. 2 shows the packing of (I). The molecules are linked *via* N—H···O hydrogen bonds (Table 2), forming a three-dimensional network.

Experimental

To a warm solution of 2-(1*H*-1,3-benzimidazol-2-yl-sulfanyl)-1- (4-methylphenyl)-1-ethanone (0.01 mol) in an ethanol/dimethylsulphoxide mixture (40 ml, 3:1 *v*/*v*), a solution of an equimolar amount of semicarbazide hydrochloride (0.07 mol) and anhydrous sodium acetate (0.07 mol) in 20 ml of water was added and refluxed for 4 h. The solution was cooled, poured on to crushed ice, filtered and washed with cold ethanol. The product, compound (I), was recrystallized from a mixture of ethanol/ethyl acetate (3:2 *v*/*v*, yield 49%).

Crystal data

$C_{17}H_{17}N_5OS$
M_r = 339.43
Tetragonal, $I4_1/a$
a = 21.525 (5) Å
c = 17.396 (4) Å
V = 8060 (4) Å^3
Z = 16
D_x = 1.119 Mg m^{-3}
D_m = 1.08 (5) Mg m^{-3}
D_m measured by flotation in a mixture of xylene and carbon tetrachloride
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 293 (2) K
Block, colourless
0.21 × 0.18 × 0.14 mm

Data collection

Nonius MACH3 diffractometer
ω–2θ scans
Absorption correction: none
4008 measured reflections
3534 independent reflections
1189 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 25.0°
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.211
S = 0.85
3534 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1015P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N11—C1	1.331 (6)	N2—N3	1.389 (5)
O12—C1	1.245 (6)	N3—C4	1.290 (6)
C1—N2	1.360 (6)		
O12—C1—N2—N3	178.2 (4)	N11—C1—N2—N3	0.0 (6)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···O12^{i}	0.86	2.18	2.901 (5)	142
N11—H11*B*···N3	0.86	2.31	2.663 (6)	105
N2—H2···N9	0.86	2.13	2.817 (6)	136
N8—H8···O12^{ii}	0.86	1.93	2.747 (6)	157

Symmetry codes: (i) $y+\frac{1}{4}, -x+\frac{3}{4}, -z+\frac{3}{4}$; (ii) $y+\frac{3}{4}, -x+\frac{3}{4}, z-\frac{1}{4}$.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). There are large accessible voids of 431 Å^3 in the structure, which tend to host disordered solvent molecules (ethylacetate and/or ethanol). This affected the diffraction pattern, mostly at low scattering angles, and this was corrected with the SQUEEZE program (*PLATON*; Spek, 2003), the number of electrons in the voids being *ca* 25.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

The authors thank the Department of Science and Technology, Government of India, for establishing the single-crystal diffractometer facility at the School of Physics, Madurai Kamaraj University, through a FIST programme. The authors also thank the UGC for the SAP programme.

References

Agarwal, K. C., Cushley, R. J., Lipsky, S. R., Wheaton, J. R. & Sartorelli, A. C. (1972). *J. Med. Chem.* **15**, 192–195.
Ali, M. A. & Livingstone, S. E. (1974). *Coord. Chem. Rev.* **13**, 101–132.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Balant, L. P. (2003). *Burger's Medicinal Chemistry and Drug Discovery*, Vol. 2, edited by D. J. Abraham, p. 516. New York: John-Wiley.
Bruker (2000). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Chattopadhyay, D., Banerjee, T., Majumdar, S. K., Ghosh, S. & Kuroda, R. (1987). *Acta Cryst.* C**43**, 974–977.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg. Germany.
Klayman, D. L., Bartosevich, J. F., Grifaen, T. S., Mason, C. J. & Scovill, J. P. (1979). *J. Med. Chem.* **22**, 855–862.
Liu, M.-C., Lin, T.-S., Penketh, P. & Sartorelli, P. (1995). *J. Med. Chem.* **38**, 4234–4241.
Lukevics, E., Jansone, D., Rubina, K., Abele, E., Germane, S., Leite, L., Shymanska, M. & Popelis, J. (1996). *Eur. J. Med. Chem.* **30**, 983–990.
Nagarajan, K., Talwaker, P. K., Kulkarni, C. L., Venkateswarlu, A., Prabhu, S. S. & Nayak, G. V. (1984). *Indian J. Chem.* **23**, 1243–1257.
Palenik, G. J. & Wester, D. W. (1978). *Inorg. Chem.* **17**, 864–870.
Pelosi, G., Pelizzi, C., Belicchi Ferrari, M., Rodríguez-Argüelles, M. C., Vieito, C. & Sanmartín, J. (2005). *Acta Cryst.* C**61**, o589–o592.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Teitz, Y., Ronen, D., Vansover, A., Stematsky, T. & Riggs, J. L. (1994). *Antiviral Res.* **24**, 305–314.
Tian, Y.-P., Wu, J.-Y., Xie, F.-X., Shanmuga Sundara Raj, S., Yang, P. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 1641–1644.