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## Key indicators

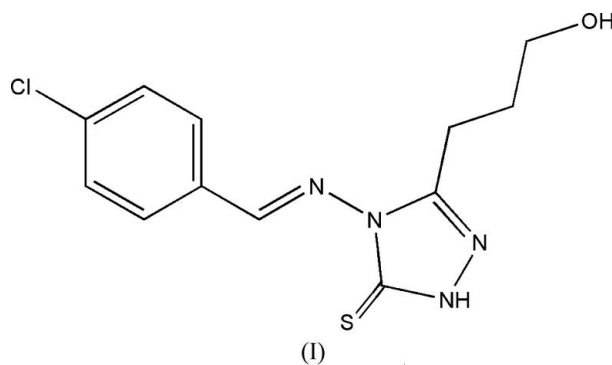
Single-crystal X-ray study  
*T* = 298 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
*R* factor = 0.047  
*wR* factor = 0.113  
Data-to-parameter ratio = 13.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.4-[(4-Chlorobenzylidene)amino]-3-(3-hydroxy-  
propyl)-1,2,4-triazole-5(4*H*)-thione

The title compound,  $\text{C}_{12}\text{H}_{13}\text{ClN}_4\text{OS}$ , was prepared by the reaction of 4-amino-3-(3-hydroxypropyl)-1,2,4-triazole-5-thione and 4-chlorobenzaldehyde. The configuration at the azomethine  $\text{C}=\text{N}$  bond is *E* and the compound can be assigned as the thione tautomeric form. The crystal packing is stabilized by  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{S}$  intermolecular hydrogen-bonding interactions.

Received 11 October 2006  
Accepted 11 November 2006

## Comment

3-Substituted-4-amino-1,2,4-triazole-5-thiones are key synthons in the formation of heterocyclic compounds. As bifunctional agents they are potential electron donors and can react with various electrophilic reagents. Their derivatives have been reported to show various biological activities (Khan & Giri, 1995; Holla & Kalluraya, 1988; Ismaiel *et al.*, 1984; Vicentini *et al.*, 1998; Maxwell *et al.*, 1984). The development of efficient methods for the synthesis of this class of compounds is, therefore, of great importance. In this paper, we report the synthesis and crystal structure of the title compound, (I).



In compound (I), the present results confirm that the configuration of the molecule is *E* at the azomethine  $\text{C}=\text{N}$  bond (Fig. 1). The  $\text{C}8-\text{S}1$  bond [ $1.677(4) \text{ \AA}$ ] is shorter than the normal covalent  $\text{S}-\text{C}$  single bond seen in some dithia-cycloalkanes ( $1.801-1.825 \text{ \AA}$ ; Setzer *et al.*, 1981) and, even though it is longer than an  $\text{S}=\text{C}$  double bond [ $1.646(5) \text{ \AA}$ ; Fujita *et al.*, 1981], it has substantial double-bond character, as shown by the conspicuous absence of an  $\text{S}-\text{H}$  vibration band ( $2500 \text{ cm}^{-1}$ ) in the IR spectrum.

The  $\text{C}-\text{N}$  bonds in compound (I) can be divided into two sets according to the observed bond lengths. The  $\text{C}8-\text{N}3$  bond [ $1.336(4) \text{ \AA}$ ] is longer than  $\text{C}9-\text{N}4$  [ $1.294(4) \text{ \AA}$ ] and the longer bonds observed for  $\text{C}8-\text{N}2$  and  $\text{C}9-\text{N}2$  suggest that the electron density is more localized among atoms  $\text{C}9/\text{N}4/\text{N}3/\text{C}8/\text{S}1$ . Taking into account all these observations, (I) can be assigned as the thione tautomeric form.

## Experimental

4-Amino-3-(3-hydroxypropyl)-1,2,4-triazole-5-thione, (II), was prepared by the reaction of 1,4-butyrolactone (0.01 mol) and thio-carbohydrazide (0.01 mol) in pyridine (40 ml) at 428 K for 4 h. A mixture of (II) (0.002 mol) and 4-chlorobenzaldehyde (0.002 mol) in absolute ethanol (20 ml) was then treated with concentrated HCl (0.1 ml) and refluxed at 433 K for 4 h. The desired product was obtained by filtration, drying and recrystallization from ethanol, in 69.5% yield. The purified product was dissolved in 95% ethanol and kept at room temperature for 5 d, and colourless crystals of (I) were formed (m.p. 411–413 K).

### Crystal data

$C_{12}H_{13}ClN_4OS$	$V = 673.05 (11) \text{ \AA}^3$
$M_r = 296.77$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.464 \text{ Mg m}^{-3}$
$a = 6.1880 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 7.5476 (7) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$c = 14.6378 (14) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 91.610 (2)^\circ$	Block, colourless
$\beta = 97.999 (2)^\circ$	$0.27 \times 0.20 \times 0.17 \text{ mm}$
$\gamma = 95.695 (2)^\circ$	

### Data collection

Bruker APEX area-detector diffractometer	3560 measured reflections
$\varphi$ and $\omega$ scans	2342 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	2117 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.891$ , $T_{\max} = 0.930$	$R_{\text{int}} = 0.014$
	$\theta_{\text{max}} = 25.0^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.3229P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
2342 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
173 parameters	
H-atom parameters constrained	

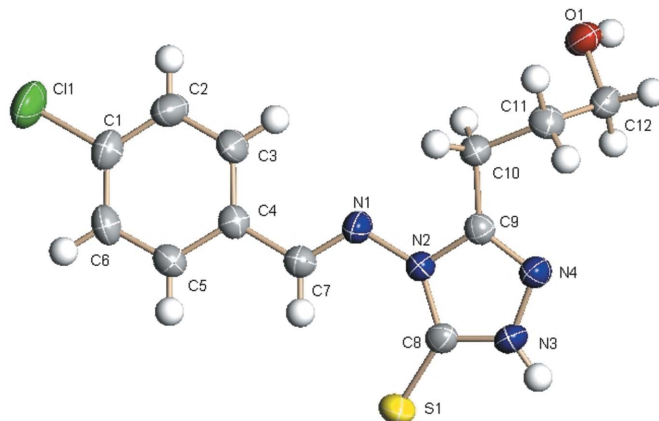
**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3 \cdots O1^i$	0.86	1.94	2.780 (3)	167
$O1-H1 \cdots S1^{ii}$	0.82	2.47	3.2922 (19)	176

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of  $Csp^2-H = 0.93 \text{ \AA}$  with  $U_{\text{iso}}(H) =$



**Figure 1**

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

$1.2U_{\text{eq}}(C)$ ,  $Csp^3-H = 0.96$  or  $0.97 \text{ \AA}$  with  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ ,  $O-H = 0.82 \text{ \AA}$  with  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$ , and  $N-H = 0.86 \text{ \AA}$  with  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(N)$ .

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2002); software used to prepare material for publication: SHELXL97.

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (grant No. M203149).

## References

- Bruker (2002). SADABS (Version 2.03), SAINT (Version 6.02), SMART (Version 5.62) and SHELXTL (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Fujita, E., Nagao, Y., Seno, K., Takao, S., Miyasaka, T., Kimura, M. & Watson, W. H. (1981). *J. Chem. Soc. Perkin Trans. 1*, pp. 914–919.
- Holla, B. S. & Kalluraya, B. (1988). *Indian J. Chem. Sect. B*, **27**, 683–685.
- Ismail, A. M., Yousif, M. Y., Metwally, M. A. & El-Kerdawy, M. M. (1984). *Indian J. Chem. Sect. B*, **23**, 489–491.
- Khan, M. H. & Giri, S. (1995). *Indian J. Chem. Sect. B*, **34**, 1007–1009.
- Maxwell, J. R., Wasdahl, D. A., Wolfson, A. C. & Stenberg, V. (1984). *J. Med. Chem.* **27**, 1565–1570.
- Setzer, W. N., Wilson, G. S. & Glass, R. S. (1981). *Tetrahedron*, **37**, 2735–2742.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Vicentini, C. B., Manfrini, M., Veronese, A. C. & Guarneri, M. (1998). *J. Heterocycl. Chem.* **35**, 29–32.