

3-(2,4-Dichlorophenyl)-4-[(1E)-(2,4-dichlorophenyl)methyleneamino]-4,5-dihydro-1H-1,2,4-triazole-5-thione dimethylformamide solvate

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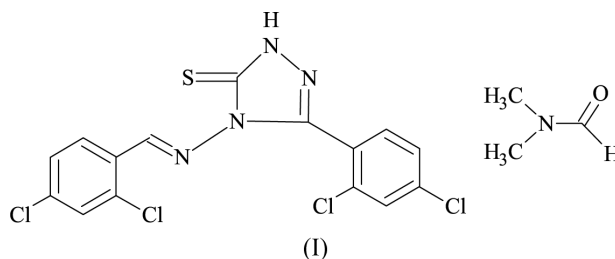
Key indicators

Single-crystal X-ray study
T = 273 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.031
wR factor = 0.039
Data-to-parameter ratio = 12.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title triazole compound, $\text{C}_{15}\text{H}_8\text{Cl}_4\text{N}_4\text{S}\cdot\text{C}_3\text{H}_7\text{NO}$, has been obtained as an unexpected product when attempting to prepare Schiff bases of thiocarbohydrazide (TCH). The triazole ring is planar within $0.004 (8) \text{ \AA}$ because of conjugation. The dihedral angles between the 1,2,4-triazole ring and the two benzene rings are $24.9 (2)$ and $70.0 (2)^\circ$. The interplanar angle between the two benzene rings is $83.4 (2)^\circ$. The packing of the molecules is stabilized both by van der Waals interactions and by $\text{N}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds between the triazole N atom and the carbonyl O atom of the dimethylformamide solvent molecule.

Comment

It is known that substituted 1,2,4-triazole-3-thione derivatives exhibit a range of antimicrobial, diuretic and antidepressant activities (Oruc *et al.*, 1999). Some of the metal complexes of these compounds also display a broad range of biological activity, finding application as antitumor, antibacterial, antifungal and antiviral agents (Bermejo *et al.*, 1999; Eweiss *et al.*, 1986). The title compound, (I), was obtained as an unexpected product when attempting to prepare the Schiff base of thiocarbohydrazide (TCH) and, to the best of our knowledge, represents a new method for the one-pot preparation of this class of triazole compounds. The triazole ring is planar within $0.004 (8) \text{ \AA}$ because of conjugation, with a maximum deviation of $0.007 (6) \text{ \AA}$ for atom C14. The dihedral angles between the 1,2,4-triazole ring and the two benzene rings are $24.9 (2)$ and $70.0 (2)^\circ$. The interplanar angle between the two benzene rings is $83.4 (2)^\circ$.



The $\text{C}=\text{S}$ bond length of $1.668 (3) \text{ \AA}$, and the $\text{N}-\text{N}$ bond lengths [$1.374 (3)$ and $1.397 (3) \text{ \AA}$] agree well with the reported values (Menzies & Squattrito, 2001). Because of conjugation, $\text{C}=\text{N}$ bond lengths range between $1.250 (4)$ and $1.380 (3) \text{ \AA}$, and $\text{C}-\text{N}$ single bond lengths between $1.445 (4)$ and $1.458 (4) \text{ \AA}$. The $\text{C}-\text{Cl}$ bond lengths [$1.724 (3)$ – $1.738 (3) \text{ \AA}$] are comparable to values found by Xu *et al.* (2005). Selected bond distances and angles are listed in Table 1.

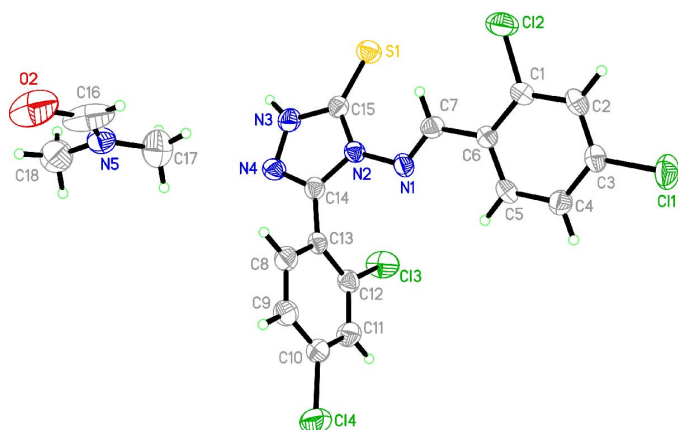


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

A packing diagram is shown in Fig. 2. The packing of the molecules is stabilized both by van der Waals interactions and by N—H···O intermolecular hydrogen bonds between the triazole N atom and the carbonyl O atom of the dimethylformamide solvent molecule [$N\cdots O^i = 2.726(2) \text{ \AA}$ and $N-H\cdots O^i = 172^\circ$] (Table 2).

Experimental

The title compound was prepared by refluxing a mixture of thio-carbohydrazide (0.212 g) and 2,4-dichlorobenzaldehyde (0.700 g) in ethanol (30 ml) for 3 h. The reaction mixture was allowed to stand undisturbed overnight in the reaction flask. Next morning, the pale yellow crystalline product was isolated (m.p. 505.5 K). The crystals were dissolved again in a mixture of dimethylformamide and MeOH (1:1). After a few days, pale yellow single crystals were obtained (m.p. 491–495 K).

Crystal data

$C_{15}H_8Cl_4N_4S \cdot C_3H_7NO$
 $M_r = 491.21$
 Orthorhombic, Pca_21
 $a = 11.3496(19) \text{ \AA}$
 $b = 18.016(3) \text{ \AA}$
 $c = 10.9165(18) \text{ \AA}$
 $V = 2232.2(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.462 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 2025 reflections
 $\theta = 4.2\text{--}20.3^\circ$
 $\mu = 0.64 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
 Block, pale yellow
 $0.27 \times 0.16 \times 0.09 \text{ mm}$

Data collection

Bruker SMART APEX-II CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 9843 measured reflections
 3377 independent reflections

1956 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -10 \rightarrow 13$
 $k = -21 \rightarrow 21$
 $l = -10 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.039$
 $S = 0.82$
 3377 reflections
 264 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0165P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1292 Friedel pairs
 Flack parameter = $-0.02(4)$

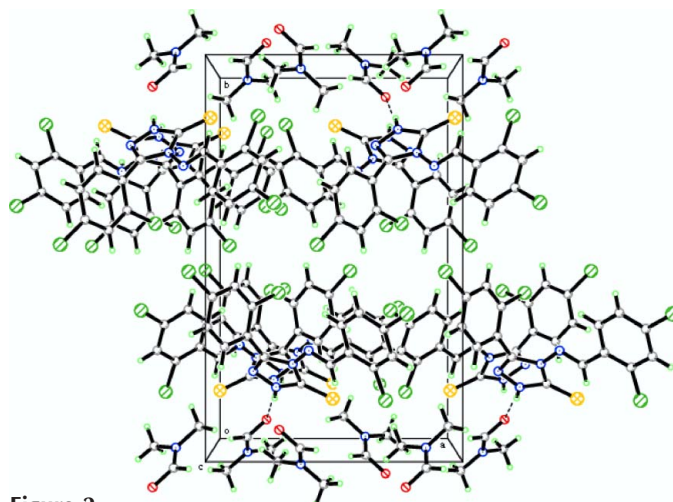


Figure 2
The packing diagram of the title compound, viewed along the c axis; hydrogen bonds are illustrated by dashed lines.

Table 1

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

S1—C15	1.668 (3)	N3—N4	1.374 (3)
N1—N2	1.397 (3)	N4—C14	1.291 (3)
N2—C14	1.369 (4)	C16—N5	1.250 (4)
N2—C15	1.380 (3)	C16—O2	1.280 (6)
N3—C15	1.357 (3)	C17—N5	1.445 (4)
C7—N1—N2	117.5 (3)	N1—C7—C6	121.5 (3)
C14—N2—C15	109.1 (3)	N4—C14—N2	111.7 (3)
C14—N2—N1	119.8 (3)	N3—C15—N2	101.2 (3)
C15—N2—N1	131.2 (3)	N3—C15—S1	126.8 (3)
C15—N3—N4	114.7 (2)	N2—C15—S1	132.0 (3)
C14—N4—N3	103.4 (3)	N5—C16—O2	123.9 (6)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3···O2 ⁱ	0.86	1.87	2.726 (2)	172

Symmetry code: (i) $1 - x, -y, z - \frac{1}{2}$.

All H atoms were positioned geometrically and refined with a riding model; C—H values were set to 0.96 and 0.93 \AA for atoms C17—C18 and C2—C15, respectively; N—H = 0.86 \AA . $U_{\text{iso}}(\text{H})$ values were constrained to be $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *APEX2*; program(s) used to refine structure: *APEX2*; molecular graphics: *APEX2*; software used to prepare material for publication: *APEX2*.

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References

Bermejo, E., Carballo, R., Castineiras, A., Dominguez, R., Maichle-Mossmar, C., Strahle, J. & West, D. (1999). *Polyhedron*, **18**, 3695–3702.

- Bruker (2004). *APEX2*. Version 1.22. Bruker AXS Inc., Madison, Wisconsin, USA.
- Eweiss, N., Bahajaj, A. & Elsherbini, E. (1986). *J. Heterocycl. Chem.* **23**, 1451–1458.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Menzies, C. M. & Squattrito, P. J. (2001). *Inorg. Chim. Acta*, **314**, 194–200.
- Oruc, E. E., Rollas, S., Kabasakal, L. & Uysal, M. K. (1999). *Drug Metabol. Drug Interact.* **15**, 127–140.
- Xu, L.-Z., Li, W.-H., Song, H.-B., Li, K. & Yu, G.-P. (2005). *Acta Cryst.* **E61**, o130–o131.