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4-(4-Chlorophenyl)-3-(3-methoxybenzyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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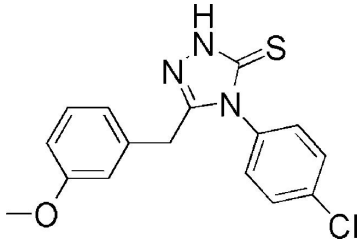
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.110; data-to-parameter ratio = 18.0.

The title compound, $C_{16}H_{14}ClN_3OS$, is an important, biologically active heterocyclic compound. The triazole ring is oriented at dihedral angles of 66.65 (3) and 82.53 (3)° with respect to the 4-chlorophenyl and 2-(3-methoxyphenyl)methyl rings, respectively. The dihedral angle between the benzene rings is 32.90 (2)°. In the crystal structure, intermolecular N—H···S hydrogen bonds link the molecules into centrosymmetric dimers.

Related literature

For related literature, see: Holla *et al.* (1998); Turan-Zitouni *et al.* (1999); Demirbas *et al.* (2002); Paulvannan *et al.* (2000); Kritsanida *et al.* (2002); Omar & Aboulwafa (1986). For related structures, see: Ozturk *et al.* (2004*a*,*b*); Zhang *et al.* (2004).



Experimental

Crystal data

$C_{16}H_{14}ClN_3OS$
M_r = 331.81
Monoclinic, $P2_1/c$
a = 14.0076 (8) Å
b = 7.4781 (3) Å
c = 14.9916 (8) Å
β = 90.536 (3)°
V = 1570.30 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 120 (2) K
0.23 × 0.13 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.917, T_{max} = 0.972
30001 measured reflections
3607 independent reflections
2815 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.110
S = 1.09
3607 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*N*···S1^{i}	0.88	2.41	3.2983 (18)	179

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

Data collection: *COLLECT* (Bruker, 2000); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2374).

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supplementary materials

Acta Cryst. (2007). E**63**, o4754 [**doi:10.1107/S1600536807058394**]

4-(4-Chlorophenyl)-3-(3-methoxybenzyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

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Comment

Substituted triazole derivatives display significant biological activities including antimicrobial (Holla *et al.*, 1998), analgesic (Turan-Zitouni *et al.*, 1999), antitumor (Demirbas *et al.*, 2002), antihypertensive (Paulvannan *et al.*, 2000) and antiviral activities (Kritsanida *et al.*, 2002). The biological activity is closely related to the structure, possibly being due to the presence of the —N—C ═S unit (Omar *et al.*, 1986). We are interested in the synthesis and biological activities of aryloxyacetyl hydrazide derivatives and report herein the synthesis and crystal structure of the title compound, (I).

In the molecule of the title compound, (I), (Fig. 1) the bond lengths and angles are comparable with those observed in related structures (Ozturk *et al.*, 2004*a*,b). The C7═S1 [1.684 (2) Å] bond agrees with the corresponding values [1.6773 (19) Å] in 4-(4-chlorophenyl)-3-(furan-2-yl) −1*H*-1,2,4-triazole-5(4*H*)-thione (Ozturk *et al.*, 2004*a*) and [1.668 (5) Å] in 4-amino-3-(1,2,3,4,5-pentahydroxypentyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (Zhang *et al.*, 2004). In the triazole ring, the N3 ═C8 [1.299 (3) Å] bond has double-bond character. The planar triazole ring A (N1—N3/C7/C8) is oriented with respect to planar 4-chlorophenyl and 2-(3-methoxyphenyl)- methyl rings; B (C1—C6) and C (C10—C15), at dihedral angles of 66.65 (3) and 82.53 (3)°, respectively. The dihedral angle between rings B and C is B/C = 32.90 (2)°.

In the crystal structure, intermolecular N—H···S hydrogen bonds (Table 1, Fig. 2) link the molecules into centrosymmetric dimers, in which they seem to be effective for the stablization of the structure.

Experimental

The synthesis of the title compound was carried out by refluxing a solution of 1-(2-(3-methoxyphenyl)acetyl)-4-(4-chlorophenyl)thiosemicarbazide (3.49 g, 10 mmol) in NaOH (2 *M*) for 5 h. Single crystals suitable for X-ray analysis were obtained by recrystallization from an aqeous ethanol solution at room temperature (yield: 81%; m.p. 432–433 K).

Refinement

The H atom (for NH) was located in difference syntheses, and constrained to ride on its parent atom, with N—H = 0.884 Å and U_{iso} = 1.5U_{eq}(N). The remaining H atoms were positioned geometrically, with C—H = 0.95, 0.99 and 0.98 Å for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

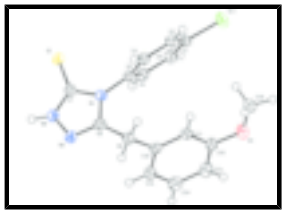


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

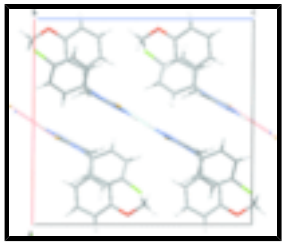


Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Fig. 3. The formation of the title compound.

4-(4-chlorophenyl)-3-(3-methoxybenzyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

$C_{16}H_{14}ClN_3OS$	F_{000} = 688
M_r = 331.81	D_x = 1.404 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 432(1) K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 14.0076 (8) Å	Cell parameters from 3607 reflections
b = 7.4781 (3) Å	θ = 2.7–27.5º
c = 14.9916 (8) Å	μ = 0.38 mm^{-1}
β = 90.536 (3)º	T = 120 (2) K
V = 1570.30 (14) Å^3	Block, colorless
Z = 4	0.23 × 0.13 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer	3607 independent reflections
Radiation source: fine-focus sealed tube	2815 reflections with $I > 2\sigma(I)$
Monochromator: horizontally mounted graphite crystal	R_{int} = 0.057
Detector resolution: 9 pixels mm^{-1}	θ_{max} = 27.5º
T = 120(2) K	θ_{min} = 2.7º
φ scans and ω scans with κ offset	h = −18→18
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	k = −8→9
T_{min} = 0.917, T_{max} = 0.972	l = −19→19

30001 measured reflections

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.044$	H-atom parameters constrained
$wR(F^2) = 0.110$	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.8817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
3607 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.15584 (4)	0.22519 (7)	0.50697 (3)	0.03371 (15)
S1	0.42366 (4)	0.17354 (6)	0.89517 (3)	0.02730 (15)
O1	0.04667 (11)	−0.3546 (2)	0.56644 (10)	0.0345 (4)
N1	0.37469 (11)	−0.1233 (2)	0.79781 (11)	0.0225 (3)
N2	0.44946 (12)	−0.1855 (2)	0.91848 (12)	0.0279 (4)
H2N	0.4835	−0.1836	0.9684	0.042*
N3	0.43084 (12)	−0.3487 (2)	0.87860 (12)	0.0274 (4)
C1	0.22361 (14)	0.1293 (2)	0.59211 (13)	0.0247 (4)
C2	0.30954 (14)	0.0465 (3)	0.57302 (14)	0.0270 (4)
H2	0.3332	0.0450	0.5138	0.032*
C3	0.36043 (14)	−0.0340 (3)	0.64189 (14)	0.0250 (4)
H3	0.4196	−0.0911	0.6304	0.030*
C4	0.32441 (13)	−0.0307 (2)	0.72754 (13)	0.0222 (4)
C5	0.23962 (14)	0.0555 (3)	0.74659 (13)	0.0249 (4)
H5	0.2165	0.0587	0.8059	0.030*
C6	0.18891 (14)	0.1372 (3)	0.67803 (13)	0.0260 (4)
H6	0.1309	0.1979	0.6900	0.031*
C7	0.41637 (14)	−0.0462 (3)	0.87139 (13)	0.0240 (4)

C8	0.38563 (14)	−0.3075 (2)	0.80539 (14)	0.0239 (4)
C9	0.34830 (14)	−0.4387 (3)	0.73827 (13)	0.0251 (4)
H9A	0.3691	−0.5605	0.7556	0.030*
H9B	0.3761	−0.4114	0.6793	0.030*
C10	0.24007 (13)	−0.4355 (2)	0.73030 (13)	0.0229 (4)
C11	0.19625 (14)	−0.3915 (2)	0.64952 (13)	0.0243 (4)
H11	0.2337	−0.3585	0.5996	0.029*
C12	0.09703 (15)	−0.3961 (3)	0.64241 (14)	0.0271 (4)
C13	0.04224 (15)	−0.4470 (3)	0.71516 (15)	0.0311 (5)
H13	−0.0253	−0.4525	0.7098	0.037*
C14	0.08652 (15)	−0.4894 (3)	0.79523 (14)	0.0317 (5)
H14	0.0492	−0.5236	0.8450	0.038*
C15	0.18521 (15)	−0.4823 (3)	0.80336 (14)	0.0279 (4)
H15	0.2152	−0.5095	0.8588	0.034*
C16	0.09854 (18)	−0.2997 (3)	0.49011 (15)	0.0370 (5)
H16A	0.1330	−0.1887	0.5035	0.056*
H16B	0.0541	−0.2795	0.4402	0.056*
H16C	0.1443	−0.3932	0.4740	0.056*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0450 (3)	0.0291 (3)	0.0268 (3)	0.0103 (2)	−0.0103 (2)	−0.0005 (2)
S1	0.0313 (3)	0.0198 (3)	0.0307 (3)	−0.00028 (19)	−0.0083 (2)	−0.00159 (19)
O1	0.0333 (8)	0.0389 (9)	0.0311 (8)	−0.0003 (6)	−0.0102 (7)	0.0047 (6)
N1	0.0241 (8)	0.0182 (8)	0.0251 (9)	0.0005 (6)	−0.0038 (7)	0.0007 (6)
N2	0.0318 (9)	0.0204 (8)	0.0314 (9)	−0.0012 (7)	−0.0121 (7)	0.0006 (7)
N3	0.0288 (9)	0.0192 (8)	0.0341 (10)	−0.0015 (6)	−0.0091 (7)	−0.0003 (7)
C1	0.0322 (10)	0.0170 (9)	0.0247 (10)	0.0018 (7)	−0.0067 (8)	0.0002 (7)
C2	0.0320 (11)	0.0223 (10)	0.0267 (10)	−0.0001 (8)	0.0017 (8)	0.0008 (8)
C3	0.0248 (10)	0.0207 (9)	0.0295 (11)	0.0003 (7)	0.0002 (8)	0.0006 (8)
C4	0.0240 (9)	0.0177 (9)	0.0247 (10)	−0.0014 (7)	−0.0047 (8)	0.0015 (7)
C5	0.0272 (10)	0.0229 (10)	0.0246 (10)	−0.0002 (8)	−0.0005 (8)	−0.0010 (8)
C6	0.0278 (10)	0.0220 (10)	0.0281 (11)	0.0034 (8)	−0.0012 (8)	−0.0015 (8)
C7	0.0227 (9)	0.0230 (10)	0.0262 (10)	−0.0008 (7)	−0.0042 (8)	0.0005 (8)
C8	0.0224 (9)	0.0194 (9)	0.0299 (11)	0.0002 (7)	−0.0025 (8)	0.0022 (8)
C9	0.0288 (10)	0.0190 (9)	0.0274 (10)	−0.0004 (8)	−0.0048 (8)	−0.0005 (7)
C10	0.0269 (10)	0.0157 (9)	0.0261 (10)	−0.0026 (7)	−0.0038 (8)	−0.0015 (7)
C11	0.0294 (10)	0.0182 (9)	0.0251 (10)	−0.0032 (7)	−0.0018 (8)	0.0006 (7)
C12	0.0303 (10)	0.0214 (10)	0.0294 (11)	0.0001 (8)	−0.0084 (8)	−0.0013 (8)
C13	0.0278 (10)	0.0320 (11)	0.0336 (12)	0.0010 (8)	−0.0014 (9)	−0.0062 (9)
C14	0.0338 (11)	0.0337 (11)	0.0276 (11)	−0.0044 (9)	0.0037 (9)	−0.0046 (9)
C15	0.0338 (11)	0.0258 (10)	0.0242 (10)	−0.0023 (8)	−0.0043 (8)	−0.0016 (8)
C16	0.0449 (13)	0.0340 (12)	0.0320 (12)	−0.0041 (10)	−0.0112 (10)	0.0065 (9)

Geometric parameters (Å, °)

Cl1—C1	1.738 (2)	C5—H5	0.9500
S1—C7	1.684 (2)	C6—H6	0.9500

O1—C12	1.370 (2)	C8—C9	1.496 (3)
O1—C16	1.422 (3)	C9—C10	1.520 (3)
N1—C7	1.370 (2)	C9—H9A	0.9900
N1—C8	1.391 (2)	C9—H9B	0.9900
N1—C4	1.439 (2)	C10—C15	1.389 (3)
N2—C7	1.339 (3)	C10—C11	1.392 (3)
N2—N3	1.382 (2)	C11—C12	1.393 (3)
N2—H2N	0.8840	C11—H11	0.9500
N3—C8	1.299 (3)	C12—C13	1.392 (3)
C1—C6	1.382 (3)	C13—C14	1.383 (3)
C1—C2	1.386 (3)	C13—H13	0.9500
C2—C3	1.387 (3)	C14—C15	1.388 (3)
C2—H2	0.9500	C14—H14	0.9500
C3—C4	1.384 (3)	C15—H15	0.9500
C3—H3	0.9500	C16—H16A	0.9800
C4—C5	1.384 (3)	C16—H16B	0.9800
C5—C6	1.386 (3)	C16—H16C	0.9800
C12—O1—C16	118.13 (17)	N1—C8—C9	123.86 (17)
C7—N1—C8	107.76 (15)	C8—C9—C10	112.61 (16)
C7—N1—C4	126.07 (16)	C8—C9—H9A	109.1
C8—N1—C4	126.10 (16)	C10—C9—H9A	109.1
C7—N2—N3	113.31 (16)	C8—C9—H9B	109.1
C7—N2—H2N	128.0	C10—C9—H9B	109.1
N3—N2—H2N	118.6	H9A—C9—H9B	107.8
C8—N3—N2	104.17 (16)	C15—C10—C11	120.20 (18)
C6—C1—C2	121.67 (18)	C15—C10—C9	119.53 (17)
C6—C1—Cl1	118.19 (15)	C11—C10—C9	120.24 (17)
C2—C1—Cl1	120.13 (16)	C10—C11—C12	119.48 (18)
C1—C2—C3	118.79 (19)	C10—C11—H11	120.3
C1—C2—H2	120.6	C12—C11—H11	120.3
C3—C2—H2	120.6	O1—C12—C13	115.46 (18)
C4—C3—C2	119.58 (18)	O1—C12—C11	124.30 (19)
C4—C3—H3	120.2	C13—C12—C11	120.24 (18)
C2—C3—H3	120.2	C14—C13—C12	119.77 (19)
C5—C4—C3	121.40 (18)	C14—C13—H13	120.1
C5—C4—N1	119.22 (17)	C12—C13—H13	120.1
C3—C4—N1	119.35 (17)	C13—C14—C15	120.4 (2)
C4—C5—C6	119.16 (19)	C13—C14—H14	119.8
C4—C5—H5	120.4	C15—C14—H14	119.8
C6—C5—H5	120.4	C14—C15—C10	119.90 (19)
C1—C6—C5	119.36 (18)	C14—C15—H15	120.0
C1—C6—H6	120.3	C10—C15—H15	120.0
C5—C6—H6	120.3	O1—C16—H16A	109.5
N2—C7—N1	103.88 (16)	O1—C16—H16B	109.5
N2—C7—S1	128.87 (15)	H16A—C16—H16B	109.5
N1—C7—S1	127.25 (15)	O1—C16—H16C	109.5
N3—C8—N1	110.87 (17)	H16A—C16—H16C	109.5
N3—C8—C9	125.27 (17)	H16B—C16—H16C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···S1^{i}	0.88	2.41	3.2983 (18)	179

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2.

Fig. 1

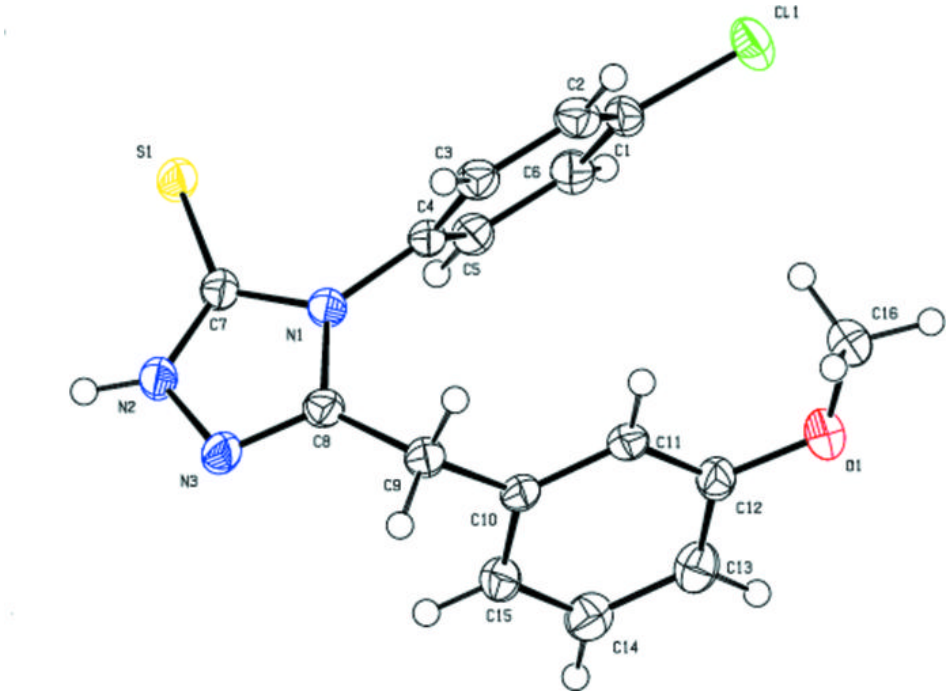

CL1
C2
C1
C6
C3
C4
C5
S1
C7
N1
N2
N3
C8
C9
C10
C11
C12
C13
C14
C15
C16
O1

Fig. 2

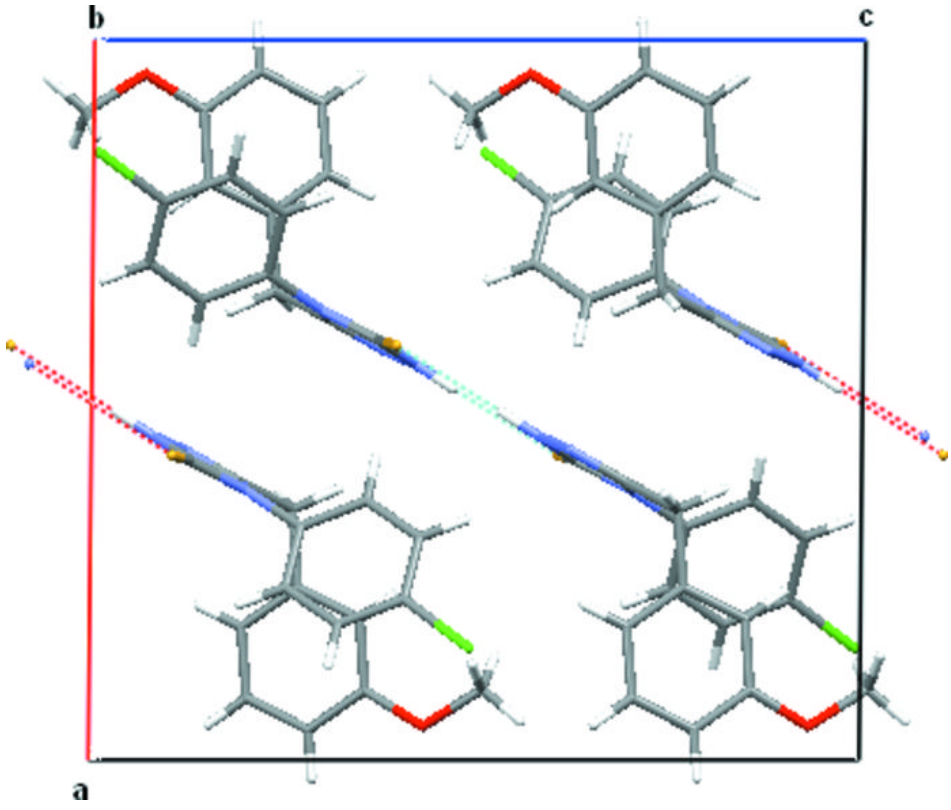
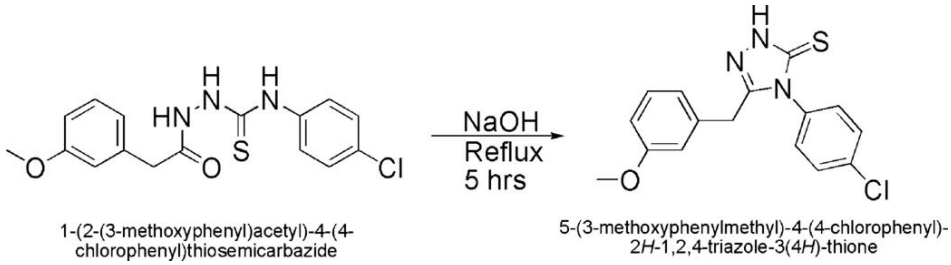


Fig. 3



1-(2-(3-methoxyphenyl)acetyl)-4-(4-chlorophenyl)thiosemicarbazide

5-(3-methoxyphenylmethyl)-4-(4-chlorophenyl)-2*H*-1,2,4-triazole-3(4*H*)-thione