Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-(4-Chlorophenyl)-1-[2-(2,4-dichlorophenoxy)propanoyl]thiosemicarbazide

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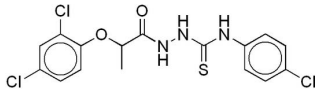
Received 9 November 2007; accepted 14 November 2007

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.042; wR factor = 0.100; data-to-parameter ratio = 18.0.

The title compound, $C_{16}H_{14}Cl_3N_3O_2S$, is an important intermediate for the synthesis of biologically active heterocyclic compounds. The chloro- and dichlorophenyl rings are oriented at a dihedral angle of 40.41 (3)°. The intramolecular N—H···O hydrogen bond results in the formation of a nearly planar five-membered ring, which is oriented at dihedral angles of 24.36 (3) and 22.27 (3)° with respect to the chloro- and dichlorophenyl rings, respectively. In the crystal structure, intermolecular N—H···O hydrogen bonds link the molecules.

Related literature

For related literature, see: Shen *et al.* (1998); Mao *et al.* (1999); Antholine & Taketa (1982). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{16}H_{14}Cl_3N_3O_2S$
M_r = 418.71
Triclinic, $P\overline{1}$
a = 7.8930 (3) Å
b = 8.9195 (3) Å
c = 13.3491 (4) Å
α = 96.514 (2)°
β = 98.681 (2)°
γ = 104.476 (2)°
V = 888.25 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.65 mm^{-1}
T = 120 (2) K
0.20 × 0.13 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.881, T_{max} = 0.926
17933 measured reflections
4083 independent reflections
3217 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.100
S = 1.04
4083 reflections
227 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1^{i}	0.87	2.02	2.854 (2)	160
N2—H2*N*···O1^{i}	0.96	1.99	2.861 (2)	150
N3—H3*N*···O2	1.00	2.04	2.526 (2)	107

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

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*.

The authors gratefully acknowledge funds from the Higher Education Commission, Islamabad, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2375).

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 doi:10.1107/S1600536807059119

supplementary materials

Acta Cryst. (2007). E**63**, o4775 [**doi:10.1107/S1600536807059119**]

4-(4-Chlorophenyl)-1-[2-(2,4-dichlorophenoxy)propanoyl]thiosemicarbazide

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Comment

Thiosemicarbazide is interesting because of the formation of complexes with biological activities (Shen *et al.*, 1998). Some substituted thiourea derivatives have shown interesting biological effects, including anti-HIV properties (Mao *et al.*, 1999), and thiourea derivatives have also been successfully screened for various biological actions (Antholine & Taketa, 1982). As a ligand with potential S– and N-atom donors, thiosemicarbazide is interesting because of the structural chemistry of its multifunctional coordination modes (N-monodentate, S-monodentate or N:*S*-bidentate). In order to investigate further this kind of ligand, we synthesized the title compound, (I), and reported herein its crystal structure.

In the molecule of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings A (C1—C6) and B (C11—C16) are, of course, planar. The intramolecular N—H···O hydrogen bond (Table 1) results in the formation of a nearly planar five-membered ring; C (N3/C8/C9/O2/H3N). The dihedral angles between them are A/B = 40.41 (3)°, A/C = 24.36 (3)° and B/C = 22.27 (3)°.

In the crystal structure, intermolecular N—H···O hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they seem to be effective in the stabilization of the structure.

Experimental

The title compound was prepared by the reaction of 2-(2,4-dichlorophenoxy) propanohydrazide (2.48 g, 20 mmol) and 4-chlorophenyl isothiocyanate (0.84 g, 20 mmol). Single crystals suitable for X-ray analysis were obtained by recrystallization from an aqeous ethanol solution at room temperature (yield; 76%; m.p. 465–466 K).

Refinement

H atoms of NH groups were located in difference syntheses and constrained to ride on their parent atoms, [N—H = 0.8725, 0.9582 and 0.9954 Å and U_{iso}(H) = 1.5U_{eq}(N)]. The remaining H atoms were positioned geometrically, with C—H = 0.95 and 1.00 Å for aromatic and methine H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

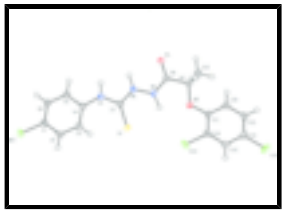
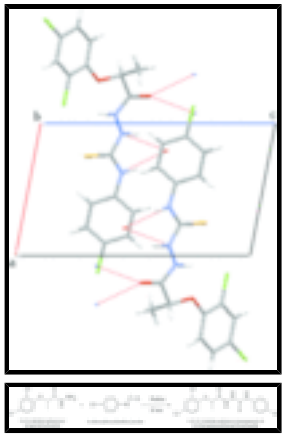


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.



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Crystal data

$C_{16}H_{14}Cl_3N_3O_2S$	$Z = 2$
$M_r = 418.71$	$F_{000} = 428$
Triclinic, $P\overline{1}$	$D_x = 1.566$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 465(1) K
$a = 7.8930$ (3) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 8.9195$ (3) Å	Cell parameters from 11915 reflections
$c = 13.3491$ (4) Å	$\theta = 1.0$–27.5º
$\alpha = 96.514$ (2)º	$\mu = 0.65$ mm^{-1}
$\beta = 98.681$ (2)º	$T = 120$ (2) K
$\gamma = 104.476$ (2)º	Block, colorless
$V = 888.25$ (5) Å^3	0.20 × 0.13 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer	4083 independent reflections
Radiation source: fine-focus sealed tube	3217 reflections with $I > 2\sigma(I)$
Monochromator: horizontally mounted graphite crystal	$R_{int} = 0.040$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 27.5$º
$T = 120(2)$ K	$\theta_{min} = 1.6$º
φ scans and ω scans with κ offset	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -11 \rightarrow 11$
$T_{min} = 0.881$, $T_{max} = 0.926$	$l = -17 \rightarrow 17$
17933 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.100$

$S = 1.04$

4083 reflections

227 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.9894P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.59$ e Å^{-3}

$\Delta\rho_{min} = -0.47$ e Å^{-3}

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 $F^2 > 2$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	1.12353 (7)	1.36448 (7)	0.36324 (5)	0.02892 (15)
Cl2	−0.13947 (8)	0.44813 (8)	0.08375 (5)	0.03269 (16)
Cl3	−0.78798 (10)	0.05093 (8)	−0.06665 (5)	0.04314 (19)
S1	0.24894 (8)	0.84661 (7)	0.21890 (5)	0.02685 (16)
O1	−0.2064 (2)	0.87470 (19)	0.44166 (12)	0.0254 (4)
O2	−0.3218 (2)	0.6062 (2)	0.21131 (12)	0.0322 (4)
N1	0.3706 (2)	1.0769 (2)	0.38554 (14)	0.0210 (4)
H1N	0.3394	1.1144	0.4410	0.031*
N2	0.0791 (2)	0.9544 (2)	0.35479 (15)	0.0225 (4)
H2N	0.0783	1.0127	0.4195	0.034*
N3	−0.0680 (2)	0.8317 (2)	0.30982 (14)	0.0210 (4)
H3N	−0.0763	0.7646	0.2434	0.031*
C1	0.9023 (3)	1.2756 (3)	0.36897 (17)	0.0196 (4)
C2	0.7841 (3)	1.2060 (3)	0.27939 (17)	0.0225 (5)
H2	0.8240	1.2052	0.2157	0.027*
C3	0.6067 (3)	1.1372 (3)	0.28158 (17)	0.0214 (5)
H3	0.5247	1.0901	0.2196	0.026*
C4	0.5497 (3)	1.1377 (2)	0.37567 (17)	0.0185 (4)
C5	0.6708 (3)	1.2093 (3)	0.46567 (17)	0.0203 (5)
H5	0.6316	1.2103	0.5296	0.024*
C6	0.8474 (3)	1.2790 (3)	0.46331 (17)	0.0210 (5)
H6	0.9295	1.3281	0.5248	0.025*
C7	0.2363 (3)	0.9647 (2)	0.32242 (17)	0.0193 (4)

C8	−0.2060 (3)	0.8005 (3)	0.35744 (17)	0.0210 (5)
C9	−0.3661 (3)	0.6672 (3)	0.30407 (17)	0.0246 (5)
H9	−0.4710	0.7097	0.2872	0.030*
C10	−0.4072 (3)	0.5491 (3)	0.37497 (19)	0.0286 (5)
H10A	−0.5123	0.4639	0.3415	0.043*
H10B	−0.4308	0.6000	0.4384	0.043*
H10C	−0.3052	0.5063	0.3913	0.043*
C11	−0.4399 (3)	0.4790 (3)	0.14855 (16)	0.0216 (5)
C12	−0.3656 (3)	0.3914 (3)	0.08300 (17)	0.0217 (5)
C13	−0.4719 (3)	0.2600 (3)	0.01604 (17)	0.0252 (5)
H13	−0.4214	0.2013	−0.0291	0.030*
C14	−0.6526 (3)	0.2161 (3)	0.01616 (18)	0.0265 (5)
C15	−0.7295 (3)	0.3017 (3)	0.07964 (18)	0.0261 (5)
H15	−0.8541	0.2700	0.0784	0.031*
C16	−0.6221 (3)	0.4346 (3)	0.14523 (18)	0.0242 (5)
H16	−0.6740	0.4956	0.1881	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0179 (3)	0.0313 (3)	0.0347 (3)	0.0013 (2)	0.0074 (2)	0.0026 (2)
Cl2	0.0211 (3)	0.0441 (4)	0.0370 (3)	0.0096 (3)	0.0122 (2)	0.0123 (3)
Cl3	0.0487 (4)	0.0326 (4)	0.0340 (4)	−0.0024 (3)	0.0001 (3)	−0.0117 (3)
S1	0.0214 (3)	0.0291 (3)	0.0257 (3)	0.0021 (2)	0.0082 (2)	−0.0078 (2)
O1	0.0244 (9)	0.0259 (9)	0.0214 (8)	0.0002 (7)	0.0080 (7)	−0.0047 (7)
O2	0.0295 (9)	0.0350 (10)	0.0211 (8)	−0.0084 (8)	0.0100 (7)	−0.0089 (7)
N1	0.0181 (9)	0.0234 (10)	0.0197 (9)	0.0016 (8)	0.0080 (7)	−0.0007 (8)
N2	0.0180 (9)	0.0222 (10)	0.0229 (10)	−0.0009 (8)	0.0068 (8)	−0.0043 (8)
N3	0.0164 (9)	0.0226 (10)	0.0198 (9)	−0.0007 (8)	0.0048 (7)	−0.0019 (8)
C1	0.0162 (11)	0.0178 (11)	0.0259 (11)	0.0048 (8)	0.0073 (9)	0.0024 (9)
C2	0.0238 (12)	0.0220 (11)	0.0216 (11)	0.0041 (9)	0.0089 (9)	0.0019 (9)
C3	0.0222 (11)	0.0200 (11)	0.0192 (11)	0.0021 (9)	0.0036 (9)	0.0002 (9)
C4	0.0176 (11)	0.0151 (10)	0.0232 (11)	0.0046 (8)	0.0058 (9)	0.0020 (8)
C5	0.0228 (11)	0.0202 (11)	0.0189 (11)	0.0068 (9)	0.0064 (9)	0.0024 (9)
C6	0.0200 (11)	0.0212 (11)	0.0197 (11)	0.0055 (9)	−0.0003 (9)	0.0004 (9)
C7	0.0194 (11)	0.0177 (11)	0.0209 (11)	0.0050 (9)	0.0044 (9)	0.0023 (8)
C8	0.0201 (11)	0.0227 (11)	0.0192 (11)	0.0036 (9)	0.0054 (9)	0.0022 (9)
C9	0.0238 (12)	0.0270 (12)	0.0192 (11)	0.0011 (10)	0.0064 (9)	−0.0021 (9)
C10	0.0306 (13)	0.0236 (12)	0.0270 (12)	−0.0002 (10)	0.0046 (10)	0.0026 (10)
C11	0.0216 (11)	0.0238 (12)	0.0150 (10)	0.0006 (9)	0.0020 (9)	−0.0007 (9)
C12	0.0195 (11)	0.0289 (12)	0.0191 (11)	0.0075 (9)	0.0065 (9)	0.0069 (9)
C13	0.0327 (13)	0.0253 (12)	0.0194 (11)	0.0098 (10)	0.0093 (10)	0.0007 (9)
C14	0.0326 (13)	0.0220 (12)	0.0203 (11)	0.0036 (10)	0.0004 (10)	−0.0006 (9)
C15	0.0195 (12)	0.0281 (13)	0.0270 (12)	0.0021 (10)	0.0020 (9)	0.0026 (10)
C16	0.0214 (12)	0.0240 (12)	0.0269 (12)	0.0059 (9)	0.0076 (9)	−0.0005 (9)

Geometric parameters (Å, °)

Cl1—C1	1.745 (2)	C3—H3	0.9500

Cl2—C12	1.727 (2)	C4—C5	1.392 (3)
Cl3—C14	1.738 (2)	C5—C6	1.384 (3)
S1—C7	1.671 (2)	C5—H5	0.9500
O1—C8	1.239 (3)	C6—H6	0.9500
O2—C11	1.370 (3)	C8—C9	1.518 (3)
O2—C9	1.423 (3)	C9—C10	1.503 (3)
N1—C7	1.358 (3)	C9—H9	1.0000
N1—C4	1.414 (3)	C10—H10A	0.9800
N1—H1N	0.8725	C10—H10B	0.9800
N2—C7	1.360 (3)	C10—H10C	0.9800
N2—N3	1.382 (3)	C11—C16	1.385 (3)
N2—H2N	0.9582	C11—C12	1.396 (3)
N3—C8	1.329 (3)	C12—C13	1.386 (3)
N3—H3N	0.9954	C13—C14	1.382 (3)
C1—C2	1.375 (3)	C13—H13	0.9500
C1—C6	1.392 (3)	C14—C15	1.382 (3)
C2—C3	1.388 (3)	C15—C16	1.389 (3)
C2—H2	0.9500	C15—H15	0.9500
C3—C4	1.396 (3)	C16—H16	0.9500
C11—O2—C9	119.48 (18)	O1—C8—C9	120.6 (2)
C7—N1—C4	130.11 (18)	N3—C8—C9	116.85 (19)
C7—N1—H1N	113.2	O2—C9—C10	113.9 (2)
C4—N1—H1N	116.6	O2—C9—C8	106.38 (18)
C7—N2—N3	119.54 (18)	C10—C9—C8	109.12 (19)
C7—N2—H2N	119.4	O2—C9—H9	109.1
N3—N2—H2N	118.8	C10—C9—H9	109.1
C8—N3—N2	118.69 (18)	C8—C9—H9	109.1
C8—N3—H3N	117.8	C9—C10—H10A	109.5
N2—N3—H3N	123.5	C9—C10—H10B	109.5
C2—C1—C6	121.1 (2)	H10A—C10—H10B	109.5
C2—C1—Cl1	119.13 (17)	C9—C10—H10C	109.5
C6—C1—Cl1	119.77 (17)	H10A—C10—H10C	109.5
C1—C2—C3	120.3 (2)	H10B—C10—H10C	109.5
C1—C2—H2	119.8	O2—C11—C16	125.2 (2)
C3—C2—H2	119.8	O2—C11—C12	115.4 (2)
C2—C3—C4	119.4 (2)	C16—C11—C12	119.3 (2)
C2—C3—H3	120.3	C13—C12—C11	120.6 (2)
C4—C3—H3	120.3	C13—C12—Cl2	119.42 (17)
C5—C4—C3	119.7 (2)	C11—C12—Cl2	119.93 (18)
C5—C4—N1	116.60 (19)	C14—C13—C12	118.8 (2)
C3—C4—N1	123.6 (2)	C14—C13—H13	120.6
C6—C5—C4	120.9 (2)	C12—C13—H13	120.6
C6—C5—H5	119.6	C13—C14—C15	121.6 (2)
C4—C5—H5	119.6	C13—C14—Cl3	119.52 (18)
C5—C6—C1	118.7 (2)	C15—C14—Cl3	118.85 (19)
C5—C6—H6	120.7	C14—C15—C16	119.1 (2)
C1—C6—H6	120.7	C14—C15—H15	120.5
N1—C7—N2	110.96 (18)	C16—C15—H15	120.5
N1—C7—S1	127.86 (17)	C11—C16—C15	120.5 (2)

N2—C7—S1	121.17 (16)	C11—C16—H16	119.8
O1—C8—N3	122.6 (2)	C15—C16—H16	119.8

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1^{i}	0.87	2.02	2.854 (2)	160
N2—H2N···O1^{i}	0.96	1.99	2.861 (2)	150
N3—H3N···O2	1.00	2.04	2.526 (2)	107

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

Fig. 1

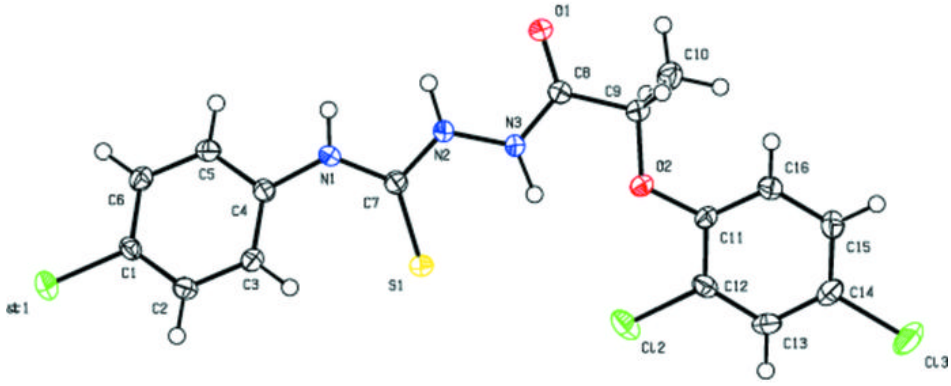

O1
C10
C8
C9
N3
N2
N1
C5
C6
C4
C7
O2
C16
C11
C15
C1
C3
S1
C12
C14
C2
CL2
C13
CL3
CL1

Fig. 2

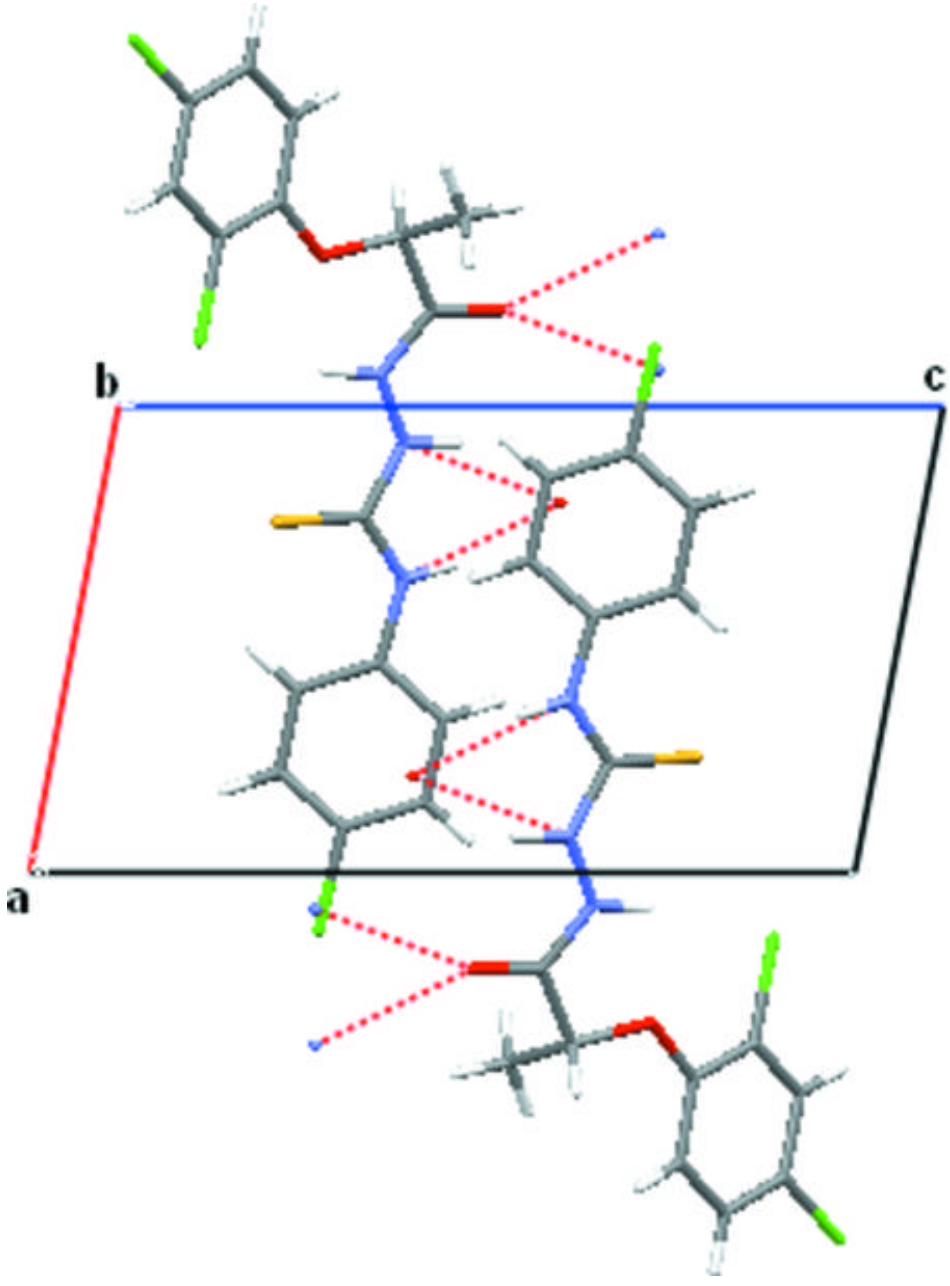
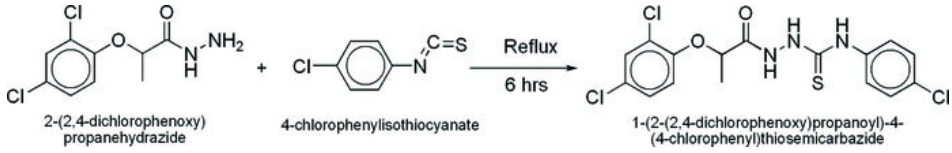


Fig. 3



2-(2,4-dichlorophenoxy) propanehydrazide

4-chlorophenylisothiocyanate

1-(2-(2,4-dichlorophenoxy)propanoyl)-4-(4-chlorophenyl)thiosemicarbazide