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1-(2,6-Dichlorobenzoyl)-3-(2-methoxyphenyl)thiourea

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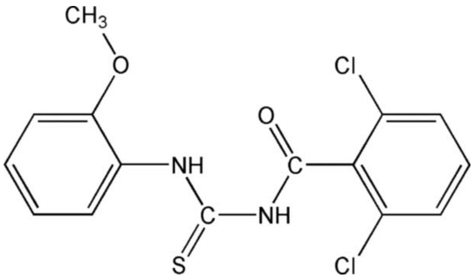
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.088; data-to-parameter ratio = 14.3.

In the title molecule, $C_{15}H_{12}Cl_2N_2O_2S$, the dihedral angle between the two benzene rings is 76.66 (5)°. The thiocarbonyl and carbonyl groups are almost coplanar, the relevant torsion angles deviating by not more than 6° from 0°; an intramolecular N—H⋯O hydrogen bond, forming a six-membered ring commonly observed in this class of compounds, may be responsible for this geometric feature. In the crystal structure, intermolecular N—H⋯S hydrogen bonds link the molecules into centrosymmetric dimers.

Related literature

The bond lengths and angles are within the ranges found for *N*,*N*′-disubstituted thiourea compounds in the Cambridge Structural Database (Version 5.28; Allen, 2002) and for a recently reported related structure (Khawar Rauf *et al.*, 2007).

For related literature, see: Darlington *et al.* (1996); Dowding & Leeds (1971); Santrucek & Krepelka (1988); Sasse *et al.* (1969); Teruhisa *et al.* (1972).



Experimental

Crystal data

$C_{15}H_{12}Cl_2N_2O_2S$
M_r = 355.23
Triclinic, $P\bar{1}$
a = 7.3748 (9) Å
b = 10.1854 (13) Å
c = 11.8404 (14) Å
α = 70.055 (9)°
β = 82.438 (11)°
γ = 74.299 (10)°
V = 804.10 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.54 mm^{-1}
T = 173 (2) K
0.49 × 0.47 × 0.47 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.778, T_{max} = 0.785
7431 measured reflections
2988 independent reflections
2762 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.088
S = 1.05
2988 reflections
209 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Selected dihedral angles (°).

C2—N2—C1—N1	−1.7 (2)	C1—N2—C2—O1	5.2 (3)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1	0.88 (2)	1.89 (2)	2.650 (2)	143 (2)
N2—H2⋯S1^i	0.85 (2)	2.60 (2)	3.4237 (15)	164.8 (19)

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

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2369).

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supplementary materials

Acta Cryst. (2007). E**63**, o2665-o2666   [**doi:10.1107/S1600536807019381**]

1-(2,6-Dichlorobenzoyl)-3-(2-methoxyphenyl)thiourea

M. Khawar Rauf, **A. Badshah** and **M. Bolte**

Comment

Thiourea and urea derivatives play an important role in developing agrochemicals and pharmacological agents. For example, ureidothiazoles are effective herbicides for a broad spectrum of weeds (Dowding & Leeds, 1971). *N*-Methylfurfurylurea herbicides give selective weed control in cereals, as well as cotton and beans (Sasse *et al.*, 1969). *N*-Methyl-*N*-(2-thiazolyl)-*N*'-alkyl substituted thioureas are plant growth regulators that inhibit stem alongation of rice and kidney bean plants without phytotoxity (Teruhisa *et al.*, 1972). 4-Aminomethyl derivatives of 2-methyl-5-hydroxybenzimidazole have been reported as an antioxidants and stimmulators of plant growth of dicotyledons under drought conditions (Santrucek & Kepelka, 1988; Darlington *et al.*, 1996).

As part of our interest in *N*,*N'*-Disubstituted thioureas, we report here the crystal structure of the title compound (I). A view of the molecular structure of (I), is shown in Fig 1. The N—C bonds (Table 1) differ significantly from one another but are short in comparison with the typical value for a N—C single bond (1.479 A°), and the C1—S1 bond is slightly shorter than a C—S double bond (1.681 A°) (Allen *et al.*, 1987), indicating partial electron delocalization in the N—C(S)—N(H)—C(O) structural segment. These distances are similar to those found in other *N*,*N'*-disubstituted thioureas in the Cambridge Structural Database, Version 5.28 (Allen, 2002) and for a recently reported structure (Khawar Rauf *et al.*, 2007). The dihedral angle between the benzene rings is 76.66 (5)°, and the corresponding angles with the thiourea plane are 25.92 (6)° for the C11–C16 ring and 77.44 (4)° for the C21–C26 ring. The thiocarbonyl and carbonyl groups are almost coplanar, as reflected by the O1—C2—N2—C1 and C2—N2— C1—N1 torsion angles (Table 1). The crystal packing is characterized by N–H···O and N–H···S hydrogen bonds (Fig.2).

Experimental

Freshly prepared 2,6-Dichlorobenzoylisothiocyanate (2.32 g, 10 mmol) was added in acetone (30 ml) and stirred for 15 minutes. Afterwards neat 2-methoxyaniline (1.23 g, 10 mmol) was added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/ 1,1-dichloromethane (1:1 *v/v*) to give fine crystals of the title compound (I), with an overall yield of 80%. Full spectroscopic and physical characterization will be reported elsewhere.

Refinement

Hydrogen atoms bonded to C were included in calculated positions and refined as riding on their parent C atom with C—H = 0.95 Å U_{iso}(H) = 1.2U(C_{eq}) or C—H = 0.98 Å and U_{iso}(H) = 1.5U(C_{eq}), respectively, for aromatic and methyl C atoms. The methyl groups were allowed to rotate but not to tip. H atoms bonded to N were refined freely.

Figures

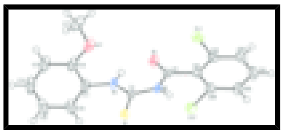

Fig. 1. Molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds showns as dashed lines.

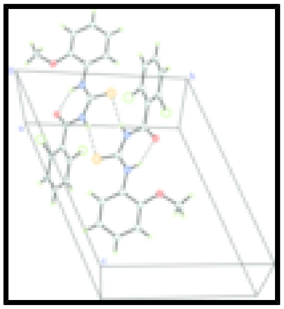

Fig. 2. Partial packing plot of (I). Hydrogen bonds shown as dashed lines.

1-(2,6-Dichlorobenzoyl)-3-(2-methoxyphenyl)thiourea

Crystal data

$C_{15}H_{12}Cl_2N_2O_2S$

$M_r = 355.23$

Triclinic, $P\overline{1}$

Hall symbol: -P 1

$a = 7.3748$ (9) Å

$b = 10.1854$ (13) Å

$c = 11.8404$ (14) Å

$\alpha = 70.055$ (9)°

$\beta = 82.438$ (11)°

$\gamma = 74.299$ (10)°

$V = 804.10$ (17) Å^3

$Z = 2$

$F_{000} = 364$

$D_x = 1.467$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 5401 reflections

$\theta = 3.7$–25.6°

$\mu = 0.54$ mm^{-1}

$T = 173$ (2) K

Block, colourless

0.49 × 0.47 × 0.47 mm

Data collection

Stoe IPDSII two-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173(2)$ K

ω scans

Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)

$T_{min} = 0.778$, $T_{max} = 0.785$

7431 measured reflections

2988 independent reflections

2762 reflections with $I > 2\sigma(I)$

$R_{int} = 0.045$

$\theta_{max} = 25.6°$

$\theta_{min} = 3.6°$

$h = -8 \rightarrow 8$

$k = -12 \rightarrow 12$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.2859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.088$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
2988 reflections	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
209 parameters	Extinction coefficient: 0.046 (4)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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}
S1	1.06353 (6)	0.36389 (4)	0.18600 (4)	0.02638 (14)
O1	0.54202 (17)	0.72852 (14)	0.19248 (11)	0.0314 (3)
Cl1	0.83368 (6)	0.93204 (5)	−0.04832 (4)	0.03324 (15)
Cl2	0.29679 (6)	0.63344 (5)	0.03232 (4)	0.03044 (14)
N1	0.7884 (2)	0.49603 (16)	0.31437 (12)	0.0250 (3)
H1	0.697 (3)	0.575 (3)	0.306 (2)	0.035 (6)*
N2	0.78676 (19)	0.59430 (14)	0.10762 (12)	0.0213 (3)
H2	0.839 (3)	0.588 (2)	0.041 (2)	0.032 (5)*
C1	0.8722 (2)	0.48715 (17)	0.20879 (14)	0.0206 (3)
C2	0.6275 (2)	0.70360 (17)	0.10366 (14)	0.0210 (3)
C11	0.8357 (2)	0.4071 (2)	0.43347 (14)	0.0275 (4)
C12	0.7695 (3)	0.4755 (2)	0.52180 (15)	0.0328 (4)
C13	0.8068 (3)	0.3994 (3)	0.64194 (16)	0.0429 (5)
H13	0.7655	0.4453	0.7016	0.051*

C14	0.9045 (3)	0.2561 (3)	0.67399 (18)	0.0509 (6)
H14	0.9319	0.2048	0.7559	0.061*
C15	0.9629 (3)	0.1865 (3)	0.58903 (19)	0.0478 (6)
H15	1.0260	0.0873	0.6131	0.057*
C16	0.9291 (3)	0.2622 (2)	0.46728 (17)	0.0358 (4)
H16	0.9697	0.2149	0.4085	0.043*
O17	0.66945 (19)	0.61556 (16)	0.47929 (11)	0.0382 (3)
C17	0.5923 (3)	0.6902 (3)	0.56413 (19)	0.0442 (5)
H17A	0.5174	0.6339	0.6270	0.066*
H17B	0.5117	0.7844	0.5229	0.066*
H17C	0.6951	0.7035	0.6006	0.066*
C21	0.5613 (2)	0.78917 (16)	−0.02152 (14)	0.0211 (3)
C22	0.6457 (2)	0.89614 (17)	−0.09868 (15)	0.0235 (3)
C23	0.5835 (3)	0.97536 (18)	−0.21395 (16)	0.0304 (4)
H23	0.6431	1.0474	−0.2655	0.037*
C24	0.4328 (3)	0.9465 (2)	−0.25165 (16)	0.0349 (4)
H24	0.3892	0.9997	−0.3302	0.042*
C25	0.3434 (3)	0.8414 (2)	−0.17707 (16)	0.0315 (4)
H25	0.2401	0.8228	−0.2041	0.038*
C26	0.4086 (2)	0.76435 (17)	−0.06253 (15)	0.0241 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0279 (2)	0.0265 (2)	0.0195 (2)	0.00321 (17)	−0.00540 (16)	−0.00678 (17)
O1	0.0333 (7)	0.0333 (7)	0.0228 (6)	0.0021 (5)	0.0015 (5)	−0.0120 (5)
Cl1	0.0321 (2)	0.0285 (2)	0.0408 (3)	−0.01124 (17)	−0.00337 (18)	−0.00953 (19)
Cl2	0.0307 (2)	0.0350 (3)	0.0280 (2)	−0.01403 (18)	0.00041 (17)	−0.00887 (18)
N1	0.0266 (7)	0.0297 (8)	0.0158 (7)	−0.0053 (6)	−0.0015 (5)	−0.0047 (6)
N2	0.0246 (7)	0.0229 (7)	0.0141 (6)	−0.0010 (5)	−0.0012 (5)	−0.0066 (5)
C1	0.0240 (8)	0.0221 (8)	0.0171 (7)	−0.0065 (6)	−0.0038 (6)	−0.0063 (6)
C2	0.0225 (8)	0.0206 (8)	0.0211 (8)	−0.0050 (6)	−0.0009 (6)	−0.0085 (6)
C11	0.0253 (8)	0.0397 (10)	0.0165 (8)	−0.0163 (7)	−0.0014 (6)	−0.0011 (7)
C12	0.0305 (9)	0.0554 (12)	0.0174 (8)	−0.0252 (9)	0.0022 (7)	−0.0074 (8)
C13	0.0467 (11)	0.0691 (15)	0.0168 (8)	−0.0338 (11)	0.0011 (8)	−0.0044 (9)
C14	0.0531 (13)	0.0748 (16)	0.0193 (9)	−0.0358 (12)	−0.0065 (9)	0.0097 (10)
C15	0.0406 (11)	0.0503 (12)	0.0366 (11)	−0.0194 (9)	−0.0089 (9)	0.0152 (10)
C16	0.0330 (10)	0.0406 (10)	0.0272 (9)	−0.0136 (8)	−0.0025 (7)	0.0016 (8)
O17	0.0457 (8)	0.0513 (8)	0.0207 (6)	−0.0139 (6)	0.0036 (5)	−0.0156 (6)
C17	0.0385 (11)	0.0728 (15)	0.0338 (10)	−0.0213 (10)	0.0097 (8)	−0.0310 (11)
C21	0.0216 (8)	0.0194 (7)	0.0198 (8)	0.0014 (6)	−0.0002 (6)	−0.0083 (6)
C22	0.0223 (8)	0.0187 (7)	0.0276 (8)	−0.0003 (6)	−0.0003 (6)	−0.0087 (7)
C23	0.0332 (9)	0.0223 (8)	0.0276 (9)	−0.0018 (7)	0.0026 (7)	−0.0029 (7)
C24	0.0380 (10)	0.0347 (10)	0.0228 (9)	−0.0008 (8)	−0.0075 (7)	−0.0017 (8)
C25	0.0286 (9)	0.0370 (10)	0.0270 (9)	−0.0033 (7)	−0.0072 (7)	−0.0092 (8)
C26	0.0230 (8)	0.0245 (8)	0.0232 (8)	−0.0027 (6)	0.0004 (6)	−0.0085 (7)

Geometric parameters (Å, °)

S1—C1	1.6771 (16)	C14—H14	0.9500
O1—C2	1.2200 (19)	C15—C16	1.403 (3)
Cl1—C22	1.7472 (17)	C15—H15	0.9500
Cl2—C26	1.7460 (17)	C16—H16	0.9500
N1—C1	1.340 (2)	O17—C17	1.431 (2)
N1—C11	1.420 (2)	C17—H17A	0.9800
N1—H1	0.88 (2)	C17—H17B	0.9800
N2—C2	1.376 (2)	C17—H17C	0.9800
N2—C1	1.399 (2)	C21—C22	1.395 (2)
N2—H2	0.85 (2)	C21—C26	1.396 (2)
C2—C21	1.508 (2)	C22—C23	1.392 (2)
C11—C16	1.390 (3)	C23—C24	1.385 (3)
C11—C12	1.412 (3)	C23—H23	0.9500
C12—O17	1.368 (3)	C24—C25	1.394 (3)
C12—C13	1.391 (3)	C24—H24	0.9500
C13—C14	1.385 (4)	C25—C26	1.388 (2)
C13—H13	0.9500	C25—H25	0.9500
C14—C15	1.381 (4)		

C1—N1—C11	130.07 (15)	C11—C16—H16	120.3
C1—N1—H1	112.5 (14)	C15—C16—H16	120.3
C11—N1—H1	117.1 (14)	C12—O17—C17	118.24 (15)
C2—N2—C1	128.23 (14)	O17—C17—H17A	109.5
C2—N2—H2	116.8 (15)	O17—C17—H17B	109.5
C1—N2—H2	115.0 (15)	H17A—C17—H17B	109.5
N1—C1—N2	114.76 (14)	O17—C17—H17C	109.5
N1—C1—S1	127.49 (13)	H17A—C17—H17C	109.5
N2—C1—S1	117.75 (11)	H17B—C17—H17C	109.5
O1—C2—N2	124.04 (15)	C22—C21—C26	117.95 (14)
O1—C2—C21	121.91 (14)	C22—C21—C2	122.10 (14)
N2—C2—C21	114.02 (13)	C26—C21—C2	119.94 (14)
C16—C11—C12	120.03 (16)	C23—C22—C21	121.91 (15)
C16—C11—N1	125.47 (16)	C23—C22—Cl1	119.24 (13)
C12—C11—N1	114.41 (16)	C21—C22—Cl1	118.85 (12)
O17—C12—C13	125.12 (18)	C24—C23—C22	118.37 (16)
O17—C12—C11	115.10 (15)	C24—C23—H23	120.8
C13—C12—C11	119.8 (2)	C22—C23—H23	120.8
C14—C13—C12	119.5 (2)	C23—C24—C25	121.58 (16)
C14—C13—H13	120.2	C23—C24—H24	119.2
C12—C13—H13	120.2	C25—C24—H24	119.2
C15—C14—C13	121.16 (18)	C26—C25—C24	118.66 (16)
C15—C14—H14	119.4	C26—C25—H25	120.7
C13—C14—H14	119.4	C24—C25—H25	120.7
C14—C15—C16	120.0 (2)	C25—C26—C21	121.53 (16)
C14—C15—H15	120.0	C25—C26—Cl2	119.16 (13)
C16—C15—H15	120.0	C21—C26—Cl2	119.31 (12)
C11—C16—C15	119.4 (2)		

C11—N1—C1—N2	−179.96 (15)	C11—C12—O17—C17	177.89 (15)
C11—N1—C1—S1	0.2 (3)	O1—C2—C21—C22	102.62 (19)
C2—N2—C1—N1	−1.7 (2)	N2—C2—C21—C22	−79.28 (18)
C2—N2—C1—S1	178.23 (12)	O1—C2—C21—C26	−76.1 (2)
C1—N2—C2—O1	5.2 (3)	N2—C2—C21—C26	102.03 (17)
C1—N2—C2—C21	−172.87 (14)	C26—C21—C22—C23	−1.0 (2)
C1—N1—C11—C16	−27.8 (3)	C2—C21—C22—C23	−179.68 (14)
C1—N1—C11—C12	155.89 (16)	C26—C21—C22—Cl1	178.61 (12)
C16—C11—C12—O17	−176.11 (15)	C2—C21—C22—Cl1	−0.1 (2)
N1—C11—C12—O17	0.4 (2)	C21—C22—C23—C24	0.4 (2)
C16—C11—C12—C13	3.4 (2)	Cl1—C22—C23—C24	−179.19 (13)
N1—C11—C12—C13	179.95 (15)	C22—C23—C24—C25	0.1 (3)
O17—C12—C13—C14	177.82 (17)	C23—C24—C25—C26	−0.1 (3)
C11—C12—C13—C14	−1.6 (3)	C24—C25—C26—C21	−0.5 (3)
C12—C13—C14—C15	−1.1 (3)	C24—C25—C26—Cl2	179.44 (14)
C13—C14—C15—C16	2.2 (3)	C22—C21—C26—C25	1.0 (2)
C12—C11—C16—C15	−2.4 (3)	C2—C21—C26—C25	179.79 (15)
N1—C11—C16—C15	−178.52 (17)	C22—C21—C26—Cl2	−178.95 (11)
C14—C15—C16—C11	−0.4 (3)	C2—C21—C26—Cl2	−0.2 (2)
C13—C12—O17—C17	−1.6 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.88 (2)	1.89 (2)	2.650 (2)	143 (2)
N2—H2···S1$^{\mathrm{i}}$	0.85 (2)	2.60 (2)	3.4237 (15)	164.8 (19)

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

Fig. 1

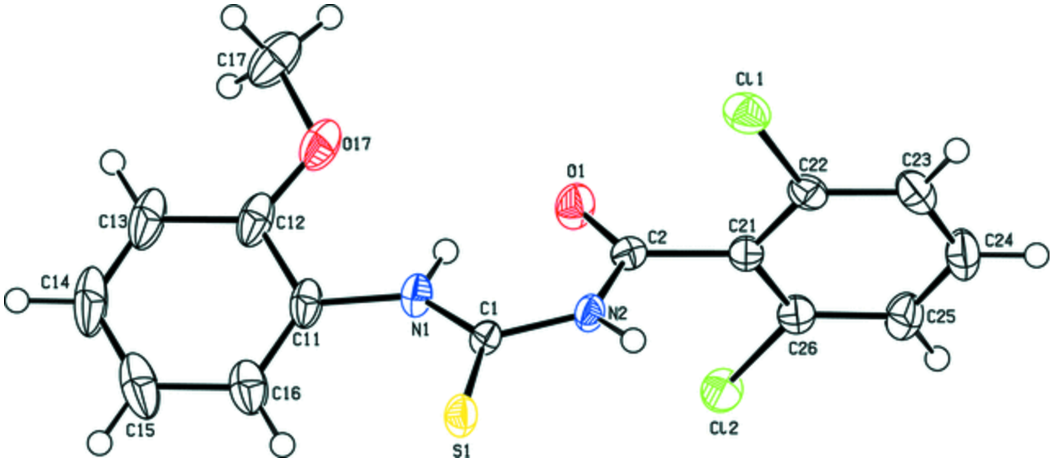
C17
O17
C13
C12
C14
C11
N1
C1
C16
C15
S1
O1
C2
N2
CL1
C22
C23
C21
C24
C26
C25
CL2

Fig. 2