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1-(3-Chlorophenyl)-3-pivaloylthiourea

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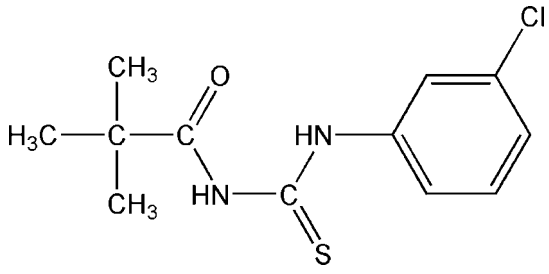
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.023; wR factor = 0.062; data-to-parameter ratio = 19.6.

The crystal structure of the title compound, $C_{12}H_{15}ClN_2OS$, is composed of discrete molecules with bond lengths and angles typical for thiourea compounds of this class. The molecule exists in the solid state in its thione form with typical thiourea C—S and C—O bond lengths, as well as shortened C—N bonds. The plane containing the thiourea group and the two attached C atoms is almost perpendicular to the benzene ring, forming a dihedral angle of 88.1 (3)°. An intramolecular N—H···O hydrogen bond stabilizes the packing arrangement and the molecules form intermolecular N—H···S hydrogen bonds to generate a chain. The *tert*-butyl group is disordered equally over two sites.

Related literature

For related literature, see: Shoukat *et al.* (2007); Khawar Rauf *et al.* (2006); Allen (2002).



Experimental

Crystal data

$C_{12}H_{15}ClN_2OS$
M_r = 270.77
Orthorhombic, $P2_12_12_1$
a = 6.1269 (2) Å
b = 10.2848 (4) Å
c = 21.1360 (9) Å
V = 1331.86 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 173 (2) K
0.49 × 0.49 × 0.47 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.817, T_{max} = 0.824
35409 measured reflections
3742 independent reflections
3700 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.062
S = 1.04
3742 reflections
191 parameters
30 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Absolute structure: Flack (1983) 1573 Friedel pairs
Flack parameter: −0.01 (4)

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.6753 (10)	N1—C11	1.4337 (13)
O1—C2	1.2272 (13)	N2—C2	1.3887 (13)
N1—C1	1.3356 (13)	N2—C1	1.3972 (12)
C2—N2—C1—N1	4.83 (15)	C1—N2—C2—O1	−0.89 (17)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.918 (19)	1.836 (19)	2.5863 (12)	137.2 (18)
N2—H2···S1^{i}	0.889 (18)	2.808 (18)	3.6560 (9)	159.8 (14)

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); 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: EZ2082).

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supplementary materials

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1-(3-Chlorophenyl)-3-pivaloylthiourea

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Comment

The background to this study has been set out in our previous work on the structural chemistry of *N*,*N*′-disubstituted thioureas (Shoukat *et al.*, 2007). Herein, as a continuation of these studies, the structure of the title compound (I) is described. A depiction of the molecule is given in Fig. 1. Bond lengths and angles, see the table of selected geometric parameters, can be regarded as typical for *N*,*N*′-disubstituted thiourea compounds as found in the Cambridge Structural Database v5.28 (Allen, 2002; Khawar Rauf *et al.*, 2006). The molecule exists in the thione form with typical thiourea C—S and C—O bonds, as well as shortened C—N bond lengths. The thiocarbonyl and carbonyl groups are almost coplanar (see selected geometric parameters table). The molecule features an intramolecular N—H···O hydrogen bond and in the crystal structure, molecules associate *via* N—H···S intermolecular hydrogen bonds to form a chain (see the table of hydrogen bond geometries; Fig 2).

Experimental

Freshly prepared pivaloylisothiocyanate (1.43 g, 10 mmol) was stirred in acetone (30 ml) for 15 minutes. Neat 3-chloroaniline (1.3 g, 10 mmol) was then added and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into acidified (pH 4) water and stirred well. The solid product was separated and washed with deionized water and purified by recrystallization from methanol/ 1,1-dichloromethane (1:10 *v/v*) to give fine crystals of (I), with an overall yield of 85%.

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_{eq}(C) or C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C), respectively, for aromatic and methyl C atoms. The H atoms bonded to N were freely refined. The *tert*-butyl group is disordered over two positions with site occupation factors of 0.50 (1)/0.50 (1). The C—C distances and C—C—C angles of the *tert*-butyl groups were restrained to be equal.

Figures

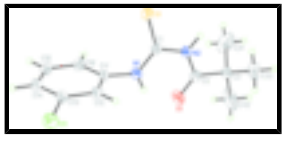

Fig. 1. Molecular structure of (I) showing atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

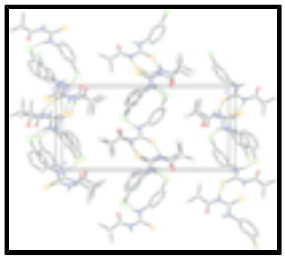

Fig. 2. Packing diagram of (I) with view onto the *bc* plane. Hydrogen bonds are shown as dashed lines.

1-(3-Chlorophenyl)-3-pivaloylthiourea

Crystal data

$C_{12}H_{15}ClN_2OS$	F_{000} = 568
M_r = 270.77	D_x = 1.350 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 34614 reflections
a = 6.1269 (2) Å	θ = 3.5–29.8º
b = 10.2848 (4) Å	μ = 0.43 mm^{-1}
c = 21.1360 (9) Å	T = 173 (2) K
V = 1331.86 (9) Å^3	Block, colourless
Z = 4	0.49 × 0.49 × 0.47 mm

Data collection

Stoe IPDSII two-circle diffractometer	3742 independent reflections
Radiation source: fine-focus sealed tube	3700 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.052
T = 173(2) K	θ_{max} = 29.6º
ω scans	θ_{min} = 3.5º
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	h = −8→8
T_{min} = 0.817, T_{max} = 0.824	k = −14→14
35409 measured reflections	l = −29→29

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.023	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.1922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.062	$(\Delta/\sigma)_{max}$ = 0.002
S = 1.04	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
3742 reflections	$\Delta\rho_{min}$ = −0.18 e Å^{-3}
191 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
30 restraints	Extinction coefficient: 0.028 (2)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack, (1983), 1573 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.01 (4)

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}	Occ. (<1)
Cl1	0.56583 (5)	0.11877 (3)	0.622329 (14)	0.03278 (8)	
S1	0.71872 (4)	0.66862 (3)	0.541901 (12)	0.02455 (7)	
O1	0.53343 (17)	0.53031 (9)	0.34538 (4)	0.0357 (2)	
N1	0.51185 (16)	0.50045 (9)	0.46671 (4)	0.02377 (17)	
H1	0.471 (3)	0.4776 (19)	0.4264 (9)	0.052 (5)*	
N2	0.72061 (15)	0.65585 (8)	0.41596 (4)	0.02134 (16)	
H2	0.821 (3)	0.7168 (17)	0.4228 (8)	0.040 (4)*	
C1	0.64372 (15)	0.60313 (9)	0.47266 (5)	0.01990 (17)	
C2	0.66320 (17)	0.61904 (11)	0.35498 (5)	0.02307 (19)	
C3	0.76111 (18)	0.69697 (11)	0.30021 (5)	0.0255 (2)	
C11	0.41745 (17)	0.43202 (9)	0.51909 (5)	0.02176 (18)	
C12	0.52851 (16)	0.32519 (10)	0.54368 (5)	0.02213 (18)	
H12	0.6688	0.3019	0.5283	0.027*	
C13	0.42847 (18)	0.25339 (10)	0.59147 (5)	0.02302 (19)	
C14	0.2224 (2)	0.28558 (11)	0.61466 (5)	0.0260 (2)	
H14	0.1563	0.2352	0.6471	0.031*	
C15	0.11545 (18)	0.39324 (12)	0.58923 (5)	0.0283 (2)	
H15	−0.0247	0.4166	0.6047	0.034*	
C16	0.21162 (18)	0.46708 (10)	0.54130 (5)	0.02590 (19)	
H16	0.1377	0.5402	0.5241	0.031*	
C31	0.6919 (19)	0.8377 (6)	0.3090 (4)	0.075 (3)	0.501 (14)
H31A	0.7498	0.8706	0.3492	0.112*	0.501 (14)
H31B	0.5322	0.8431	0.3095	0.112*	0.501 (14)
H31C	0.7491	0.8903	0.2741	0.112*	0.501 (14)
C32	0.6826 (14)	0.6375 (10)	0.2402 (3)	0.072 (3)	0.501 (14)
H32A	0.7430	0.6855	0.2041	0.108*	0.501 (14)
H32B	0.5229	0.6411	0.2387	0.108*	0.501 (14)
H32C	0.7303	0.5466	0.2381	0.108*	0.501 (14)
C33	1.0128 (9)	0.6913 (7)	0.3023 (3)	0.0448 (12)	0.501 (14)
H33A	1.0646	0.7296	0.3420	0.067*	0.501 (14)
H33B	1.0729	0.7401	0.2665	0.067*	0.501 (14)
H33C	1.0606	0.6005	0.2998	0.067*	0.501 (14)
C31'	0.6110 (11)	0.8150 (7)	0.2875 (3)	0.0556 (14)	0.499 (14)

H31D	0.4607	0.7849	0.2814	0.083*	0.499 (14)
H31E	0.6605	0.8604	0.2493	0.083*	0.499 (14)
H31F	0.6168	0.8746	0.3236	0.083*	0.499 (14)
C32'	0.7525 (16)	0.6115 (6)	0.2407 (3)	0.058 (2)	0.499 (14)
H32D	0.6026	0.5814	0.2338	0.087*	0.499 (14)
H32E	0.8488	0.5363	0.2462	0.087*	0.499 (14)
H32F	0.8007	0.6622	0.2040	0.087*	0.499 (14)
C33'	0.9919 (10)	0.7433 (11)	0.3097 (3)	0.0562 (19)	0.499 (14)
H33D	1.0396	0.7918	0.2722	0.084*	0.499 (14)
H33E	1.0880	0.6682	0.3161	0.084*	0.499 (14)
H33F	0.9985	0.7999	0.3469	0.084*	0.499 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.04062 (15)	0.02760 (12)	0.03014 (13)	0.00457 (11)	−0.00164 (11)	0.00577 (10)
S1	0.02621 (11)	0.02688 (12)	0.02055 (11)	−0.00204 (9)	−0.00021 (9)	−0.00280 (9)
O1	0.0454 (5)	0.0378 (5)	0.0238 (4)	−0.0202 (4)	−0.0028 (4)	0.0016 (3)
N1	0.0308 (4)	0.0221 (4)	0.0184 (4)	−0.0057 (3)	0.0028 (3)	−0.0004 (3)
N2	0.0240 (4)	0.0209 (3)	0.0191 (4)	−0.0036 (3)	0.0014 (3)	0.0001 (3)
C1	0.0200 (4)	0.0185 (4)	0.0212 (4)	0.0025 (3)	0.0025 (3)	0.0009 (3)
C2	0.0266 (4)	0.0229 (4)	0.0197 (4)	−0.0017 (4)	0.0002 (3)	0.0014 (4)
C3	0.0312 (5)	0.0255 (4)	0.0198 (4)	−0.0044 (4)	0.0005 (4)	0.0033 (4)
C11	0.0247 (4)	0.0215 (4)	0.0190 (4)	−0.0034 (4)	0.0031 (4)	−0.0006 (3)
C12	0.0220 (4)	0.0238 (4)	0.0207 (4)	−0.0019 (3)	0.0014 (3)	−0.0013 (4)
C13	0.0274 (5)	0.0214 (4)	0.0203 (4)	−0.0014 (4)	−0.0018 (4)	0.0002 (3)
C14	0.0296 (5)	0.0278 (5)	0.0205 (4)	−0.0051 (4)	0.0051 (4)	0.0003 (4)
C15	0.0261 (5)	0.0324 (5)	0.0264 (5)	0.0012 (4)	0.0074 (4)	−0.0012 (4)
C16	0.0276 (4)	0.0254 (4)	0.0247 (5)	0.0029 (4)	0.0025 (4)	0.0006 (4)
C31	0.118 (6)	0.039 (2)	0.068 (4)	0.031 (3)	0.045 (4)	0.032 (2)
C32	0.077 (4)	0.120 (6)	0.019 (2)	−0.063 (4)	−0.013 (2)	0.018 (3)
C33	0.0357 (15)	0.060 (3)	0.0384 (19)	−0.0093 (19)	0.0065 (13)	0.016 (2)
C31'	0.067 (3)	0.052 (3)	0.048 (3)	0.025 (2)	0.018 (2)	0.027 (2)
C32'	0.106 (6)	0.0388 (18)	0.029 (2)	−0.036 (3)	0.022 (3)	−0.0107 (15)
C33'	0.043 (2)	0.092 (5)	0.034 (2)	−0.034 (3)	−0.0109 (18)	0.030 (3)

Geometric parameters (Å, °)

Cl1—C13	1.7466 (11)	C14—H14	0.9500
S1—C1	1.6753 (10)	C15—C16	1.3965 (15)
O1—C2	1.2272 (13)	C15—H15	0.9500
N1—C1	1.3356 (13)	C16—H16	0.9500
N1—C11	1.4337 (13)	C31—H31A	0.9800
N1—H1	0.918 (19)	C31—H31B	0.9800
N2—C2	1.3887 (13)	C31—H31C	0.9800
N2—C1	1.3972 (12)	C32—H32A	0.9800
N2—H2	0.889 (18)	C32—H32B	0.9800
C2—C3	1.5304 (14)	C32—H32C	0.9800
C3—C32	1.489 (6)	C33—H33A	0.9800

C3—C33'	1.506 (5)	C33—H33B	0.9800
C3—C31	1.520 (5)	C33—H33C	0.9800
C3—C32'	1.536 (5)	C31'—H31D	0.9800
C3—C33	1.544 (5)	C31'—H31E	0.9800
C3—C31'	1.547 (5)	C31'—H31F	0.9800
C11—C16	1.3931 (14)	C32'—H32D	0.9800
C11—C12	1.3930 (14)	C32'—H32E	0.9800
C12—C13	1.3932 (14)	C32'—H32F	0.9800
C12—H12	0.9500	C33'—H33D	0.9800
C13—C14	1.3940 (16)	C33'—H33E	0.9800
C14—C15	1.3945 (16)	C33'—H33F	0.9800
C1—N1—C11	124.02 (9)	C11—C16—C15	119.05 (10)
C1—N1—H1	117.0 (12)	C11—C16—H16	120.5
C11—N1—H1	118.8 (13)	C15—C16—H16	120.5
C2—N2—C1	127.23 (9)	C3—C31—H31A	109.5
C2—N2—H2	121.2 (11)	C3—C31—H31B	109.5
C1—N2—H2	111.5 (11)	H31A—C31—H31B	109.5
N1—C1—N2	115.47 (9)	C3—C31—H31C	109.5
N1—C1—S1	124.48 (8)	H31A—C31—H31C	109.5
N2—C1—S1	120.05 (7)	H31B—C31—H31C	109.5
O1—C2—N2	121.35 (9)	C3—C32—H32A	109.5
O1—C2—C3	121.22 (9)	C3—C32—H32B	109.5
N2—C2—C3	117.39 (9)	H32A—C32—H32B	109.5
C32—C3—C31	114.0 (4)	C3—C32—H32C	109.5
C32—C3—C2	107.6 (3)	H32A—C32—H32C	109.5
C33'—C3—C2	115.7 (2)	H32B—C32—H32C	109.5
C31—C3—C2	107.3 (2)	C3—C33—H33A	109.5
C32—C3—C32'	19.1 (5)	C3—C33—H33B	109.5
C33'—C3—C32'	108.8 (4)	H33A—C33—H33B	109.5
C2—C3—C32'	107.8 (3)	C3—C33—H33C	109.5
C32—C3—C33	109.4 (4)	H33A—C33—H33C	109.5
C31—C3—C33	108.1 (4)	H33B—C33—H33C	109.5
C2—C3—C33	110.5 (3)	C3—C31'—H31D	109.5
C33'—C3—C31'	109.5 (4)	C3—C31'—H31E	109.5
C2—C3—C31'	108.0 (2)	H31D—C31'—H31E	109.5
C32'—C3—C31'	106.6 (3)	C3—C31'—H31F	109.5
C16—C11—C12	121.37 (9)	H31D—C31'—H31F	109.5
C16—C11—N1	119.89 (9)	H31E—C31'—H31F	109.5
C12—C11—N1	118.57 (9)	C3—C32'—H32D	109.5
C11—C12—C13	118.27 (9)	C3—C32'—H32E	109.5
C11—C12—H12	120.9	H32D—C32'—H32E	109.5
C13—C12—H12	120.9	C3—C32'—H32F	109.5
C12—C13—C14	121.83 (10)	H32D—C32'—H32F	109.5
C12—C13—Cl1	118.61 (8)	H32E—C32'—H32F	109.5
C14—C13—Cl1	119.56 (8)	C3—C33'—H33D	109.5
C13—C14—C15	118.60 (10)	C3—C33'—H33E	109.5
C13—C14—H14	120.7	H33D—C33'—H33E	109.5
C15—C14—H14	120.7	C3—C33'—H33F	109.5
C14—C15—C16	120.87 (10)	H33D—C33'—H33F	109.5

C14—C15—H15	119.6	H33E—C33'—H33F	109.5
C16—C15—H15	119.6		
C11—N1—C1—N2	179.50 (9)	N2—C2—C3—C33	58.8 (3)
C11—N1—C1—S1	−0.31 (15)	O1—C2—C3—C31'	90.7 (4)
C2—N2—C1—N1	4.83 (15)	N2—C2—C3—C31'	−87.0 (4)
C2—N2—C1—S1	−175.35 (8)	C1—N1—C11—C16	92.59 (13)
C1—N2—C2—O1	−0.89 (17)	C1—N1—C11—C12	−92.01 (13)
C1—N2—C2—C3	176.75 (9)	C16—C11—C12—C13	−0.02 (15)
O1—C2—C3—C32	−4.2 (5)	N1—C11—C12—C13	−175.36 (9)
N2—C2—C3—C32	178.2 (5)	C11—C12—C13—C14	0.19 (15)
O1—C2—C3—C33'	−146.3 (5)	C11—C12—C13—Cl1	179.68 (7)
N2—C2—C3—C33'	36.1 (5)	C12—C13—C14—C15	−0.34 (16)
O1—C2—C3—C31	118.8 (6)	Cl1—C13—C14—C15	−179.83 (9)
N2—C2—C3—C31	−58.8 (6)	C13—C14—C15—C16	0.33 (17)
O1—C2—C3—C32'	−24.3 (4)	C12—C11—C16—C15	0.02 (16)
N2—C2—C3—C32'	158.1 (4)	N1—C11—C16—C15	175.29 (10)
O1—C2—C3—C33	−123.5 (3)	C14—C15—C16—C11	−0.18 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.918 (19)	1.836 (19)	2.5863 (12)	137.2 (18)
N2—H2···S1^{i}	0.889 (18)	2.808 (18)	3.6560 (9)	159.8 (14)

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+1.

Fig. 1

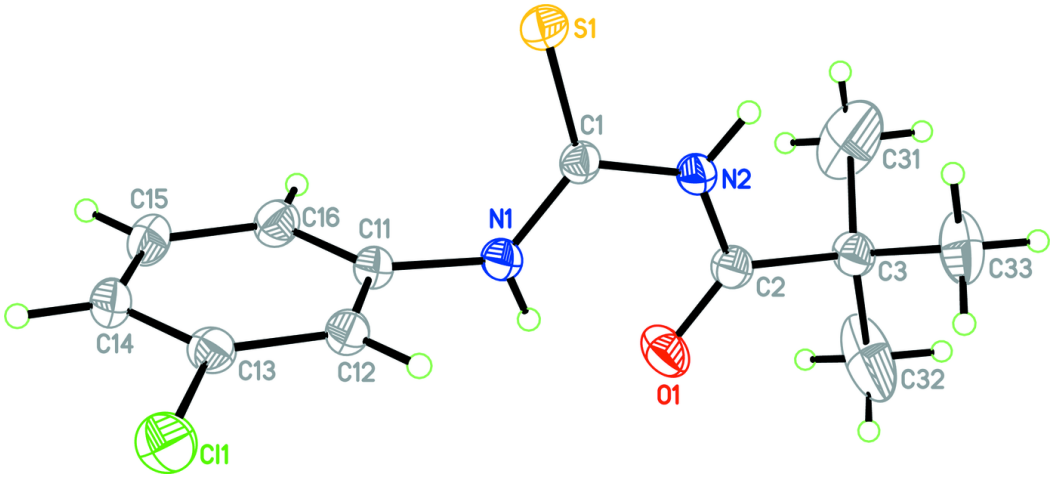

Fig. 2