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1-(4-Chlorophenyl)-3-(2-thienylcarbonyl)thiourea

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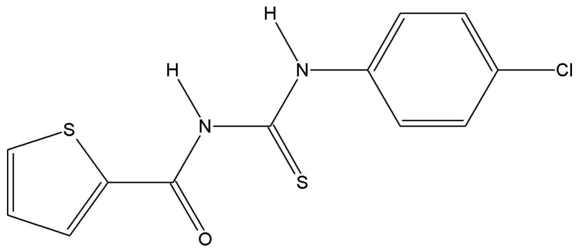
Key indicators: single-crystal X-ray study; T = 300 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.107; data-to-parameter ratio = 18.0.

The title compound, $C_{12}H_9ClN_2OS_2$, exists in the thioamide form with an intramolecular N—H···O hydrogen bond across the thiourea and the carbonyl group. The dihedral angle between the rings is 10.36 (11)°. In the crystal structure, molecules are linked into chains by weak intermolecular C—H···Cl hydrogen-bonding interactions.

Related literature

For general background to the biological activity of thiourea derivatives, see: Xu *et al.* (2004); Gu *et al.* (2007). For related structures, see: Saeed *et al.* (2008, 2009). For the cytotoxicity of anticancer drugs to normal cells in cancer therapy, see: Saeed *et al.* (2010).



Experimental

Crystal data

$C_{12}H_9ClN_2OS_2$
M_r = 296.78
Monoclinic, $P2_1/n$
a = 4.6552 (7) Å
b = 11.660 (2) Å
c = 23.630 (4) Å
β = 95.626 (2)°
V = 1276.4 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.61 mm^{-1}
T = 300 K
0.42 × 0.19 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.783, $T_{\max}$ = 0.953
8549 measured reflections
3102 independent reflections
2578 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.107
S = 1.07
3102 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O1	0.87 (2)	1.91 (2)	2.651 (2)	143 (2)
C12—H12···Cl1$^{\rm i}$	0.93	2.69	3.523 (2)	149

Symmetry code: (i) $x - \frac{5}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* and *CrystalStructure* (Rigaku/MSC and Rigaku, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976) and *DIAMOND* (Brandenburg, 1998); 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: LX2142).

References

Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (1998). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Gu, C.-L., Liu, L., Sui, Y., Zhao, J.-L. D., Wang, D. & Chen, Y.-J. (2007). *Tetrahedron*, **18**, 455–463.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rigaku/MSC and Rigaku (2006). *CrystalStructure*. Rigaku/MSC, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Saeed, S., Bhatti, M. H., Yunus, U. & Jones, P. G. (2008). *Acta Cryst.* E**64**, o1485.
Saeed, S., Rashid, N., Jones, P. G., Ali, M. & Hussain, R. (2010). *Eur. J. Med. Chem.* **45**, 1323–1331.
Saeed, S., Rashid, N., Tahir, A. & Jones, P. G. (2009). *Acta Cryst.* E**65**, o1870–o1871.
Sheldrick, G. M. (1996). *SADABS*, Göttingen University, Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Xu, Y., Hua, W., Liu, X. & Zhu, D. (2004). *Chin. J. Org. Chem.* **24**, 1217–1222.

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supplementary materials

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1-(4-Chlorophenyl)-3-(2-thienylcarbonyl)thiourea

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Comment

Thiourea and its derivatives are an important class of organic compounds in which sulfur is the major ligand atom which plays an important role in coordination chemistry with transition metals. Thiourea and its derivatives have found extensive applications in the fields of medicine, agriculture and analytical chemistry. Thioureas are also known to exhibit a wide range of biological activities including anticancer (Saeed *et al.*, 2010), antifungal (Saeed *et al.*, 2008), antiviral, antibacterial, anti-tubercular, anti-thyroidal, herbicidal and insecticidal activities, organocatalyst (Gu *et al.*, 2007) and as agrochemicals (Xu *et al.*, 2004).

The 4-chlorophenyl ring is slightly twisted {15.04 (8)°} from the thiourea plane. The thioureido group is also slightly twisted {5.0 (1)°} from the thiophene ring plane of S2/C9/C10/C11/C12. The molecular packing (Fig. 2) exhibits the thioamide form with an intramolecular N–H···O hydrogen bond across the thiourea system, with a N1–H1N···O1 (Table 1). The crystal packing (Fig. 2) is stabilized by weak intermolecular C–H···Cl hydrogen bonds between the thiophene H atom and the chlorine of an adjacent molecule, with a C12–H12···Cl1^{i} (Table 1).

Experimental

A solution of 2-thiophenecarbonyl chloride (0.01 mol) in anhydrous acetone (80 ml) was added dropwise to a suspension of ammonium thiocyanate (0.01 mol) in anhydrous acetone (50 ml) and the reaction mixture was refluxed for 50 minutes. After cooling to room temperature, a solution of 4-chloroaniline (0.01 mol) in dry acetone (25 ml) was added and the resulting mixture refluxed for 2 h. The reaction mixture was poured into five times its volume of cold water, upon which the thiourea precipitated. The product was recrystallized from ethanol as white block crystals.

Refinement

The H atoms bound C atoms were located from difference Fourier map and refined freely. All H atoms of C atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å for aryl and thiophenyl H atoms. U_{iso}(H) = 1.2U_{eq}(C) for aryl thiophenyl H atoms.

Figures

Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are presented as a small spheres of arbitrary radius.

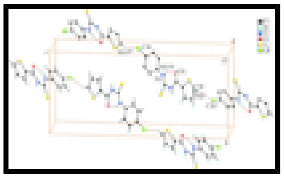

Fig. 2. N–H···O and C–H···Cl interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) x - 5/2, - y + 1/2, z - 1/2 (ii) x + 5/2, - y + 1/2, z + 1/2.]

1-(4-Chlorophenyl)-3-(2-thienylcarbonyl)thiourea

Crystal data

$C_{12}H_9ClN_2OS_2$	$F(000) = 608$
$M_r = 296.78$	$D_x = 1.544$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 412 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.6552$ (7) Å	Cell parameters from 8801 reflections
$b = 11.660$ (2) Å	$\theta = 1.7$–28.3°
$c = 23.630$ (4) Å	$\mu = 0.61$ mm^{-1}
$\beta = 95.626$ (2)°	$T = 300$ K
$V = 1276.4$ (4) Å^3	Prism, yellow
$Z = 4$	0.42 × 0.19 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer	3102 independent reflections
Radiation source: fine-focus sealed tube	2578 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.019$
ω scan	$\theta_{max} = 28.3°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -6 \rightarrow 6$
$T_{min} = 0.783$, $T_{max} = 0.953$	$k = -9 \rightarrow 15$
8549 measured reflections	$l = -30 \rightarrow 31$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.3548P]$ where $P = (F_o^2 + 2F_c^2)/3$
3102 reflections	$(\Delta/\sigma)_{max} < 0.001$
172 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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	1.37357 (11)	0.14501 (5)	0.54454 (2)	0.06174 (17)
S1	0.42417 (13)	0.54355 (4)	0.38816 (3)	0.06558 (19)
S2	−0.38487 (12)	0.23708 (4)	0.20193 (2)	0.05870 (17)
O1	0.0745 (3)	0.22204 (11)	0.29637 (6)	0.0549 (3)
N1	0.4375 (3)	0.31315 (13)	0.37757 (6)	0.0426 (3)
H1N	0.357 (5)	0.2572 (18)	0.3578 (9)	0.053 (6)*
N2	0.0880 (3)	0.41119 (13)	0.32158 (7)	0.0446 (3)
H2N	0.001 (5)	0.475 (2)	0.3134 (10)	0.063 (7)*
C1	1.1034 (4)	0.19841 (16)	0.49542 (8)	0.0448 (4)
C2	0.9940 (4)	0.12913 (16)	0.45099 (8)	0.0470 (4)
H2	1.0655	0.0554	0.4470	0.056*
C3	0.7761 (4)	0.17123 (15)	0.41242 (7)	0.0446 (4)
H3	0.7010	0.1254	0.3823	0.053*
C4	0.6685 (4)	0.28161 (15)	0.41829 (7)	0.0395 (3)
C5	0.7819 (4)	0.34955 (16)	0.46329 (8)	0.0486 (4)
H5	0.7111	0.4233	0.4677	0.058*
C6	1.0007 (4)	0.30746 (17)	0.50170 (8)	0.0506 (4)
H6	1.0777	0.3531	0.5317	0.061*
C7	0.3216 (4)	0.41540 (14)	0.36378 (7)	0.0409 (4)
C8	−0.0182 (4)	0.32019 (15)	0.28912 (7)	0.0408 (4)
C9	−0.2510 (4)	0.34711 (15)	0.24497 (7)	0.0413 (4)
C10	−0.3865 (4)	0.44880 (17)	0.22982 (8)	0.0499 (4)
H10	−0.3439	0.5183	0.2481	0.060*
C11	−0.5988 (5)	0.43535 (18)	0.18316 (9)	0.0574 (5)
H11	−0.7109	0.4952	0.1671	0.069*
C12	−0.6202 (5)	0.32616 (19)	0.16464 (9)	0.0586 (5)
H12	−0.7503	0.3022	0.1346	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0533 (3)	0.0688 (3)	0.0585 (3)	−0.0017 (2)	−0.0177 (2)	0.0113 (2)

S1	0.0745 (4)	0.0364 (2)	0.0783 (4)	−0.0039 (2)	−0.0311 (3)	−0.0049 (2)
S2	0.0706 (3)	0.0434 (3)	0.0563 (3)	0.0030 (2)	−0.0228 (2)	−0.0074 (2)
O1	0.0672 (9)	0.0381 (6)	0.0547 (8)	0.0023 (6)	−0.0187 (6)	−0.0028 (6)
N1	0.0463 (8)	0.0358 (7)	0.0429 (8)	−0.0042 (6)	−0.0088 (6)	−0.0016 (6)
N2	0.0469 (8)	0.0372 (7)	0.0466 (8)	0.0002 (6)	−0.0105 (6)	−0.0020 (6)
C1	0.0384 (8)	0.0518 (10)	0.0427 (9)	−0.0060 (7)	−0.0035 (7)	0.0076 (7)
C2	0.0494 (10)	0.0429 (9)	0.0473 (9)	0.0012 (8)	−0.0023 (7)	0.0025 (7)
C3	0.0491 (9)	0.0403 (9)	0.0423 (9)	−0.0046 (7)	−0.0060 (7)	−0.0026 (7)
C4	0.0387 (8)	0.0392 (8)	0.0394 (8)	−0.0047 (6)	−0.0026 (6)	0.0029 (7)
C5	0.0552 (10)	0.0416 (9)	0.0465 (9)	−0.0005 (8)	−0.0075 (8)	−0.0035 (7)
C6	0.0526 (10)	0.0501 (10)	0.0460 (9)	−0.0084 (8)	−0.0113 (8)	−0.0045 (8)
C7	0.0418 (8)	0.0395 (8)	0.0401 (8)	−0.0048 (7)	−0.0030 (6)	−0.0010 (7)
C8	0.0428 (8)	0.0395 (8)	0.0388 (8)	−0.0031 (7)	−0.0020 (6)	0.0002 (7)
C9	0.0436 (8)	0.0394 (9)	0.0392 (8)	−0.0041 (7)	−0.0042 (6)	0.0001 (7)
C10	0.0528 (10)	0.0419 (10)	0.0519 (10)	0.0004 (8)	−0.0098 (8)	0.0005 (8)
C11	0.0578 (11)	0.0509 (11)	0.0595 (12)	0.0041 (9)	−0.0146 (9)	0.0077 (9)
C12	0.0620 (12)	0.0570 (12)	0.0514 (10)	−0.0013 (9)	−0.0214 (9)	0.0007 (9)

Geometric parameters (Å, °)

Cl1—C1	1.7408 (18)	C2—H2	0.9300
S1—C7	1.6548 (17)	C3—C4	1.393 (2)
S2—C12	1.693 (2)	C3—H3	0.9300
S2—C9	1.7158 (17)	C4—C5	1.388 (2)
O1—C8	1.229 (2)	C5—C6	1.386 (3)
N1—C7	1.336 (2)	C5—H5	0.9300
N1—C4	1.419 (2)	C6—H6	0.9300
N1—H1N	0.87 (2)	C8—C9	1.463 (2)
N2—C8	1.373 (2)	C9—C10	1.374 (2)
N2—C7	1.402 (2)	C10—C11	1.415 (3)
N2—H2N	0.86 (2)	C10—H10	0.9300
C1—C6	1.372 (3)	C11—C12	1.347 (3)
C1—C2	1.382 (3)	C11—H11	0.9300
C2—C3	1.385 (2)	C12—H12	0.9300
C12—S2—C9	91.64 (10)	C1—C6—C5	119.94 (17)
C7—N1—C4	131.12 (15)	C1—C6—H6	120.0
C7—N1—H1N	113.5 (14)	C5—C6—H6	120.0
C4—N1—H1N	115.4 (14)	N1—C7—N2	114.12 (15)
C8—N2—C7	129.51 (16)	N1—C7—S1	128.69 (13)
C8—N2—H2N	113.9 (16)	N2—C7—S1	117.15 (13)
C7—N2—H2N	116.5 (16)	O1—C8—N2	122.64 (16)
C6—C1—C2	121.18 (16)	O1—C8—C9	121.65 (16)
C6—C1—Cl1	119.75 (14)	N2—C8—C9	115.71 (15)
C2—C1—Cl1	119.06 (15)	C10—C9—C8	131.32 (16)
C1—C2—C3	118.96 (17)	C10—C9—S2	111.10 (13)
C1—C2—H2	120.5	C8—C9—S2	117.57 (13)
C3—C2—H2	120.5	C9—C10—C11	112.03 (17)
C2—C3—C4	120.61 (16)	C9—C10—H10	124.0
C2—C3—H3	119.7	C11—C10—H10	124.0

C4—C3—H3	119.7	C12—C11—C10	112.44 (18)
C5—C4—C3	119.35 (16)	C12—C11—H11	123.8
C5—C4—N1	125.26 (16)	C10—C11—H11	123.8
C3—C4—N1	115.33 (15)	C11—C12—S2	112.79 (15)
C6—C5—C4	119.96 (18)	C11—C12—H12	123.6
C6—C5—H5	120.0	S2—C12—H12	123.6
C4—C5—H5	120.0		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1	0.87 (2)	1.91 (2)	2.651 (2)	143 (2)
C12—H12···Cl1^{i}	0.93	2.69	3.523 (2)	149

Symmetry codes: (i) *x*−5/2, −*y*+1/2, *z*−1/2.

Fig. 1

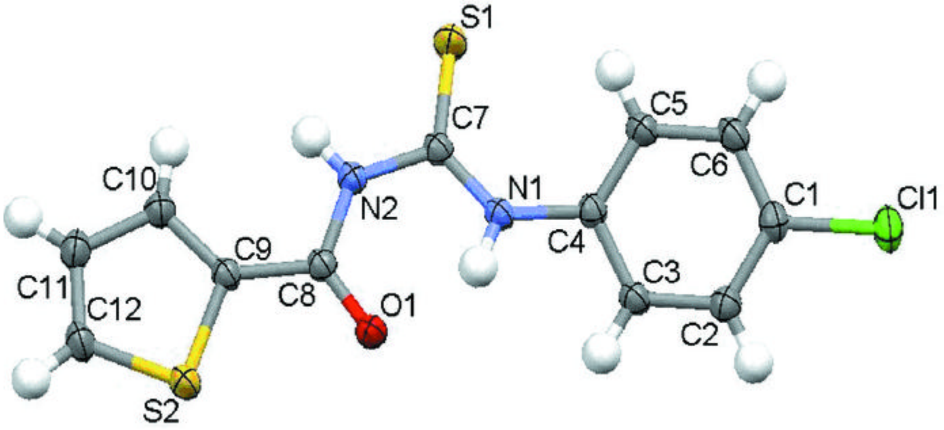

Fig. 2