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N-(2-Chlorobenzoyl)-*N*′-(3-pyridyl)thiourea

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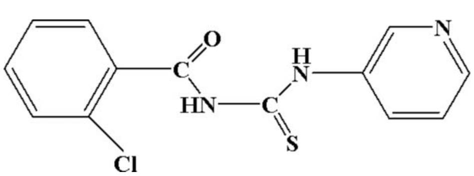
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.100; data-to-parameter ratio = 13.5.

In the molecule of the title compound, $C_{13}H_{10}ClN_3OS$, the dihedral angles between the plane through the thiourea group and the pyridine and benzene rings are 53.08 (3) and 87.12 (3)°, respectively. The molecules are linked by intermolecular N—H···N hydrogen-bonding interactions to form a supramolecular chain structure along the *a* axis. An intramolecular N—H···O hydrogen bond is also present.

Related literature

For related literature, see: Campo *et al.* (2002); Dong *et al.* (2006, 2008); Foss *et al.* (2004); Guillon *et al.* (1996); Koch (2001); Krepps *et al.* (2001); Su *et al.* (2004, 2006); Teoh *et al.* (1999); Venkatachalam *et al.* (2004); West *et al.* (2000); Xian *et al.* (2004).



Experimental

Crystal data

$C_{13}H_{10}ClN_3OS$
M_r = 291.75
Triclinic, $P\overline{1}$
a = 8.421 (3) Å
b = 9.282 (4) Å
c = 10.512 (4) Å
α = 98.336 (4)°
β = 110.797 (4)°
γ = 112.532 (4)°
V = 670.9 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.43 mm^{-1}
T = 298 (2) K
0.32 × 0.11 × 0.07 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.874, T_{max} = 0.972
3504 measured reflections
2319 independent reflections
1734 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.02
2319 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1	0.86	1.98	2.671 (3)	137
N1—H1···N3^{i}	0.86	2.08	2.886 (4)	157

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2227).

References

Campo, R., Criado, J. J. & Garcia, E. (2002). *J. Inorg. Biochem.* **89**, 74–82.
Dong, W. K., Yang, X. Q., Chai, L. Q., Tian, Y. Q. & Feng, J. H. (2008). *Phosphorus Sulfur Silicon*, **183**, 1181–1187.
Dong, W.-K., Yang, X.-Q. & Feng, J.-H. (2006). *Acta Cryst.* E**62**, o3459–o3460.
Foss, O., Husebye, S., Törnroos, K. W. & Fanwick, P. E. (2004). *Polyhedron*, **23**, 3021–3032.
Guillon, E., Mohamadou, G. & Déchamps-Olivier, I. (1996). *Polyhedron*, **15**, 947–952.
Koch, K. R. (2001). *Coord. Chem. Rev.* **216–217**, 473–488.
Krepps, M. K., Parkin, S. & Atwood, D. A. (2001). *Cryst. Growth Des.* **1**, 291–297.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Su, B. Q., Liu, G. L. & Sheng, L. (2006). *Phosphorus Sulfur Silicon*, **181**, 745–750.
Su, B.-Q., Xian, L., Song, H.-B. & Sheng, L. (2004). *Acta Cryst.* C**60**, m661–m662.
Teoh, S. G., Ang, S. H. & Fun, H. K. (1999). *J. Organomet. Chem.* **580**, 17–21.
Venkatachalam, T. K., Sudbeck, E. & Uckun, F. M. (2004). *J. Mol. Struct.* **687**, 45–51.
West, D. X., Castiñeiras, A. & Bermejo, E. (2000). *J. Mol. Struct.* **520**, 103–106.
Xian, L., Wei, T. B. & Zhang, Y. M. (2004). *J. Coord. Chem.* **57**, 453–457.

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N-(2-Chlorobenzoyl)-*N*′-(3-pyridyl)thiourea

Lan-Qin Chai, Yu-Jie Ding, Xiao-Qing Yang, Hai-Bo Yan and Wen-Kui Dong

S1. Comment

Thiourea and its substituted derivatives have attracted much attention because of their unique properties, such as the strong coordination ability (Su *et al.*, 2004; Su *et al.*, 2006; Xian *et al.*, 2004; West *et al.*, 2000). They are used as selective analytical reagents, especially for the determination of transition metals in complex interfering matrices (Koch, 2001; Foss *et al.*, 2004). It has been shown that the redox properties of thiourea are markedly influenced by electronic factors (Guillon *et al.*, 1996), and the biological activity of thiourea derivatives has also been reported in the literature (Teoh *et al.*, 1999; Campo *et al.*, 2002). However, the study of S···H interactions may have fundamental importance in biochemical research due to the fact that living systems contain several important sulfur-containing molecules, such as the aminoacids cysteine and methionine (Krepps *et al.*, 2001). Related to the biological relevance of S···H interactions, Uckum and coworkers have recently reported a structural study of a series of thiourea compounds (Venkatachalam *et al.*, 2004). Here we report the synthesis and crystal structure of a new benzoylthiourea derivative, *N*-(*o*-chloro)benzoyl-*N*′-(3-pyridyl)thiourea. The molecular structure of the title compound is shown in Figure 1.

The dihedral angles formed by the plane through the thiourea group and the pyridine and benzene rings of 53.08 (3) and 87.12 (3)°, respectively. The molecular conformation is stabilized by an intramolecular N—H···O hydrogen bonding interaction (Table 1), forming a planar six-membered ring. In contrast to other thiourea compounds, the H1···S1 separation is 2.662 (2) Å, indicating that S1 is not involved in hydrogen bonding. This situation is similar to that found in the structure of *N*-benzoyl-*N*′-(3-pyridyl)thiourea (Dong *et al.*, 2006). The C=O bond length of 1.217 (3) Å is just significantly longer than the average C=O bond length (1.200 Å) due to the intramolecular hydrogen bond. In the crystal structure, molecules are linked by intermolecular by N—H···N hydrogen interactions to form supramolecular chains along the *a* axis.

S2. Experimental

N-(*o*-Chloro)benzoyl-*N*′-(3-pyridyl)thiourea was synthesized according the method reported in the literature (Dong *et al.*, 2008). *o*-Chlorobenzoyl chloride (3.61 g, 0.02 mol) was reacted with ammonium thiocyanate (2.28 g, 0.03 mol) in CH_2Cl_2 (25 ml) under solid-liquid phase transfer catalysis, using 3% polyethylene glycol-400 (0.36 g) as catalyst, to give the corresponding benzoyl isothiocyanate, which was reacted with 3-aminopyridine (1.72 g, 0.02 mol). The title compound precipitated immediately. The product was filtered, washed with water and CH_2Cl_2 and dried. Colourless needle-shaped single crystals were obtained by slow evaporation of an acetone solution after several weeks at room temperature. M.p. 442 - 444 K. Anal. Calcd. for $C_{13}H_{10}ClN_3OS$: C, 53.52; H, 3.45; N, 14.40. Found: C, 53.28; H, 3.48; N, 14.15%.

S3. Refinement

H atoms were treated as riding atoms with C—H = 0.93 Å, N—H = 0.86 Å, and U_{iso}(H) = 1.2 U_{eq}(C, N).

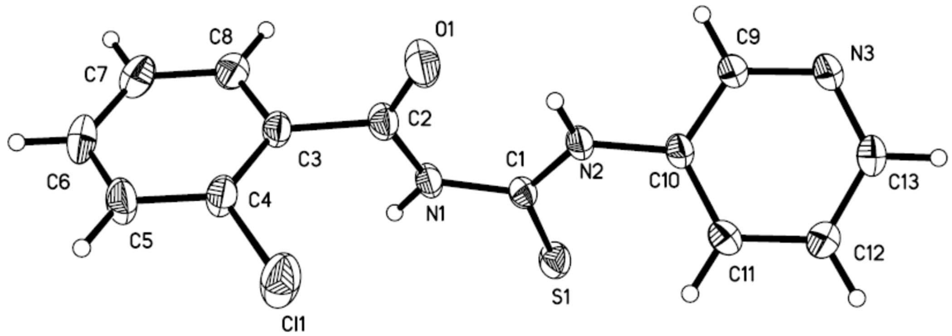

Figure 1

The molecule structure of the title compound with atom numbering. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

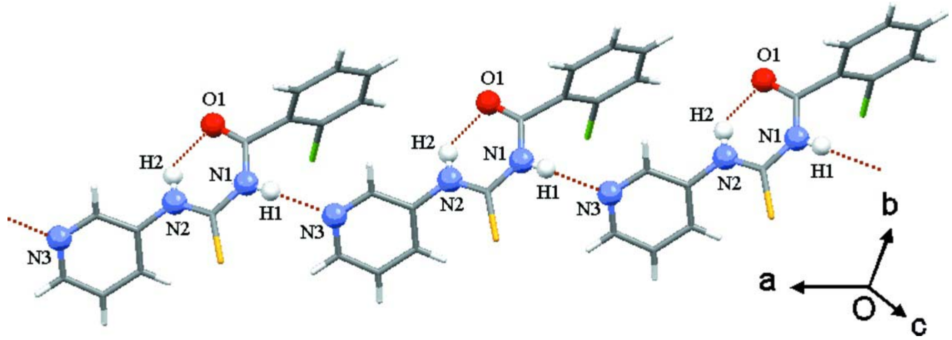

Figure 2

The supramolecular chain structure of the title compound constructed by intermolecular N—H···N hydrogen bonding interactions (dotted lines).

N-(2-Chlorobenzoyl)-*N*′-(3-pyridyl)thiourea

Crystal data

$C_{13}H_{10}ClN_3OS$
M_r = 291.75
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.421 (3) Å
b = 9.282 (4) Å
c = 10.512 (4) Å
α = 98.336 (4)°
β = 110.797 (4)°
γ = 112.532 (4)°
V = 670.9 (5) Å^3
Z = 2
F(000) = 300
D_x = 1.444 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1514 reflections
θ = 2.5–26.6°
μ = 0.43 mm^{-1}
T = 298 K
Needle, colourless
0.32 × 0.11 × 0.07 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.874, T_{max} = 0.972

3504 measured reflections
2319 independent reflections
1734 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -10 \to 9$
$k = -11 \to 9$
$l = -12 \to 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.100$
$S = 1.02$
2319 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 0.2146P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.41414 (14)	0.64074 (11)	0.50918 (8)	0.0781 (3)
N1	0.4306 (3)	0.5361 (2)	0.1841 (2)	0.0397 (5)
H1	0.3077	0.4966	0.1477	0.048*
N2	0.6871 (3)	0.4903 (2)	0.2029 (2)	0.0416 (5)
H2	0.7561	0.5927	0.2548	0.050*
N3	1.0366 (3)	0.3871 (2)	0.1394 (2)	0.0481 (5)
O1	0.7112 (3)	0.7734 (2)	0.3311 (2)	0.0630 (5)
S1	0.33789 (9)	0.24252 (8)	0.02568 (7)	0.0500 (2)
C1	0.4967 (3)	0.4294 (3)	0.1432 (2)	0.0370 (5)
C2	0.5364 (4)	0.6956 (3)	0.2748 (3)	0.0422 (6)
C3	0.4139 (3)	0.7708 (3)	0.2962 (2)	0.0400 (5)
C4	0.3540 (4)	0.7557 (3)	0.4027 (3)	0.0476 (6)
C5	0.2449 (4)	0.8281 (3)	0.4233 (3)	0.0560 (7)
H5	0.2062	0.8177	0.4955	0.067*
C6	0.1944 (4)	0.9154 (3)	0.3359 (3)	0.0613 (8)
H6	0.1211	0.9644	0.3490	0.074*
C7	0.2513 (4)	0.9307 (3)	0.2296 (3)	0.0593 (7)
H7	0.2157	0.9895	0.1705	0.071*
C8	0.3611 (4)	0.8595 (3)	0.2093 (3)	0.0495 (6)
H8	0.3997	0.8711	0.1371	0.059*
C9	0.9299 (3)	0.4610 (3)	0.1477 (2)	0.0411 (6)

H9	0.9551	0.5586	0.1259	0.049*
C10	0.7848 (3)	0.3985 (3)	0.1872 (2)	0.0380 (5)
C11	0.7442 (4)	0.2524 (3)	0.2178 (3)	0.0481 (6)
H11	0.6456	0.2070	0.2436	0.058*
C12	0.8523 (4)	0.1757 (3)	0.2093 (3)	0.0542 (7)
H12	0.8291	0.0776	0.2300	0.065*
C13	0.9953 (4)	0.2463 (3)	0.1697 (3)	0.0537 (7)
H13	1.0674	0.1930	0.1636	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1271 (8)	0.0975 (6)	0.0704 (5)	0.0861 (6)	0.0617 (5)	0.0496 (5)
N1	0.0341 (10)	0.0395 (11)	0.0488 (11)	0.0192 (9)	0.0225 (9)	0.0076 (9)
N2	0.0372 (11)	0.0368 (10)	0.0569 (12)	0.0195 (9)	0.0271 (10)	0.0101 (9)
N3	0.0439 (12)	0.0496 (12)	0.0650 (14)	0.0268 (10)	0.0339 (11)	0.0184 (11)
O1	0.0406 (11)	0.0539 (11)	0.0758 (13)	0.0192 (9)	0.0209 (10)	−0.0069 (10)
S1	0.0487 (4)	0.0416 (4)	0.0571 (4)	0.0206 (3)	0.0259 (3)	0.0051 (3)
C1	0.0437 (14)	0.0408 (13)	0.0405 (13)	0.0244 (11)	0.0273 (11)	0.0160 (10)
C2	0.0426 (15)	0.0419 (13)	0.0447 (14)	0.0219 (12)	0.0227 (12)	0.0074 (11)
C3	0.0408 (13)	0.0356 (12)	0.0459 (14)	0.0206 (11)	0.0213 (11)	0.0071 (11)
C4	0.0624 (17)	0.0491 (14)	0.0487 (14)	0.0376 (13)	0.0297 (13)	0.0177 (12)
C5	0.0712 (19)	0.0653 (17)	0.0544 (16)	0.0448 (16)	0.0386 (15)	0.0170 (14)
C6	0.0686 (19)	0.0596 (17)	0.0696 (19)	0.0464 (16)	0.0307 (16)	0.0129 (15)
C7	0.0712 (19)	0.0516 (16)	0.0672 (18)	0.0404 (15)	0.0291 (16)	0.0236 (14)
C8	0.0577 (16)	0.0438 (14)	0.0540 (15)	0.0264 (13)	0.0293 (13)	0.0168 (12)
C9	0.0374 (13)	0.0396 (13)	0.0515 (14)	0.0198 (11)	0.0238 (12)	0.0142 (11)
C10	0.0388 (13)	0.0410 (13)	0.0432 (13)	0.0231 (11)	0.0236 (11)	0.0120 (10)
C11	0.0507 (15)	0.0512 (15)	0.0599 (16)	0.0269 (13)	0.0380 (13)	0.0222 (13)
C12	0.0630 (17)	0.0487 (15)	0.0750 (18)	0.0351 (14)	0.0422 (15)	0.0300 (14)
C13	0.0556 (16)	0.0537 (16)	0.0732 (18)	0.0373 (14)	0.0378 (15)	0.0220 (14)

Geometric parameters (Å, º)

Cl1—C4	1.734 (2)	C5—C6	1.372 (4)
N1—C2	1.368 (3)	C5—H5	0.9300
N1—C1	1.394 (3)	C6—C7	1.369 (4)
N1—H1	0.8600	C6—H6	0.9300
N2—C1	1.331 (3)	C7—C8	1.380 (4)
N2—C10	1.422 (3)	C7—H7	0.9300
N2—H2	0.8600	C8—H8	0.9300
N3—C13	1.335 (3)	C9—C10	1.375 (3)
N3—C9	1.340 (3)	C9—H9	0.9300
O1—C2	1.217 (3)	C10—C11	1.381 (3)
S1—C1	1.659 (2)	C11—C12	1.371 (3)
C2—C3	1.508 (3)	C11—H11	0.9300
C3—C4	1.385 (3)	C12—C13	1.373 (3)
C3—C8	1.386 (3)	C12—H12	0.9300

C4—C5	1.384 (3)	C13—H13	0.9300

C2—N1—C1	128.3 (2)	C7—C6—H6	119.8
C2—N1—H1	115.9	C5—C6—H6	119.8
C1—N1—H1	115.9	C6—C7—C8	120.5 (2)
C1—N2—C10	124.83 (19)	C6—C7—H7	119.7
C1—N2—H2	117.6	C8—C7—H7	119.7
C10—N2—H2	117.6	C7—C8—C3	120.1 (2)
C13—N3—C9	117.2 (2)	C7—C8—H8	119.9
N2—C1—N1	115.4 (2)	C3—C8—H8	119.9
N2—C1—S1	125.54 (17)	N3—C9—C10	122.6 (2)
N1—C1—S1	119.02 (17)	N3—C9—H9	118.7
O1—C2—N1	124.8 (2)	C10—C9—H9	118.7
O1—C2—C3	122.1 (2)	C9—C10—C11	119.2 (2)
N1—C2—C3	113.1 (2)	C9—C10—N2	119.10 (19)
C4—C3—C8	118.6 (2)	C11—C10—N2	121.6 (2)
C4—C3—C2	121.6 (2)	C12—C11—C10	118.6 (2)
C8—C3—C2	119.8 (2)	C12—C11—H11	120.7
C5—C4—C3	121.1 (2)	C10—C11—H11	120.7
C5—C4—Cl1	119.9 (2)	C11—C12—C13	118.8 (2)
C3—C4—Cl1	118.97 (18)	C11—C12—H12	120.6
C6—C5—C4	119.2 (2)	C13—C12—H12	120.6
C6—C5—H5	120.4	N3—C13—C12	123.6 (2)
C4—C5—H5	120.4	N3—C13—H13	118.2
C7—C6—C5	120.4 (2)	C12—C13—H13	118.2

C10—N2—C1—N1	173.77 (19)	C4—C5—C6—C7	0.0 (4)
C10—N2—C1—S1	−7.1 (3)	C5—C6—C7—C8	−0.4 (4)
C2—N1—C1—N2	1.6 (3)	C6—C7—C8—C3	0.4 (4)
C2—N1—C1—S1	−177.58 (18)	C4—C3—C8—C7	0.0 (4)
C1—N1—C2—O1	3.2 (4)	C2—C3—C8—C7	−179.1 (2)
C1—N1—C2—C3	−178.6 (2)	C13—N3—C9—C10	0.8 (4)
O1—C2—C3—C4	−93.6 (3)	N3—C9—C10—C11	−1.0 (4)
N1—C2—C3—C4	88.1 (3)	N3—C9—C10—N2	175.7 (2)
O1—C2—C3—C8	85.4 (3)	C1—N2—C10—C9	129.9 (2)
N1—C2—C3—C8	−92.8 (3)	C1—N2—C10—C11	−53.4 (3)
C8—C3—C4—C5	−0.4 (4)	C9—C10—C11—C12	0.8 (4)
C2—C3—C4—C5	178.7 (2)	N2—C10—C11—C12	−175.8 (2)
C8—C3—C4—Cl1	178.40 (18)	C10—C11—C12—C13	−0.5 (4)
C2—C3—C4—Cl1	−2.5 (3)	C9—N3—C13—C12	−0.5 (4)
C3—C4—C5—C6	0.4 (4)	C11—C12—C13—N3	0.4 (4)
Cl1—C4—C5—C6	−178.4 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1	0.86	1.98	2.671 (3)	137

N1—H1···N3^{i}	0.86	2.08	2.886 (4)	157

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