organic papers

N-(4-Chloro-3-nitrophenyl)-N'-(3-nitro-benzoyl)thiourea

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In the title molecule, $C_{14}H_9ClN_4O_5S$, all bond lengths and angles show normal values. The mean plane of the central thiourea unit, N_2CS, makes dihedral angles of 9.54 (12) and 56.60 (10)°, respectively, with the mean planes of the 3-nitrobenzoyl and 4-chloro-3-nitrophenyl groups. The crystal packing is stabilized by weak intermolecular N—H···O and C—H···O hydrogen bonds.

Comment

Substituted thiourea compounds have found applications in the rubber and dye industries (Ramadas *et al.*, 1993). Some of their derivatives exhibit biological activity (Baruah *et al.*, 2002). The title compound, (I), is analogous to *N*-benzoyl-*N'*-phenylthiourea, (II) (Yamin & Yusof, 2003). The molecule has a *trans–cis* configuration with respect to the positions of the 3-nitrobenzoyl and 4-chloro-3-nitrophenyl groups relative to the thiono S1 atom across the C8—N3 and C8—N4 bonds, respectively (Fig. 1). The bond lengths and angles (Table 1) are in normal ranges (Allen *et al.*, 1987) and are comparable with those in (II). The mean plane of the central thiourea unit, N_2CS, makes dihedral angles of 9.54 (12) and 56.60 (10)°, respectively, with the mean planes of the 3-nitrobenzoyl and 4-chloro-3-nitrophenyl groups. The dihedral angle between the two aromatic rings is 62.09 (13)°.

(I)
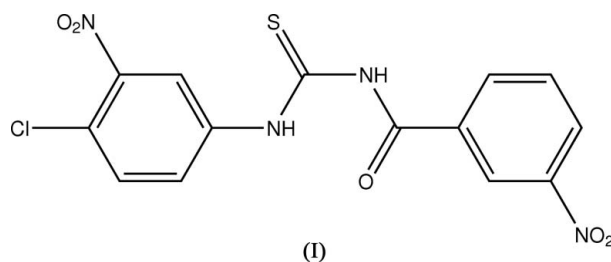
There is an intramolecular hydrogen bond (N3—H3···O3; Table 2) which forms a pseudo-six-membered ring (N3—H3···O3—C7—N2—C8). In the crystal structure, the molecules are linked by intermolecular N—H···O and C—H···O hydrogen bonds (Table 2) into a two-dimensional network parallel to the *bc* plane (Fig. 2).

Experimental

An equimolar amount of 4-chloro-3-nitroaniline (1.86 g, 11 mmol) in 20 ml acetone was added dropwise to a stirred acetone solution (75 ml) containing 3-nitrobenzoyl chloride (2.0 g, 11 mmol) and ammonium thiocyanate (0.82 g, 11 mmol). The solution was refluxed for 1 h and then poured into a beaker containing some ice blocks. The

resulting light-yellow precipitate was filtered off and washed with distilled water and cold ethanol before being dried under vacuum. Good quality crystals were obtained by recrystallization from chloroform (yield 72%, 2.63 g; m.p. 489.3–491.7 K).

Crystal data

$C_{14}H_9ClN_4O_5S$	$V = 779.5$ (2) Å^3
$M_r = 380.77$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.622$ Mg m^{-3}
$a = 7.7327$ (14) Å	Mo $K\alpha$ radiation
$b = 7.8617$ (14) Å	$\mu = 0.42$ mm^{-1}
$c = 14.368$ (3) Å	$T = 298$ (2) K
$\alpha = 102.041$ (3)°	Slab, light yellow
$\beta = 94.257$ (3)°	$0.40 \times 0.18 \times 0.11$ mm
$\gamma = 112.213$ (3)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	7444 measured reflections
	2744 independent reflections
ω scans	2230 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$R_{int} = 0.019$
$T_{min} = 0.852$, $T_{max} = 0.956$	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.2966P]$
$wR(F^2) = 0.113$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2744 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
226 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.650 (2)	N3—C8	1.334 (3)
N2—C8	1.397 (3)	N3—C9	1.416 (3)
O3—C7—N2	122.1 (2)	N3—C8—S1	125.45 (17)
N3—C8—N2	115.1 (2)	N2—C8—S1	119.48 (17)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$O3	0.86	1.92	2.616 (3)	138
N2—H2$\cdots$O2^i	0.86	2.50	3.165 (3)	135
C1—H1$A\cdots$O2^i	0.93	2.47	3.279 (4)	146
C3—H3$A\cdots$O4^{ii}	0.93	2.34	3.264 (3)	175
C10—H10$\cdots$O5^{iii}	0.93	2.59	3.242 (4)	128
C14—H14$\cdots$O1^{iv}	0.93	2.48	3.401 (3)	169

Symmetry codes: (i) $x, y + 1, z$; (ii) $x + 1, y, z + 1$; (iii) $x + 1, y, z$; (iv) $-x + 1, -y, -z + 2$.

After their location in a difference map, all H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93–0.96 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics:
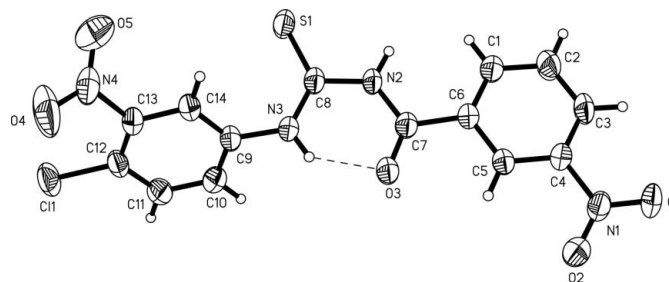

Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids. The dashed line denotes an intramolecular hydrogen bond.
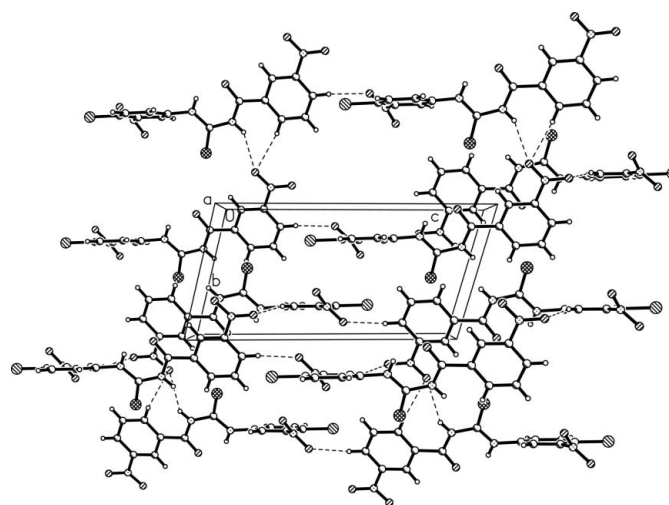

Figure 2
Packing diagram for (I), viewed down the a axis. The dashed lines denote N—H$\cdots$O and C—H$\cdots$O hydrogen bonds.

SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2003).

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