

Crystal structure of 4-fluoro-*N*-[2-(4-fluorobenzoyl)hydrazine-1-carbonothioyl]benzamide

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In the title compound, $C_{15}H_{11}F_2N_3O_2S$, the dihedral angle between the fluorobenzene rings is $88.43(10)^\circ$ and that between the central semithiocarbazide grouping is $47.00(11)^\circ$. The dihedral angle between the amide group and attached fluorobenzene ring is $50.52(11)^\circ$; the equivalent angle between the carbonylthioamide group and its attached ring is $12.98(10)^\circ$. The major twists in the molecule occur about the C–N–N–C bonds [torsion angle = $-138.7(2)^\circ$] and the C_{ar}–C_{ar}–C–N (ar = aromatic) bonds [$-132.0(2)^\circ$]. An intramolecular N–H···O hydrogen bond occurs, which generates an *S*(6) ring. In the crystal, the molecules are linked by N–H···O and N–H···S hydrogen bonds, generating (001) sheets. Weak C–H···O and C–H···F interactions are also observed.

Keywords: crystal structure; hydrogen bonds; semithiocarbazide.

CCDC reference: 1012471

1. Related literature

For further synthetic details and the crystal structures of related thiourea derivatives, see: Yamin & Yusof (2003*a,b*); Yusof *et al.* (2003); For a metal complex with a similar ligand, see: Ke *et al.* (2007).

2. Experimental

2.1. Crystal data

$C_{15}H_{11}F_2N_3O_2S$	$V = 2930.6(3) \text{ \AA}^3$
$M_r = 335.33$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 11.6172(6) \text{ \AA}$	$\mu = 0.26 \text{ mm}^{-1}$
$b = 8.4086(5) \text{ \AA}$	$T = 296 \text{ K}$
$c = 30.0002(16) \text{ \AA}$	$0.50 \times 0.12 \times 0.08 \text{ mm}$

2.2. Data collection

Bruker SMART APEX CCD diffractometer	76830 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	2886 independent reflections
$T_{\min} = 0.883$, $T_{\max} = 0.980$	2024 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.137$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	208 parameters
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
2886 reflections	$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N2–H2A···O1	0.86	1.89	2.571(2)	135
N2–H2A···S1 ⁱ	0.86	2.84	3.3875(18)	123
N1–H1A···O2 ⁱⁱ	0.86	2.33	3.165(2)	165
N3–H3···O2 ⁱⁱⁱ	0.86	2.10	2.942(2)	166
C4–H4···F1 ^{iv}	0.93	2.49	3.409(3)	169
C5–H5···O2 ⁱⁱ	0.93	2.45	3.345(3)	160

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iv) $-x + 2, -y + 1, -z + 2$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); 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* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7245).

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Crystal structure of 4-fluoro-*N*-[2-(4-fluorobenzoyl)hydrazine-1-carbonothioyl]benzamide

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S1. Experimental

30 ml acetone containing 4-fluorobenzoyl isothiocyanate (1.81 g, 0.01 mol) was mixed with hydrazine (0.16 g, 0.005 mol). The mixture was refluxed for 2 hours. The solution was filtered and left to evaporate at room temperature. The white precipitate obtained after a few days, was washed with water and cold ethanol. Colourless blocks of the title compound were obtained by recrystallization from ethanol solution.

S2. Refinement

After location in the difference map, the H-atoms attached to the C and N atoms were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H = 0.93–0.97 Å, N—H = 0.86 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$.

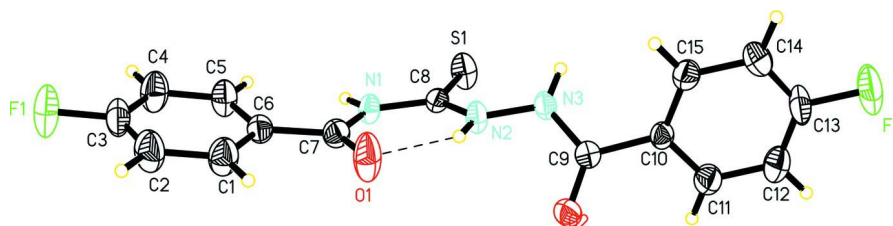
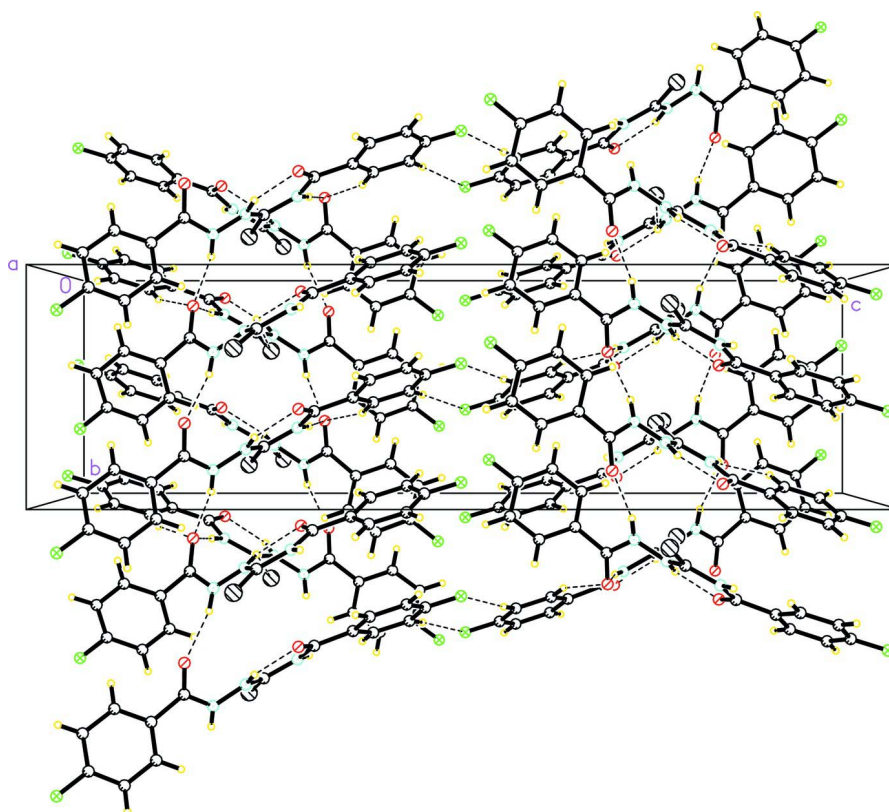


Figure 1

Molecular structure of (I) with 50% probability displacement ellipsoids. The dashes line indicates the intramolecular hydrogen bond.

**Figure 2**

Unit-cell packing for (I) in the unit cell viewed down a axis. The dashes lines indicate hydrogen bonds.

4-Fluoro-N-[2-(4-fluorobenzoyl)hydrazine-1-carbonthioyl]benzamide

Crystal data

$C_{15}H_{11}F_2N_3O_2S$

$M_r = 335.33$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 11.6172 (6) \text{ \AA}$

$b = 8.4086 (5) \text{ \AA}$

$c = 30.0002 (16) \text{ \AA}$

$V = 2930.6 (3) \text{ \AA}^3$

$Z = 8$

$F(000) = 1376$

$D_x = 1.520 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

$\mu = 0.26 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colorless

$0.50 \times 0.12 \times 0.08 \text{ mm}$

Data collection

Bruker SMART APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.883$, $T_{\max} = 0.980$

76830 measured reflections

2886 independent reflections

2024 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.137$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -14 \rightarrow 14$

$k = -10 \rightarrow 10$

$l = -37 \rightarrow 37$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.099$
 $S = 1.04$
 2886 reflections
 208 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
 $w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 2.0394P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.98887 (5)	0.15863 (8)	0.73680 (2)	0.04054 (19)
O1	0.69608 (15)	0.4074 (2)	0.80598 (6)	0.0585 (6)
O2	0.64343 (13)	0.34844 (18)	0.67414 (5)	0.0328 (4)
N1	0.88035 (15)	0.3239 (2)	0.79937 (6)	0.0283 (4)
H1A	0.9472	0.3290	0.8116	0.034*
N2	0.76928 (15)	0.2357 (2)	0.74100 (6)	0.0308 (5)
H2A	0.7137	0.2871	0.7533	0.037*
N3	0.74823 (15)	0.1473 (2)	0.70307 (5)	0.0278 (4)
H3	0.7784	0.0548	0.6995	0.033*
C1	0.7245 (2)	0.5302 (3)	0.88928 (8)	0.0444 (7)
H1	0.6558	0.5469	0.8741	0.053*
C2	0.7347 (2)	0.5802 (3)	0.93299 (8)	0.0511 (7)
H2	0.6738	0.6303	0.9474	0.061*
C3	0.8362 (2)	0.5540 (3)	0.95425 (8)	0.0430 (7)
C4	0.9276 (2)	0.4826 (3)	0.93441 (8)	0.0479 (7)
H4	0.9959	0.4667	0.9500	0.057*
C5	0.9171 (2)	0.4339 (3)	0.89050 (8)	0.0402 (6)
H5	0.9792	0.3861	0.8762	0.048*
C6	0.81520 (19)	0.4557 (3)	0.86779 (7)	0.0300 (5)
C7	0.79209 (19)	0.3964 (3)	0.82191 (7)	0.0315 (5)
C8	0.87407 (18)	0.2428 (3)	0.75895 (7)	0.0258 (5)
C9	0.67935 (17)	0.2104 (3)	0.67201 (7)	0.0254 (5)
C10	0.64585 (18)	0.1018 (3)	0.63505 (7)	0.0263 (5)
C11	0.6553 (2)	0.1549 (3)	0.59144 (7)	0.0383 (6)
H11	0.6838	0.2563	0.5858	0.046*

supporting information

C12	0.6228 (2)	0.0589 (3)	0.55647 (8)	0.0481 (7)
H12	0.6300	0.0931	0.5271	0.058*
C13	0.5797 (2)	-0.0878 (3)	0.56616 (9)	0.0503 (7)
C15	0.6004 (2)	-0.0473 (3)	0.64350 (8)	0.0360 (6)
H15	0.5929	-0.0828	0.6727	0.043*
F1	0.84583 (15)	0.6012 (2)	0.99733 (5)	0.0681 (5)
F2	0.54797 (19)	-0.1828 (2)	0.53146 (6)	0.0870 (7)
C14	0.5660 (2)	-0.1434 (3)	0.60860 (9)	0.0491 (7)
H14	0.5344	-0.2433	0.6139	0.059*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0271 (3)	0.0533 (4)	0.0412 (4)	0.0032 (3)	-0.0018 (3)	-0.0162 (3)
O1	0.0387 (11)	0.0887 (16)	0.0482 (11)	0.0263 (10)	-0.0169 (9)	-0.0332 (11)
O2	0.0344 (9)	0.0280 (9)	0.0359 (9)	0.0044 (8)	-0.0042 (7)	-0.0043 (7)
N1	0.0248 (9)	0.0357 (11)	0.0242 (9)	-0.0003 (8)	-0.0042 (8)	-0.0055 (8)
N2	0.0269 (10)	0.0392 (12)	0.0262 (10)	0.0057 (9)	-0.0042 (8)	-0.0118 (9)
N3	0.0280 (9)	0.0286 (10)	0.0270 (10)	0.0032 (9)	-0.0059 (8)	-0.0073 (8)
C1	0.0390 (15)	0.0567 (18)	0.0374 (14)	0.0123 (13)	-0.0061 (12)	-0.0095 (13)
C2	0.0505 (17)	0.0635 (19)	0.0394 (15)	0.0131 (15)	0.0054 (13)	-0.0154 (14)
C3	0.0531 (17)	0.0494 (17)	0.0265 (13)	-0.0062 (14)	-0.0001 (12)	-0.0112 (12)
C4	0.0389 (14)	0.067 (2)	0.0377 (15)	0.0004 (14)	-0.0096 (12)	-0.0118 (14)
C5	0.0347 (14)	0.0535 (17)	0.0323 (13)	0.0045 (12)	-0.0021 (11)	-0.0116 (12)
C6	0.0316 (13)	0.0303 (13)	0.0280 (12)	-0.0002 (10)	-0.0017 (10)	-0.0027 (11)
C7	0.0300 (12)	0.0332 (14)	0.0314 (13)	0.0042 (10)	-0.0046 (10)	-0.0026 (11)
C8	0.0294 (12)	0.0253 (12)	0.0228 (11)	-0.0025 (10)	-0.0034 (10)	0.0009 (9)
C9	0.0214 (11)	0.0280 (13)	0.0267 (12)	-0.0014 (10)	0.0019 (9)	-0.0010 (10)
C10	0.0233 (11)	0.0289 (13)	0.0267 (12)	0.0027 (10)	-0.0056 (9)	-0.0036 (10)
C11	0.0464 (14)	0.0374 (15)	0.0313 (13)	-0.0068 (13)	-0.0024 (11)	0.0013 (12)
C12	0.0634 (18)	0.0546 (18)	0.0261 (13)	-0.0020 (15)	-0.0060 (12)	-0.0041 (13)
C13	0.0603 (18)	0.0505 (18)	0.0399 (16)	-0.0067 (15)	-0.0182 (13)	-0.0189 (14)
C15	0.0390 (14)	0.0368 (15)	0.0321 (13)	-0.0051 (12)	-0.0082 (11)	0.0020 (11)
F1	0.0741 (11)	0.0980 (14)	0.0322 (8)	-0.0006 (10)	-0.0036 (8)	-0.0258 (9)
F2	0.1324 (18)	0.0781 (14)	0.0506 (11)	-0.0280 (12)	-0.0284 (11)	-0.0258 (10)
C14	0.0589 (18)	0.0370 (16)	0.0514 (17)	-0.0158 (14)	-0.0154 (14)	-0.0037 (13)

Geometric parameters (\AA , $^\circ$)

S1—C8	1.650 (2)	C4—C5	1.385 (3)
O1—C7	1.217 (3)	C4—H4	0.9300
O2—C9	1.235 (3)	C5—C6	1.378 (3)
N1—C7	1.371 (3)	C5—H5	0.9300
N1—C8	1.393 (3)	C6—C7	1.488 (3)
N1—H1A	0.8600	C9—C10	1.488 (3)
N2—C8	1.333 (3)	C10—C15	1.384 (3)
N2—N3	1.381 (2)	C10—C11	1.387 (3)
N2—H2A	0.8600	C11—C12	1.377 (3)

supporting information

N3—C9	1.338 (3)	C11—H11	0.9300
N3—H3	0.8600	C12—C13	1.362 (4)
C1—C2	1.382 (3)	C12—H12	0.9300
C1—C6	1.385 (3)	C13—F2	1.363 (3)
C1—H1	0.9300	C13—C14	1.366 (4)
C2—C3	1.359 (4)	C15—C14	1.381 (3)
C2—H2	0.9300	C15—H15	0.9300
C3—F1	1.357 (3)	C14—H14	0.9300
C3—C4	1.358 (4)		
C7—N1—C8	127.43 (18)	O1—C7—N1	121.7 (2)
C7—N1—H1A	116.3	O1—C7—C6	120.2 (2)
C8—N1—H1A	116.3	N1—C7—C6	118.04 (19)
C8—N2—N3	121.27 (18)	N2—C8—N1	114.95 (18)
C8—N2—H2A	119.4	N2—C8—S1	123.80 (16)
N3—N2—H2A	119.4	N1—C8—S1	121.23 (15)
C9—N3—N2	117.80 (18)	O2—C9—N3	122.6 (2)
C9—N3—H3	121.1	O2—C9—C10	121.8 (2)
N2—N3—H3	121.1	N3—C9—C10	115.58 (19)
C2—C1—C6	121.0 (2)	C15—C10—C11	119.7 (2)
C2—C1—H1	119.5	C15—C10—C9	121.3 (2)
C6—C1—H1	119.5	C11—C10—C9	119.0 (2)
C3—C2—C1	118.0 (2)	C12—C11—C10	120.5 (2)
C3—C2—H2	121.0	C12—C11—H11	119.7
C1—C2—H2	121.0	C10—C11—H11	119.7
F1—C3—C4	118.8 (2)	C13—C12—C11	118.0 (2)
F1—C3—C2	118.1 (2)	C13—C12—H12	121.0
C4—C3—C2	123.0 (2)	C11—C12—H12	121.0
C3—C4—C5	118.6 (2)	C12—C13—F2	117.8 (2)
C3—C4—H4	120.7	C12—C13—C14	123.5 (2)
C5—C4—H4	120.7	F2—C13—C14	118.7 (3)
C6—C5—C4	120.5 (2)	C14—C15—C10	120.1 (2)
C6—C5—H5	119.8	C14—C15—H15	119.9
C4—C5—H5	119.8	C10—C15—H15	119.9
C5—C6—C1	118.9 (2)	C13—C14—C15	118.2 (3)
C5—C6—C7	124.6 (2)	C13—C14—H14	120.9
C1—C6—C7	116.4 (2)	C15—C14—H14	120.9
C8—N2—N3—C9	-138.7 (2)	C7—N1—C8—N2	-0.5 (3)
C6—C1—C2—C3	0.0 (4)	C7—N1—C8—S1	-178.67 (18)
C1—C2—C3—F1	-179.2 (3)	N2—N3—C9—O2	6.9 (3)
C1—C2—C3—C4	0.5 (5)	N2—N3—C9—C10	-171.47 (17)
F1—C3—C4—C5	179.6 (3)	O2—C9—C10—C15	-127.2 (2)
C2—C3—C4—C5	-0.1 (4)	N3—C9—C10—C15	51.2 (3)
C3—C4—C5—C6	-0.9 (4)	O2—C9—C10—C11	49.5 (3)
C4—C5—C6—C1	1.4 (4)	N3—C9—C10—C11	-132.0 (2)
C4—C5—C6—C7	-175.0 (2)	C15—C10—C11—C12	-1.9 (4)
C2—C1—C6—C5	-1.0 (4)	C9—C10—C11—C12	-178.6 (2)

supporting information

C2—C1—C6—C7	175.7 (3)	C10—C11—C12—C13	1.1 (4)
C8—N1—C7—O1	-6.0 (4)	C11—C12—C13—F2	-179.8 (3)
C8—N1—C7—C6	171.2 (2)	C11—C12—C13—C14	0.7 (4)
C5—C6—C7—O1	172.8 (3)	C11—C10—C15—C14	0.9 (4)
C1—C6—C7—O1	-3.6 (4)	C9—C10—C15—C14	177.6 (2)
C5—C6—C7—N1	-4.4 (4)	C12—C13—C14—C15	-1.7 (4)
C1—C6—C7—N1	179.1 (2)	F2—C13—C14—C15	178.8 (3)
N3—N2—C8—N1	-174.21 (18)	C10—C15—C14—C13	0.8 (4)
N3—N2—C8—S1	3.9 (3)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots O1	0.86	1.89	2.571 (2)	135
N2—H2A \cdots S1 ⁱ	0.86	2.84	3.3875 (18)	123
N1—H1A \cdots O2 ⁱⁱ	0.86	2.33	3.165 (2)	165
N3—H3 \cdots O2 ⁱⁱⁱ	0.86	2.10	2.942 (2)	166
C4—H4 \cdots F1 ^{iv}	0.93	2.49	3.409 (3)	169
C5—H5 \cdots O2 ⁱⁱ	0.93	2.45	3.345 (3)	160

Symmetry codes: (i) $x-1/2, y, -z+3/2$; (ii) $x+1/2, y, -z+3/2$; (iii) $-x+3/2, y-1/2, z$; (iv) $-x+2, -y+1, -z+2$.