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

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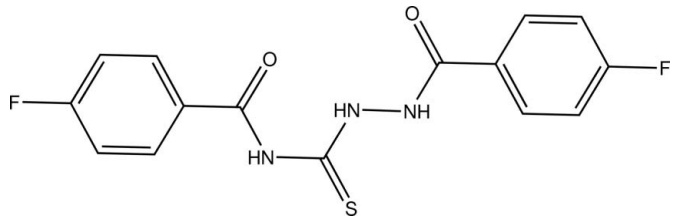
In the title compound, $C_{15}H_{11}F_2N_3O_2S$, the dihedral angle between the fluorobenzene rings is 88.43 (10)° and that between the central semithiocarbazide grouping is 47.00 (11)°. The dihedral angle between the amide group and attached fluorobenzene ring is 50.52 (11)°; the equivalent angle between the carbonylthioamide group and its attached ring is 12.98 (10)°. The major twists in the molecule occur about the C—N—N—C bonds [torsion angle = −138.7 (2)°] and the C_{ar}—C_{ar}—C—N (ar = aromatic) bonds [−132.0 (2)°]. 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

$C_{15}H_{11}F_2N_3O_2S$
M_r = 335.33
Orthorhombic, *Pbca*
a = 11.6172 (6) Å
b = 8.4086 (5) Å
c = 30.0002 (16) Å
V = 2930.6 (3) Å^3
Z = 8
Mo *Kα* radiation
μ = 0.26 mm^{-1}
T = 296 K
0.50 × 0.12 × 0.08 mm

2.2. Data collection

Bruker SMART APEX CCD diffractometer
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_{int} = 0.137

2.3. Refinement

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1	0.86	1.89	2.571 (2)	135
N2—H2*A*···S1^{i}	0.86	2.84	3.3875 (18)	123
N1—H1*A*···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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supporting information

Acta Cryst. (2014). E**70**, o915–o916 [doi:10.1107/S1600536814015761]

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_{iso}(H)=1.2U_{eq}(C or N).

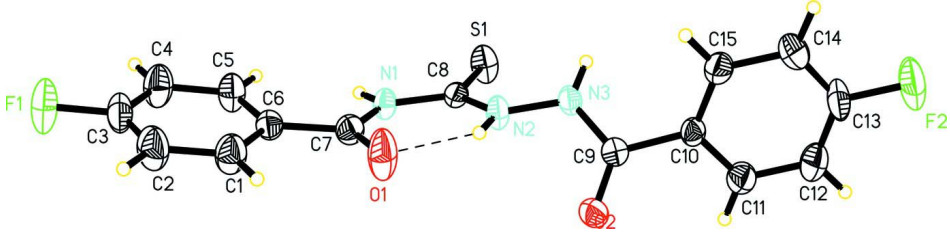

Figure 1

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

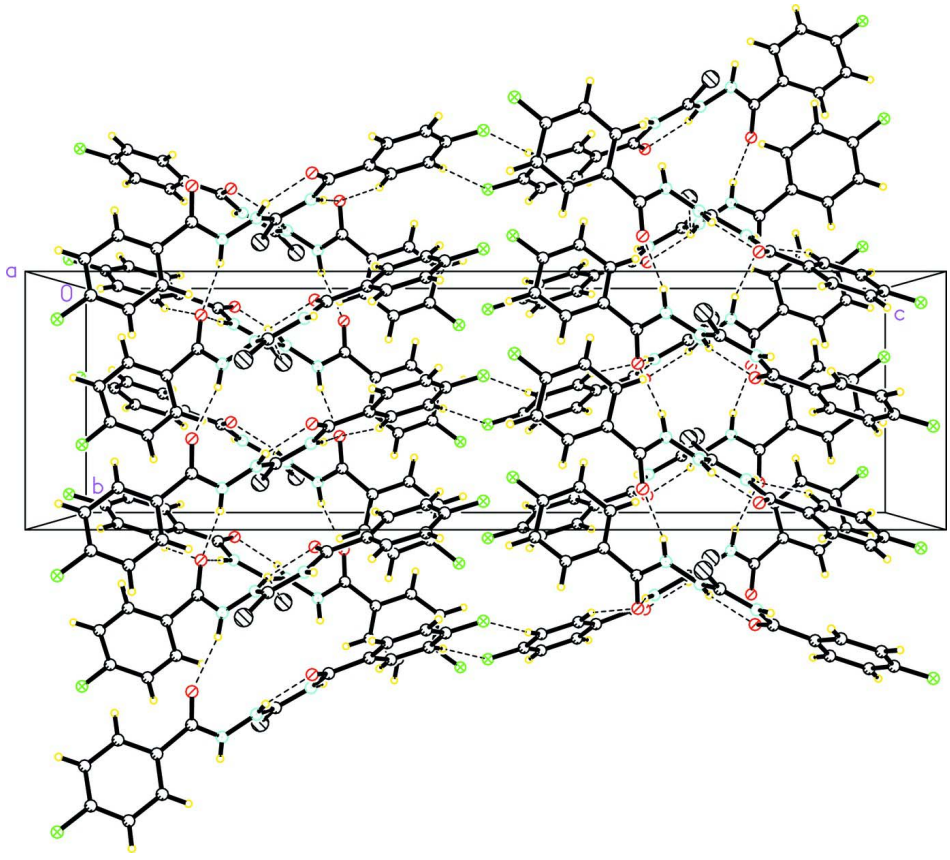

Figure 2

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-carbonothioyl]benzamide

Crystal data

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V = 2930.6 (3) Å^3
Z = 8
F(000) = 1376
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Mo $K\alpha$ radiation, λ = 0.71073 Å
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Block, colorless
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ω scans
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76830 measured reflections
2886 independent reflections
2024 reflections with $I > 2\sigma(I)$
R_{int} = 0.137
θ_{max} = 26.0°, θ_{min} = 3.1°
h = −14→14
k = −10→10
l = −37→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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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 $F^2 > 2$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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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*

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 (Å²)

	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 (Å, º)

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)

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)

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 (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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N2—H2*A*···S1^{i}	0.86	2.84	3.3875 (18)	123
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N3—H3···O2^{iii}	0.86	2.10	2.942 (2)	166
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