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(Z)-2-(5-Fluoro-2-oxoindolin-3-ylidene)-N-methylhydrazinecarbothioamide

Amna Qasem Ali,^a Naser Eltaher Eltayeb^{b*} and Siang Guan Teoh^c

^aDepartment of Chemistry, Faculty of Science, Sebha University, Libya, ^bDepartment of Chemistry, Rabigh College of Science and Arts, King Abdulaziz University, PO Box 344, Rabigh 21911, Saudi Arabia, and ^cSchool of Chemical Sciences, Universiti Sains Malaysia, Minden, Penang, Malaysia. *Correspondence e-mail: nasertaha90@hotmail.com

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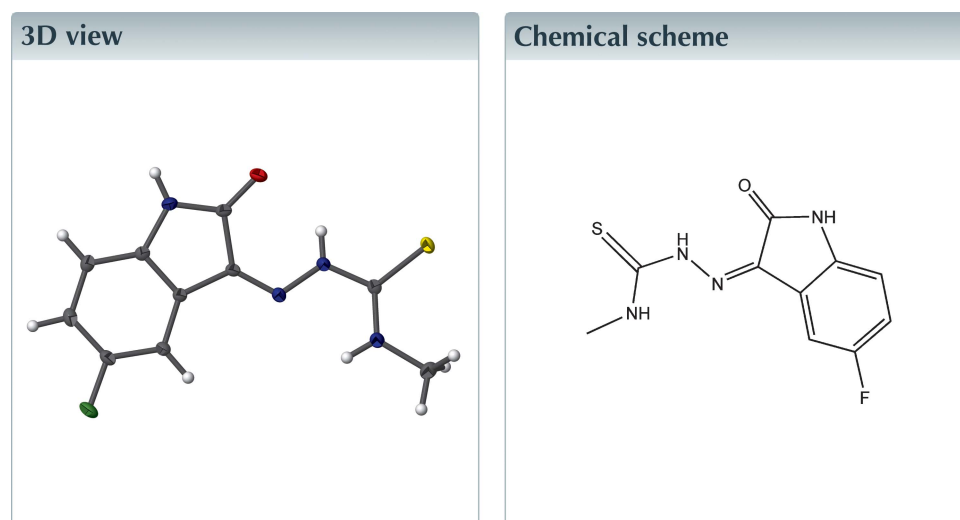
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Keywords: crystal structure; Schiff base; isatin.

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Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, C₁₀H₉FN₄OS, which is approximately planar with a maximum deviation of 0.0881 (10) Å from the mean plane of the non-H atoms, an intramolecular N—H···O hydrogen bond generates an S(6) ring. In the crystal, molecules are linked *via* N—H···O hydrogen bonds, forming a helical chain along the *a* axis. The chains are linked by N—H···S, C—H···S and C—H···F hydrogen bonds and C—H···π interactions into a three-dimensional network.



Structure description

The title Schiff base was synthesized by the condensation reaction of 5-fluoroisatin with 4-methyl-3-thiosemicarbazide. In numerous cases, isatins react with nucleophiles, even in the absence of any catalyst, either at room temperature or by heating for a few hours (Singh & Desta, 2012). Thiosemicarbazones are a class of small molecules that display numerous biological activities as antivirals and as anticancer therapeutics, as well as parasiticidal action against *Plasmodium falciparum* and *Trypanosoma cruzi* which are the causative agents of malaria and Chagas's disease, respectively (Er *et al.*, 2008). The crystal structures of (Z)-2-(5-fluoro-2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamide (Ali *et al.*, 2012a) and bis[2-(2-oxoindolin-3-ylidene)-N-phenylhydrazinecarbothioamidato-κ³O,N²,S]nickel(II) dimethylformamide monosolvate (Ali *et al.*, 2012b), closely related to the title compound, have been reported.

The title compound is approximately planar (Fig. 1); the dihedral angle between the benzene C1–C6 ring and the five-membered ring C1/C6/N1/C7/C8 is 1.24 (7)°, and the C8–N2–N3–C9, N2–N3–C9–N4 and N2–N3–C9–S1 torsion angles are 176.91 (12), 0.33 (18) and –178.81 (9)°, respectively.

Table 1

Hydrogen-bond geometry (Å, °).

Cg2 is the centroid of the C1–C6 ring.

<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>
N3–H1N3...O1	0.83 (2)	2.09 (2)	2.7407 (15)	135 (2)
N1–H1N1...O1 ⁱ	0.86 (2)	1.96 (2)	2.8173 (15)	178 (3)
N4–H1N4...S1 ⁱⁱ	0.86 (2)	2.67 (2)	3.4718 (11)	157.0 (19)
C2–H2A...S1 ⁱⁱ	0.95	2.78	3.6979 (13)	163
C10–H10C...F1 ⁱⁱⁱ	0.98	2.55	3.1746 (19)	122
C4–H4A...Cg2 ^{iv}	0.95	2.62	3.4291 (15)	143

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

In the crystal (Fig. 2), the molecules are linked through N1–H1N1...O1ⁱ hydrogen bonds, forming a helical chain along the *a* axis. The chains are linked by N4–H1N4...S1ⁱⁱ, C2–H2A...S1ⁱⁱ and C10–H10C...F1ⁱⁱⁱ hydrogen bonds and a C4–H4A...Cg2^{iv} interaction (symmetry codes as given in Table 1), forming a three-dimensional network. No significant aromatic π – π stacking

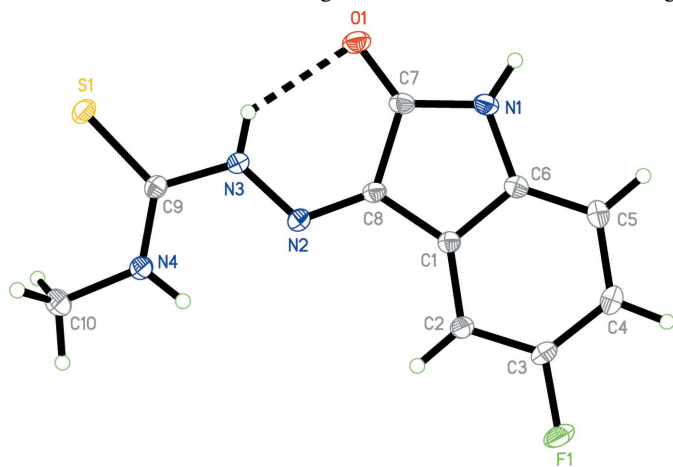


Figure 1

The molecular structure of the title compound, with 50% probability displacement ellipsoids and the atom-numbering scheme.

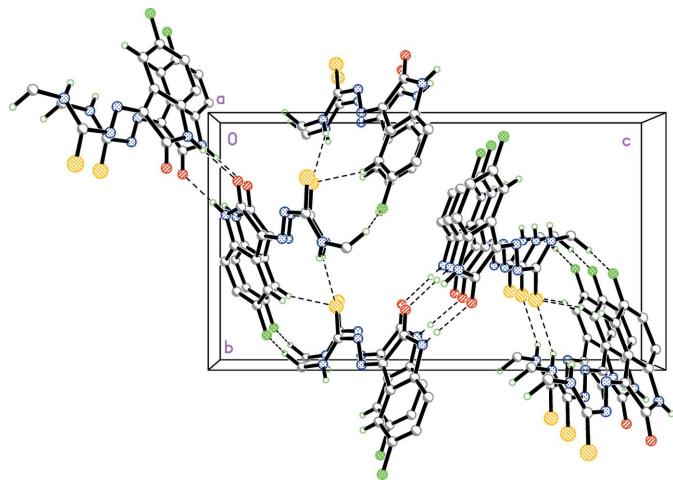


Figure 2

The crystal packing of the title compound, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₀ H ₉ FN ₄ OS
<i>M_r</i>	252.27
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.7058 (1), 10.6201 (2), 18.8688 (4)
<i>V</i> (Å ³)	1143.38 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.29
Crystal size (mm)	0.53 × 0.30 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2005)
<i>T_{min}</i> , <i>T_{max}</i>	0.782, 0.854
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	16340, 4144, 3953
<i>R_{int}</i>	0.019
(sin θ/ λ) _{max} (Å ⁻¹)	0.758
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.069, 1.05
No. of reflections	4144
No. of parameters	167
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.31, -0.19
Absolute structure	Flack <i>x</i> determined using 1583 quotients [(<i>I</i> ⁺) – (<i>I</i> [–])] / [(<i>I</i> ⁺) + (<i>I</i> [–])] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.031 (15)

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS2014* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

interactions are observed, the shortest centroid–centroid separation being 4.715 Å.

Synthesis and crystallization

The title compound was synthesized by refluxing the reaction mixture of hot ethanolic solutions (30 ml each) of 4-methyl-3-thiosemicarbazide (0.01 mol) and 5-fluoroisatin (0.01 mol) for 2 h. The precipitates formed during reflux were filtered and washed with cold ethanol and finally stored in a vacuum desiccator over P₂O₅ (yield 94%, m.p. 512.4–513.8 K). Yellow crystals were grown from acetone–dimethylformamide (3:1) by slow evaporation at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160659 [doi:10.1107/S2414314616006593]

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(Z)-2-(5-Fluoro-2-oxoindolin-3-ylidene)-N-methylhydrazinecarbothioamide*Crystal data*

$C_{10}H_9FN_4OS$

$M_r = 252.27$

Orthorhombic, $P2_12_12_1$

$a = 5.7058$ (1) Å

$b = 10.6201$ (2) Å

$c = 18.8688$ (4) Å

$V = 1143.38$ (4) Å³

$Z = 4$

$F(000) = 520$

$D_x = 1.466$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9924 reflections

$\theta = 3.7\text{--}32.6^\circ$

$\mu = 0.28$ mm⁻¹

$T = 100$ K

Block, yellow

$0.53 \times 0.30 \times 0.17$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.782$, $T_{\max} = 0.854$

16340 measured reflections

4144 independent reflections

3953 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 32.6^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -8 \rightarrow 8$

$k = -16 \rightarrow 14$

$l = -28 \rightarrow 28$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.069$

$S = 1.05$

4144 reflections

167 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.2071P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å⁻³

$\Delta\rho_{\min} = -0.19$ e Å⁻³

Absolute structure: Flack x determined using

1583 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.031 (15)

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.

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	0.74472 (6)	0.26837 (3)	0.22344 (2)	0.01730 (8)
F1	-0.37420 (18)	0.87584 (8)	0.12143 (5)	0.0246 (2)
O1	0.13905 (19)	0.26894 (10)	0.06783 (5)	0.0189 (2)
N1	-0.1734 (2)	0.39611 (11)	0.03438 (6)	0.0166 (2)
N2	0.2390 (2)	0.48908 (9)	0.16490 (5)	0.01366 (19)
N3	0.3829 (2)	0.39002 (10)	0.17279 (6)	0.0149 (2)
N4	0.6013 (2)	0.50266 (10)	0.25329 (6)	0.0156 (2)
C1	-0.1048 (2)	0.57160 (12)	0.10271 (6)	0.0129 (2)
C2	-0.1426 (2)	0.69283 (12)	0.12782 (7)	0.0150 (2)
H2A	-0.0423	0.7308	0.1619	0.018*
C3	-0.3354 (2)	0.75503 (12)	0.10026 (7)	0.0165 (2)
C4	-0.4878 (3)	0.70357 (13)	0.05128 (7)	0.0176 (3)
H4A	-0.6193	0.7504	0.0352	0.021*
C5	-0.4470 (2)	0.58177 (13)	0.02560 (7)	0.0166 (2)
H5A	-0.5480	0.5444	-0.0084	0.020*
C6	-0.2538 (3)	0.51798 (11)	0.05173 (6)	0.0140 (2)
C7	0.0219 (2)	0.36665 (12)	0.07190 (7)	0.0150 (2)
C8	0.0724 (2)	0.47780 (12)	0.11870 (6)	0.0135 (2)
C9	0.5714 (2)	0.39599 (11)	0.21827 (7)	0.0135 (2)
C10	0.7908 (3)	0.52261 (14)	0.30366 (8)	0.0211 (3)
H10A	0.7855	0.6095	0.3211	0.032*
H10B	0.9414	0.5074	0.2802	0.032*
H10C	0.7730	0.4644	0.3436	0.032*
H1N3	0.362 (4)	0.324 (2)	0.1503 (10)	0.022 (5)*
H1N1	-0.234 (5)	0.346 (2)	0.0038 (11)	0.035 (6)*
H1N4	0.502 (4)	0.562 (2)	0.2464 (12)	0.027 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01617 (14)	0.01296 (12)	0.02276 (14)	0.00254 (12)	-0.00245 (14)	0.00152 (10)
F1	0.0294 (5)	0.0163 (4)	0.0280 (4)	0.0105 (4)	-0.0010 (4)	-0.0041 (3)
O1	0.0242 (5)	0.0144 (4)	0.0181 (4)	0.0039 (4)	0.0004 (4)	-0.0035 (4)
N1	0.0205 (6)	0.0137 (4)	0.0157 (5)	-0.0002 (4)	-0.0029 (4)	-0.0032 (4)
N2	0.0144 (5)	0.0122 (4)	0.0144 (4)	0.0011 (4)	0.0003 (4)	0.0011 (3)
N3	0.0164 (5)	0.0117 (4)	0.0167 (5)	0.0019 (4)	-0.0028 (4)	-0.0011 (4)
N4	0.0152 (5)	0.0137 (5)	0.0180 (5)	0.0008 (4)	-0.0015 (4)	-0.0002 (4)
C1	0.0139 (5)	0.0125 (5)	0.0125 (5)	0.0002 (4)	0.0003 (4)	0.0001 (4)
C2	0.0168 (6)	0.0133 (5)	0.0150 (5)	0.0023 (4)	-0.0005 (5)	-0.0010 (4)
C3	0.0178 (6)	0.0142 (5)	0.0175 (5)	0.0045 (5)	0.0023 (5)	-0.0001 (4)
C4	0.0142 (6)	0.0200 (6)	0.0186 (5)	0.0028 (5)	0.0005 (5)	0.0038 (5)
C5	0.0141 (6)	0.0193 (6)	0.0163 (5)	-0.0013 (5)	-0.0017 (5)	0.0018 (4)
C6	0.0152 (5)	0.0135 (4)	0.0131 (4)	-0.0013 (5)	0.0007 (5)	0.0002 (4)
C7	0.0195 (6)	0.0129 (5)	0.0125 (5)	-0.0002 (5)	0.0003 (5)	-0.0018 (4)
C8	0.0157 (6)	0.0119 (4)	0.0129 (5)	0.0012 (4)	0.0009 (4)	-0.0011 (4)

C9	0.0134 (5)	0.0130 (5)	0.0140 (5)	0.0001 (4)	0.0010 (4)	0.0021 (4)
C10	0.0189 (7)	0.0212 (6)	0.0232 (6)	-0.0033 (5)	-0.0049 (5)	-0.0026 (5)

Geometric parameters (Å, °)

S1—C9	1.6804 (13)	C1—C6	1.4043 (18)
F1—C3	1.3618 (15)	C1—C8	1.4509 (18)
O1—C7	1.2366 (16)	C2—C3	1.3843 (19)
N1—C7	1.3567 (18)	C2—H2A	0.9500
N1—C6	1.4116 (16)	C3—C4	1.3819 (19)
N1—H1N1	0.86 (2)	C4—C5	1.4009 (19)
N2—C8	1.2957 (17)	C4—H4A	0.9500
N2—N3	1.3426 (15)	C5—C6	1.3847 (19)
N3—C9	1.3775 (17)	C5—H5A	0.9500
N3—H1N3	0.83 (2)	C7—C8	1.5020 (17)
N4—C9	1.3225 (16)	C10—H10A	0.9800
N4—C10	1.4549 (18)	C10—H10B	0.9800
N4—H1N4	0.86 (2)	C10—H10C	0.9800
C1—C2	1.3887 (17)		
C7—N1—C6	110.94 (11)	C6—C5—C4	117.45 (12)
C7—N1—H1N1	122.6 (16)	C6—C5—H5A	121.3
C6—N1—H1N1	126.5 (16)	C4—C5—H5A	121.3
C8—N2—N3	116.80 (10)	C5—C6—C1	121.83 (12)
N2—N3—C9	120.70 (11)	C5—C6—N1	128.66 (12)
N2—N3—H1N3	121.2 (15)	C1—C6—N1	109.51 (12)
C9—N3—H1N3	118.1 (14)	O1—C7—N1	127.23 (12)
C9—N4—C10	123.16 (12)	O1—C7—C8	126.33 (12)
C9—N4—H1N4	117.9 (15)	N1—C7—C8	106.43 (11)
C10—N4—H1N4	118.9 (15)	N2—C8—C1	126.00 (11)
C2—C1—C6	121.04 (12)	N2—C8—C7	127.51 (12)
C2—C1—C8	132.37 (12)	C1—C8—C7	106.49 (11)
C6—C1—C8	106.60 (11)	N4—C9—N3	116.83 (11)
C3—C2—C1	115.96 (12)	N4—C9—S1	125.88 (10)
C3—C2—H2A	122.0	N3—C9—S1	117.29 (9)
C1—C2—H2A	122.0	N4—C10—H10A	109.5
F1—C3—C4	117.79 (12)	N4—C10—H10B	109.5
F1—C3—C2	117.95 (12)	H10A—C10—H10B	109.5
C4—C3—C2	124.24 (13)	N4—C10—H10C	109.5
C3—C4—C5	119.46 (13)	H10A—C10—H10C	109.5
C3—C4—H4A	120.3	H10B—C10—H10C	109.5
C5—C4—H4A	120.3		
C8—N2—N3—C9	176.91 (12)	C6—N1—C7—O1	-177.89 (13)
C6—C1—C2—C3	0.79 (19)	C6—N1—C7—C8	0.88 (14)
C8—C1—C2—C3	-179.31 (13)	N3—N2—C8—C1	178.69 (12)
C1—C2—C3—F1	-177.62 (11)	N3—N2—C8—C7	-0.75 (19)
C1—C2—C3—C4	0.7 (2)	C2—C1—C8—N2	2.3 (2)

F1—C3—C4—C5	176.88 (12)	C6—C1—C8—N2	-177.77 (13)
C2—C3—C4—C5	-1.4 (2)	C2—C1—C8—C7	-178.15 (14)
C3—C4—C5—C6	0.64 (19)	C6—C1—C8—C7	1.76 (13)
C4—C5—C6—C1	0.80 (19)	O1—C7—C8—N2	-3.3 (2)
C4—C5—C6—N1	-179.45 (13)	N1—C7—C8—N2	177.88 (13)
C2—C1—C6—C5	-1.56 (19)	O1—C7—C8—C1	177.15 (13)
C8—C1—C6—C5	178.52 (12)	N1—C7—C8—C1	-1.64 (14)
C2—C1—C6—N1	178.64 (12)	C10—N4—C9—N3	179.35 (12)
C8—C1—C6—N1	-1.28 (14)	C10—N4—C9—S1	-1.59 (19)
C7—N1—C6—C5	-179.55 (13)	N2—N3—C9—N4	0.33 (18)
C7—N1—C6—C1	0.23 (15)	N2—N3—C9—S1	-178.81 (9)

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C1—C6 ring.

<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>
N3—H1N3...O1	0.83 (2)	2.09 (2)	2.7407 (15)	135 (2)
N1—H1N1...O1 ⁱ	0.86 (2)	1.96 (2)	2.8173 (15)	178 (3)
N4—H1N4...S1 ⁱⁱ	0.86 (2)	2.67 (2)	3.4718 (11)	157.0 (19)
C2—H2A...S1 ⁱⁱ	0.95	2.78	3.6979 (13)	163
C10—H10C...F1 ⁱⁱⁱ	0.98	2.55	3.1746 (19)	122
C4—H4A...Cg2 ^{iv}	0.95	2.62	3.4291 (15)	143

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