4-(3-Nitrophenyl)-1-(2-oxoindolin-3-yl-idene)thiosemicarbazide

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In the title compound, $C_{15}H_{11}N_5O_3S$, intramolecular N—H⋯N hydrogen bonding forms an $S(5)$ ring motif, whereas N—H⋯O and C—H⋯S interactions type complete $S(6)$ ring motifs. The 2-oxoindoline and 3-methoxyphenyl rings are almost planar, with r.m.s. deviations of 0.0178 and 0.0149 Å, respectively, and form a dihedral angle of 33.59 (3)°. In the crystal, molecules are interlinked through the nitro groups in an end-to-end fashion *via* N—H⋯O and C—H⋯O interactions.

Related literature

For the preparation and structures of biologically important N^4-aryl-substituted isatin-3-thiosemicarbazones, see: Pervez *et al.* (2007). For related structures, see: (Pervez *et al.* 2010*a,b*). For graph-set notation, see: Bernstein *et al.* (1995).
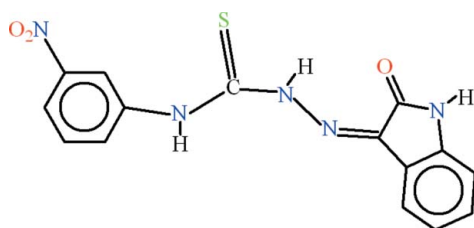
Experimental

Crystal data

$C_{15}H_{11}N_5O_3S$	$V = 1523.44$ (16) Å³
$M_r = 341.35$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 18.5545$ (10) Å	$\mu = 0.24$ mm⁻¹
$b = 15.3852$ (8) Å	$T = 296$ K
$c = 5.3367$ (4) Å	$0.24 \times 0.16 \times 0.14$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	7285 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	2751 independent reflections
$T_{min} = 0.957$, $T_{max} = 0.966$	1957 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.096$	$\Delta\rho_{max} = 0.16$ e Å⁻³
$S = 1.00$	$\Delta\rho_{min} = -0.27$ e Å⁻³
2751 reflections	Absolute structure: Flack (1983),
217 parameters	992 Friedel pairs
1 restraint	Flack parameter: -0.05 (11)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O3[i]	0.86	2.21	3.058 (3)	170
N3—H3⋯O1	0.86	2.13	2.797 (3)	134
N4—H4A⋯N2	0.86	2.12	2.580 (3)	113
C7—H7⋯O2[i]	0.93	2.55	3.358 (4)	145
C11—H11⋯S1	0.93	2.56	3.204 (3)	127

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + 2$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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supporting information

4-(3-Nitrophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide

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S1. Comment

As a part of our work on the synthesis of certain biologically important isatin derivatives (Pervez *et al.*, 2007), we report herein the structure and synthesis of the title compound (I, Fig. 1).

The crystal structure of (II) i.e. 4-(2-fluorophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide (Pervez *et al.*, 2010b) and (III) i.e. 4-(3-methoxyphenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide (Pervez *et al.*, 2010a) have been reported. The title compound (I) differs from (II) due to the attachment of nitro group at position-3 instead of fluoro at position-2 of the phenyl ring substituted at N^4 of the thiosemicarbazone moiety. Similarly (I) differs from (III) due to the presence of nitro instead of methoxy function at position-3 of the phenyl ring. In (I) the 2-oxoindolin A (C1–C8/N1/O1), thiosemicarbazide B (N2/N3/C9/S1/N4) and the 3-methoxyphenyl C (C10—C16/O2) are planar with r. m. s. deviations of 0.0178, 0.0244 and 0.0149 Å, respectively. The dihedral angle between A/B, A/C and B/C is 8.71 (5)°, 33.59 (3)° and 39.32 (3)°, respectively. Due to intramolecular H-bondings (Table 1, Fig. 1), one S(5) and two S(6) (Bernstein *et al.*, 1995) ring motifs are formed. The molecules are interlinked through nitro groups (Fig. 2) in end to end fashion due to N—H···O and C–H···O interactions completing $R_2^2(8)$ ring motifs. The N=O···π and C=S···π interaction play role in stabilizing the molecules.

S2. Experimental

To a hot solution of isatin (0.74 g, 5.0 mmol) in ethanol (10 ml) containing a few drops of glacial acetic acid was added 4-(3-nitrophenyl)thiosemicarbazide (1.06 g, 5.0 mmol) dissolved in ethanol (10 ml) under stirring. The reaction mixture was then heated under reflux for 2 h. The orange crystalline solid formed during heating was collected by suction filtration. Thorough washing with hot ethanol followed by ether provided the desired compound (I) in pure form (1.08 g, 63%), m.p. 539 K. The single crystals of (I) were grown in ethyl acetate by slow evaporation at room temperature.

S3. Refinement

The H-atoms were positioned geometrically (N–H = 0.86 Å, C–H = 0.93 Å) and refined as riding with $U_{iso}(H) = xU_{eq}(C, N)$, where x = 1.2 for all H-atoms.
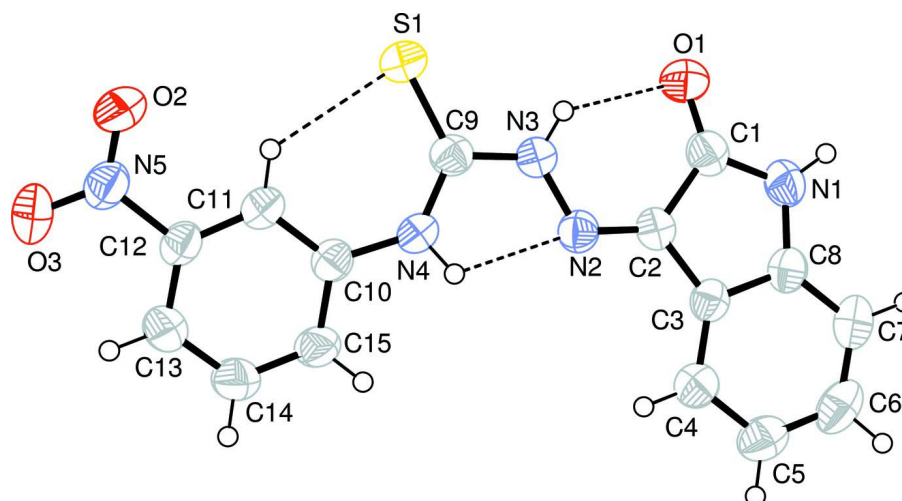
Figure 1

View of the title compound with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. The dotted lines indicate the intra-molecular H-bondings.
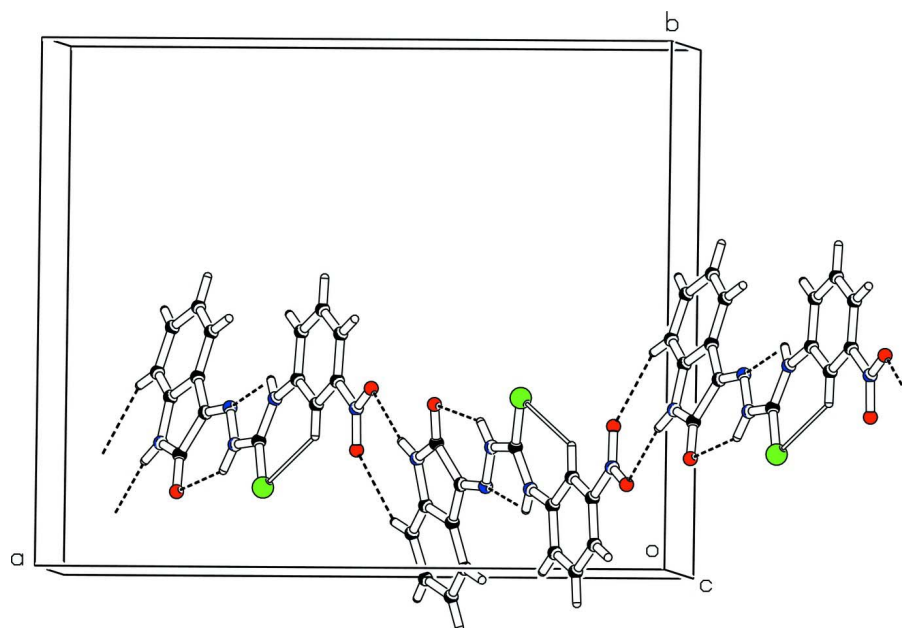
Figure 2

The partial packing (*PLATON*; Spek, 2009) which shows that molecules form dimers which are interlinked.

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Crystal data

$C_{15}H_{11}N_5O_3S$	$V = 1523.44\ (16)$ Å³
$M_r = 341.35$	$Z = 4$
Orthorhombic, $Pna2_1$	$F(000) = 704$
Hall symbol: P 2c -2n	$D_x = 1.488$ Mg m⁻³
$a = 18.5545\ (10)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 15.3852\ (8)$ Å	Cell parameters from 2751 reflections
$c = 5.3367\ (4)$ Å	$\theta = 2.6$–$26.5°$

$\mu = 0.24$ mm^{-1}

$T = 296$ K

Prism, light yellow

$0.24 \times 0.16 \times 0.14$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	7285 measured reflections
Radiation source: fine-focus sealed tube	2751 independent reflections
Graphite monochromator	1957 reflections with $I > 2\sigma(I)$
Detector resolution: 7.80 pixels mm^{-1}	$R_{int} = 0.036$
ω scans	$\theta_{max} = 26.5°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -23 \rightarrow 23$
	$k = -19 \rightarrow 18$
$T_{min} = 0.957$, $T_{max} = 0.966$	$l = -6 \rightarrow 5$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.036$	H-atom parameters constrained
$wR(F^2) = 0.096$	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$
$S = 1.00$	where $P = (F_o^2 + 2F_c^2)/3$
2751 reflections	$(\Delta/\sigma)_{max} < 0.001$
217 parameters	$\Delta\rho_{max} = 0.16$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 992 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: −0.05 (11)

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 $F^2 > \sigma(F^2)$ 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}
S1	0.22195 (4)	0.31899 (4)	−0.2161 (2)	0.0691 (3)
O1	0.38865 (11)	0.31688 (13)	0.4271 (5)	0.0693 (6)
O2	0.04767 (14)	0.25693 (14)	−0.7833 (6)	0.0987 (11)
O3	0.01628 (11)	0.14340 (14)	−0.9884 (5)	0.0691 (6)
N1	0.42883 (11)	0.21951 (15)	0.7293 (5)	0.0584 (7)
H1	0.4577	0.2529	0.8109	0.070*
N2	0.29869 (10)	0.15983 (12)	0.2774 (5)	0.0462 (5)
N3	0.28351 (11)	0.23206 (14)	0.1419 (5)	0.0511 (6)
H3	0.3036	0.2806	0.1808	0.061*
N4	0.21013 (11)	0.14865 (14)	−0.0938 (5)	0.0485 (6)
H4A	0.2223	0.1111	0.0179	0.058*
N5	0.04756 (12)	0.17858 (16)	−0.8135 (5)	0.0573 (7)

C1	0.38904 (15)	0.24541 (19)	0.5275 (6)	0.0526 (8)
C2	0.34565 (13)	0.16630 (16)	0.4526 (6)	0.0443 (6)
C3	0.36668 (12)	0.09693 (16)	0.6207 (6)	0.0440 (6)
C4	0.34648 (14)	0.01067 (17)	0.6375 (6)	0.0529 (7)
H4	0.3137	−0.0131	0.5247	0.063*
C5	0.37617 (16)	−0.03939 (19)	0.8262 (7)	0.0627 (9)
H5	0.3632	−0.0975	0.8415	0.075*
C6	0.42479 (16)	−0.0037 (2)	0.9915 (7)	0.0666 (9)
H6	0.4435	−0.0385	1.1182	0.080*
C7	0.44684 (14)	0.0822 (2)	0.9761 (6)	0.0596 (8)
H7	0.4802	0.1054	1.0876	0.072*
C8	0.41680 (12)	0.13180 (17)	0.7871 (7)	0.0483 (6)
C9	0.23686 (13)	0.22885 (16)	−0.0549 (6)	0.0463 (7)
C10	0.16580 (12)	0.11539 (16)	−0.2849 (5)	0.0448 (7)
C11	0.12759 (13)	0.16537 (16)	−0.4543 (6)	0.0475 (7)
H11	0.1294	0.2257	−0.4476	0.057*
C12	0.08673 (13)	0.12370 (18)	−0.6333 (6)	0.0467 (7)
C13	0.08131 (14)	0.03494 (18)	−0.6548 (7)	0.0594 (9)
H13	0.0538	0.0090	−0.7799	0.071*
C14	0.11867 (17)	−0.01353 (19)	−0.4821 (8)	0.0669 (10)
H14	0.1158	−0.0738	−0.4884	0.080*
C15	0.16025 (13)	0.02508 (17)	−0.3002 (7)	0.0564 (8)
H15	0.1850	−0.0094	−0.1859	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0952 (5)	0.0440 (4)	0.0682 (6)	0.0028 (4)	−0.0217 (6)	0.0061 (4)
O1	0.0843 (14)	0.0538 (12)	0.0697 (17)	−0.0173 (10)	−0.0095 (13)	0.0108 (11)
O2	0.1169 (18)	0.0549 (14)	0.124 (3)	−0.0056 (12)	−0.060 (2)	0.0259 (15)
O3	0.0610 (12)	0.0922 (16)	0.0540 (15)	0.0020 (11)	−0.0169 (12)	0.0025 (12)
N1	0.0572 (13)	0.0627 (15)	0.055 (2)	−0.0116 (10)	−0.0129 (13)	−0.0018 (13)
N2	0.0479 (11)	0.0467 (13)	0.0439 (15)	0.0030 (8)	−0.0014 (13)	−0.0011 (13)
N3	0.0608 (14)	0.0423 (13)	0.0501 (17)	−0.0004 (9)	−0.0107 (13)	0.0009 (11)
N4	0.0552 (12)	0.0424 (12)	0.0478 (16)	0.0017 (10)	−0.0072 (11)	0.0080 (10)
N5	0.0487 (12)	0.0632 (17)	0.060 (2)	−0.0013 (11)	−0.0065 (13)	0.0151 (14)
C1	0.0522 (15)	0.0573 (18)	0.048 (2)	−0.0067 (13)	0.0022 (15)	−0.0028 (15)
C2	0.0422 (13)	0.0482 (16)	0.0425 (18)	−0.0008 (10)	−0.0003 (13)	−0.0025 (12)
C3	0.0435 (13)	0.0491 (16)	0.0396 (18)	0.0049 (11)	0.0015 (13)	−0.0005 (13)
C4	0.0522 (15)	0.0536 (18)	0.053 (2)	0.0024 (12)	0.0011 (14)	0.0009 (14)
C5	0.0688 (17)	0.0548 (17)	0.064 (3)	0.0099 (13)	0.0049 (19)	0.0084 (16)
C6	0.0682 (19)	0.079 (2)	0.053 (2)	0.0252 (16)	0.0012 (17)	0.0140 (17)
C7	0.0555 (16)	0.080 (2)	0.043 (2)	0.0080 (15)	−0.0047 (15)	−0.0012 (15)
C8	0.0467 (12)	0.0569 (17)	0.0414 (18)	0.0025 (11)	0.0002 (16)	−0.0004 (15)
C9	0.0505 (13)	0.0425 (15)	0.0458 (19)	0.0059 (12)	0.0039 (15)	−0.0024 (13)
C10	0.0415 (12)	0.0475 (16)	0.045 (2)	0.0023 (10)	0.0007 (12)	0.0028 (12)
C11	0.0471 (14)	0.0470 (15)	0.0482 (19)	0.0040 (11)	−0.0006 (13)	0.0067 (13)
C12	0.0391 (11)	0.0543 (16)	0.047 (2)	0.0007 (12)	−0.0016 (12)	0.0111 (13)

C13	0.0543 (15)	0.0562 (18)	0.068 (3)	−0.0087 (13)	−0.0116 (17)	0.0010 (15)
C14	0.0692 (18)	0.0454 (16)	0.086 (3)	−0.0022 (14)	−0.0198 (19)	0.0051 (17)
C15	0.0495 (14)	0.0459 (16)	0.074 (2)	−0.0006 (12)	−0.0134 (16)	0.0120 (14)

Geometric parameters (Å, º)

S1—C9	1.655 (3)	C4—C5	1.382 (4)
O1—C1	1.223 (3)	C4—H4	0.9300
O2—N5	1.216 (3)	C5—C6	1.376 (5)
O3—N5	1.225 (3)	C5—H5	0.9300
N1—C1	1.365 (4)	C6—C7	1.386 (4)
N1—C8	1.402 (3)	C6—H6	0.9300
N1—H1	0.8600	C7—C8	1.382 (4)
N2—C2	1.282 (4)	C7—H7	0.9300
N2—N3	1.355 (3)	C10—C11	1.382 (4)
N3—C9	1.362 (4)	C10—C15	1.396 (3)
N3—H3	0.8600	C11—C12	1.378 (4)
N4—C9	1.346 (3)	C11—H11	0.9300
N4—C10	1.407 (3)	C12—C13	1.374 (4)
N4—H4A	0.8600	C13—C14	1.373 (4)
N5—C12	1.472 (4)	C13—H13	0.9300
C1—C2	1.513 (4)	C14—C15	1.375 (4)
C2—C3	1.448 (4)	C14—H14	0.9300
C3—C4	1.382 (3)	C15—H15	0.9300
C3—C8	1.393 (4)		
C1—N1—C8	111.6 (2)	C5—C6—H6	118.8
C1—N1—H1	124.2	C7—C6—H6	118.8
C8—N1—H1	124.2	C8—C7—C6	116.8 (3)
C2—N2—N3	117.8 (2)	C8—C7—H7	121.6
N2—N3—C9	120.9 (2)	C6—C7—H7	121.6
N2—N3—H3	119.5	C7—C8—C3	121.4 (2)
C9—N3—H3	119.5	C7—C8—N1	128.9 (3)
C9—N4—C10	131.3 (2)	C3—C8—N1	109.7 (3)
C9—N4—H4A	114.3	N4—C9—N3	112.7 (2)
C10—N4—H4A	114.3	N4—C9—S1	128.8 (2)
O2—N5—O3	122.7 (3)	N3—C9—S1	118.5 (2)
O2—N5—C12	118.7 (3)	C11—C10—C15	118.5 (3)
O3—N5—C12	118.6 (2)	C11—C10—N4	124.9 (2)
O1—C1—N1	127.7 (3)	C15—C10—N4	116.6 (2)
O1—C1—C2	127.2 (3)	C12—C11—C10	118.5 (2)
N1—C1—C2	105.2 (2)	C12—C11—H11	120.8
N2—C2—C3	125.3 (2)	C10—C11—H11	120.8
N2—C2—C1	128.1 (2)	C13—C12—C11	124.1 (3)
C3—C2—C1	106.6 (2)	C13—C12—N5	118.6 (3)
C4—C3—C8	120.6 (3)	C11—C12—N5	117.3 (2)
C4—C3—C2	132.5 (3)	C14—C13—C12	116.5 (3)
C8—C3—C2	106.9 (2)	C14—C13—H13	121.7

C3—C4—C5	118.3 (3)	C12—C13—H13	121.7
C3—C4—H4	120.8	C13—C14—C15	121.5 (3)
C5—C4—H4	120.8	C13—C14—H14	119.2
C6—C5—C4	120.4 (3)	C15—C14—H14	119.2
C6—C5—H5	119.8	C14—C15—C10	120.8 (3)
C4—C5—H5	119.8	C14—C15—H15	119.6
C5—C6—C7	122.4 (3)	C10—C15—H15	119.6

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3[i]	0.86	2.21	3.058 (3)	170
N3—H3···O1	0.86	2.13	2.797 (3)	134
N4—H4A···N2	0.86	2.12	2.580 (3)	113
C7—H7···O2[i]	0.93	2.55	3.358 (4)	145
C11—H11···S1	0.93	2.56	3.204 (3)	127

Symmetry code: (i) $x+1/2, -y+1/2, z+2$.