Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

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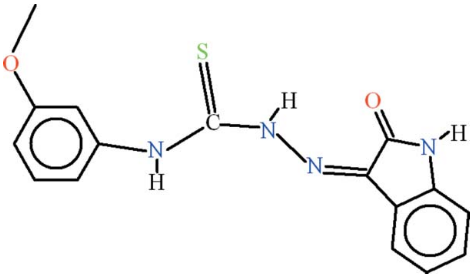
Received 6 May 2010; accepted 15 May 2010

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.125; data-to-parameter ratio = 18.8.

In the title compound, $C_{16}H_{14}N_4O_2S$, intramolecular N—H···N hydrogen bonding forms an S(5) ring, whereas N—H···O and C—H···S interactions complete S(6) ring motifs. In the crystal, molecules form inversion dimers due to N—H···O interactions. The dimers are interlinked through N—H···S hydrogen bonds and π–π interactions occur with a centroid–centroid distance of 3.8422 (11) Å between the methoxy-containing benzene ring and the five-membered heterocyclic ring.

Related literature

For the preparation and structures of biologically important N^4-aryl-substituted isatin-3-thiosemicarbazones, see: Pervez *et al.* (2007, 2008, 2009, 2010*a*). For a related structure, see: Pervez *et al.* (2010*b*). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{16}H_{14}N_4O_2S$
M_r = 326.37
Monoclinic, $P2_1/n$
a = 15.1793 (5) Å
b = 7.2473 (2) Å
c = 15.4764 (5) Å
β = 111.179 (2)°
V = 1587.55 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 296 K
0.34 × 0.22 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.946, T_{max} = 0.960
13861 measured reflections
3925 independent reflections
2898 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.125
S = 1.04
3925 reflections
209 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.86	2.04	2.875 (2)	164
N3—H3A···O1	0.86	2.06	2.7441 (19)	136
N4—H4A···N2	0.86	2.19	2.620 (2)	110
N4—H4A···S1^{ii}	0.86	2.87	3.5806 (16)	141
C11—H11···S1	0.93	2.74	3.212 (2)	112

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

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*.

HP, MSI and NS thank the Higher Education Commission (HEC), Pakistan, for financial assistance under the National Research Program for Universities (project No. 20–873/R&D/07/452).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2262).

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doi:10.1107/S1600536810018052

supporting information

Acta Cryst. (2010). E**66**, o1404   [https://doi.org/10.1107/S1600536810018052]

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

Humayun Pervez, Mohammad S. Iqbal, Naveeda Saira, Muhammad Yaqub and M. Nawaz Tahir

S1. Comment

In continuation of our work on the synthesis of medicinally important organic molecules (Pervez *et al.*, 2007, 2008, 2009, 2010*a*), 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 has been published (Pervez *et al.*, 2010*b*). The title compound (I) differs from (II) due to the attachment of methoxy group at position-3 instead of fluoro at position-2 of the phenyl ring substituted at N^4^ of the thiosemicarbazone moiety.

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 dimerised (Fig. 2) due to intermolecular H-bonding of N—H···O type with $R_2^2(8)$ ring motifs. The dimers are interlinked through N—H···S type of H-bonding. There exist $\pi\cdots\pi$ interaction at a distance of 3.8422 (11) Å between the benzene ring (C10—C15) and the heterocyclic ring (N1/C7/C2/C1/C8).

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-methoxyphenyl)thiosemicarbazide (0.99 g, 5.0 mmol) dissolved in ethanol (10 ml) under stirring. The reaction mixture was then heated under reflux for 2 h. The yellow crystalline solid formed during refluxing was collected by suction filtration. Thorough washing with hot ethanol followed by ether afforded the target compound (I) in pure form (1.25 g, 77%), m. p. 477 K (d). The single crystals of (I) were grown in acetone by slow evaporation at room temperature.

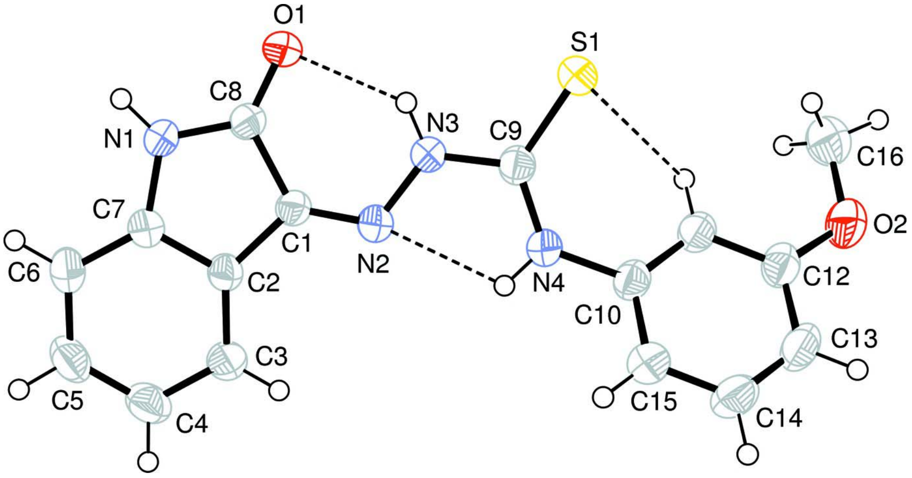

Figure 1

View of the title compound with the atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radii. The dotted lines indicate the intra-molecular H-bondings.

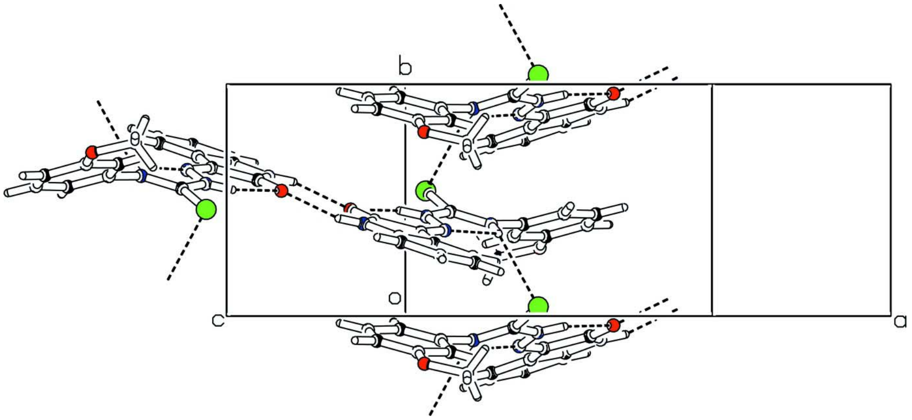

Figure 2

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

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

Crystal data

$C_{16}H_{14}N_4O_2S$
$M_r = 326.37$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 15.1793\ (5)$ Å
$b = 7.2473\ (2)$ Å
$c = 15.4764\ (5)$ Å
$\beta = 111.179\ (2)°$
$V = 1587.55\ (9)$ Å^3
$Z = 4$

$F(000) = 680$
$D_x = 1.366$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2898 reflections
$\theta = 3.2–28.3°$
$\mu = 0.22$ mm^{-1}
$T = 296$ K
Prism, yellow
0.34 × 0.22 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.40 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min} = 0.946$, $T_{\max} = 0.960$

13861 measured reflections
3925 independent reflections
2898 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 28.3°$, $\theta_{\min} = 3.2°$
$h = -20 \rightarrow 20$
$k = -9 \rightarrow 9$
$l = -20 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.125$
$S = 1.04$
3925 reflections
209 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
$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 0.6227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ 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 $F^2 > \sigma(F^2)$ 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	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.19826 (11)	0.3610 (2)	0.45348 (11)	0.0329 (3)
C2	0.26044 (11)	0.3126 (2)	0.54720 (11)	0.0345 (3)
C3	0.35347 (12)	0.2547 (3)	0.58412 (12)	0.0434 (4)
H3	0.3882	0.2332	0.5464	0.052*
C4	0.39313 (14)	0.2298 (3)	0.67919 (13)	0.0515 (5)
H4	0.4555	0.1908	0.7057	0.062*
C5	0.34181 (15)	0.2617 (3)	0.73516 (13)	0.0529 (5)
H5	0.3705	0.2446	0.7988	0.063*
C6	0.24859 (14)	0.3187 (3)	0.69884 (12)	0.0491 (5)
H6	0.2140	0.3403	0.7367	0.059*
C7	0.20928 (11)	0.3419 (2)	0.60448 (11)	0.0382 (4)
C8	0.10524 (11)	0.4125 (2)	0.46058 (11)	0.0359 (4)
C9	0.17432 (11)	0.4498 (2)	0.22293 (11)	0.0360 (4)
C10	0.30202 (12)	0.3962 (2)	0.16100 (12)	0.0388 (4)
C11	0.24941 (12)	0.3445 (2)	0.07119 (12)	0.0407 (4)
H11	0.1865	0.3103	0.0552	0.049*

C12	0.29128 (13)	0.3440 (3)	0.00497 (13)	0.0446 (4)
C13	0.38568 (14)	0.3931 (3)	0.02993 (15)	0.0539 (5)
H13	0.4139	0.3948	−0.0143	0.065*
C14	0.43705 (14)	0.4392 (3)	0.11998 (16)	0.0554 (5)
H14	0.5006	0.4689	0.1366	0.066*
C15	0.39605 (13)	0.4423 (3)	0.18678 (14)	0.0477 (4)
H15	0.4313	0.4748	0.2476	0.057*
C16	0.14733 (15)	0.2526 (3)	−0.11290 (15)	0.0613 (6)
H16A	0.1142	0.3578	−0.1023	0.092*
H16B	0.1387	0.1496	−0.0777	0.092*
H16C	0.1230	0.2222	−0.1776	0.092*
N1	0.11680 (10)	0.3984 (2)	0.55058 (10)	0.0429 (4)
H1	0.0733	0.4210	0.5725	0.051*
N2	0.22156 (9)	0.36975 (19)	0.38155 (9)	0.0351 (3)
N3	0.15482 (9)	0.4293 (2)	0.30214 (9)	0.0374 (3)
H3A	0.0992	0.4548	0.3013	0.045*
N4	0.26118 (10)	0.3955 (2)	0.23067 (10)	0.0416 (4)
H4A	0.2966	0.3552	0.2842	0.050*
O1	0.03312 (8)	0.45962 (19)	0.39631 (8)	0.0452 (3)
O2	0.24526 (10)	0.2944 (2)	−0.08484 (9)	0.0610 (4)
S1	0.09025 (3)	0.53985 (8)	0.13109 (3)	0.04856 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0311 (7)	0.0360 (8)	0.0318 (8)	0.0010 (6)	0.0115 (6)	−0.0041 (6)
C2	0.0357 (8)	0.0370 (9)	0.0304 (8)	0.0024 (6)	0.0115 (6)	−0.0028 (6)
C3	0.0409 (9)	0.0480 (10)	0.0403 (9)	0.0111 (7)	0.0136 (7)	−0.0015 (8)
C4	0.0456 (10)	0.0572 (12)	0.0423 (10)	0.0146 (9)	0.0045 (8)	0.0006 (9)
C5	0.0585 (12)	0.0603 (12)	0.0312 (9)	0.0100 (9)	0.0060 (8)	0.0039 (8)
C6	0.0547 (11)	0.0628 (12)	0.0320 (9)	0.0061 (9)	0.0182 (8)	−0.0004 (8)
C7	0.0370 (8)	0.0444 (9)	0.0329 (8)	0.0019 (7)	0.0123 (7)	−0.0013 (7)
C8	0.0306 (7)	0.0442 (9)	0.0335 (8)	−0.0012 (6)	0.0121 (6)	−0.0050 (7)
C9	0.0361 (8)	0.0396 (9)	0.0331 (8)	−0.0034 (7)	0.0136 (7)	−0.0010 (7)
C10	0.0408 (9)	0.0398 (9)	0.0411 (9)	0.0054 (7)	0.0211 (7)	0.0075 (7)
C11	0.0412 (9)	0.0431 (10)	0.0421 (9)	0.0028 (7)	0.0200 (7)	0.0032 (7)
C12	0.0518 (10)	0.0442 (10)	0.0445 (10)	0.0062 (8)	0.0253 (8)	0.0032 (8)
C13	0.0548 (11)	0.0636 (13)	0.0570 (12)	0.0033 (10)	0.0367 (10)	0.0059 (10)
C14	0.0414 (10)	0.0658 (13)	0.0656 (13)	−0.0035 (9)	0.0272 (10)	0.0046 (10)
C15	0.0415 (9)	0.0565 (12)	0.0465 (10)	0.0005 (8)	0.0174 (8)	0.0036 (9)
C16	0.0634 (13)	0.0705 (15)	0.0487 (12)	−0.0020 (11)	0.0187 (10)	−0.0053 (10)
N1	0.0337 (7)	0.0646 (10)	0.0332 (7)	0.0050 (7)	0.0154 (6)	−0.0018 (7)
N2	0.0345 (7)	0.0396 (8)	0.0317 (7)	0.0018 (6)	0.0124 (6)	−0.0014 (6)
N3	0.0303 (6)	0.0520 (9)	0.0304 (7)	0.0027 (6)	0.0114 (5)	0.0015 (6)
N4	0.0355 (7)	0.0579 (10)	0.0330 (7)	0.0072 (6)	0.0143 (6)	0.0079 (6)
O1	0.0303 (6)	0.0680 (9)	0.0342 (6)	0.0061 (5)	0.0081 (5)	−0.0031 (6)
O2	0.0614 (9)	0.0838 (11)	0.0445 (8)	0.0019 (8)	0.0272 (7)	−0.0089 (7)
S1	0.0377 (2)	0.0708 (4)	0.0363 (2)	0.0074 (2)	0.01228 (18)	0.0104 (2)

Geometric parameters (Å, º)

C1—N2	1.286 (2)	C10—C11	1.381 (2)
C1—C2	1.459 (2)	C10—N4	1.425 (2)
C1—C8	1.503 (2)	C11—C12	1.387 (2)
C2—C3	1.383 (2)	C11—H11	0.9300
C2—C7	1.390 (2)	C12—O2	1.359 (2)
C3—C4	1.386 (3)	C12—C13	1.389 (3)
C3—H3	0.9300	C13—C14	1.370 (3)
C4—C5	1.378 (3)	C13—H13	0.9300
C4—H4	0.9300	C14—C15	1.386 (3)
C5—C6	1.384 (3)	C14—H14	0.9300
C5—H5	0.9300	C15—H15	0.9300
C6—C7	1.374 (2)	C16—O2	1.422 (3)
C6—H6	0.9300	C16—H16A	0.9600
C7—N1	1.410 (2)	C16—H16B	0.9600
C8—O1	1.2319 (19)	C16—H16C	0.9600
C8—N1	1.343 (2)	N1—H1	0.8600
C9—N4	1.339 (2)	N2—N3	1.3504 (18)
C9—N3	1.369 (2)	N3—H3A	0.8600
C9—S1	1.6624 (17)	N4—H4A	0.8600
C10—C15	1.377 (2)		

N2—C1—C2	126.25 (14)	C10—C11—H11	120.3
N2—C1—C8	127.64 (14)	C12—C11—H11	120.3
C2—C1—C8	105.94 (13)	O2—C12—C11	123.55 (17)
C3—C2—C7	120.33 (15)	O2—C12—C13	116.72 (17)
C3—C2—C1	132.91 (15)	C11—C12—C13	119.72 (18)
C7—C2—C1	106.72 (13)	C14—C13—C12	119.75 (18)
C2—C3—C4	117.73 (17)	C14—C13—H13	120.1
C2—C3—H3	121.1	C12—C13—H13	120.1
C4—C3—H3	121.1	C13—C14—C15	121.26 (18)
C5—C4—C3	121.22 (17)	C13—C14—H14	119.4
C5—C4—H4	119.4	C15—C14—H14	119.4
C3—C4—H4	119.4	C10—C15—C14	118.52 (18)
C4—C5—C6	121.48 (17)	C10—C15—H15	120.7
C4—C5—H5	119.3	C14—C15—H15	120.7
C6—C5—H5	119.3	O2—C16—H16A	109.5
C7—C6—C5	117.13 (17)	O2—C16—H16B	109.5
C7—C6—H6	121.4	H16A—C16—H16B	109.5
C5—C6—H6	121.4	O2—C16—H16C	109.5
C6—C7—C2	122.09 (16)	H16A—C16—H16C	109.5
C6—C7—N1	128.44 (16)	H16B—C16—H16C	109.5
C2—C7—N1	109.47 (14)	C8—N1—C7	111.39 (14)
O1—C8—N1	127.11 (15)	C8—N1—H1	124.3
O1—C8—C1	126.47 (15)	C7—N1—H1	124.3
N1—C8—C1	106.42 (13)	C1—N2—N3	116.95 (13)
N4—C9—N3	114.35 (14)	N2—N3—C9	121.05 (13)

N4—C9—S1	128.21 (13)	N2—N3—H3A	119.5
N3—C9—S1	117.43 (12)	C9—N3—H3A	119.5
C15—C10—C11	121.28 (16)	C9—N4—C10	127.93 (14)
C15—C10—N4	118.06 (16)	C9—N4—H4A	116.0
C11—C10—N4	120.61 (15)	C10—N4—H4A	116.0
C10—C11—C12	119.44 (16)	C12—O2—C16	117.57 (15)

N2—C1—C2—C3	−4.6 (3)	C10—C11—C12—C13	0.8 (3)
C8—C1—C2—C3	179.95 (19)	O2—C12—C13—C14	−178.02 (19)
N2—C1—C2—C7	172.98 (16)	C11—C12—C13—C14	0.9 (3)
C8—C1—C2—C7	−2.51 (18)	C12—C13—C14—C15	−1.6 (3)
C7—C2—C3—C4	−0.8 (3)	C11—C10—C15—C14	1.2 (3)
C1—C2—C3—C4	176.49 (19)	N4—C10—C15—C14	178.50 (17)
C2—C3—C4—C5	0.0 (3)	C13—C14—C15—C10	0.6 (3)
C3—C4—C5—C6	0.4 (3)	O1—C8—N1—C7	−179.55 (17)
C4—C5—C6—C7	0.1 (3)	C1—C8—N1—C7	0.0 (2)
C5—C6—C7—C2	−0.9 (3)	C6—C7—N1—C8	177.47 (19)
C5—C6—C7—N1	−179.92 (19)	C2—C7—N1—C8	−1.6 (2)
C3—C2—C7—C6	1.3 (3)	C2—C1—N2—N3	−175.68 (15)
C1—C2—C7—C6	−176.60 (17)	C8—C1—N2—N3	−1.2 (2)
C3—C2—C7—N1	−179.52 (16)	C1—N2—N3—C9	177.49 (15)
C1—C2—C7—N1	2.6 (2)	N4—C9—N3—N2	3.9 (2)
N2—C1—C8—O1	5.7 (3)	S1—C9—N3—N2	−175.20 (12)
C2—C1—C8—O1	−178.91 (17)	N3—C9—N4—C10	178.85 (16)
N2—C1—C8—N1	−173.84 (17)	S1—C9—N4—C10	−2.1 (3)
C2—C1—C8—N1	1.57 (19)	C15—C10—N4—C9	142.08 (19)
C15—C10—C11—C12	−1.8 (3)	C11—C10—N4—C9	−40.6 (3)
N4—C10—C11—C12	−179.12 (16)	C11—C12—O2—C16	4.2 (3)
C10—C11—C12—O2	179.65 (17)	C13—C12—O2—C16	−176.89 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.86	2.04	2.875 (2)	164
N3—H3*A*···O1	0.86	2.06	2.7441 (19)	136
N4—H4*A*···N2	0.86	2.19	2.620 (2)	110
N4—H4*A*···S1^{ii}	0.86	2.87	3.5806 (16)	141
C11—H11···S1	0.93	2.74	3.212 (2)	112
C8—O1···*Cg*3^{iii}	1.23 (1)	3.64 (1)	3.7399 (17)	85 (1)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iii) −*x*+1/2, *y*+1/2, −*z*+1/2.