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Crystal structure of 2-[2-(hydroxyimino)-1-phenylpropylidene]-*N*-phenylhydrazinecarbothioamide

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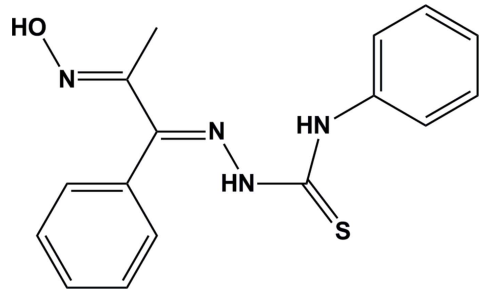
In the title compound, $C_{16}H_{16}N_4OS$, an intramolecular C—H···S hydrogen bond is observed. With the exception of the phenyl ring of the phenylpropylidene unit, the remainder of the molecule has an almost planar skeleton with an r.m.s. deviation of 0.121 (5) Å from the plane through the remaining 16 atoms. In the crystal O—H···N hydrogen bonds are observed between the terminal hydroxyimino groups, forming inverson dimers with $R_2^2(6)$ graph-set motifs. Additional C—H···N contacts stack the dimers along [100]. While no π—π interactions are present, weak C—H···O and O—H···*Cg* interactions are also observed and help stabilize the crystal packing.

Keywords: crystal structure; thiosemicarbazone; weak intermolecular interactions; O—H···π interactions.

CCDC reference: 1426205

1. Related literature

For thiosemicarbazone ligands and their metal complexes, see: Lobana *et al.* (2009, 2012). For the biological, anti-tumor and anti-fungal activity of palladium complexes with thiosemicarbazone ligands, see: Chellan *et al.* (2010). For the biological activity of a thiosemicarbazone ligand with terminal dimethyl substitution, see: Kowol *et al.* (2009). For related structures, see Anderson *et al.* (2012, 2013).



2. Experimental

2.1. Crystal data

$C_{16}H_{16}N_4OS$
M_r = 312.39
Monoclinic, $P2_1/n$
a = 5.4955 (6) Å
b = 27.973 (2) Å
c = 10.4175 (9) Å
β = 92.444 (9)°
V = 1600.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 173 K
0.42 × 0.14 × 0.08 mm

2.2. Data collection

Agilent Eos, Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min} = 0.747, T_{max} = 1.000
17587 measured reflections
5402 independent reflections
4006 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.182
S = 1.04
5402 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

*Cg*1 is the centroid of the C4–C9 phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N4^{i}	0.82	2.20	2.867 (2)	139
C5—H5···O1^{ii}	0.93	2.84	3.451 (3)	124
C5—H5···N4^{ii}	0.93	2.85	3.472 (2)	125
C6—H6···O1^{ii}	0.93	2.82	3.442 (3)	125
C11—H11···S1	0.93	2.54	3.193 (2)	127
O1—H1···*Cg*1^{i}		2.78	3.3309 (17)	126

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

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SJ5476).

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Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

supporting information

Acta Cryst. (2015). E**71**, o796–o797 [doi:10.1107/S2056989015017739]

Crystal structure of 2-[2-(hydroxyimino)-1-phenylpropylidene]-*N*-phenylhydrazinecarbothioamide

Brian J. Anderson, Michael B. Freedman, Sean P. Millikan, Victoria A. Smolenski and Jerry P. Jasinski

S1. Comment

In the title compound, $C_{16}H_{16}N_4OS$, (I), one independent molecule crystallizes in the asymmetric unit and forms an intramolecular C11—H11···S1 hydrogen bond, (Fig. 1). With the exception of the C4···.C9 phenyl ring of the phenylpropylidene unit, the remainder of the molecule has an almost planar skeleton with an *rms* deviation of 0.121 (5) Å from the plane through the remaining 16 atoms. In the crystal O1—H1···N4 hydrogen bonds are observed between the terminal hydroxyimino groups forming inverson dimers with $R_2^2(6)$ graph-set motifs (Table 1) Additional C5—H5···N4 contacts stack the dimers along [1 0 0]. While no π–π interactions are present, weak C5—H5···O1, C6—H6···O1 and O1—H1···π interactions are also observed, and help stablize the crystal packing.

S2. Experimental

In a 25 ml round bottom flask 0.205 g (1.26 mmol) of 1-phenyl-1, 2-propanedione 2-oxine and 0.211 g (1.26 mmol) of 4-phenylthiosemicarbazide were dissolved in 20 ml of methanol. One drop of sulfuric acid was added to catalyze the reaction. The resulting clear solution was refluxed for 12 h and there was a noticeable yellow color change. The reaction was removed from the heat and cooled to room temperature. The resulting yellow solution was transferred to a 125 ml separatory funnel. Dichloromethane (10 ml) and water (10 ml) were added, and the organic layer was separated. The aqueous layer was extracted with an additional 10 ml of dichloromethane, and then the organic layers were combined, washed with brine (2 *x* 10 ml), dried with magnesium sulfate, and the solvent was removed *in vacuo* to give a yellow solid. The product was recrystallized from hot acetonitrile. m.p. 463–464 K.

S3. Refinement

Crystal data, data collection and structure refinement details are summarizedin Table 1. A l l H atoms were located in difference maps. The C–H and N–H atoms were treated as riding atoms in geometrically idealized positions with C—H, N—H distances of 0.93 Å, 0.86 Å and refined with $U_{iso}(H) = 1.2U_{eq}(C, N)$. The CH_3 and O–H atoms were also treated as riding atoms in geometrically idealized positions with the CH_3, O—H distances of 0.96 Å, 0.84 Å and refined with $U_{iso}(H) = 1.5U_{eq}(C, O)$.

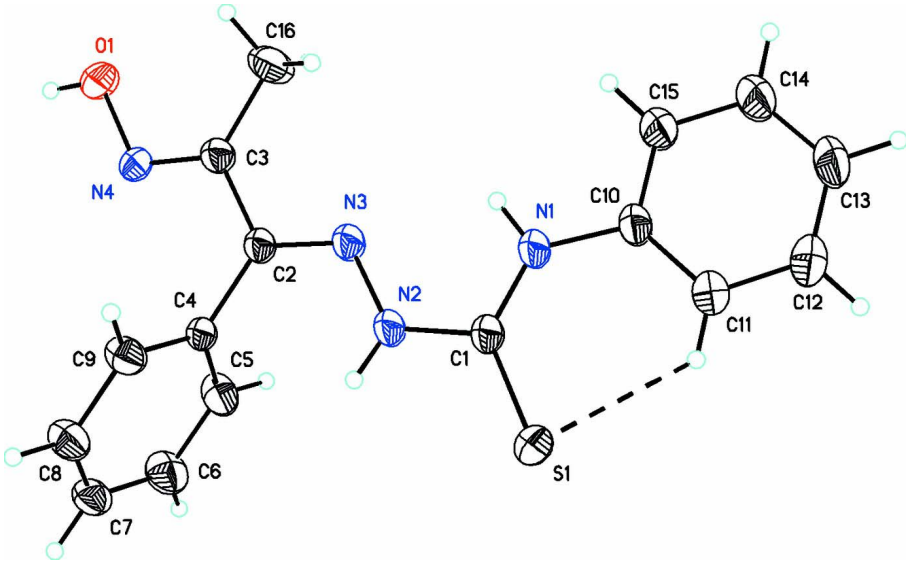

Figure 1

The molecular structure of $C_{16}H_{16}N_4OS$, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The dashed line indicates a weak C11—H11···S1 intramolecular contact.

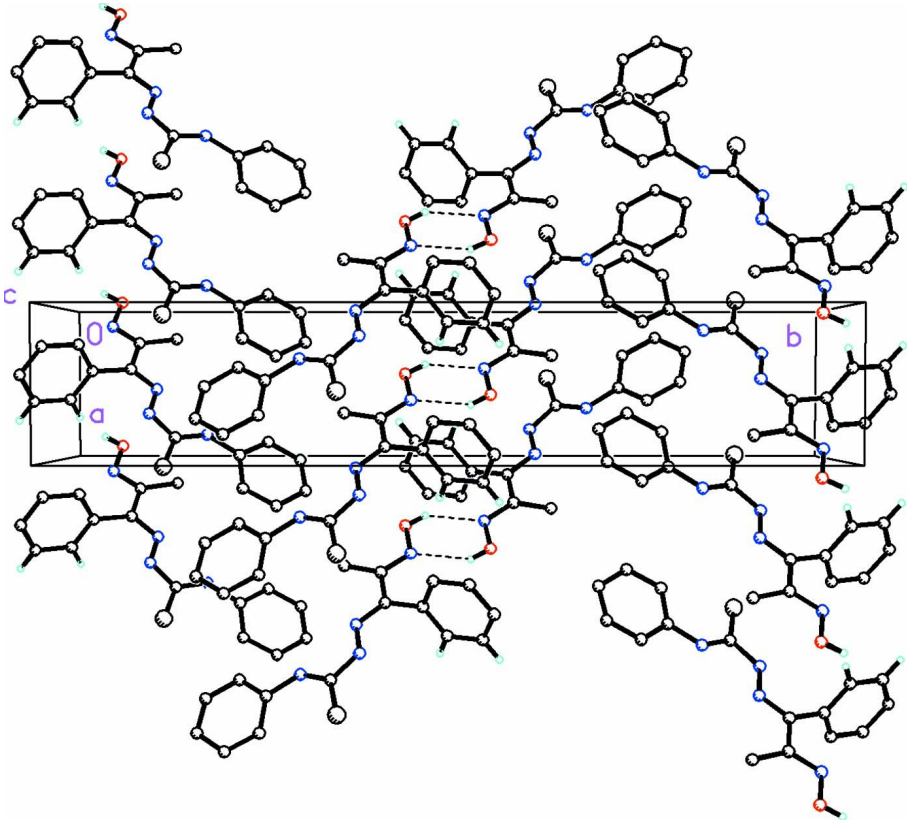

Figure 2

Packing diagram of (I) viewed along the *c* axis. Dashed lines indicate O—H—N hydrogen bonds between the terminal hydroxy amino groups forming $R_2^2(6)$ inverson dimers stacked along [1 0 0]. The H atoms not involved in these interactions have been omitted for clarity.

2-[2-(Hydroxyimino)-1-phenylpropylidene]-*N*-phenylhydrazinecarbothioamide

Crystal data

$C_{16}H_{16}N_4OS$
$M_r = 312.39$
Monoclinic, $P2_1/n$
$a = 5.4955$ (6) Å
$b = 27.973$ (2) Å
$c = 10.4175$ (9) Å
$\beta = 92.444$ (9)°
$V = 1600.0$ (3) Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.297$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4571 reflections
$\theta = 3.5$–$32.9°$
$\mu = 0.21$ mm^{-1}
$T = 173$ K
Needle, colourless
0.42 × 0.14 × 0.08 mm

Data collection

Agilent Eos, Gemini diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2014)
$T_{min} = 0.747$, $T_{max} = 1.000$
17587 measured reflections
5402 independent reflections
4006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 33.0°$, $\theta_{min} = 3.5°$
$h = -7 \rightarrow 6$
$k = -39 \rightarrow 42$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.182$
$S = 1.04$
5402 reflections
201 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 0.6623P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.45822 (11)	0.63428 (2)	0.03118 (5)	0.04249 (17)
O1	1.5672 (3)	0.55466 (5)	0.56408 (13)	0.0352 (3)
H1	1.6317	0.5292	0.5847	0.053*
N1	0.6605 (3)	0.68290 (6)	0.23282 (16)	0.0396 (4)
H1A	0.7732	0.6814	0.2925	0.047*
N2	0.8045 (3)	0.60886 (5)	0.19247 (14)	0.0317 (3)
H2	0.8036	0.5826	0.1497	0.038*
N3	0.9654 (3)	0.61454 (5)	0.29421 (14)	0.0292 (3)

N4	1.3985 (3)	0.54711 (5)	0.46248 (13)	0.0261 (3)
C1	0.6445 (3)	0.64429 (6)	0.15726 (16)	0.0283 (3)
C2	1.1020 (3)	0.57835 (5)	0.32323 (15)	0.0248 (3)
C3	1.2802 (3)	0.58508 (6)	0.43056 (16)	0.0275 (3)
C4	1.0875 (3)	0.53131 (5)	0.25667 (14)	0.0234 (3)
C5	0.8957 (4)	0.50060 (6)	0.27837 (19)	0.0351 (4)
H5	0.7749	0.5097	0.3333	0.042*
C6	0.8837 (4)	0.45653 (7)	0.2185 (2)	0.0398 (4)
H6	0.7553	0.4359	0.2335	0.048*
C7	1.0618 (4)	0.44308 (6)	0.13634 (18)	0.0327 (4)
H7	1.0540	0.4133	0.0968	0.039*
C8	1.2505 (4)	0.47357 (7)	0.11285 (18)	0.0344 (4)
H8	1.3697	0.4645	0.0570	0.041*
C9	1.2637 (4)	0.51787 (6)	0.17228 (17)	0.0311 (4)
H9	1.3908	0.5386	0.1556	0.037*
C10	0.5243 (4)	0.72573 (6)	0.23153 (18)	0.0365 (4)
C11	0.3061 (6)	0.73214 (9)	0.1637 (3)	0.0676 (9)
H11	0.2395	0.7075	0.1136	0.081*
C12	0.1862 (6)	0.77580 (10)	0.1708 (3)	0.0749 (10)
H12	0.0384	0.7801	0.1256	0.090*
C13	0.2824 (6)	0.81243 (9)	0.2433 (3)	0.0648 (8)
H13	0.2094	0.8424	0.2422	0.078*
C14	0.4845 (7)	0.80392 (10)	0.3160 (4)	0.0897 (14)
H14	0.5435	0.8275	0.3721	0.108*
C15	0.6072 (6)	0.76113 (9)	0.3097 (3)	0.0695 (10)
H15	0.7492	0.7566	0.3601	0.083*
C16	1.3123 (5)	0.63254 (7)	0.4947 (2)	0.0491 (6)
H16A	1.1963	0.6358	0.5605	0.074*
H16B	1.2872	0.6575	0.4323	0.074*
H16C	1.4743	0.6348	0.5325	0.074*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0480 (3)	0.0359 (3)	0.0417 (3)	0.0114 (2)	−0.0199 (2)	−0.00529 (18)
O1	0.0361 (7)	0.0355 (7)	0.0326 (6)	0.0052 (5)	−0.0142 (5)	−0.0002 (5)
N1	0.0474 (10)	0.0274 (8)	0.0420 (9)	0.0158 (7)	−0.0197 (7)	−0.0071 (6)
N2	0.0390 (9)	0.0235 (7)	0.0316 (7)	0.0117 (6)	−0.0107 (6)	−0.0037 (5)
N3	0.0349 (8)	0.0248 (7)	0.0272 (6)	0.0086 (6)	−0.0069 (5)	−0.0020 (5)
N4	0.0256 (7)	0.0276 (7)	0.0244 (6)	0.0044 (5)	−0.0055 (5)	−0.0006 (5)
C1	0.0322 (9)	0.0226 (7)	0.0297 (8)	0.0055 (6)	−0.0040 (6)	0.0024 (6)
C2	0.0273 (8)	0.0221 (7)	0.0248 (7)	0.0046 (6)	−0.0024 (6)	0.0000 (5)
C3	0.0311 (9)	0.0240 (7)	0.0271 (7)	0.0032 (6)	−0.0035 (6)	−0.0012 (5)
C4	0.0256 (8)	0.0206 (7)	0.0236 (7)	0.0045 (5)	−0.0037 (5)	0.0002 (5)
C5	0.0335 (10)	0.0273 (8)	0.0453 (10)	0.0007 (7)	0.0102 (7)	−0.0021 (7)
C6	0.0398 (11)	0.0264 (9)	0.0535 (11)	−0.0069 (7)	0.0074 (9)	−0.0015 (8)
C7	0.0405 (10)	0.0221 (7)	0.0349 (8)	0.0011 (6)	−0.0036 (7)	−0.0030 (6)
C8	0.0383 (10)	0.0321 (9)	0.0332 (8)	0.0006 (7)	0.0059 (7)	−0.0070 (6)

C9	0.0320 (9)	0.0286 (8)	0.0332 (8)	−0.0041 (6)	0.0059 (7)	−0.0051 (6)
C10	0.0435 (11)	0.0274 (8)	0.0375 (9)	0.0130 (7)	−0.0100 (8)	−0.0034 (6)
C11	0.0659 (18)	0.0420 (12)	0.091 (2)	0.0249 (12)	−0.0401 (15)	−0.0243 (12)
C12	0.074 (2)	0.0538 (15)	0.093 (2)	0.0350 (14)	−0.0419 (17)	−0.0214 (14)
C13	0.078 (2)	0.0420 (12)	0.0712 (16)	0.0336 (13)	−0.0279 (14)	−0.0210 (11)
C14	0.103 (3)	0.0505 (15)	0.109 (3)	0.0422 (16)	−0.066 (2)	−0.0462 (16)
C15	0.078 (2)	0.0453 (13)	0.0806 (18)	0.0310 (13)	−0.0487 (15)	−0.0319 (12)
C16	0.0690 (16)	0.0278 (9)	0.0481 (12)	0.0066 (9)	−0.0249 (11)	−0.0100 (8)

Geometric parameters (Å, º)

S1—C1	1.6543 (18)	C7—H7	0.9300
O1—H1	0.8200	C7—C8	1.373 (3)
O1—N4	1.3930 (17)	C8—H8	0.9300
N1—H1A	0.8600	C8—C9	1.386 (2)
N1—C1	1.337 (2)	C9—H9	0.9300
N1—C10	1.412 (2)	C10—C11	1.377 (3)
N2—H2	0.8600	C10—C15	1.349 (3)
N2—N3	1.3604 (19)	C11—H11	0.9300
N2—C1	1.365 (2)	C11—C12	1.391 (3)
N3—C2	1.288 (2)	C12—H12	0.9300
N4—C3	1.282 (2)	C12—C13	1.366 (4)
C2—C3	1.467 (2)	C13—H13	0.9300
C2—C4	1.488 (2)	C13—C14	1.339 (4)
C3—C16	1.493 (2)	C14—H14	0.9300
C4—C5	1.386 (2)	C14—C15	1.377 (3)
C4—C9	1.387 (2)	C15—H15	0.9300
C5—H5	0.9300	C16—H16A	0.9600
C5—C6	1.382 (3)	C16—H16B	0.9600
C6—H6	0.9300	C16—H16C	0.9600
C6—C7	1.379 (3)		
N4—O1—H1	109.5	C7—C8—H8	120.0
C1—N1—H1A	114.4	C7—C8—C9	120.09 (18)
C1—N1—C10	131.15 (15)	C9—C8—H8	120.0
C10—N1—H1A	114.4	C4—C9—H9	120.0
N3—N2—H2	119.5	C8—C9—C4	120.06 (17)
N3—N2—C1	120.97 (14)	C8—C9—H9	120.0
C1—N2—H2	119.5	C11—C10—N1	124.38 (18)
C2—N3—N2	116.34 (14)	C15—C10—N1	116.84 (18)
C3—N4—O1	112.67 (13)	C15—C10—C11	118.60 (19)
N1—C1—S1	128.83 (13)	C10—C11—H11	120.3
N1—C1—N2	113.76 (15)	C10—C11—C12	119.4 (2)
N2—C1—S1	117.40 (13)	C12—C11—H11	120.3
N3—C2—C3	116.19 (14)	C11—C12—H12	119.5
N3—C2—C4	124.51 (14)	C13—C12—C11	121.0 (2)
C3—C2—C4	119.30 (13)	C13—C12—H12	119.5
N4—C3—C2	113.98 (14)	C12—C13—H13	120.9

N4—C3—C16	124.84 (16)	C14—C13—C12	118.1 (2)
C2—C3—C16	121.17 (15)	C14—C13—H13	120.9
C5—C4—C2	119.88 (15)	C13—C14—H14	119.2
C5—C4—C9	119.45 (15)	C13—C14—C15	121.6 (2)
C9—C4—C2	120.67 (15)	C15—C14—H14	119.2
C4—C5—H5	120.0	C10—C15—C14	120.9 (2)
C6—C5—C4	120.09 (17)	C10—C15—H15	119.6
C6—C5—H5	120.0	C14—C15—H15	119.6
C5—C6—H6	119.9	C3—C16—H16A	109.5
C7—C6—C5	120.12 (18)	C3—C16—H16B	109.5
C7—C6—H6	119.9	C3—C16—H16C	109.5
C6—C7—H7	119.9	H16A—C16—H16B	109.5
C8—C7—C6	120.17 (16)	H16A—C16—H16C	109.5
C8—C7—H7	119.9	H16B—C16—H16C	109.5

O1—N4—C3—C2	179.66 (14)	C3—C2—C4—C9	−75.1 (2)
O1—N4—C3—C16	−0.9 (3)	C4—C2—C3—N4	−4.6 (2)
N1—C10—C11—C12	179.2 (3)	C4—C2—C3—C16	176.00 (19)
N1—C10—C15—C14	−179.2 (3)	C4—C5—C6—C7	−0.4 (3)
N2—N3—C2—C3	178.26 (15)	C5—C4—C9—C8	−1.6 (3)
N2—N3—C2—C4	−2.4 (3)	C5—C6—C7—C8	−0.6 (3)
N3—N2—C1—S1	179.26 (14)	C6—C7—C8—C9	0.4 (3)
N3—N2—C1—N1	−1.4 (3)	C7—C8—C9—C4	0.7 (3)
N3—C2—C3—N4	174.81 (16)	C9—C4—C5—C6	1.4 (3)
N3—C2—C3—C16	−4.6 (3)	C10—N1—C1—S1	1.7 (4)
N3—C2—C4—C5	−74.1 (2)	C10—N1—C1—N2	−177.6 (2)
N3—C2—C4—C9	105.6 (2)	C10—C11—C12—C13	0.4 (6)
C1—N1—C10—C11	14.2 (4)	C11—C10—C15—C14	−3.9 (5)
C1—N1—C10—C15	−170.8 (3)	C11—C12—C13—C14	−5.6 (6)
C1—N2—N3—C2	177.18 (17)	C12—C13—C14—C15	6.1 (7)
C2—C4—C5—C6	−178.89 (17)	C13—C14—C15—C10	−1.4 (7)
C2—C4—C9—C8	178.75 (16)	C15—C10—C11—C12	4.3 (5)
C3—C2—C4—C5	105.27 (19)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C4–C9 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N4^{i}	0.82	2.20	2.867 (2)	139
C5—H5···O1^{ii}	0.93	2.84	3.451 (3)	124
C5—H5···N4^{ii}	0.93	2.85	3.472 (2)	125
C6—H6···O1^{ii}	0.93	2.82	3.442 (3)	125
C11—H11···S1	0.93	2.54	3.193 (2)	127
O1—H1···*Cg*1^{i}		2.78	3.3309 (17)	126

Symmetry codes: (i) −*x*+3, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*+1, −*z*+1.