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## Structure Reports

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# N-Ethyl-2-[1-(2-hydroxy-6-methoxyphenyl)ethylidene]hydrazinecarbothioamide

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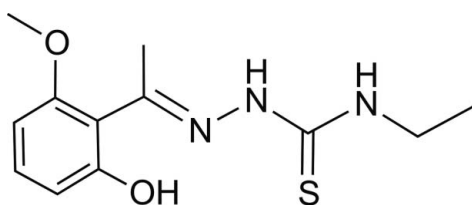
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Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å; R factor = 0.047;  $wR$  factor = 0.128; data-to-parameter ratio = 23.0.

In the title compound,  $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ , the dihedral angle between the mean planes of the hydrazinecarbothioamide group and the benzene ring is  $86.8(4)^\circ$ . In the crystal, intermolecular  $\text{O}-\text{H}\cdots\text{S}$  hydrogen bonds link the molecules into chains along  $[001]$ . The crystal studied was an inversion twin, the refined ratio of the twin components being 0.98021 (3):0.01978 (7).

## Related literature

For thiosemicarbazone structures and their biological activity, see: Lobana *et al.* (2009). For thiosemicarbazones as ligands for metal-catalyzed reactions or hydrogenations, see: Xie *et al.* (2010); Pelagatti *et al.* (1998). For reference bond-length data, see: Allen *et al.* (1987).



## Experimental

### Crystal data

$\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$   
 $M_r = 267.35$

Monoclinic,  $Pc$   
 $a = 8.5681(6)$  Å

$b = 8.0393(5)$  Å  
 $c = 10.3808(8)$  Å  
 $\beta = 103.510(7)^\circ$   
 $V = 695.26(8)$  Å<sup>3</sup>  
 $Z = 2$

Mo  $K\alpha$  radiation  
 $\mu = 0.23$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.46 \times 0.32 \times 0.24$  mm

### Data collection

Oxford Xcalibur (Eos, Gemini) diffractometer  
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)  
 $T_{\min} = 0.974$ ,  $T_{\max} = 1.000$

7338 measured reflections  
3987 independent reflections  
3287 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.128$   
 $S = 1.05$   
3987 reflections  
173 parameters  
2 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.63$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.21$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983), with 1510 Friedel pairs  
Flack parameter: 0.00 (8)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{S1}^i$	0.82	2.35	3.1655 (19)	175

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); 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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5339).

## References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Lobana, T. S., Sharma, R., Bawa, G. & Khanna, S. (2009). *Coord. Chem. Rev.* **253**, 977–1055.
- Oxford Diffraction (2010). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Pelagatti, P., Venturini, A., Carcelli, M., Costa, M., Bacchi, A., Pelizzi, G. & Pelizza, C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2715–2721.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Xie, G., Chellan, P., Mao, J., Chibale, K. & Smith, G. S. (2010). *Adv. Synth. Catal.* **352**, 1641–1647.

## supporting information

*Acta Cryst.* (2012). E68, o2982 [https://doi.org/10.1107/S1600536812039323]

***N*-Ethyl-2-[1-(2-hydroxy-6-methoxyphenyl)ethylidene]hydrazinecarbothioamide****Brian J. Anderson, Christopher J. Kennedy and Jerry P. Jasinski****S1. Comment**

Thiosemicarbazones are an important class of ligands whose metal complex structures and biological activity have been extensively investigated (Lobana *et al.*, 2009). Recently, thiosemicarbazones have been studied as ligands for metal catalyzed reactions such as Mizoroki–Heck couplings (Xie *et al.*, 2010) and hydrogenations (Pelagatti *et al.*, 1998). The crystal structure of a novel thiosemicarbazone molecule is reported here.

In the title compound, C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S (Fig. 1), the dihedral angle between the mean plane of the hydrazinecarbothioamide group (N1/S1/C3/N2/N3) and benzene ring is 86.8 (4)°. Bond lengths are in normal ranges (Allen *et al.*, 1987). In the crystal, the intermolecular O—H⋯S hydrogen bonds (Table 1) link the molecules into chains in [001] (Fig. 2).

**S2. Experimental**

A 50 ml round-bottomed flask was charged with 0.507 g (3.05 mmol) of 2'-hydroxy-6'-methoxyacetophenone and 0.363 g (3.05 mmol) of 4-ethyl-3-thiosemicarbazide followed by 35 ml of methanol, resulting in a clear yellow solution. The solution was refluxed for 5 h, and then the solvent was removed by rotary evaporation. The product was dissolved into 40°C acetonitrile and slowly allowed to cool to 0°C. Translucent crystals were observed after 48 h. (m.p. 458–460 K).

**S3. Refinement**

Atoms H1A and H2 were located on a difference map and refined isotropically. The remaining H atoms were placed in their calculated positions and then refined using the riding model, with C—H lengths of 0.93 Å (CH), 0.97 Å (CH<sub>2</sub>) or 0.96 Å (CH<sub>3</sub>) and the O—H length of 0.82 Å. The isotropic displacement parameters for these atoms were set to 1.2 (CH, CH<sub>2</sub>) or 1.5 (CH<sub>3</sub>, OH) times  $U_{eq}$  of the parent atom. The structure was refined as an inversion twin, with the twin law -1 0 0 0 -1 0 0 0 -1 2 and the refined ratio of twin components being 0.98021 (3):0.01978 (7).

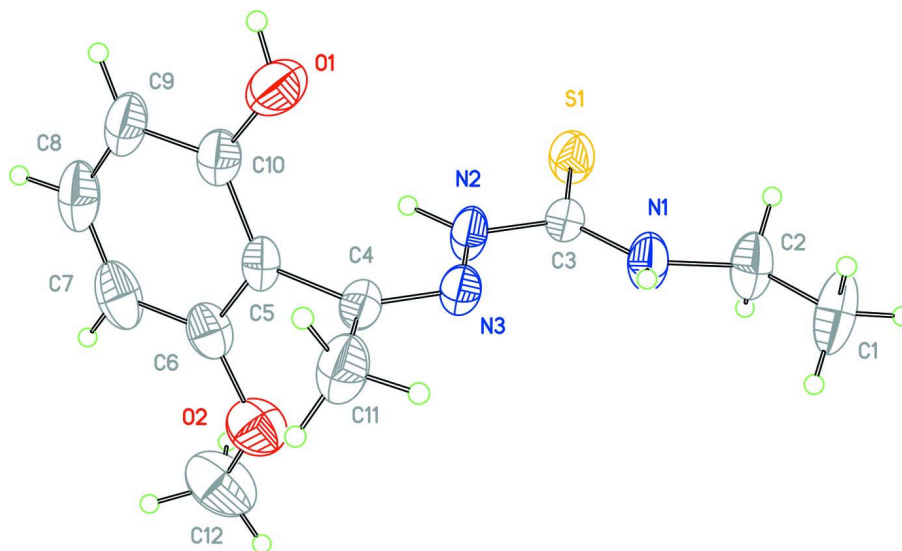


Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

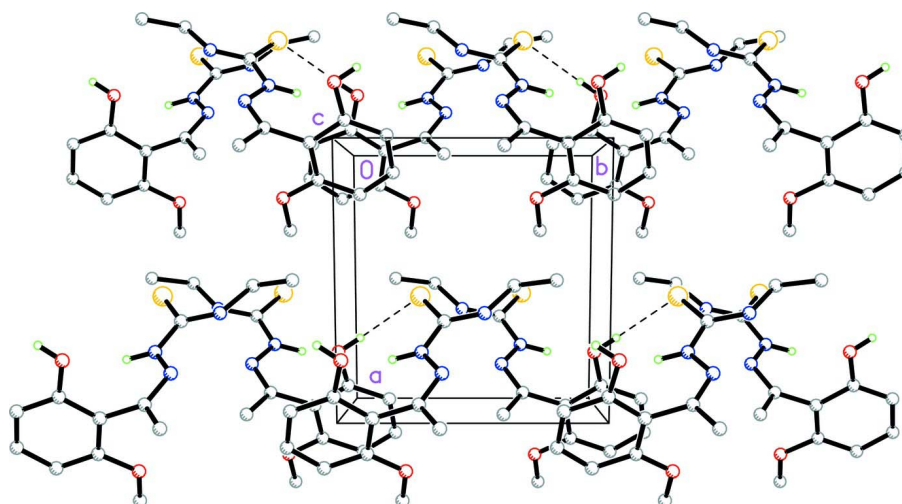


Figure 2

Packing diagram viewed along the *c* axis. Weak O—H...S intermolecular interactions are shown by dashed lines. C-bound H atoms were omitted for clarity.

### *N*-Ethyl-2-[1-(2-hydroxy-6-methoxyphenyl)ethylidene]hydrazinecarbothioamide

#### Crystal data

$C_{12}H_{17}N_3O_2S$

$M_r = 267.35$

Monoclinic, *Pc*

Hall symbol: *P* -2yc

$a = 8.5681$  (6) Å

$b = 8.0393$  (5) Å

$c = 10.3808$  (8) Å

$\beta = 103.510$  (7)°

$V = 695.26$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 284$

$D_x = 1.277$  Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda = 0.71070$  Å

Cell parameters from 2153 reflections

$\theta = 3.2$ – $32.3$ °

$\mu = 0.23$  mm<sup>-1</sup>

$T = 173$  K  $0.46 \times 0.32 \times 0.24$  mm  
 Chunk, colourless

*Data collection*

Oxford Xcalibur (Eos, Gemini) diffractometer	7338 measured reflections 3987 independent reflections
Radiation source: Enhance (Mo) X-ray Source	3287 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.030$
Detector resolution: 16.1500 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 32.3^\circ$ , $\theta_{\text{min}} = 3.2^\circ$
$\omega$ scans	$h = -12 \rightarrow 11$
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2010)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.974$ , $T_{\text{max}} = 1.000$	$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.0627P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3987 reflections	$\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
173 parameters	$\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
2 restraints	Absolute structure: Flack (1983), with 1510 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.00 (8)
Secondary atom site location: difference Fourier map	

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.55727 (6)	0.29581 (7)	0.59523 (6)	0.04628 (16)
O1	0.7690 (2)	0.0256 (2)	1.0893 (2)	0.0585 (5)
H1	0.7155	-0.0595	1.0865	0.088*
O2	1.1860 (2)	0.2488 (3)	0.92524 (19)	0.0549 (5)
N1	0.6144 (3)	0.5442 (3)	0.7677 (2)	0.0457 (5)
H1A	0.637 (4)	0.575 (4)	0.839 (3)	0.050 (9)*
N2	0.7546 (2)	0.3070 (2)	0.83163 (19)	0.0379 (4)
H2	0.782 (3)	0.198 (4)	0.823 (3)	0.047 (8)*
N3	0.8239 (2)	0.3855 (2)	0.94956 (18)	0.0344 (4)
C1	0.4947 (5)	0.8165 (4)	0.7392 (3)	0.0657 (9)
H1B	0.4404	0.7948	0.8086	0.098*
H1C	0.4323	0.8925	0.6764	0.098*

H1D	0.5980	0.8644	0.7765	0.098*
C2	0.5155 (4)	0.6584 (4)	0.6716 (3)	0.0568 (7)
H2A	0.4116	0.6086	0.6348	0.068*
H2B	0.5674	0.6800	0.5996	0.068*
C3	0.6451 (2)	0.3906 (2)	0.7390 (2)	0.0346 (4)
C4	0.9297 (2)	0.3025 (2)	1.0323 (2)	0.0333 (4)
C5	0.9822 (2)	0.1311 (3)	1.0085 (2)	0.0345 (4)
C6	1.1173 (3)	0.1064 (3)	0.9568 (2)	0.0415 (5)
C7	1.1719 (3)	-0.0556 (4)	0.9435 (3)	0.0523 (6)
H7	1.2623	-0.0731	0.9102	0.063*
C8	1.0913 (4)	-0.1879 (3)	0.9799 (3)	0.0532 (7)
H8	1.1301	-0.2948	0.9731	0.064*
C9	0.9556 (3)	-0.1677 (3)	1.0258 (3)	0.0494 (6)
H9	0.9002	-0.2595	1.0464	0.059*
C10	0.9014 (3)	-0.0067 (3)	1.0412 (2)	0.0411 (5)
C11	1.0021 (3)	0.3811 (3)	1.1618 (3)	0.0510 (6)
H11A	0.9585	0.4908	1.1644	0.077*
H11B	1.1163	0.3883	1.1730	0.077*
H11C	0.9782	0.3151	1.2319	0.077*
C12	1.3067 (4)	0.2315 (5)	0.8506 (3)	0.0717 (9)
H12A	1.3976	0.1733	0.9029	0.107*
H12B	1.3397	0.3398	0.8281	0.107*
H12C	1.2636	0.1700	0.7710	0.107*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0464 (3)	0.0416 (3)	0.0444 (3)	0.0038 (3)	-0.0023 (2)	-0.0014 (3)
O1	0.0607 (11)	0.0363 (9)	0.0872 (14)	0.0008 (8)	0.0352 (11)	0.0062 (10)
O2	0.0481 (10)	0.0661 (12)	0.0562 (12)	0.0008 (9)	0.0238 (9)	0.0002 (9)
N1	0.0463 (10)	0.0360 (10)	0.0482 (12)	0.0125 (8)	-0.0027 (9)	0.0005 (9)
N2	0.0434 (9)	0.0266 (8)	0.0390 (10)	0.0100 (7)	0.0001 (8)	0.0012 (7)
N3	0.0367 (8)	0.0284 (8)	0.0371 (9)	0.0056 (7)	0.0066 (7)	0.0024 (7)
C1	0.100 (3)	0.0467 (15)	0.0512 (15)	0.0374 (16)	0.0185 (16)	0.0129 (12)
C2	0.0634 (16)	0.0465 (14)	0.0556 (16)	0.0212 (12)	0.0042 (13)	0.0089 (12)
C3	0.0312 (9)	0.0284 (9)	0.0433 (11)	0.0026 (8)	0.0066 (8)	0.0047 (8)
C4	0.0366 (10)	0.0291 (9)	0.0344 (10)	0.0049 (7)	0.0089 (8)	0.0048 (8)
C5	0.0378 (10)	0.0314 (10)	0.0319 (9)	0.0105 (8)	0.0031 (8)	0.0030 (8)
C6	0.0382 (10)	0.0493 (13)	0.0344 (10)	0.0081 (9)	0.0034 (9)	-0.0021 (9)
C7	0.0464 (12)	0.0651 (17)	0.0438 (12)	0.0242 (12)	0.0074 (10)	-0.0085 (12)
C8	0.0653 (16)	0.0414 (13)	0.0442 (13)	0.0226 (12)	-0.0046 (12)	-0.0054 (10)
C9	0.0603 (15)	0.0317 (11)	0.0504 (14)	0.0123 (10)	0.0012 (12)	0.0045 (10)
C10	0.0426 (11)	0.0355 (10)	0.0432 (12)	0.0084 (9)	0.0062 (9)	0.0030 (9)
C11	0.0660 (15)	0.0382 (12)	0.0429 (13)	0.0100 (11)	0.0007 (11)	-0.0026 (10)
C12	0.0528 (16)	0.114 (3)	0.0560 (17)	-0.0008 (17)	0.0279 (14)	-0.0007 (18)

*Geometric parameters (Å, °)*

S1—C3	1.688 (2)	C4—C11	1.484 (3)
O1—C10	1.367 (3)	C4—C5	1.487 (3)
O1—H1	0.8200	C5—C10	1.389 (3)
O2—C6	1.362 (3)	C5—C6	1.399 (3)
O2—C12	1.436 (3)	C6—C7	1.402 (4)
N1—C3	1.311 (3)	C7—C8	1.368 (4)
N1—C2	1.471 (3)	C7—H7	0.9300
N1—H1A	0.76 (3)	C8—C9	1.365 (4)
N2—C3	1.355 (3)	C8—H8	0.9300
N2—N3	1.382 (2)	C9—C10	1.396 (3)
N2—H2	0.92 (3)	C9—H9	0.9300
N3—C4	1.281 (3)	C11—H11A	0.9600
C1—C2	1.482 (4)	C11—H11B	0.9600
C1—H1B	0.9600	C11—H11C	0.9600
C1—H1C	0.9600	C12—H12A	0.9600
C1—H1D	0.9600	C12—H12B	0.9600
C2—H2A	0.9700	C12—H12C	0.9600
C2—H2B	0.9700		
C10—O1—H1	109.5	C6—C5—C4	120.3 (2)
C6—O2—C12	117.1 (3)	O2—C6—C5	114.6 (2)
C3—N1—C2	123.2 (2)	O2—C6—C7	125.7 (2)
C3—N1—H1A	121 (2)	C5—C6—C7	119.7 (2)
C2—N1—H1A	116 (2)	C8—C7—C6	119.6 (2)
C3—N2—N3	119.04 (16)	C8—C7—H7	120.2
C3—N2—H2	124.0 (18)	C6—C7—H7	120.2
N3—N2—H2	116.8 (18)	C9—C8—C7	122.0 (2)
C4—N3—N2	116.48 (17)	C9—C8—H8	119.0
C2—C1—H1B	109.5	C7—C8—H8	119.0
C2—C1—H1C	109.5	C8—C9—C10	118.9 (3)
H1B—C1—H1C	109.5	C8—C9—H9	120.5
C2—C1—H1D	109.5	C10—C9—H9	120.5
H1B—C1—H1D	109.5	O1—C10—C5	116.17 (19)
H1C—C1—H1D	109.5	O1—C10—C9	123.0 (2)
N1—C2—C1	109.1 (2)	C5—C10—C9	120.8 (2)
N1—C2—H2A	109.9	C4—C11—H11A	109.5
C1—C2—H2A	109.9	C4—C11—H11B	109.5
N1—C2—H2B	109.9	H11A—C11—H11B	109.5
C1—C2—H2B	109.9	C4—C11—H11C	109.5
H2A—C2—H2B	108.3	H11A—C11—H11C	109.5
N1—C3—N2	116.6 (2)	H11B—C11—H11C	109.5
N1—C3—S1	123.69 (17)	O2—C12—H12A	109.5
N2—C3—S1	119.71 (15)	O2—C12—H12B	109.5
N3—C4—C11	117.74 (18)	H12A—C12—H12B	109.5
N3—C4—C5	124.46 (19)	O2—C12—H12C	109.5
C11—C4—C5	117.79 (18)	H12A—C12—H12C	109.5

C10—C5—C6	119.0 (2)	H12B—C12—H12C	109.5
C10—C5—C4	120.74 (18)		
C3—N2—N3—C4	-178.22 (19)	C10—C5—C6—O2	178.6 (2)
C3—N1—C2—C1	175.6 (3)	C4—C5—C6—O2	-3.4 (3)
C2—N1—C3—N2	171.6 (2)	C10—C5—C6—C7	-2.3 (3)
C2—N1—C3—S1	-8.0 (3)	C4—C5—C6—C7	175.6 (2)
N3—N2—C3—N1	1.3 (3)	O2—C6—C7—C8	179.7 (2)
N3—N2—C3—S1	-179.12 (15)	C5—C6—C7—C8	0.7 (4)
N2—N3—C4—C11	-177.9 (2)	C6—C7—C8—C9	1.8 (4)
N2—N3—C4—C5	0.6 (3)	C7—C8—C9—C10	-2.7 (4)
N3—C4—C5—C10	-87.9 (3)	C6—C5—C10—O1	-179.0 (2)
C11—C4—C5—C10	90.5 (3)	C4—C5—C10—O1	3.0 (3)
N3—C4—C5—C6	94.1 (3)	C6—C5—C10—C9	1.5 (3)
C11—C4—C5—C6	-87.4 (3)	C4—C5—C10—C9	-176.5 (2)
C12—O2—C6—C5	-169.3 (2)	C8—C9—C10—O1	-178.5 (2)
C12—O2—C6—C7	11.7 (4)	C8—C9—C10—C5	1.0 (4)

Hydrogen-bond geometry (Å, °)

<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>
O1—H1...S1 <sup>i</sup>	0.82	2.35	3.1655 (19)	175

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