2-[1-(1,3-Dioxo-1,3-dihydro-2H-inden-2-ylidene)-ethyl]hydrazinecarbothioamide

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The title compound, $C_{12}H_{11}N_3O_2S$, was synthesized by a condensation reaction of 2-acetylindan-1,3-dione and thiosemicarbazide in ethanol in the presence of glacial acetic acid. The molecule adopts a thioketone form. The dihedral angle between the mean planes of 1H-inden-1,3(2H)-dione and hydrazinecarbothioamide units is 86.32 (7)°. Weak intramolecular N—H⋯O and C—H⋯O hydrogen bonds are observed. In the crystal, molecules are linked via pairs of weak intermolecular N—H⋯O hydrogen bonds, forming inversion dimers. The dimers are further linked into a three-dimensional network through N—H⋯S and N—H⋯O hydrogen bonds, and π–π interactions [centroid–centroid distances = 3.5619 (10)–3.9712 (9) Å].

3D view

Chemical scheme
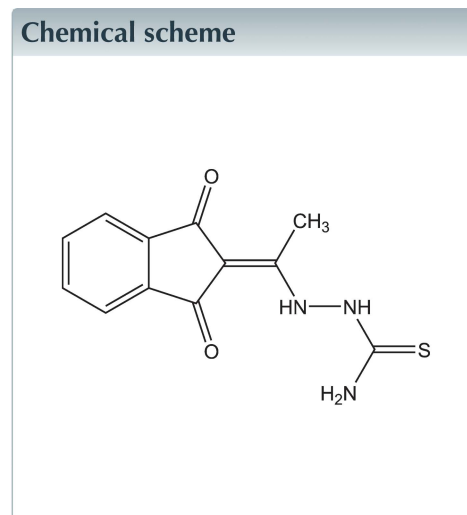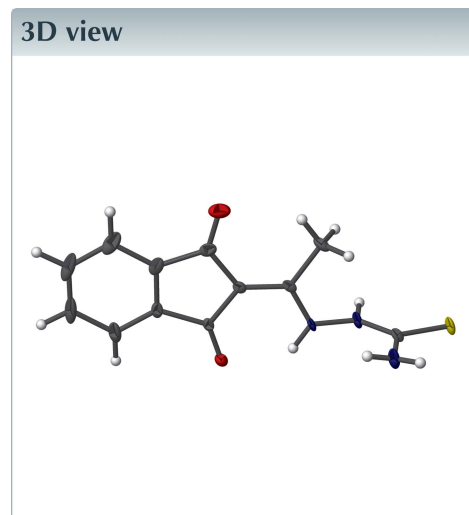
Structure description

Derivatives obtained from the reaction of 2-acetylindan-1,3-dione and thiosemicarbazide in the literature (Sawhney & Lemke, 1983; Kumar *et al.*, 2014). It is predicted that the reaction with thiosemicarbazide at the acetyl group will produce a thiosemicarbazone as a Schiff base, but in this work, we report the formation of the title compound, an enamine of 2-acetylindan-1,3-dionethiosemicarbazone.

The title compound is completely in a thioketone form and weak intramolecular N—H⋯O and C—H⋯O hydrogen bonds (N3—HN4⋯O2 and C12—H12B⋯O1; Table 1) are observed (Fig. 1). The dihedral angle between the mean planes of the 1H-indene-1,3(2H)-dione and hydrazinecarbothioamide units is 86.32 (7)°. The length of the C1—S1 bond [1.705 (2) Å] is intermediate between a single bond C—S (1.82 Å) and a double bond C=S (1.67 Å) (Allen *et al.*, 1987), which implies that it possesses partial double-bond character indicative of possible delocalization over atoms S1, C1 and N1. This notion is supported by the C1—N1 bond length [1.318 (2) Å], which is shorter than C1—
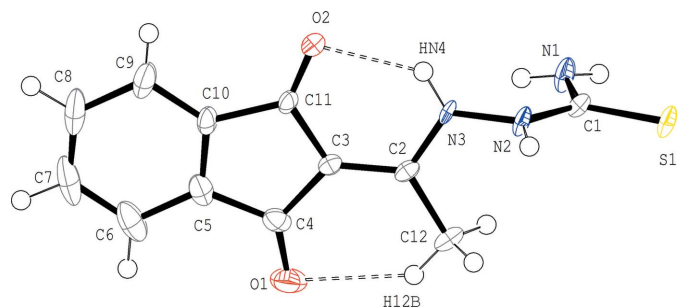
Figure 1
The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at 50% probability level. Intramolecular N—H···O and C—H···O hydrogen bonds are shown as dashed lines.

N2 [1.340 (2) Å], again indicative of some double-bond character of C1—N1. A similar feature has been observed in a thiosemicarbazone (Jouad *et al.*, 2001).

In the crystal, two molecules are bound by a pair of N—H···O hydrogen bonds (N3—HN4···O2^{iv}; Table 1), forming a centrosymmetric dimeric structure (Fig. 2). The dimers are further connected by two N—H···S hydrogen bonds and one N—H···O hydrogen bond (N2—HN3···S1^{i}, N1—HN1···S1^{ii}, and N1—HN2···O1^{iii}; Table 1). The crystal packing also features π–π stacking interactions. The centroid–centroid distances are 3.8487 (10), 3.6271 (11), 3.5619 (10), 3.8614 (11) and 3.9712 (9) Å, respectively, for $Cg1\cdots Cg1^{v}$, $Cg1\cdots Cg2^{vi}$,
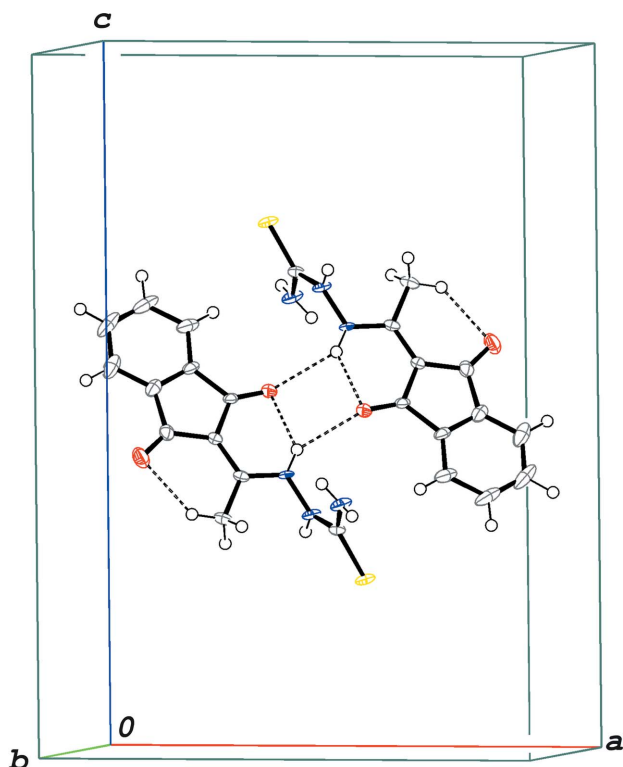

Figure 2
The inversion dimer of the title compound formed by a pair of N—H···O hydrogen bonds (dashed lines).

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···O1	0.98	2.26	3.033 (3)	135
N2—HN3···S1^{i}	0.84 (2)	2.47 (2)	3.2796 (16)	163 (2)
N1—HN1···S1^{ii}	0.85 (3)	2.63 (3)	3.3764 (19)	147 (2)
N1—HN2···O1^{iii}	0.84 (3)	2.11 (3)	2.816 (2)	142 (2)
N3—HN4···O2	0.89 (3)	2.05 (3)	2.7592 (19)	135 (2)
N3—HN4···O2^{iv}	0.89 (3)	2.30 (2)	3.0107 (19)	137 (2)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{11}N_3O_2S$
M_r	261.30
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	99
a, b, c (Å)	15.0751 (6), 7.6891 (4), 20.7891 (9)
V (Å^3)	2409.75 (19)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.27
Crystal size (mm)	0.76 × 0.25 × 0.25
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.824, 0.937
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18247, 3382, 2712
R_{int}	0.073
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.173, 1.07
No. of reflections	3382
No. of parameters	181
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.79, −1.00

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *ORTEP-3 for Windows* (Farrugia, 2012).

$Cg1\cdots Cg3^{vi}$, $Cg2\cdots Cg3^{v}$ and $Cg3\cdots Cg3^{v}$; $Cg1$, $Cg2$ and $Cg3$ are the centroids of the C3–C5/C10/C11 and C5–C10 rings, and the C3–C11 ring system, respectively [symmetry codes: (v) $\frac{3}{2} - x, -\frac{1}{2} + y, z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, z$].

Synthesis and crystallization

The title compound was prepared by heating a mixed solution of 2-acetylindan-1,3-dione (0.50 g, 2.66 mmol) in absolute ethanol (20 ml) and thiosemicarbazide (0.24 g, 2.66 mmol) in absolute ethanol (55 ml). Three drops of glacial acetic acid were then added and the mixture was refluxed for 30 min. A yellow microcrystalline powder was obtained and it was recrystallized from an acetonitrile/methanol mixture solvent. The pale-brown crystals obtained were filtered, washed with

cold acetonitrile and dried *in vacuo* [yield: 0.57 g (82%), m.p. 486–487 K]. Single crystals of the title compound suitable for X-ray analysis were grown by slow evaporation at room temperature from an acetonitrile/methanol mixture solvent.

IR (v, cm^{-1}): 3336–3112 (*w*, N—H), 2945 (*w*, Ar C—H), 1696 (*m*, C=O), 1654 (*s*, C=O), 1573 and 1502 (*s*, aromatic C=C), 858 (*s*, C=S). EI–MS calculated for $C_{12}H_{11}N_3O_2S$, $M^{+\cdot}$: 261.30, found: 261. ^{1}H NMR (DMSO-d_6) δ (p.p.m.): 11.48 (*br*, 1H, –N*H*), 10.00 (*s*, 1H, –N*H*), 7.99 (*br*, 2H, –N*H*$_2$), 7.67–7.72 (*m*, 4H, Ar-*H*), 3.33 (*s*, 3H, –C*H*$_3$). ^{13}C NMR (DMSO-d_6) δ (p.p.m.): 192.34, 189.44, 182.36, 139.65, 138.09, 133.61, 133.53, 121.20, 120.94, 12.59. Analysis calculated for $C_{12}H_{11}N_3O_2S$: C 55.16, H 4.24, N 16.08%. Found: C 55.12, H 3.96, N 15.42%.

Refinement

Crystal data, data collection and structure refinement details of the title compound are summarized in Table 2.

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.
Bruker (2014). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Jouad, E. M., Riou, A., Allain, M., Khan, M. A. & Bouet, G. M. (2001). *Polyhedron*, **20**, 67–74.
Kumar, D., Singh, V. K., Khiwar, S. S. & Saxena, N. (2014). *J. Drug Deliv. Ther.* **4**, 73–83.
Sawhney, K. N. & Lemke, T. L. (1983). *J. Org. Chem.* **48**, 4326–4329.
Sheldrick, G. M. (2015a). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015b). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

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2-[1-(1,3-Dioxo-1,3-dihydro-2*H*-inden-2-ylidene)ethyl]hydrazinecarbothioamide

Crystal data

$C_{12}H_{11}N_3O_2S$	$D_x = 1.440$ Mg m^{-3}
$M_r = 261.30$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 6090 reflections
$a = 15.0751$ (6) Å	$\theta = 2.4$–29.6°
$b = 7.6891$ (4) Å	$\mu = 0.27$ mm^{-1}
$c = 20.7891$ (9) Å	$T = 99$ K
$V = 2409.75$ (19) Å^3	Rod, brown
$Z = 8$	$0.76 \times 0.25 \times 0.25$ mm
$F(000) = 1088$	

Data collection

Bruker D8 Venture diffractometer	3382 independent reflections
profile data from $\theta/2\theta$ scans	2712 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2014)	$R_{int} = 0.073$
	$\theta_{max} = 29.6°$, $\theta_{min} = 2.4°$
$T_{min} = 0.824$, $T_{max} = 0.937$	$h = -20 \rightarrow 18$
18247 measured reflections	$k = -8 \rightarrow 10$
	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.063$	Hydrogen site location: mixed
$wR(F^2) = 0.173$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	
3382 reflections	$w = 1/[\sigma^2(F_o^2) + (0.117P)^2 + 0.3104P]$
181 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.79$ e Å^{-3}
	$\Delta\rho_{min} = -1.00$ 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.

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

	x	y	z	U_{iso}*/U_{eq}
S1	0.43388 (3)	0.69858 (6)	0.75750 (2)	0.01816 (17)
O1	0.86124 (9)	0.5148 (2)	0.58244 (8)	0.0294 (4)
O2	0.58261 (8)	0.40510 (17)	0.48472 (6)	0.0202 (3)
N1	0.50396 (12)	0.8510 (2)	0.65405 (8)	0.0213 (4)
HN1	0.4960 (17)	0.948 (4)	0.6726 (15)	0.043 (8)*
HN2	0.5428 (16)	0.853 (3)	0.6251 (14)	0.025 (6)*
N2	0.52093 (10)	0.5557 (2)	0.66273 (7)	0.0162 (3)
HN3	0.5202 (14)	0.465 (3)	0.6853 (13)	0.024 (6)*
N3	0.57075 (10)	0.5469 (2)	0.60634 (7)	0.0150 (3)
HN4	0.5434 (15)	0.516 (3)	0.5700 (14)	0.027 (6)*
C1	0.49117 (11)	0.7065 (2)	0.68685 (8)	0.0152 (4)
C2	0.66012 (11)	0.5365 (2)	0.60836 (8)	0.0141 (3)
C3	0.70518 (11)	0.4833 (2)	0.55397 (8)	0.0151 (3)
C4	0.80153 (11)	0.4714 (2)	0.54558 (10)	0.0191 (4)
C5	0.81627 (12)	0.3939 (2)	0.48089 (10)	0.0209 (4)
C6	0.89580 (14)	0.3553 (3)	0.45015 (12)	0.0308 (5)
H6	0.951321	0.377395	0.470159	0.037*
C7	0.89078 (15)	0.2830 (3)	0.38902 (12)	0.0366 (6)
H7	0.944060	0.256797	0.366630	0.044*
C8	0.81003 (16)	0.2482 (3)	0.35982 (11)	0.0349 (5)
H8	0.809265	0.197883	0.318095	0.042*
C9	0.72982 (15)	0.2855 (3)	0.39040 (10)	0.0268 (5)
H9	0.674394	0.261752	0.370510	0.032*
C10	0.73498 (12)	0.3592 (2)	0.45145 (8)	0.0177 (4)
C11	0.66251 (11)	0.4159 (2)	0.49572 (8)	0.0149 (3)
C12	0.70463 (12)	0.5863 (3)	0.67010 (9)	0.0215 (4)
H12A	0.684628	0.702208	0.683240	0.026*
H12B	0.769069	0.587450	0.663875	0.026*
H12C	0.689323	0.501675	0.703566	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0289 (3)	0.0173 (3)	0.0083 (2)	−0.00088 (16)	0.00634 (15)	−0.00102 (15)
O1	0.0189 (7)	0.0388 (9)	0.0304 (9)	0.0005 (6)	−0.0073 (6)	0.0053 (6)
O2	0.0190 (6)	0.0289 (7)	0.0128 (6)	0.0048 (5)	−0.0024 (5)	−0.0033 (5)
N1	0.0347 (9)	0.0172 (8)	0.0120 (8)	0.0020 (7)	0.0095 (6)	0.0015 (6)
N2	0.0263 (8)	0.0151 (7)	0.0073 (7)	0.0003 (6)	0.0054 (6)	0.0000 (6)
N3	0.0190 (7)	0.0219 (8)	0.0042 (7)	0.0015 (5)	0.0020 (5)	−0.0013 (5)
C1	0.0193 (8)	0.0168 (8)	0.0094 (8)	−0.0013 (6)	−0.0018 (6)	−0.0021 (6)
C2	0.0188 (8)	0.0141 (8)	0.0095 (8)	−0.0012 (6)	−0.0021 (6)	0.0032 (6)
C3	0.0164 (8)	0.0179 (8)	0.0110 (8)	0.0020 (6)	−0.0013 (6)	0.0028 (6)
C4	0.0167 (8)	0.0207 (9)	0.0200 (9)	0.0026 (6)	0.0004 (6)	0.0086 (7)
C5	0.0232 (9)	0.0171 (9)	0.0223 (10)	0.0058 (7)	0.0088 (7)	0.0080 (7)
C6	0.0256 (10)	0.0230 (10)	0.0436 (13)	0.0052 (8)	0.0169 (9)	0.0101 (9)

C7	0.0424 (13)	0.0228 (11)	0.0444 (14)	0.0086 (9)	0.0313 (11)	0.0070 (9)
C8	0.0565 (14)	0.0243 (11)	0.0239 (11)	0.0098 (10)	0.0237 (10)	0.0024 (9)
C9	0.0420 (12)	0.0239 (10)	0.0146 (9)	0.0070 (8)	0.0083 (8)	0.0011 (7)
C10	0.0240 (9)	0.0173 (8)	0.0118 (8)	0.0053 (7)	0.0066 (6)	0.0043 (7)
C11	0.0200 (8)	0.0164 (8)	0.0082 (8)	0.0048 (6)	0.0020 (6)	0.0029 (6)
C12	0.0263 (9)	0.0268 (10)	0.0113 (8)	−0.0015 (7)	−0.0062 (7)	−0.0009 (7)

Geometric parameters (Å, º)

S1—C1	1.7050 (18)	C4—C5	1.488 (3)
O1—C4	1.228 (2)	C5—C6	1.391 (3)
O2—C11	1.229 (2)	C5—C10	1.395 (3)
N1—C1	1.318 (2)	C6—C7	1.389 (4)
N1—HN1	0.85 (3)	C6—H6	0.9500
N1—HN2	0.84 (3)	C7—C8	1.386 (4)
N2—C1	1.340 (2)	C7—H7	0.9500
N2—N3	1.394 (2)	C8—C9	1.396 (3)
N2—HN3	0.84 (2)	C8—H8	0.9500
N3—C2	1.350 (2)	C9—C10	1.392 (3)
N3—HN4	0.89 (3)	C9—H9	0.9500
C2—C3	1.381 (2)	C10—C11	1.493 (2)
C2—C12	1.498 (2)	C12—H12A	0.9800
C3—C11	1.466 (2)	C12—H12B	0.9800
C3—C4	1.466 (2)	C12—H12C	0.9800
C1—N1—HN1	119 (2)	C7—C6—C5	117.3 (2)
C1—N1—HN2	119.0 (17)	C7—C6—H6	121.3
HN1—N1—HN2	114 (2)	C5—C6—H6	121.3
C1—N2—N3	122.48 (15)	C8—C7—C6	121.71 (18)
C1—N2—HN3	120.3 (17)	C8—C7—H7	119.1
N3—N2—HN3	115.8 (16)	C6—C7—H7	119.1
C2—N3—N2	120.94 (15)	C7—C8—C9	121.4 (2)
C2—N3—HN4	118.1 (15)	C7—C8—H8	119.3
N2—N3—HN4	118.4 (15)	C9—C8—H8	119.3
N1—C1—N2	119.14 (16)	C10—C9—C8	116.8 (2)
N1—C1—S1	123.34 (14)	C10—C9—H9	121.6
N2—C1—S1	117.46 (13)	C8—C9—H9	121.6
N3—C2—C3	118.86 (15)	C9—C10—C5	121.78 (17)
N3—C2—C12	117.30 (15)	C9—C10—C11	129.77 (18)
C3—C2—C12	123.84 (16)	C5—C10—C11	108.44 (16)
C2—C3—C11	124.43 (15)	O2—C11—C3	127.43 (15)
C2—C3—C4	127.10 (16)	O2—C11—C10	125.64 (16)
C11—C3—C4	108.34 (15)	C3—C11—C10	106.93 (14)
O1—C4—C3	129.43 (19)	C2—C12—H12A	109.5
O1—C4—C5	124.29 (17)	C2—C12—H12B	109.5
C3—C4—C5	106.28 (16)	H12A—C12—H12B	109.5
C6—C5—C10	121.0 (2)	C2—C12—H12C	109.5
C6—C5—C4	129.0 (2)	H12A—C12—H12C	109.5

C10—C5—C4	109.99 (15)	H12B—C12—H12C	109.5

C1—N2—N3—C2	97.7 (2)	C4—C5—C6—C7	−179.82 (18)
N3—N2—C1—N1	4.8 (3)	C5—C6—C7—C8	−0.9 (3)
N3—N2—C1—S1	−178.07 (12)	C6—C7—C8—C9	0.5 (3)
N2—N3—C2—C3	163.37 (16)	C7—C8—C9—C10	0.0 (3)
N2—N3—C2—C12	−17.4 (2)	C8—C9—C10—C5	−0.2 (3)
N3—C2—C3—C11	−7.9 (3)	C8—C9—C10—C11	179.00 (18)
C12—C2—C3—C11	172.90 (16)	C6—C5—C10—C9	−0.2 (3)
N3—C2—C3—C4	176.93 (16)	C4—C5—C10—C9	−179.77 (17)
C12—C2—C3—C4	−2.3 (3)	C6—C5—C10—C11	−179.53 (16)
C2—C3—C4—O1	−4.8 (3)	C4—C5—C10—C11	0.9 (2)
C11—C3—C4—O1	179.40 (19)	C2—C3—C11—O2	4.2 (3)
C2—C3—C4—C5	175.41 (17)	C4—C3—C11—O2	−179.82 (17)
C11—C3—C4—C5	−0.42 (19)	C2—C3—C11—C10	−175.02 (16)
O1—C4—C5—C6	0.3 (3)	C4—C3—C11—C10	0.94 (19)
C3—C4—C5—C6	−179.83 (19)	C9—C10—C11—O2	0.3 (3)
O1—C4—C5—C10	179.86 (18)	C5—C10—C11—O2	179.61 (16)
C3—C4—C5—C10	−0.3 (2)	C9—C10—C11—C3	179.59 (18)
C10—C5—C6—C7	0.7 (3)	C5—C10—C11—C3	−1.14 (19)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C12—H12B⋯O1	0.98	2.26	3.033 (3)	135
N2—HN3⋯S1[i]	0.84 (2)	2.47 (2)	3.2796 (16)	163 (2)
N1—HN1⋯S1[ii]	0.85 (3)	2.63 (3)	3.3764 (19)	147 (2)
N1—HN2⋯O1[iii]	0.84 (3)	2.11 (3)	2.816 (2)	142 (2)
N3—HN4⋯O2	0.89 (3)	2.05 (3)	2.7592 (19)	135 (2)
N3—HN4⋯O2[iv]	0.89 (3)	2.30 (2)	3.0107 (19)	137 (2)

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