research communications

Spontaneous resolution and crystal structure of (2S)-2-(3-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-one; crystal structure of rac-2-(4-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-one

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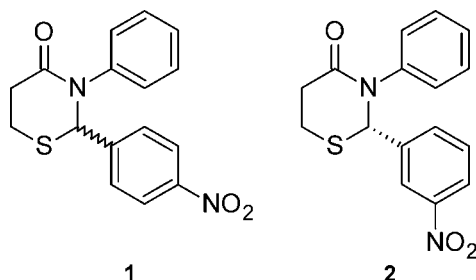
The crystal structures of isomeric rac-2-(4-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-one ($C_{16}H_{14}N_2O_3S$) (**1**) and (2S)-2-(3-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-one ($C_{16}H_{14}N_2O_3S$) (**2**) are reported here. While **1** crystallizes in a centrosymmetric space group, the crystal of **2** chosen for data collection has molecules only with (2S) chirality. This is the result of spontaneous resolution during crystallization, as the synthesis produces a racemic mixture. A crystal with (2R) molecules was also found in the same crystallization vial (structure factors available). The six-membered thiazine ring in both **1** and **2** displays an envelope conformation with the S atom forming the flap. The aryl rings in both structures adopt an approximate V shape with angles between their planes of 46.97 (14)° in **1** and 58.37 (10)° in **2**. In both structures, the molecules form layers in the *ab* plane. Within such a layer in **1**, one of the O atoms of the nitrophenyl group accepts a C—H⋯O hydrogen bond from the CH group at position 5 of the thiazine ring of a molecule of opposite chirality, forming chains along the *a*-axis direction. Each of the thiazine rings also participate in C—H⋯O bonds with the same carbon atom as above, resulting in chains along the *b*-axis direction, albeit of monochiral type. Adjacent layers are consolidated along the *c*-axis direction by pairs of parallel hydrogen bonds (C—H⋯O type) between the nitrophenyl groups of enantiomers. In **2**, the two C—H⋯O hydrogen bonds contribute to chain formation along the *b*-axis direction. Weak edge-to-face interactions between the aryl groups of neighbouring molecules in **1**, and C—H⋯π interactions between a thiazine ring CH group and a phenyl group of a neighboring molecule in **2** are also observed.

1. Chemical context

Compounds with an N-aryl-2,3,5,6-tetrahydro-4H-1,3-thiazin-4-one scaffold have been shown to have a wide variety of bioactivities, including antifungal (Qu *et al.*, 2013; Dandia *et al.*, 2004; Krumkains, 1984), antitubercular (Dandia *et al.*, 2004), antitumor (Chen *et al.*, 2012), antidiabetic (Arya *et al.*, 2012), regulation of plant growth (Krumkains, 1984), cleavage of DNA (possible antitumor) (Dandia *et al.*, 2013), inhibition of cannabinoid receptor 1 (CB1) (Choi *et al.*, 2008), and inhibition of angiogenesis (possible treatment of eye disease, neoplasm, arteriosclerosis, arthritis, psoriasis, diabetes, and mellitus) (Chen *et al.*, 2012).

The spontaneous resolution of a racemic solution by direct crystallization to form a conglomerate, a mechanical mixture of separate homochiral crystals, is an uncommon but well-known phenomenon, recognized first by Pasteur in 1848 (Pasteur, 1848; Jacques *et al.*, 1981; Eliel & Wilen, 1994; Pérez-Garcia & Amabilino, 2007). It has even been used in the production of chiral active pharmaceutical ingredients (Bredikhin & Bredikhina, 2017). However, the reasons why this occurs with a minority of molecules are not well understood (Pérez-Garcia & Amabilino, 2007) and have not yet yielded to attempts to predict occurrence (D'Oria, Karanertzanis & Price, 2010; Pérez-Garcia & Amabilino, 2007).

1   **2**

In this work, we report the spontaneous resolution and crystal structure of (2*S*)-2-(3-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one, **2**. We later collected another crystal from the vial and confirmed that it had the (2*R*) configuration (identical packing, structure factors available upon request). We also report the racemic (centrosymmetric) structure of the isomeric 2-(4-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one, **1**. We have previously reported the crystal structure of *rac*-2,3-diphenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (Yennawar & Silverberg, 2014).
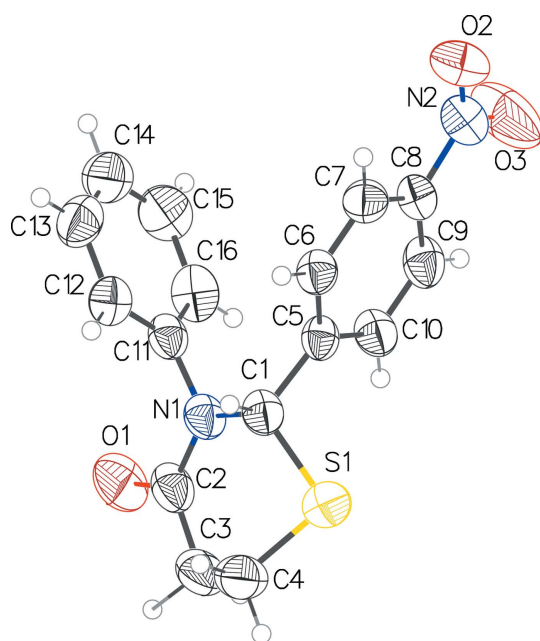
2. Structural commentary

Both structures **1** and **2** (Figs. 1 and 2) exhibit an envelope pucker conformation of the thiazine ring with the sulfur atom forming the flap. The Cremer & Pole (1975) puckering parameters in **1** are: $Q = 0.638$ (3) Å, $\theta = 47.0$ (3)°, $\varphi = 339.8$ (4)° and in **2**: $Q = 0.6654$ (16) Å, $\theta = 44.20$ (17)°, $\varphi = 353.8$ (3)°. The aryl rings in both structures form an approximate V shape with inter-centroid distances of 3.964 (2) and 4.160 (2) Å, and interplanar angles of 46.97 (14) and 58.37 (10)°, in **1** and **2**, respectively.

3. Supramolecular features

In both structures, C—H···O interactions are observed (Tables 1 and 2, Figs. 3 and 4), resulting in layering of molecules in planes parallel to (001). In each layer of structure **1**, one of the oxygen atoms of the nitrophenyl group accepts a C—H···O hydrogen bond from the CH group at position 5 of the thiazine ring of a molecule of opposite chirality. This results in infinite chains of mixed chirality along the *a*-axis direction. The second oxygen atom of the nitrophenyl group also accepts a hydrogen bond from the thiazine 5-carbon atom, resulting this time in monochiral chains along the *b*-axis direction. Further, the stacking of layers along the *c*-axis direction is consolidated by pairs of parallel hydrogen bonds between the nitrophenyl groups of enantiomers. In **2**, a monochiral structure, the C—H···O hydrogen bonds between the chiral carbon atom and the 4-oxygen atom on the neigh-
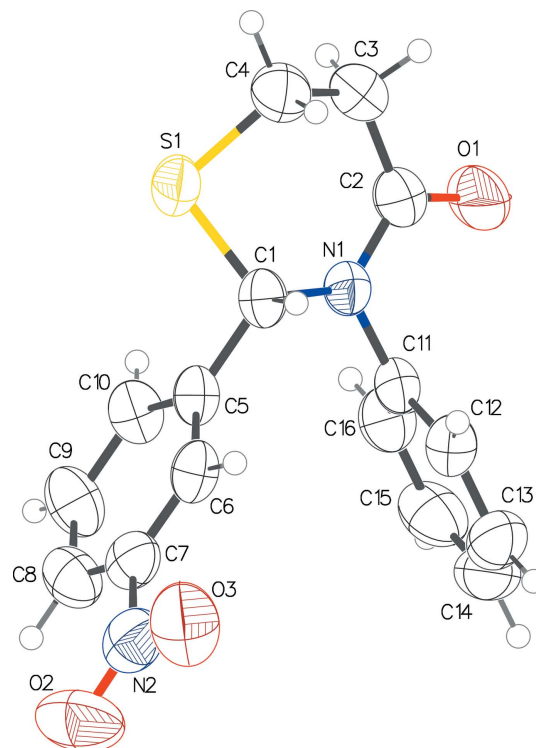

Figure 1
The molecular structure of **1**, with displacement ellipsoids drawn at the 50% probability level.

Figure 2
The molecular structure of **2**, with displacement ellipsoids drawn at the 50% probability level.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$A\cdots$O2^i	0.97	2.62	3.405 (4)	139
C3—H3$B\cdots$O3^{ii}	0.97	2.57	3.253 (5)	128
C7—H7$\cdots$O2^{iii}	0.93	2.50	3.417 (4)	170

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

Table 2
Hydrogen-bond geometry (Å, °) for **2**.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$O1^i	0.98	2.19	3.158 (2)	170
C15—H15$\cdots$O3^{ii}	0.93	2.58	3.501 (3)	174

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

boring thiazine ring results in a chain along the *b*-axis direction. The second hydrogen bond loops back to the second molecule in the reverse direction of the same chain. While weak edge-to-face interactions [$Cg\cdots Cg$ distance of 5.340 (3) Å and an interplanar angle of 84.99 (2)°] between the aryl groups of neighboring molecules is observed in **1**, in **2**, the 6-carbon atom of the thiazine ring interacts with the phenyl group in a C—H$\cdots\pi$ type interaction [$C4\cdots Cg = 3.581 (2)$ Å].

4. Database survey

No substantially similar crystal structures were found other than certain ones we have published, including 2,3-diphenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (Yennawar & Silverberg, 2014, 2015), 2-(3-nitrophenyl)-3-phenyl-2,3-dihydro-4*H*-1,3-benzothiazin-4-one (Yennawar *et al.*, 2013), and 2-(4-nitrophenyl)-3-phenyl-2,3-dihydro-4*H*-1,3-benzothiazin-4-one (Yennawar *et al.*, 2015).

5. Synthesis and crystallization

General: A two-necked 25 ml round-bottom flask was oven-dried, cooled under N$_2$, and charged with a stir bar and the imine (6 mmol). 3-Mercaptopropionic acid (0.52 ml, 6 mmol) and then 2-methyltetrahydrofuran (2.3 ml) were added and
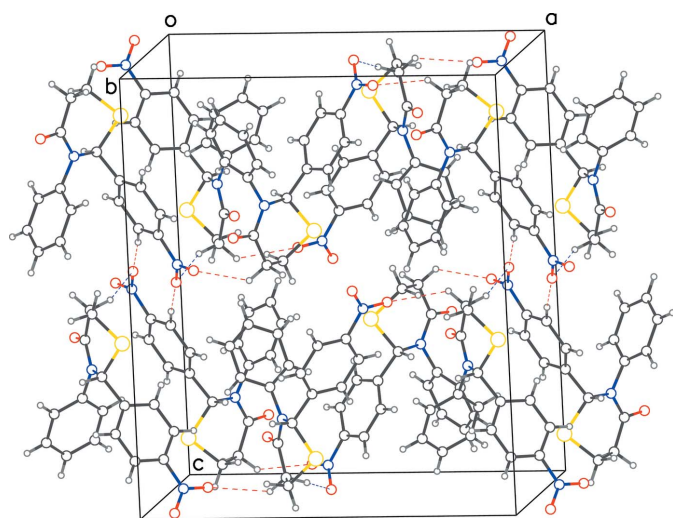
the solution was stirred. Pyridine (1.95 ml, 24 mmol) and finally, 2,4,6-tripropyl-1,3,5,2,4,6-trioxatriphosphorinane-2,4,6-trioxide (T3P) in 2-methyltetrahydrofuran (50 weight percent; 7.3 ml, 12 mmol) were added. The reaction was stirred at room temperature and followed by TLC. The mixture was poured into a separatory funnel with dichloromethane and distilled water. The layers were separated and the aqueous was then extracted twice with dichloromethane. The organics were combined and washed with saturated sodium bicarbonate and then saturated sodium chloride. The organic was dried over sodium sulfate and concentrated under vacuum to give crude product.

2-(4-Nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**1**): the crude product was recrystallized from 2-propanol to give a white powder. Yield: 1.397 g (74%). m.p. 410–412 K. Colorless blocks for data collection were grown by slow evaporation from 2-propanol solution.

2-(3-Nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one (**2**): The crude product was recrystallized from 2-propanol to give a yellow powder. Yield: 1.121 g (59%). m.p. 415 K. Colorless blocks were grown by slow evaporation from ethanol solution; the (2*S*) and (2*R*) crystals had identical morphology. The stereochemical configuration of individual crystals was identified by solving the crystal structure. After several were found to be (2*S*), a crystal was found that was (2*R*).

Figure 3
Packing diagram for **1**, showing the layering of molecules in the *ab* plane. Red dotted lines show hydrogen bonds between enantiomers and blue dotted lines show interactions between molecules of same chirality.
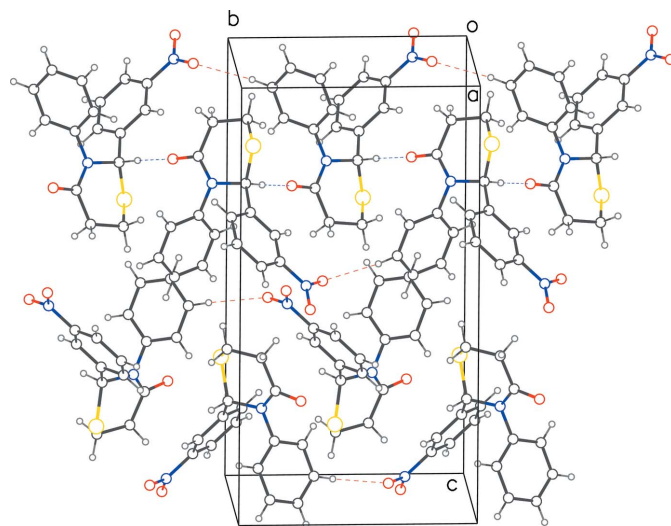

Figure 4
Packing diagram for **2**, showing the layering of molecules in the *ab* plane. Blue dotted lines show hydrogen bonds between molecules forming a chain in the *b*-axis direction and red dotted lines show a loop-back interaction within each chain.

Table 3
Experimental details.

	1	2
Crystal data		
Chemical formula	$C_{16}H_{14}N_2O_3S$	$C_{16}H_{14}N_2O_3S$
M_r	314.35	314.35
Crystal system, space group	Orthorhombic, $Pbca$	Orthorhombic, $P2_12_12_1$
Temperature (K)	298	298
a, b, c (Å)	15.801 (6), 10.280 (4), 18.460 (7)	8.6877 (17), 9.6547 (19), 18.137 (4)
V (Å^3)	2998.4 (19)	1521.3 (5)
Z	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.23	0.23
Crystal size (mm)	$0.2 \times 0.16 \times 0.09$	$0.21 \times 0.19 \times 0.18$
Data collection		
Diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.154, 0.9	0.341, 0.9
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26571, 3769, 2297	14176, 3775, 3144
R_{int}	0.057	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.670	0.667
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.078, 0.216, 1.19	0.045, 0.121, 1.01
No. of reflections	3769	3775
No. of parameters	199	199
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.24, −0.48	0.32, −0.16
Absolute structure	–	Flack (1983), 4055 Friedel pairs
Absolute structure parameter	–	0.09 (7)

Computer programs: *SMART* and *SAINT* (Bruker, 2016), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

6. Refinement

Crystal data, data collection and structure refinement details for both structures **1** and **2** are summarized in Table 3. The H atoms were placed geometrically and allowed to ride on their parent C atoms during refinement, with C—H distances of 0.93 Å (aromatic), 0.97 Å (methylene) and 0.98 (methyl) and with $U_{iso}(H) = 1.2U_{eq}$(aromatic or methylene C) or $1.5U_{eq}$(methyl C). In structure **2**, the absolute configuration for the chiral centres in the molecule was determined as (2*S*) with a Flack absolute structure parameter of 0.09 (7) for 4055 Friedel pairs.

Acknowledgements

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supporting information

Spontaneous resolution and crystal structure of (2*S*)-2-(3-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one; crystal structure of *rac*-2-(4-nitrophenyl)-3-phenyl-2,3,5,6-tetrahydro-4*H*-1,3-thiazin-4-one

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Computing details

For both structures, data collection: *SMART* (Bruker, 2001). Cell refinement: *SAINT* (Bruker, 2016) for (1); *SAINT* (Bruker, 2001) for (2). Data reduction: *SAINT* (Bruker, 2016) for (1); *SAINT* (Bruker, 2001) for (2). Program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015) for (1); *SHELXS97* (Sheldrick, 2008) for (2). For both structures, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

(2*S*)-2-(3-Nitrophenyl)-3-phenyl-3,4,5,6-tetrahydro-2*H*-1,3-thiazin-4-one (1)

Crystal data

$C_{16}H_{14}N_2O_3S$	$D_x = 1.393$ Mg m^{-3}
$M_r = 314.35$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 3516 reflections
$a = 15.801$ (6) Å	$\theta = 2.6$–$27.5°$
$b = 10.280$ (4) Å	$\mu = 0.23$ mm^{-1}
$c = 18.460$ (7) Å	$T = 298$ K
$V = 2998.4$ (19) Å^3	Block, colorless
$Z = 8$	$0.2 \times 0.16 \times 0.09$ mm
$F(000) = 1312$	

Data collection

Bruker SMART CCD area detector diffractometer	26571 measured reflections
	3769 independent reflections
Radiation source: fine-focus sealed tube	2297 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.057$
phi and ω scans	$\theta_{max} = 28.5°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$h = -20 \rightarrow 21$
	$k = -13 \rightarrow 13$
$T_{min} = 0.154$, $T_{max} = 0.9$	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	3769 reflections
Least-squares matrix: full	199 parameters
$R[F^2 > 2\sigma(F^2)] = 0.078$	0 restraints
$wR(F^2) = 0.216$	Primary atom site location: iterative
$S = 1.19$	

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.24$ e Å^{-3}
H-atom parameters constrained	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Special details

Experimental. The data collection nominally covered a full sphere of reciprocal space by a combination of 4 sets of ω scans each set at different φ and/or 2θ angles and each scan (10 s exposure) covering -0.300° degrees in ω. The crystal to detector distance was 5.82 cm.

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
C1	0.38874 (16)	0.8032 (2)	0.80475 (15)	0.0493 (7)
H1	0.3458	0.8713	0.7995	0.059*
C2	0.32207 (18)	0.6103 (3)	0.86948 (17)	0.0613 (8)
C3	0.3466 (2)	0.6614 (3)	0.94234 (17)	0.0744 (10)
H3A	0.3941	0.6104	0.9597	0.089*
H3B	0.2998	0.6462	0.9752	0.089*
C4	0.3704 (2)	0.8027 (4)	0.94716 (18)	0.0746 (10)
H4A	0.3901	0.8224	0.9957	0.090*
H4B	0.3212	0.8562	0.9373	0.090*
C5	0.44572 (15)	0.8058 (2)	0.73915 (15)	0.0446 (6)
C6	0.42995 (16)	0.8917 (2)	0.68348 (15)	0.0482 (7)
H6	0.3860	0.9513	0.6880	0.058*
C7	0.47813 (18)	0.8909 (3)	0.62117 (15)	0.0551 (7)
H7	0.4674	0.9495	0.5839	0.066*
C8	0.54241 (16)	0.8013 (3)	0.61555 (15)	0.0525 (7)
C9	0.56167 (17)	0.7155 (3)	0.67046 (18)	0.0584 (8)
H9	0.6058	0.6563	0.6658	0.070*
C10	0.51327 (17)	0.7203 (3)	0.73259 (16)	0.0546 (7)
H10	0.5262	0.6650	0.7709	0.066*
C11	0.31097 (16)	0.6326 (2)	0.73959 (15)	0.0488 (7)
C12	0.24278 (18)	0.6965 (3)	0.71096 (17)	0.0572 (7)
H12	0.2159	0.7612	0.7375	0.069*
C13	0.2139 (2)	0.6647 (3)	0.64262 (19)	0.0679 (9)
H13	0.1672	0.7078	0.6235	0.082*
C14	0.2530 (2)	0.5712 (3)	0.6032 (2)	0.0747 (10)
H14	0.2336	0.5511	0.5569	0.090*
C15	0.3214 (2)	0.5062 (3)	0.6317 (2)	0.0770 (10)
H15	0.3484	0.4423	0.6045	0.092*

C16	0.3502 (2)	0.5354 (3)	0.70058 (19)	0.0660 (8)
H16	0.3955	0.4899	0.7204	0.079*
N1	0.34542 (14)	0.6745 (2)	0.80829 (12)	0.0514 (6)
N2	0.59028 (18)	0.7939 (3)	0.54789 (16)	0.0700 (7)
O1	0.28131 (16)	0.5087 (2)	0.86495 (14)	0.0905 (8)
O2	0.57444 (17)	0.8711 (3)	0.49997 (13)	0.0870 (8)
O3	0.6441 (2)	0.7111 (3)	0.54203 (18)	0.1312 (13)
S1	0.45206 (5)	0.83866 (9)	0.88301 (4)	0.0706 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0452 (15)	0.0467 (14)	0.0561 (17)	0.0018 (11)	0.0019 (12)	0.0096 (11)
C2	0.0498 (16)	0.0657 (18)	0.068 (2)	0.0000 (14)	0.0077 (14)	0.0223 (16)
C3	0.065 (2)	0.099 (3)	0.060 (2)	0.0073 (18)	0.0096 (16)	0.0301 (18)
C4	0.072 (2)	0.100 (3)	0.0521 (19)	0.0153 (19)	0.0029 (16)	0.0062 (17)
C5	0.0395 (13)	0.0399 (12)	0.0543 (16)	−0.0048 (10)	−0.0009 (11)	0.0045 (11)
C6	0.0439 (14)	0.0458 (13)	0.0550 (17)	0.0024 (11)	−0.0026 (12)	0.0079 (12)
C7	0.0550 (16)	0.0586 (16)	0.0517 (17)	−0.0010 (14)	−0.0036 (13)	0.0106 (13)
C8	0.0445 (15)	0.0585 (16)	0.0545 (17)	−0.0061 (12)	0.0055 (13)	0.0029 (13)
C9	0.0436 (15)	0.0584 (16)	0.073 (2)	0.0060 (12)	0.0027 (14)	0.0090 (15)
C10	0.0481 (15)	0.0545 (15)	0.0613 (18)	0.0053 (13)	0.0041 (13)	0.0188 (13)
C11	0.0438 (14)	0.0466 (14)	0.0559 (17)	−0.0038 (11)	0.0047 (13)	0.0097 (12)
C12	0.0496 (16)	0.0574 (16)	0.065 (2)	0.0008 (13)	−0.0008 (14)	−0.0009 (14)
C13	0.0625 (19)	0.0674 (19)	0.074 (2)	−0.0120 (16)	−0.0130 (17)	0.0057 (17)
C14	0.083 (2)	0.073 (2)	0.069 (2)	−0.0263 (19)	−0.0012 (19)	−0.0034 (18)
C15	0.086 (3)	0.063 (2)	0.083 (3)	−0.0113 (18)	0.012 (2)	−0.0183 (18)
C16	0.0600 (18)	0.0513 (16)	0.087 (2)	0.0032 (14)	0.0041 (17)	0.0009 (15)
N1	0.0475 (13)	0.0509 (12)	0.0558 (15)	−0.0010 (10)	0.0032 (11)	0.0165 (10)
N2	0.0613 (16)	0.0829 (19)	0.0657 (19)	−0.0036 (15)	0.0121 (14)	0.0036 (15)
O1	0.0943 (18)	0.0839 (17)	0.0934 (19)	−0.0271 (14)	0.0132 (14)	0.0336 (14)
O2	0.0969 (18)	0.1087 (19)	0.0554 (15)	−0.0039 (15)	0.0103 (13)	0.0133 (14)
O3	0.124 (3)	0.155 (3)	0.115 (3)	0.062 (2)	0.061 (2)	0.030 (2)
S1	0.0682 (6)	0.0868 (6)	0.0569 (6)	−0.0123 (4)	−0.0040 (4)	0.0004 (4)

Geometric parameters (Å, º)

C1—H1	0.9800	C8—C9	1.378 (4)
C1—C5	1.509 (4)	C8—N2	1.462 (4)
C1—N1	1.491 (3)	C9—H9	0.9300
C1—S1	1.795 (3)	C9—C10	1.379 (4)
C2—C3	1.495 (5)	C10—H10	0.9300
C2—N1	1.359 (3)	C11—C12	1.368 (4)
C2—O1	1.230 (4)	C11—C16	1.379 (4)
C3—H3A	0.9700	C11—N1	1.446 (4)
C3—H3B	0.9700	C12—H12	0.9300
C3—C4	1.503 (5)	C12—C13	1.381 (4)
C4—H4A	0.9700	C13—H13	0.9300

C4—H4B	0.9700	C13—C14	1.355 (5)
C4—S1	1.790 (3)	C14—H14	0.9300
C5—C6	1.378 (4)	C14—C15	1.375 (5)
C5—C10	1.388 (4)	C15—H15	0.9300
C6—H6	0.9300	C15—C16	1.384 (4)
C6—C7	1.379 (4)	C16—H16	0.9300
C7—H7	0.9300	N2—O2	1.215 (3)
C7—C8	1.375 (4)	N2—O3	1.208 (4)
C5—C1—H1	108.7	C9—C8—N2	118.7 (3)
C5—C1—S1	108.04 (18)	C8—C9—H9	121.1
N1—C1—H1	108.7	C8—C9—C10	117.8 (3)
N1—C1—C5	109.0 (2)	C10—C9—H9	121.1
N1—C1—S1	113.65 (17)	C5—C10—H10	119.3
S1—C1—H1	108.7	C9—C10—C5	121.4 (3)
N1—C2—C3	120.4 (3)	C9—C10—H10	119.3
O1—C2—C3	119.7 (3)	C12—C11—C16	120.0 (3)
O1—C2—N1	119.9 (3)	C12—C11—N1	119.5 (2)
C2—C3—H3A	108.0	C16—C11—N1	120.3 (3)
C2—C3—H3B	108.0	C11—C12—H12	120.0
C2—C3—C4	117.2 (2)	C11—C12—C13	120.0 (3)
H3A—C3—H3B	107.2	C13—C12—H12	120.0
C4—C3—H3A	108.0	C12—C13—H13	119.7
C4—C3—H3B	108.0	C14—C13—C12	120.5 (3)
C3—C4—H4A	109.7	C14—C13—H13	119.7
C3—C4—H4B	109.7	C13—C14—H14	120.1
C3—C4—S1	109.9 (2)	C13—C14—C15	119.8 (3)
H4A—C4—H4B	108.2	C15—C14—H14	120.1
S1—C4—H4A	109.7	C14—C15—H15	119.8
S1—C4—H4B	109.7	C14—C15—C16	120.3 (3)
C6—C5—C1	120.1 (2)	C16—C15—H15	119.8
C6—C5—C10	118.7 (2)	C11—C16—C15	119.3 (3)
C10—C5—C1	121.2 (2)	C11—C16—H16	120.3
C5—C6—H6	119.4	C15—C16—H16	120.3
C5—C6—C7	121.2 (2)	C2—N1—C1	126.3 (3)
C7—C6—H6	119.4	C2—N1—C11	118.8 (2)
C6—C7—H7	120.8	C11—N1—C1	113.49 (19)
C8—C7—C6	118.3 (3)	O2—N2—C8	118.8 (3)
C8—C7—H7	120.8	O3—N2—C8	118.5 (3)
C7—C8—C9	122.4 (3)	O3—N2—O2	122.7 (3)
C7—C8—N2	118.8 (3)	C4—S1—C1	95.08 (15)
C1—C5—C6—C7	−176.2 (2)	C12—C11—N1—C1	−69.7 (3)
C1—C5—C10—C9	175.0 (3)	C12—C11—N1—C2	97.7 (3)
C2—C3—C4—S1	−54.0 (4)	C12—C13—C14—C15	0.8 (5)
C3—C2—N1—C1	−5.9 (4)	C13—C14—C15—C16	0.3 (5)
C3—C2—N1—C11	−171.6 (3)	C14—C15—C16—C11	−1.7 (5)
C3—C4—S1—C1	63.8 (2)	C16—C11—C12—C13	−0.9 (4)

C5—C1—N1—C2	147.8 (3)	C16—C11—N1—C1	105.6 (3)
C5—C1—N1—C11	−45.9 (3)	C16—C11—N1—C2	−87.0 (3)
C5—C1—S1—C4	−171.67 (19)	N1—C1—C5—C6	115.7 (3)
C5—C6—C7—C8	0.4 (4)	N1—C1—C5—C10	−62.5 (3)
C6—C5—C10—C9	−3.3 (4)	N1—C1—S1—C4	−50.6 (2)
C6—C7—C8—C9	−1.9 (4)	N1—C2—C3—C4	20.1 (4)
C6—C7—C8—N2	176.0 (3)	N1—C11—C12—C13	174.4 (2)
C7—C8—C9—C10	0.7 (4)	N1—C11—C16—C15	−173.3 (3)
C7—C8—N2—O2	3.4 (4)	N2—C8—C9—C10	−177.1 (3)
C7—C8—N2—O3	−176.7 (3)	O1—C2—C3—C4	−160.7 (3)
C8—C9—C10—C5	1.9 (4)	O1—C2—N1—C1	174.9 (3)
C9—C8—N2—O2	−178.6 (3)	O1—C2—N1—C11	9.3 (4)
C9—C8—N2—O3	1.3 (4)	S1—C1—C5—C6	−120.4 (2)
C10—C5—C6—C7	2.1 (4)	S1—C1—C5—C10	61.4 (3)
C11—C12—C13—C14	−0.5 (5)	S1—C1—N1—C2	27.3 (3)
C12—C11—C16—C15	1.9 (4)	S1—C1—N1—C11	−166.44 (18)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O2^i	0.97	2.62	3.405 (4)	139
C3—H3B···O3^ii	0.97	2.57	3.253 (5)	128
C7—H7···O2^iii	0.93	2.50	3.417 (4)	170

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

rac-**2-(4-Nitrophenyl)-3-phenyl-3,4,5,6-tetrahydro-2*H*-1,3-thiazin-4-one (2)**

Crystal data

C$_{16}$H$_{14}$N$_2$O$_3$S
M_r = 314.35
Orthorhombic, $P2_12_12_1$
a = 8.6877 (17) Å
b = 9.6547 (19) Å
c = 18.137 (4) Å
V = 1521.3 (5) Å^3
Z = 4
$F(000)$ = 656

D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1695 reflections
θ = 2.6–27.4°
μ = 0.23 mm^{-1}
T = 298 K
Block, colorless
0.21 × 0.19 × 0.18 mm

Data collection

Bruker SMART CCD area detector
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.34 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan
  (SADABS; Bruker, 2001)
T_{min} = 0.341, T_{max} = 0.9

14176 measured reflections
3775 independent reflections
3144 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 28.3°, θ_{min} = 2.3°
h = −11→11
k = −12→12
l = −24→22

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0783P)^2]$
$wR(F^2) = 0.121$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
3775 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 4055 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.09 (7)
Secondary atom site location: difference Fourier map	

Special details

Experimental. The data collection nominally covered a full sphere of reciprocal space by a combination of 4 sets of ω scans each set at different φ and/or 2θ angles and each scan (10 s exposure) covering -0.300° degrees in ω. The crystal to detector distance was 5.82 cm.

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 > 2sigma(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	$U_{iso}*/U_{eq}$
C1	0.26199 (19)	0.53305 (17)	0.75480 (10)	0.0468 (4)
H1	0.1885	0.6066	0.7426	0.056*
C2	0.0844 (3)	0.3448 (2)	0.79727 (12)	0.0640 (5)
C3	0.0753 (3)	0.4045 (3)	0.87435 (13)	0.0688 (6)
H3A	−0.0321	0.4053	0.8889	0.083*
H3B	0.1283	0.3413	0.9073	0.083*
C4	0.1385 (2)	0.5458 (2)	0.88739 (13)	0.0685 (6)
H4A	0.1435	0.5638	0.9400	0.082*
H4B	0.0710	0.6143	0.8653	0.082*
C5	0.39844 (19)	0.54561 (17)	0.70401 (10)	0.0462 (4)
C6	0.3973 (2)	0.64968 (18)	0.65124 (11)	0.0499 (4)
H6	0.3133	0.7089	0.6470	0.060*
C7	0.5226 (2)	0.6638 (2)	0.60521 (11)	0.0535 (5)
C8	0.6496 (2)	0.5792 (2)	0.60899 (13)	0.0614 (5)
H8	0.7326	0.5913	0.5773	0.074*
C9	0.6499 (2)	0.4757 (2)	0.66142 (14)	0.0648 (6)
H9	0.7343	0.4168	0.6653	0.078*
C10	0.5258 (2)	0.45870 (19)	0.70826 (12)	0.0546 (5)
H10	0.5274	0.3881	0.7431	0.066*
C11	0.17339 (19)	0.34283 (18)	0.67247 (10)	0.0464 (4)
C12	0.0949 (2)	0.4149 (2)	0.61946 (11)	0.0541 (4)

H12	0.0456	0.4973	0.6315	0.065*
C13	0.0889 (3)	0.3649 (3)	0.54785 (13)	0.0697 (6)
H13	0.0360	0.4136	0.5116	0.084*
C14	0.1617 (3)	0.2433 (3)	0.53116 (13)	0.0784 (8)
H14	0.1574	0.2088	0.4833	0.094*
C15	0.2404 (3)	0.1724 (3)	0.58378 (16)	0.0748 (7)
H15	0.2902	0.0903	0.5715	0.090*
C16	0.2472 (2)	0.2211 (2)	0.65527 (13)	0.0601 (5)
H16	0.3009	0.1723	0.6912	0.072*
N1	0.18311 (17)	0.39713 (15)	0.74654 (8)	0.0473 (3)
N2	0.5185 (3)	0.7744 (2)	0.54921 (11)	0.0695 (5)
O1	0.0060 (2)	0.2427 (2)	0.78250 (10)	0.1044 (8)
O2	0.6279 (3)	0.7859 (2)	0.50693 (12)	0.1032 (7)
O3	0.4078 (2)	0.8498 (2)	0.54701 (13)	0.0971 (7)
S1	0.32852 (6)	0.56010 (6)	0.84780 (3)	0.06274 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0395 (8)	0.0424 (9)	0.0586 (10)	0.0006 (7)	−0.0046 (8)	0.0003 (8)
C2	0.0585 (11)	0.0712 (13)	0.0624 (12)	−0.0210 (11)	0.0031 (10)	−0.0021 (10)
C3	0.0573 (11)	0.0877 (16)	0.0613 (12)	−0.0131 (12)	0.0106 (9)	−0.0027 (11)
C4	0.0561 (11)	0.0838 (15)	0.0655 (12)	−0.0010 (11)	0.0092 (10)	−0.0206 (12)
C5	0.0399 (8)	0.0400 (8)	0.0587 (10)	−0.0030 (7)	−0.0068 (7)	−0.0026 (8)
C6	0.0473 (8)	0.0417 (9)	0.0606 (11)	−0.0030 (7)	−0.0123 (9)	−0.0026 (8)
C7	0.0648 (11)	0.0428 (9)	0.0529 (11)	−0.0117 (9)	−0.0069 (9)	−0.0005 (8)
C8	0.0599 (11)	0.0527 (11)	0.0717 (13)	−0.0094 (10)	0.0122 (10)	−0.0040 (10)
C9	0.0482 (9)	0.0530 (11)	0.0932 (16)	0.0051 (8)	0.0087 (11)	0.0020 (11)
C10	0.0489 (9)	0.0449 (10)	0.0701 (12)	0.0015 (8)	−0.0016 (9)	0.0080 (9)
C11	0.0377 (7)	0.0471 (9)	0.0544 (9)	−0.0070 (7)	−0.0012 (8)	−0.0017 (7)
C12	0.0478 (9)	0.0525 (10)	0.0621 (11)	−0.0027 (8)	−0.0081 (9)	0.0016 (9)
C13	0.0786 (14)	0.0757 (15)	0.0547 (12)	−0.0185 (13)	−0.0091 (12)	0.0099 (11)
C14	0.0955 (18)	0.0839 (17)	0.0556 (12)	−0.0344 (16)	0.0165 (13)	−0.0110 (12)
C15	0.0721 (14)	0.0633 (13)	0.0891 (17)	−0.0018 (12)	0.0275 (13)	−0.0183 (13)
C16	0.0514 (10)	0.0550 (11)	0.0741 (13)	0.0058 (9)	−0.0007 (10)	0.0007 (11)
N1	0.0431 (7)	0.0500 (8)	0.0489 (8)	−0.0088 (6)	−0.0029 (6)	−0.0002 (7)
N2	0.0846 (14)	0.0604 (11)	0.0637 (11)	−0.0208 (11)	−0.0131 (10)	0.0075 (9)
O1	0.1126 (16)	0.1198 (15)	0.0807 (11)	−0.0768 (14)	0.0227 (11)	−0.0220 (11)
O2	0.133 (2)	0.0990 (14)	0.0779 (11)	−0.0127 (13)	0.0272 (13)	0.0221 (11)
O3	0.0867 (12)	0.0827 (13)	0.1218 (16)	−0.0107 (11)	−0.0210 (12)	0.0455 (12)
S1	0.0486 (2)	0.0780 (4)	0.0616 (3)	−0.0121 (2)	−0.0044 (2)	−0.0156 (3)

Geometric parameters (Å, º)

C1—H1	0.9800	C8—H8	0.9300
C1—C5	1.506 (2)	C8—C9	1.380 (3)
C1—N1	1.488 (2)	C9—H9	0.9300
C1—S1	1.802 (2)	C9—C10	1.383 (3)

C2—C3	1.514 (3)	C10—H10	0.9300
C2—N1	1.356 (3)	C11—C12	1.369 (3)
C2—O1	1.228 (3)	C11—C16	1.375 (3)
C3—H3A	0.9700	C11—N1	1.444 (2)
C3—H3B	0.9700	C12—H12	0.9300
C3—C4	1.490 (3)	C12—C13	1.386 (3)
C4—H4A	0.9700	C13—H13	0.9300
C4—H4B	0.9700	C13—C14	1.368 (4)
C4—S1	1.806 (2)	C14—H14	0.9300
C5—C6	1.388 (3)	C14—C15	1.359 (4)
C5—C10	1.391 (2)	C15—H15	0.9300
C6—H6	0.9300	C15—C16	1.380 (4)
C6—C7	1.379 (3)	C16—H16	0.9300
C7—C8	1.375 (3)	N2—O2	1.226 (3)
C7—N2	1.474 (3)	N2—O3	1.207 (3)
C5—C1—H1	108.4	C9—C8—H8	121.1
C5—C1—S1	107.96 (11)	C8—C9—H9	119.7
N1—C1—H1	108.4	C8—C9—C10	120.51 (19)
N1—C1—C5	111.83 (14)	C10—C9—H9	119.7
N1—C1—S1	111.70 (12)	C5—C10—H10	119.5
S1—C1—H1	108.4	C9—C10—C5	121.00 (18)
N1—C2—C3	121.17 (18)	C9—C10—H10	119.5
O1—C2—C3	118.6 (2)	C12—C11—C16	120.49 (19)
O1—C2—N1	120.1 (2)	C12—C11—N1	119.87 (16)
C2—C3—H3A	107.7	C16—C11—N1	119.61 (18)
C2—C3—H3B	107.7	C11—C12—H12	120.0
H3A—C3—H3B	107.1	C11—C12—C13	120.0 (2)
C4—C3—C2	118.4 (2)	C13—C12—H12	120.0
C4—C3—H3A	107.7	C12—C13—H13	120.4
C4—C3—H3B	107.7	C14—C13—C12	119.2 (2)
C3—C4—H4A	109.6	C14—C13—H13	120.4
C3—C4—H4B	109.6	C13—C14—H14	119.7
C3—C4—S1	110.09 (15)	C15—C14—C13	120.6 (2)
H4A—C4—H4B	108.2	C15—C14—H14	119.7
S1—C4—H4A	109.6	C14—C15—H15	119.7
S1—C4—H4B	109.6	C14—C15—C16	120.6 (2)
C6—C5—C1	118.31 (16)	C16—C15—H15	119.7
C6—C5—C10	118.75 (17)	C11—C16—C15	119.0 (2)
C10—C5—C1	122.93 (16)	C11—C16—H16	120.5
C5—C6—H6	120.5	C15—C16—H16	120.5
C7—C6—C5	118.90 (17)	C2—N1—C1	123.49 (16)
C7—C6—H6	120.5	C2—N1—C11	117.31 (15)
C6—C7—N2	118.02 (19)	C11—N1—C1	116.14 (14)
C8—C7—C6	123.01 (18)	O2—N2—C7	118.5 (2)
C8—C7—N2	119.0 (2)	O3—N2—C7	118.6 (2)
C7—C8—H8	121.1	O3—N2—O2	122.8 (2)
C7—C8—C9	117.81 (19)	C1—S1—C4	93.89 (9)

C1—C5—C6—C7	178.90 (16)	C12—C11—N1—C1	−61.8 (2)
C1—C5—C10—C9	−178.72 (19)	C12—C11—N1—C2	99.1 (2)
C2—C3—C4—S1	−48.3 (3)	C12—C13—C14—C15	−0.6 (4)
C3—C2—N1—C1	−14.7 (3)	C13—C14—C15—C16	0.6 (4)
C3—C2—N1—C11	−174.1 (2)	C14—C15—C16—C11	−0.2 (4)
C3—C4—S1—C1	63.17 (18)	C16—C11—C12—C13	0.3 (3)
C5—C1—N1—C2	162.42 (18)	C16—C11—N1—C1	116.17 (18)
C5—C1—N1—C11	−37.9 (2)	C16—C11—N1—C2	−82.9 (2)
C5—C1—S1—C4	177.36 (13)	N1—C1—C5—C6	118.45 (17)
C5—C6—C7—C8	0.1 (3)	N1—C1—C5—C10	−62.3 (2)
C5—C6—C7—N2	179.58 (16)	N1—C1—S1—C4	−59.28 (14)
C6—C5—C10—C9	0.5 (3)	N1—C2—C3—C4	18.6 (4)
C6—C7—C8—C9	0.1 (3)	N1—C11—C12—C13	178.24 (18)
C6—C7—N2—O2	−178.4 (2)	N1—C11—C16—C15	−178.26 (19)
C6—C7—N2—O3	1.7 (3)	N2—C7—C8—C9	−179.38 (18)
C7—C8—C9—C10	0.0 (3)	O1—C2—C3—C4	−165.2 (2)
C8—C7—N2—O2	1.1 (3)	O1—C2—N1—C1	169.2 (2)
C8—C7—N2—O3	−178.8 (2)	O1—C2—N1—C11	9.8 (3)
C8—C9—C10—C5	−0.4 (3)	S1—C1—C5—C6	−118.27 (14)
C10—C5—C6—C7	−0.4 (3)	S1—C1—C5—C10	61.0 (2)
C11—C12—C13—C14	0.2 (3)	S1—C1—N1—C2	41.3 (2)
C12—C11—C16—C15	−0.3 (3)	S1—C1—N1—C11	−159.05 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1[i]	0.98	2.19	3.158 (2)	170
C15—H15···O3[ii]	0.93	2.58	3.501 (3)	174

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