Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Buthalital and methitural – 5,5-substituted derivatives of 2-thiobarbituric acid forming the same type of hydrogen-bonded chain

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Received 10 November 2017
Accepted 16 November 2017

Edited by D. Chopra, Indian Institute of Science Education and Research Bhopal, India

Keywords: crystal structure; hydrogen bonding; barbiturates; pharmaceuticals.

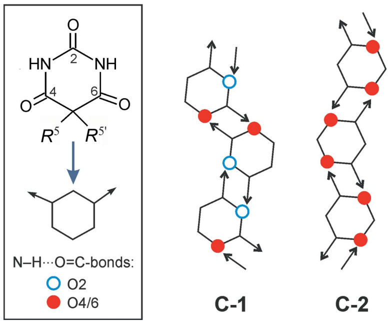
CCDC references: 1586016; 1586015

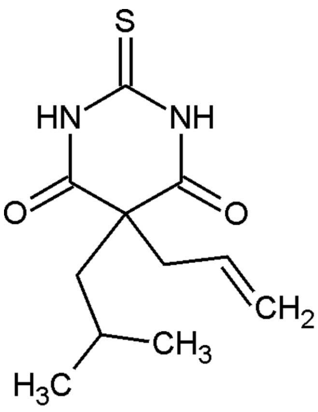
Supporting information: this article has supporting information at journals.iucr.org/e

The molecule of buthalital, (I) [systematic name: 5-(2-methylpropyl)-5-(prop-2-en-1-yl)-2-sulfanylidene-1,3-diazinane-4,6-dione], $C_{11}H_{16}N_2O_2S$, exhibits a planar pyrimidine ring, whereas the pyrimidine ring of methitural, (II) [systematic name: 5-(1-methylbutyl)-5-[2-(methylsulfanyl)ethyl]-2-sulfanylidene-1,3-diazinane-4,6-dione], $C_{12}H_{20}N_2O_2S_2$, is slightly puckered. (I) and (II) contain the same hydrogen-bonded chain structure in which each molecule is connected, *via* four N—H⋯O═C hydrogen bonds, to two other molecules, resulting in a hydrogen-bonded chain displaying a sequence of $R_2^2(8)$ rings. The same type of N—H⋯O═C hydrogen-bonded chain has previously been found in several 5,5-disubstituted derivatives of barbituric acid which are chemically closely related to (I) and (II).

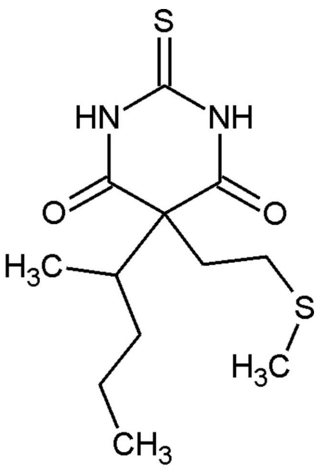
1. Chemical context

Buthalital (I) and methitural (II) are 5,5-disubstituted derivatives of 2-thiobarbituric acid. Compounds of the thiobarbiturate class differ from the corresponding barbiturates in that the ketone group at the 2-position is replaced by a thione group. Thiobarbiturates are used as injection narcotics for the induction of general anaesthesia or to produce complete anaesthesia of short duration. The sodium salt of (I) was originally developed as a short-acting anaesthetic but was found to have an extremely rapid elimination rate. Similarly, (II) was marketed in the 1950s as an ultra-short-acting intravenous anaesthetic.





(I)



(II)

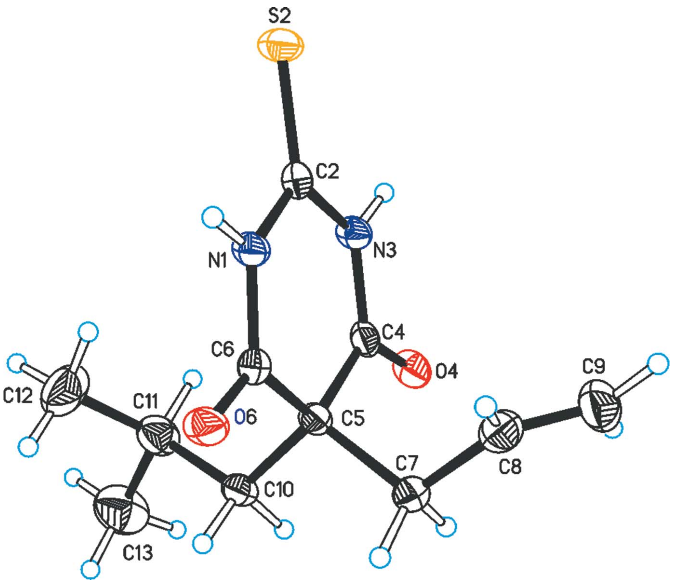


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms drawn as spheres of arbitrary size.

2. Structural commentary

The molecular structure of (I), Fig. 1, shows an almost planar pyrimidine ring (N1, C2, N3, C4 C5, C6) with a root-mean-square (r.m.s.) deviation of its six atoms from the mean plane of 0.016 Å (Fig. 1). The (C7, C8, C5, C10, C11) unit defined by ring atom C5 and two atoms of each of the allyl and isobutyl substituents is nearly planar (r.m.s. deviation = 0.050 Å). The mean plane of this fragment forms an angle of 87.5 (1)° with the plane of the six-membered ring. Additionally, it forms an angle of 77.8 (2)° with the plane of the allyl group defined by C7, C8 and C9. The terminal torsion angles C5—C10—C11—C12 and C5—C10— C11—C13 of the isobutyl substituent are −71.7 (3)° and 165.6 (2)°, respectively.

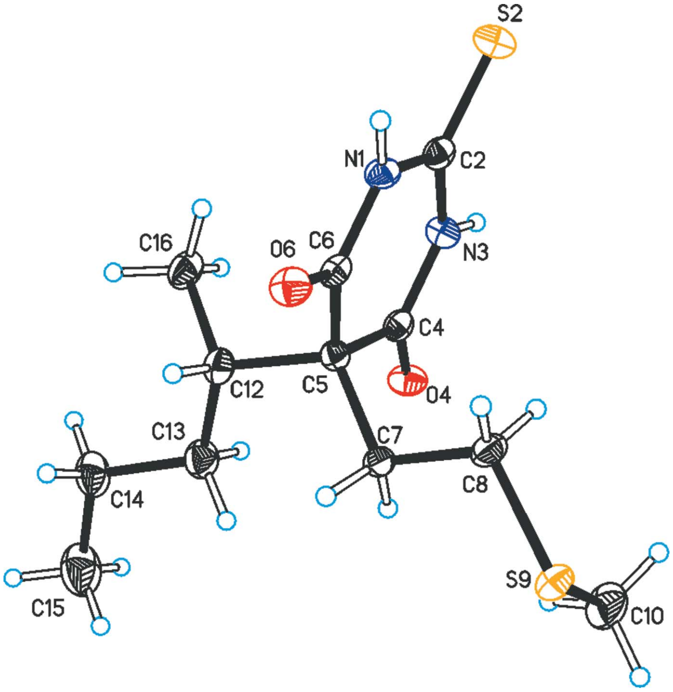


Figure 2
The molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level and H atoms drawn as spheres of arbitrary size.

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{N1-H1}\cdots\mathrm{O4}^{\mathrm{i}}$	0.87 (2)	1.95 (2)	2.815 (2)	174 (2)
$\mathrm{N3-H3}\cdots\mathrm{O6}^{\mathrm{ii}}$	0.86 (2)	2.10 (2)	2.922 (2)	160 (2)

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

The pyrimidine ring (N1, C2, N3, C4 C5, C6) in the molecule of (II) deviates somewhat from planarity (r.m.s. deviation = 0.030 Å); specifically, the distance between C6 and the mean plane defined by the other five ring atoms (r.m.s deviation = 0.005 Å) is 0.104 (2) Å (Fig. 2). The mean plane of the (S9, C8, C7, C5, C12, C16) chain, defined by ring atom C6, three atoms of the 2-(methylthio)ethyl substituent and two atoms of the *sec*-butyl group (r.m.s. deviation = 0.091 Å) forms an angle of 88.64 (5)° with the mean plane of the pyrimidine ring and an angle of 39.0 (1)° with the mean plane of the (C5, C12, C13, C14, C15) fragment of the nearly planar (r.m.s. deviation = 0.070) *sec*-butyl group. In the 2-(methylthio)ethyl substituent, the C10—S9 and C8—S9 bond lengths are 1.794 (2) and 1.803 (2) Å, respectively, and the C7—C8—S9—C10 torsion angle is 82.5 (2)°. The bond between ring atom C5 and atom C12 of the *sec*-butyl group [1.582 (2) Å] is somewhat longer than the analogous distance between C5 and atom C7 of the 2-(methylthio)ethyl group [1.547 (2) Å]. This difference is reminiscent of the difference between equatorial and axial bonds at ring atom C5 found in several 5,5-disubstituted barbituric acid derivatives that exhibit a puckered pyrimidine ring (Gelbrich *et al.*, 2016*b*).

3. Supramolecular features

The crystal structure of (I) contains $\mathrm{N1-H1}\cdots\mathrm{O4}^{\mathrm{i}}$ and $\mathrm{N3-H3}\cdots\mathrm{O6}^{\mathrm{ii}}$ bonds (Fig. 3, Table 1). Each molecule is linked to two neighbouring molecules *via* two-point connections and $R_2^2(8)$ rings (Etter *et al.* 1990, Bernstein *et al.*, 1995). The resulting chain structure (topological type 2C1) contains a twofold screw axis and runs parallel to the *b* axis. The mean planes of neighbouring pyrimidine rings in the chain form an angle of approximately 40° with one another. The chain structure of (I) belongs to the **C-2** type, which also occurs in a number of 5,5-disubstituted barbituric acid derivatives (Gelbrich *et al.*, 2016*a*). The four shortest intermolecular contacts of the sulfur atom (S···H distances between 2.97 and 3.01 Å; close to the sum of van der Waals radii) involve both $\mathrm{CH_2}$ groups of a neighbouring molecule and one $\mathrm{CH_3}$ group belonging to the isobutyl substituent of two other molecules.

Two independent hydrogen bonds, $\mathrm{N1-H1}\cdots\mathrm{O6}^{\mathrm{i}}$ and $\mathrm{N3-H3}\cdots\mathrm{O4}^{\mathrm{ii}}$, are present in the crystal structure of (II). As in (I), each molecule is linked, by two-point connections, to two

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O6^{i}	0.86 (2)	2.07 (2)	2.921 (2)	170 (2)
N3—H3$\cdots$O4^{ii}	0.86 (2)	2.14 (2)	2.963 (2)	160 (2)

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

neighbouring molecules so that a **C-2** chain structure is formed that propagates parallel to the c axis. In this case, the **C-2** chain contains two crystallographically distinct $R_2^2(8)$ rings which are centred either by a twofold axis or an inversion centre (Fig. 4, Table 2). The mean planes of adjacent pyrimidine rings in the same chain are either coplanar with one another (if the corresponding molecules are related by an inversion operation), or they form an angle of 75° (if the molecules are related by a 180° rotation). The sulfur atom S9 of the 2-(methylthio)ethyl substituent forms an intermolecular contact (S$\cdots$H = 2.86 Å) with the *sec*-butyl group of a molecule belonging to a neighbouring chain and S2 lies in close proximity to the methyl group of a 2-(methylthio)ethyl substituent (S$\cdots$H = 2.96 Å).

4. Database survey

The crystal structures of three polymorphs of the keto form of 2-thiobarbituric acid, which is a close structural analogue of (I) and (II), have been determined (Chierotti *et al.*, 2010). Polymorph III (CSD refcode THBARB01) contains an N—H$\cdots$O-bonded layer structure having the **hcb** topology and polymorph IV (THBARB02) an N—H$\cdots$O-bonded framework. Both these structures contain N—H$\cdots$O-bonded $R_2^2(8)$ rings analogous to those present in the hydrogen-bonded chains of (I) and (II), and additionally they contain one-point hydrogen-bond connections between molecules. Form VI of 2-thiobarbituric acid (THBARB03) displays two distinct hydrogen-bonded structures, an N—H$\cdots$O-bonded layer with **sql** topology whose molecules are linked exclusively by one-point connections and an **hcb**-type layer based on N—H$\cdots$O

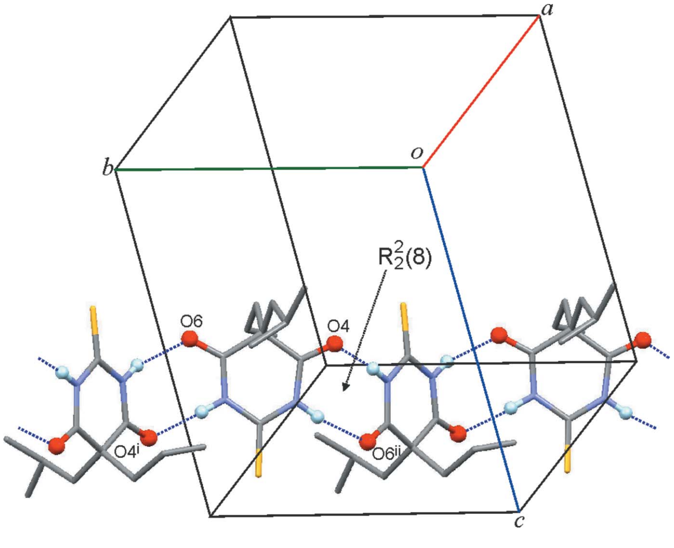


Figure 3
The **C-2**-type bonded chain of (I). O and H atoms directly involved in N—H$\cdots$O interactions are drawn as balls and H atoms bonded to C atoms are omitted for clarity. The chain displays a twofold screw symmetry and contains just one type of $R_2^2(8)$ ring. [Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.]

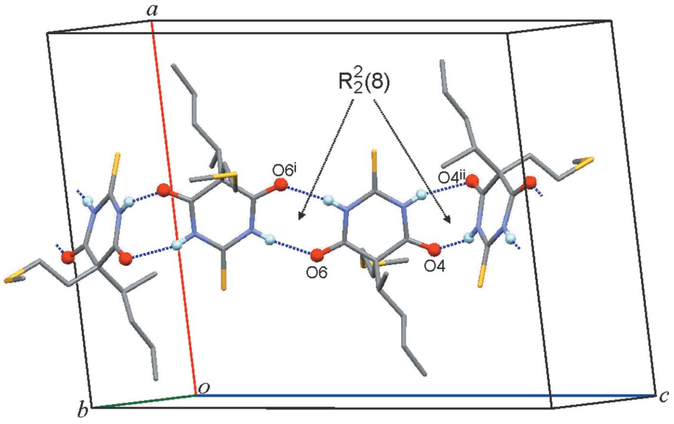


Figure 4
The **C-2**-type bonded chain of (II). O and H atoms directly involved in N—H$\cdots$O interactions are drawn as balls and H atoms bonded to C atoms are omitted for clarity. The chain displays two types of $R_2^2(8)$ ring, which contain an inversion centre (N1—H1$\cdots$O6^{i}) or a twofold axis (N3—H3$\cdots$O4^{ii}). [Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, y, -z+\frac{1}{2}$.]

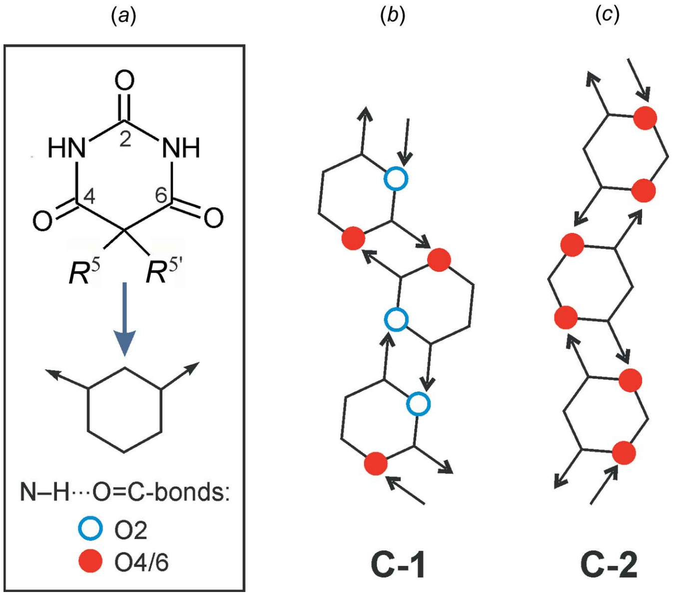


Figure 5
(*a*) Simplified representation of a molecule of a 5,5-disubstituted derivative of barbituric acid. The same scheme can be applied for analogous thiobarbiturates such as (I) and (II) if the O atom of the carbonyl group in position 2 is replaced by a thioxo S atom. (*b*) and (*c*) Schematic representation of the N—H$\cdots$O═C-bonded chain types **C-1** and **C-2** with an underlying 2C1 topology, which are frequently found in barbiturates. The thiobarbiturates (I) and (II) contain chains of the **C-2** type.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{11}H_{16}N_2O_2S$	$C_{12}H_{20}N_2O_2S_2$
M_r	240.32	288.42
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$
Temperature (K)	120	120
a, b, c (Å)	8.7271 (6), 11.6521 (4), 12.5400 (8)	15.1873 (2), 9.0920 (1), 20.8684 (3)
β (°)	96.539 (2)	96.083 (1)
V (Å^3)	1266.89 (13)	2865.34 (6)
Z	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.24	0.37
Crystal size (mm)	0.40 × 0.10 × 0.05	0.15 × 0.15 × 0.10
Data collection		
Diffractometer	Bruker–Nonius Roper CCD camera on κ-goniostat	Bruker–Nonius APEXII CCD camera on κ-goniostat
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2007)	Multi-scan (*SADABS*; Sheldrick, 2007)
T_{min}, T_{max}	0.924, 1.000	0.974, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9476, 2519, 1833	24772, 2813, 2630
R_{int}	0.067	0.034
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.108, 1.04	0.038, 0.084, 1.14
No. of reflections	2519	2813
No. of parameters	170	192
No. of restraints	2	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, −0.27	0.53, −0.30

Computer programs: *DENZO* (Otwinowski & Minor, 1997), *COLLECT* (Hooft, 1998), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008) *Mercury* (Macrae *et al.*, 2006), *PLATON* (Spek, 2009), *publCIF* (Westrip, 2010) and *TOPOS* (Blatov, 2006).

as well as N—H···S bonds, with the latter interaction resulting in $R_2^2(8)$ rings.

Numerous 5,5-substituted derivatives of barbituric acid are known to form N—H···O=C-bonded chains exhibiting the 2C1 topology, with their molecules being linked by two-point connections resulting in the formation of characteristic $R_2^2(8)$ rings. Chains exhibiting these specific properties can be classified into two distinct types, denoted as **C-1** and **C-2** (Gelbrich *et al.*, 2016*a*; see Fig. 5). The less frequent of these two types, **C-2**, is also the chain motif of (I) and (II). It is characterized by the employment of each of the topologically equivalent C4 and C6 carbonyl groups, but not the C2 group, as a hydrogen-bond acceptor.

C-2 chains containing a 2_1 screw axis occur in polymorph III of phenobarbital (PHBARB09), the CH_2Cl_2 solvate of the same compound (EPUDEA) (Zencirci *et al.*, 2010, 2014) and in 5-fluoro-5-phenylbarbituric acid (HEKTOG) (DesMarteau *et al.*, 1994) as well as in (I). By contrast, the **C-2** chains of 6-oxocyclobarbital (OXCBAR) (Chentli-Benchikha *et al.*, 1977) and polymorph III of pentobarbital (FUFTEG02) (Rossi *et al.*, 2012) exhibit glide symmetry. Moreover, polymorph II of barbital (DETBAA02) (Craven *et al.*, 1969) as well as forms I and II of phenobarbital (Zencirci *et al.*, 2010) exhibit **C-2** chains whose $R_2^2(8)$ rings contain crystallographic inversion centres. The crystal structure of methitural (II) is the first example of a **C-2** chain whose $R_2^2(8)$ rings are centred alternately by a twofold rotational axis and an inversion centre.

5. Synthesis and crystallization

Single crystals of (I) were produced by sublimation between two glass slides separated by a spacer ring (height: 1 cm), using a hot bench at a temperature of 403 K. As confirmed by PXRD, the phase investigated by us is identical with that of the original sample from the1940s obtained from our archive. The melting point of this phase of 422 K was determined with hot-stage microscopy. Heating the quench-cooled melt of (I) above 323 K resulted in the crystallization of a second form. Isolated, individual crystals of this second form melted at approximately 387 K. In other experiments, a phase transition from the low-melting form II to a high-melting form I occurred on heating, usually between 378 and 383 K (see Supporting information). These observations are consistent with a previous description by Brandstätter-Kuhnert & Aepkers (1962).

The crystals of (II) investigated in this study were taken from a sample obtained from Merck AG, Darmstadt, Germany. These crystals melted within a relatively broad temperature range between 361 and 366 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were identified in difference maps. Methyl H atoms were idealized and included as rigid groups allowed to rotate but not tip and all other H atoms bonded to carbon atoms were positioned geometrically (C—H = 0.95–0.99 Å). The hydrogen atoms in NH groups were refined with restrained distances [N—H = 0.88 (2) Å]. The $U_{\rm iso}$ parameters of all H atoms were refined freely.

Acknowledgements

We thank Professor S. Coles (Southampton) for providing access to the X-ray diffractometers used in this study.

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supporting information

Acta Cryst. (2017). E**73**, 1908-1912   [https://doi.org/10.1107/S205698901701653X]

Buthalital and methitural – 5,5-substituted derivatives of 2-thiobarbituric acid forming the same type of hydrogen-bonded chain

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Computing details

For both structures, data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006). Software used to prepare material for publication: *PLATON* (Spek, 2009), *publCIF* (Westrip, 2010) and *TOPOS* (Blatov, 2006) for (I); *PLATON* (Spek, 2009) and *publCIF* Westrip (2010) for (II).

5-(2-Methylpropyl)-5-(prop-2-en-1-yl)-2-sulfanylidene-1,3-diazinane-4,6-dione (I)

Crystal data

$C_{11}H_{16}N_2O_2S$
$M_r = 240.32$
Monoclinic, $P2_1/n$
$a = 8.7271\ (6)$ Å
$b = 11.6521\ (4)$ Å
$c = 12.5400\ (8)$ Å
$\beta = 96.539\ (2)°$
$V = 1266.89\ (13)$ Å^3
$Z = 4$

$F(000) = 512$
$D_x = 1.260$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 10435 reflections
$\theta = 2.9–27.5°$
$\mu = 0.24$ mm^{-1}
$T = 120$ K
Prism, colourless
0.40 × 0.10 × 0.05 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)

$T_{min} = 0.924$, $T_{max} = 1.000$
9476 measured reflections
2519 independent reflections
1833 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 26.4°$, $\theta_{min} = 3.3°$
$h = -9 \rightarrow 10$
$k = -12 \rightarrow 13$
$l = -15 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.04$

2519 reflections
170 parameters
2 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.281P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.011 (2)

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}
S2	0.13456 (7)	0.87633 (4)	0.94050 (5)	0.0259 (2)
O4	0.42805 (18)	0.66380 (11)	0.69496 (13)	0.0256 (4)
O6	0.26955 (18)	1.04475 (11)	0.60757 (12)	0.0261 (4)
N1	0.2119 (2)	0.95525 (14)	0.75707 (14)	0.0197 (4)
H1	0.162 (3)	1.0169 (17)	0.771 (2)	0.036 (7)*
N3	0.2876 (2)	0.76850 (14)	0.79944 (14)	0.0192 (4)
H3	0.282 (3)	0.7101 (16)	0.8409 (17)	0.030 (7)*
C2	0.2138 (2)	0.86637 (16)	0.82860 (17)	0.0181 (5)
C4	0.3650 (2)	0.75482 (16)	0.71139 (17)	0.0196 (5)
C5	0.3698 (2)	0.85445 (16)	0.63413 (17)	0.0187 (5)
C6	0.2810 (2)	0.95949 (16)	0.66426 (17)	0.0193 (5)
C7	0.2939 (3)	0.81243 (17)	0.52224 (17)	0.0225 (5)
H7A	0.3022	0.8740	0.4689	0.034 (7)*
H7B	0.3518	0.7451	0.5000	0.034 (7)*
C8	0.1275 (3)	0.7801 (2)	0.52146 (18)	0.0286 (5)
H8	0.0538	0.8398	0.5236	0.038 (7)*
C9	0.0781 (3)	0.6733 (2)	0.5180 (2)	0.0397 (7)
H9A	0.1494	0.6119	0.5157	0.054 (9)*
H9B	−0.0287	0.6576	0.5176	0.051 (8)*
C10	0.5409 (3)	0.88428 (17)	0.62406 (17)	0.0221 (5)
H10A	0.5867	0.8189	0.5884	0.029 (6)*
H10B	0.5423	0.9512	0.5756	0.025 (6)*
C11	0.6456 (3)	0.9114 (2)	0.7264 (2)	0.0322 (6)
H11	0.6314	0.8501	0.7802	0.052 (8)*
C12	0.6132 (3)	1.0262 (3)	0.7760 (2)	0.0494 (8)
H12A	0.6195	1.0872	0.7228	0.074 (11)*
H12B	0.6895	1.0404	0.8382	0.076 (10)*
H12C	0.5096	1.0254	0.7990	0.074 (11)*
C13	0.8130 (3)	0.9075 (3)	0.7015 (3)	0.0484 (8)
H13A	0.8366	0.8305	0.6764	0.068 (10)*
H13B	0.8819	0.9256	0.7666	0.069 (10)*
H13C	0.8278	0.9639	0.6456	0.049 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0311 (4)	0.0251 (3)	0.0237 (3)	0.0012 (2)	0.0123 (3)	0.0027 (2)
O4	0.0280 (9)	0.0144 (7)	0.0365 (10)	0.0023 (6)	0.0129 (7)	0.0001 (6)
O6	0.0392 (10)	0.0170 (8)	0.0238 (9)	0.0019 (6)	0.0113 (7)	0.0035 (6)
N1	0.0239 (11)	0.0145 (9)	0.0222 (10)	0.0010 (7)	0.0086 (8)	0.0010 (7)
N3	0.0234 (10)	0.0139 (9)	0.0212 (10)	0.0015 (7)	0.0063 (8)	0.0034 (7)
C2	0.0164 (11)	0.0172 (10)	0.0203 (11)	−0.0026 (8)	0.0002 (9)	−0.0009 (8)
C4	0.0164 (11)	0.0178 (11)	0.0248 (12)	−0.0042 (8)	0.0031 (9)	−0.0019 (8)
C5	0.0214 (12)	0.0154 (10)	0.0205 (11)	−0.0015 (8)	0.0074 (9)	−0.0004 (8)
C6	0.0222 (12)	0.0160 (10)	0.0200 (12)	−0.0020 (8)	0.0042 (9)	−0.0018 (8)
C7	0.0262 (13)	0.0213 (11)	0.0207 (12)	−0.0024 (9)	0.0063 (10)	−0.0025 (8)
C8	0.0259 (13)	0.0358 (13)	0.0240 (13)	−0.0013 (10)	0.0028 (10)	−0.0040 (10)
C9	0.0355 (16)	0.0477 (16)	0.0343 (15)	−0.0172 (13)	−0.0032 (12)	0.0032 (11)
C10	0.0238 (12)	0.0215 (11)	0.0225 (12)	−0.0024 (8)	0.0088 (10)	0.0005 (8)
C11	0.0269 (14)	0.0405 (14)	0.0287 (14)	−0.0073 (10)	0.0016 (11)	0.0039 (10)
C12	0.0388 (18)	0.068 (2)	0.0405 (17)	−0.0152 (14)	0.0031 (14)	−0.0245 (15)
C13	0.0291 (16)	0.066 (2)	0.0496 (19)	−0.0035 (13)	0.0025 (14)	0.0078 (15)

Geometric parameters (Å, º)

S2—C2	1.638 (2)	C8—C9	1.315 (3)
O4—C4	1.223 (2)	C8—H8	0.9500
O6—C6	1.219 (2)	C9—H9A	0.9500
N1—C2	1.369 (3)	C9—H9B	0.9500
N1—C6	1.371 (3)	C10—C11	1.522 (3)
N1—H1	0.867 (16)	C10—H10A	0.9900
N3—C4	1.367 (3)	C10—H10B	0.9900
N3—C2	1.379 (3)	C11—C12	1.515 (4)
N3—H3	0.861 (16)	C11—C13	1.529 (4)
C4—C5	1.516 (3)	C11—H11	1.0000
C5—C6	1.519 (3)	C12—H12A	0.9800
C5—C10	1.552 (3)	C12—H12B	0.9800
C5—C7	1.561 (3)	C12—H12C	0.9800
C7—C8	1.499 (3)	C13—H13A	0.9800
C7—H7A	0.9900	C13—H13B	0.9800
C7—H7B	0.9900	C13—H13C	0.9800
C2—N1—C6	127.57 (17)	C7—C8—H8	118.3
C2—N1—H1	117.7 (17)	C8—C9—H9A	120.0
C6—N1—H1	114.8 (17)	C8—C9—H9B	120.0
C4—N3—C2	126.79 (17)	H9A—C9—H9B	120.0
C4—N3—H3	117.7 (16)	C11—C10—C5	117.95 (18)
C2—N3—H3	115.5 (16)	C11—C10—H10A	107.8
N1—C2—N3	115.02 (18)	C5—C10—H10A	107.8
N1—C2—S2	122.21 (15)	C11—C10—H10B	107.8
N3—C2—S2	122.77 (15)	C5—C10—H10B	107.8

O4—C4—N3	120.68 (18)	H10A—C10—H10B	107.2
O4—C4—C5	120.70 (19)	C12—C11—C10	114.0 (2)
N3—C4—C5	118.62 (17)	C12—C11—C13	109.7 (2)
C4—C5—C6	113.95 (17)	C10—C11—C13	108.5 (2)
C4—C5—C10	108.69 (17)	C12—C11—H11	108.1
C6—C5—C10	111.26 (16)	C10—C11—H11	108.1
C4—C5—C7	107.13 (16)	C13—C11—H11	108.1
C6—C5—C7	107.46 (17)	C11—C12—H12A	109.5
C10—C5—C7	108.11 (16)	C11—C12—H12B	109.5
O6—C6—N1	120.64 (18)	H12A—C12—H12B	109.5
O6—C6—C5	121.44 (18)	C11—C12—H12C	109.5
N1—C6—C5	117.91 (17)	H12A—C12—H12C	109.5
C8—C7—C5	113.35 (17)	H12B—C12—H12C	109.5
C8—C7—H7A	108.9	C11—C13—H13A	109.5
C5—C7—H7A	108.9	C11—C13—H13B	109.5
C8—C7—H7B	108.9	H13A—C13—H13B	109.5
C5—C7—H7B	108.9	C11—C13—H13C	109.5
H7A—C7—H7B	107.7	H13A—C13—H13C	109.5
C9—C8—C7	123.4 (2)	H13B—C13—H13C	109.5
C9—C8—H8	118.3		

C6—N1—C2—N3	−3.7 (3)	C10—C5—C6—O6	59.5 (3)
C6—N1—C2—S2	176.16 (17)	C7—C5—C6—O6	−58.7 (2)
C4—N3—C2—N1	4.2 (3)	C4—C5—C6—N1	2.0 (3)
C4—N3—C2—S2	−175.64 (17)	C10—C5—C6—N1	−121.3 (2)
C2—N3—C4—O4	178.9 (2)	C7—C5—C6—N1	120.6 (2)
C2—N3—C4—C5	−1.6 (3)	C4—C5—C7—C8	62.7 (2)
O4—C4—C5—C6	177.91 (19)	C6—C5—C7—C8	−60.1 (2)
N3—C4—C5—C6	−1.6 (3)	C10—C5—C7—C8	179.67 (17)
O4—C4—C5—C10	−57.4 (2)	C5—C7—C8—C9	−106.1 (3)
N3—C4—C5—C10	123.1 (2)	C4—C5—C10—C11	−55.6 (2)
O4—C4—C5—C7	59.2 (3)	C6—C5—C10—C11	70.6 (2)
N3—C4—C5—C7	−120.3 (2)	C7—C5—C10—C11	−171.58 (18)
C2—N1—C6—O6	179.9 (2)	C5—C10—C11—C12	−71.7 (3)
C2—N1—C6—C5	0.6 (3)	C5—C10—C11—C13	165.64 (19)
C4—C5—C6—O6	−177.20 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.87 (2)	1.95 (2)	2.815 (2)	174 (2)
N3—H3···O6^{ii}	0.86 (2)	2.10 (2)	2.922 (2)	160 (2)

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

5-(1-Methylbutyl)-5-[2-(methylsulfanyl)ethyl]-2-sulfanylidene-1,3-diazinane-4,6-dione (II)

Crystal data

$C_{12}H_{20}N_2O_2S_2$
$M_r = 288.42$
Monoclinic, $C2/c$
$a = 15.1873$ (2) Å
$b = 9.0920$ (1) Å
$c = 20.8684$ (3) Å
$\beta = 96.083$ (1)°
$V = 2865.34$ (6) Å^3
$Z = 8$
$F(000) = 1232$
$D_x = 1.337$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 29667 reflections
$\theta = 2.9$–27.5°
$\mu = 0.37$ mm^{-1}
$T = 120$ K
Block, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Bruker–Nonius APEXII CCD camera on κ-goniostat diffractometer
Radiation source: Bruker-Nonius FR591 rotating anode
10cm confocal mirrors monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ & ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)
$T_{\min} = 0.974$, $T_{\max} = 1.000$
24772 measured reflections
2813 independent reflections
2630 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 26.0°$, $\theta_{\min} = 3.2°$
$h = -18 \rightarrow 18$
$k = -11 \rightarrow 11$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.084$
$S = 1.14$
2813 reflections
192 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2 + 6.3729P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ 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 (Å^2)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
S2	−0.17769 (3)	0.62565 (6)	0.34779 (2)	0.02411 (13)
S9	0.14236 (3)	1.10685 (5)	0.51192 (2)	0.02392 (13)
O4	0.09157 (9)	0.87624 (15)	0.30012 (6)	0.0218 (3)
O6	0.09747 (9)	0.59147 (14)	0.49086 (6)	0.0220 (3)
N1	−0.02312 (10)	0.60656 (17)	0.41868 (7)	0.0177 (3)
H1	−0.0510 (14)	0.551 (2)	0.4430 (10)	0.031 (6)*
N3	−0.02774 (10)	0.75738 (17)	0.32870 (7)	0.0181 (3)
H3	−0.0574 (14)	0.798 (2)	0.2962 (9)	0.029 (6)*
C2	−0.07264 (12)	0.6645 (2)	0.36566 (8)	0.0173 (4)

C4	0.06055 (12)	0.79499 (19)	0.33818 (8)	0.0167 (4)
C6	0.06356 (12)	0.63907 (19)	0.43924 (8)	0.0171 (4)
C7	0.16068 (12)	0.85980 (19)	0.43567 (8)	0.0161 (4)
H7A	0.2088	0.8208	0.4667	0.020 (5)*
H7B	0.1875	0.9281	0.4063	0.021 (5)*
C5	0.11666 (11)	0.73082 (19)	0.39593 (8)	0.0158 (4)
C8	0.09525 (13)	0.9443 (2)	0.47235 (9)	0.0218 (4)
H8A	0.0735	0.8786	0.5051	0.029 (6)*
H8B	0.0437	0.9733	0.4419	0.031 (6)*
C10	0.13117 (16)	1.2337 (2)	0.44571 (12)	0.0345 (5)
H10A	0.1605	1.1935	0.4099	0.071 (10)*
H10B	0.1586	1.3277	0.4594	0.053 (8)*
H10C	0.0682	1.2492	0.4316	0.047 (8)*
C12	0.18817 (13)	0.6231 (2)	0.37204 (9)	0.0217 (4)
H12	0.2155	0.5694	0.4110	0.033 (6)*
C13	0.26315 (13)	0.7017 (2)	0.34349 (10)	0.0258 (4)
H13A	0.2880	0.7777	0.3742	0.040 (7)*
H13B	0.2390	0.7523	0.3034	0.043 (7)*
C14	0.33787 (14)	0.5984 (2)	0.32810 (11)	0.0308 (5)
H14A	0.3564	0.5368	0.3662	0.029 (6)*
H14B	0.3159	0.5324	0.2922	0.054 (8)*
C15	0.41659 (17)	0.6846 (3)	0.30960 (13)	0.0438 (6)
H15A	0.3988	0.7425	0.2708	0.072 (10)*
H15B	0.4640	0.6164	0.3011	0.053 (8)*
H15C	0.4380	0.7508	0.3449	0.073 (10)*
C16	0.14371 (14)	0.5061 (2)	0.32611 (9)	0.0250 (4)
H16A	0.1226	0.5521	0.2849	0.036 (7)*
H16B	0.0935	0.4628	0.3452	0.038 (7)*
H16C	0.1867	0.4290	0.3190	0.040 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0188 (2)	0.0307 (3)	0.0228 (2)	−0.0057 (2)	0.00256 (18)	0.0002 (2)
S9	0.0251 (3)	0.0196 (2)	0.0270 (3)	−0.00207 (19)	0.00215 (19)	−0.00781 (19)
O4	0.0228 (7)	0.0243 (7)	0.0184 (6)	−0.0061 (6)	0.0029 (5)	0.0052 (5)
O6	0.0248 (7)	0.0210 (7)	0.0195 (7)	−0.0020 (6)	−0.0006 (5)	0.0056 (5)
N1	0.0194 (8)	0.0159 (7)	0.0183 (8)	−0.0032 (6)	0.0045 (6)	0.0025 (6)
N3	0.0177 (8)	0.0212 (8)	0.0152 (7)	−0.0008 (6)	0.0009 (6)	0.0030 (6)
C2	0.0211 (9)	0.0159 (9)	0.0152 (8)	−0.0005 (7)	0.0038 (7)	−0.0027 (7)
C4	0.0200 (9)	0.0157 (9)	0.0145 (8)	0.0003 (7)	0.0028 (7)	−0.0030 (7)
C6	0.0209 (9)	0.0119 (8)	0.0186 (9)	−0.0001 (7)	0.0029 (7)	−0.0018 (7)
C7	0.0164 (9)	0.0147 (8)	0.0172 (8)	−0.0012 (7)	0.0023 (7)	−0.0011 (7)
C5	0.0153 (8)	0.0155 (8)	0.0169 (8)	0.0004 (7)	0.0026 (7)	0.0000 (7)
C8	0.0230 (10)	0.0169 (9)	0.0266 (10)	−0.0043 (8)	0.0081 (8)	−0.0067 (8)
C10	0.0388 (13)	0.0191 (10)	0.0469 (13)	0.0002 (9)	0.0106 (11)	0.0060 (10)
C12	0.0222 (10)	0.0183 (9)	0.0250 (10)	0.0029 (8)	0.0047 (8)	−0.0032 (8)
C13	0.0249 (10)	0.0237 (10)	0.0299 (10)	0.0025 (8)	0.0081 (8)	0.0006 (8)

C14	0.0283 (11)	0.0317 (12)	0.0345 (12)	0.0080 (9)	0.0122 (9)	−0.0006 (9)
C15	0.0387 (14)	0.0430 (14)	0.0528 (15)	0.0091 (12)	0.0189 (12)	0.0070 (13)
C16	0.0312 (11)	0.0189 (9)	0.0258 (10)	0.0007 (8)	0.0078 (8)	−0.0048 (8)

Geometric parameters (Å, º)

S2—C2	1.6381 (19)	C8—H8B	0.9900
S9—C10	1.794 (2)	C10—H10A	0.9800
S9—C8	1.8033 (19)	C10—H10B	0.9800
O4—C4	1.216 (2)	C10—H10C	0.9800
O6—C6	1.223 (2)	C12—C13	1.519 (3)
N1—C6	1.373 (2)	C12—C16	1.539 (3)
N1—C2	1.375 (2)	C12—H12	1.0000
N1—H1	0.858 (16)	C13—C14	1.533 (3)
N3—C2	1.373 (2)	C13—H13A	0.9900
N3—C4	1.378 (2)	C13—H13B	0.9900
N3—H3	0.856 (16)	C14—C15	1.513 (3)
C4—C5	1.517 (2)	C14—H14A	0.9900
C6—C5	1.522 (2)	C14—H14B	0.9900
C7—C8	1.525 (2)	C15—H15A	0.9800
C7—C5	1.547 (2)	C15—H15B	0.9800
C7—H7A	0.9900	C15—H15C	0.9800
C7—H7B	0.9900	C16—H16A	0.9800
C5—C12	1.582 (2)	C16—H16B	0.9800
C8—H8A	0.9900	C16—H16C	0.9800
C10—S9—C8	99.99 (10)	S9—C10—H10B	109.5
C6—N1—C2	126.40 (15)	H10A—C10—H10B	109.5
C6—N1—H1	117.3 (16)	S9—C10—H10C	109.5
C2—N1—H1	116.1 (16)	H10A—C10—H10C	109.5
C2—N3—C4	127.29 (16)	H10B—C10—H10C	109.5
C2—N3—H3	117.3 (16)	C13—C12—C16	112.25 (16)
C4—N3—H3	115.4 (16)	C13—C12—C5	113.62 (15)
N3—C2—N1	115.21 (16)	C16—C12—C5	110.71 (15)
N3—C2—S2	122.31 (14)	C13—C12—H12	106.6
N1—C2—S2	122.47 (14)	C16—C12—H12	106.6
O4—C4—N3	119.72 (16)	C5—C12—H12	106.6
O4—C4—C5	121.92 (16)	C12—C13—C14	113.35 (17)
N3—C4—C5	118.36 (15)	C12—C13—H13A	108.9
O6—C6—N1	119.97 (16)	C14—C13—H13A	108.9
O6—C6—C5	121.12 (16)	C12—C13—H13B	108.9
N1—C6—C5	118.89 (15)	C14—C13—H13B	108.9
C8—C7—C5	112.56 (14)	H13A—C13—H13B	107.7
C8—C7—H7A	109.1	C15—C14—C13	111.01 (19)
C5—C7—H7A	109.1	C15—C14—H14A	109.4
C8—C7—H7B	109.1	C13—C14—H14A	109.4
C5—C7—H7B	109.1	C15—C14—H14B	109.4
H7A—C7—H7B	107.8	C13—C14—H14B	109.4

C4—C5—C6	113.21 (15)	H14A—C14—H14B	108.0
C4—C5—C7	107.99 (14)	C14—C15—H15A	109.5
C6—C5—C7	108.86 (14)	C14—C15—H15B	109.5
C4—C5—C12	109.53 (14)	H15A—C15—H15B	109.5
C6—C5—C12	105.81 (14)	C14—C15—H15C	109.5
C7—C5—C12	111.49 (14)	H15A—C15—H15C	109.5
C7—C8—S9	113.25 (13)	H15B—C15—H15C	109.5
C7—C8—H8A	108.9	C12—C16—H16A	109.5
S9—C8—H8A	108.9	C12—C16—H16B	109.5
C7—C8—H8B	108.9	H16A—C16—H16B	109.5
S9—C8—H8B	108.9	C12—C16—H16C	109.5
H8A—C8—H8B	107.7	H16A—C16—H16C	109.5
S9—C10—H10A	109.5	H16B—C16—H16C	109.5

C4—N3—C2—N1	1.7 (3)	N1—C6—C5—C7	128.90 (16)
C4—N3—C2—S2	−178.33 (14)	O6—C6—C5—C12	67.0 (2)
C6—N1—C2—N3	3.8 (3)	N1—C6—C5—C12	−111.17 (17)
C6—N1—C2—S2	−176.19 (14)	C8—C7—C5—C4	73.15 (18)
C2—N3—C4—O4	178.09 (17)	C8—C7—C5—C6	−50.13 (19)
C2—N3—C4—C5	−1.0 (3)	C8—C7—C5—C12	−166.48 (15)
C2—N1—C6—O6	172.51 (17)	C5—C7—C8—S9	−173.66 (12)
C2—N1—C6—C5	−9.3 (3)	C10—S9—C8—C7	82.54 (16)
O4—C4—C5—C6	176.79 (16)	C4—C5—C12—C13	73.5 (2)
N3—C4—C5—C6	−4.2 (2)	C6—C5—C12—C13	−164.15 (16)
O4—C4—C5—C7	56.2 (2)	C7—C5—C12—C13	−46.0 (2)
N3—C4—C5—C7	−124.77 (16)	C4—C5—C12—C16	−53.9 (2)
O4—C4—C5—C12	−65.4 (2)	C6—C5—C12—C16	68.47 (19)
N3—C4—C5—C12	113.64 (17)	C7—C5—C12—C16	−173.34 (15)
O6—C6—C5—C4	−173.00 (16)	C16—C12—C13—C14	−60.5 (2)
N1—C6—C5—C4	8.8 (2)	C5—C12—C13—C14	172.91 (17)
O6—C6—C5—C7	−52.9 (2)	C12—C13—C14—C15	−171.28 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O6^{i}	0.86 (2)	2.07 (2)	2.921 (2)	170 (2)
N3—H3···O4^{ii}	0.86 (2)	2.14 (2)	2.963 (2)	160 (2)

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