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Crystal structure of a new monoclinic polymorph of 2,4-dihydroxybenzaldehyde 4-methylthiosemicarbazone

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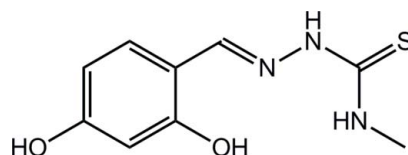
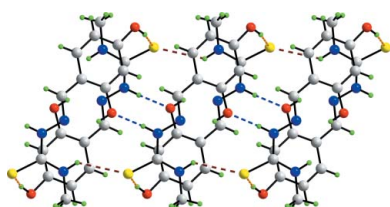
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The title compound, C₉H₁₁N₃O₂S, is a second monoclinic (*P*₂₁/*c*) polymorph of the previously reported *Cc* form [Tan *et al.* (2008*b*). *Acta Cryst.* **E64**, o2224]. The molecule is non-planar, with the dihedral angle between the N₃CS residue (r.m.s. deviation = 0.0816 Å) and the benzene ring being 21.36 (4)°. The conformation about the C=N bond [1.292 (2) Å] is *E*, the two N-bound H atoms are *anti*, and the inner hydroxy O-bound and outer amide N-bound H atoms form intramolecular hydrogen bonds to the imine N atom. Crucially, the H atom of the outer hydroxy group is approximately *syn* to the H atom of the benzene C atom connecting the two C atoms bearing the hydroxy substituents. This arrangement enables the formation of supramolecular tubes aligned along [010] and sustained by N—H···O, O—H···S and N—H···S hydrogen bonds; the tubes pack with no specific interactions between them. While the molecular structure in the *Cc* form is comparable, the H atom of the outer hydroxy group is approximately *anti*, rather than *syn*. This different orientation leads to the formation a three-dimensional architecture based on N—H···O and O—H···S hydrogen bonds.

1. Chemical context

In a review of the biological applications of metal complexes of thiosemicarbazone derivatives, Dilworth & Hueting (2012) highlighted the various biological roles exhibited by this class of compound. Thus, these may have therapeutic potential, for example being cytotoxic and capable of inhibiting both ribonuclease reductase and topoisomerase II. Metal complexes of thiosemicarbazones can also function as diagnostic agents in imaging/diagnostic applications. In the context of this biological relevance, the specific title compound of the present report has been coordinated as an *N,O,S*-tridentate dianion to zinc(II) and the resultant complex explored for activity against prostate cancer (Tan *et al.*, 2012).



The crystal structure of the title molecule has been reported previously as a *Cc* polymorph (Tan *et al.*, 2008*b*). Following on from previous structural work on related compounds (Affan *et al.*, 2013), the title compound was prepared and routine screening of the crystals indicated that this crystallizes as a second monoclinic (*P*₂₁/*c*) polymorph. The crystal and mol-

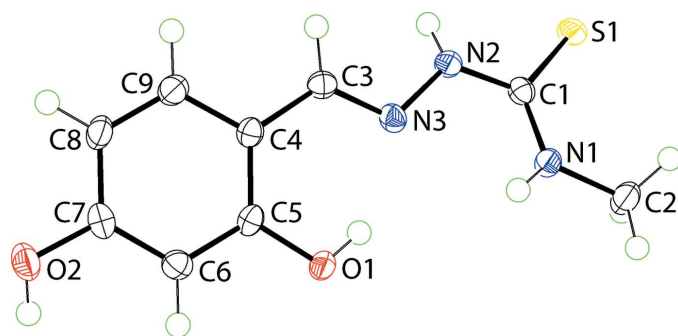


Figure 1
The molecular structure of the title compound in the $P2_1/c$ polymorph, showing the atom labelling and displacement ellipsoids at the 70% probability level.

ecular structure of the second form of the title compound is reported herein and compared with the original Cc polymorph.

2. Structural commentary

The molecular structure found in the new monoclinic ($P2_1/c$) polymorph is shown in Fig. 1. The molecule is non-planar with a twist about the C1–N2 bond being evident as seen in (i) the N3–N2–C1–S1 torsion angle of $164.83(11)^\circ$ and (ii) the dihedral angle between the N₃CS residue (r.m.s. deviation = 0.0816 \AA) and benzene ring of $21.36(4)^\circ$. The conformation about the C3=C=N3 bond [$1.292(2) \text{ \AA}$] is *E*, the two N-bound H atoms are *anti*, and within the molecule, both the O1- and N1-bound H atoms form intramolecular hydrogen bonds to the imine-N3 atom, Table 1. The O2–H_{2o} H atom is approximately *syn* to the C6–H₆ H atom.

To a first approximation, the molecular structure found in the Cc polymorph (Tan *et al.*, 2008*b*), reported to be isolated also from an ethanol solution, is similar, but two significant differences are noted. These are highlighted in the overlay diagram shown in Fig. 2. With the N3–N2–C1–S1 torsion angle being $-172.5(2)^\circ$, the twist about the C1–N2 bond deviates by about 8° , toward planarity, from that in the $P2_1/c$ form. However, the dihedral angle between the N₃CS residue and benzene ring of $23.1(9)^\circ$ is a little wider in the Cc form as the terminal methyl group is slightly twisted out of the CN₃S plane: the C2–N1–C1–S1 torsion angle is $-3.1(5)^\circ$ *cf.* to

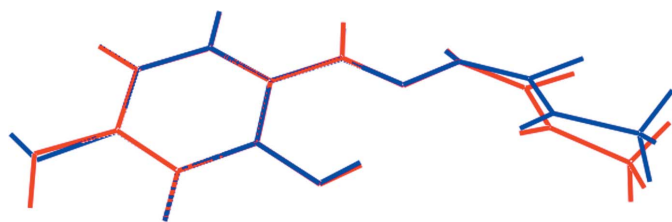


Figure 2
Overlay diagram of the molecules in the $P2_1/n$ polymorph (red image) and in the Cc form (blue). The molecules have been overlapped so the benzene rings are coincident.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 o ···N3	0.83 (2)	1.97 (2)	2.6992 (17)	147 (2)
N1–H1 n ···N3	0.815 (19)	2.35 (2)	2.7080 (19)	107.1 (16)
O2–H2 o ···S1 ⁱ	0.90 (2)	2.37 (2)	3.1918 (12)	152 (2)
N1–H1 n ···S1 ⁱⁱ	0.815 (19)	2.763 (18)	3.3883 (13)	134.9 (17)
N2–H2 n ···O1 ⁱⁱⁱ	0.90 (2)	2.08 (2)	2.9527 (17)	162 (2)

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

$1.2(2)^\circ$ in the $P2_1/c$ form. The major and most significant difference arises in the relative orientation of the outer hydroxy group where the H_{2o} atom is *anti* to the C6–H₆ H atom *cf.* approximately *syn* in the $P2_1/c$ form. This has a major consequence upon the crystal packing in the two forms as discussed in §3.

The calculated density for the $P2_1/c$ form is 1.496 g cm^{-3} and the packing efficiency (KPI), calculated by *PLATON* (Spek, 2009), is 73.1%. These values are lower than the comparable values in the Cc form, *i.e.* 1.521 g cm^{-3} and 74.4%, respectively, suggesting that the Cc form is the more stable.

3. Supramolecular features

In the crystal packing of the $P2_1/c$ polymorph, conventional hydrogen bonding interactions lead to the formation of a supramolecular tube, Fig. 3 and Table 1. Here, the inner N2–H_{2n} atom forms a hydrogen bond to a translationally related inner O1 atom, and the bifurcated S1 atom accepts hydrogen bonds from the outer, centrosymmetrically related, O2–H_{2o} and a translationally related, outer N1–H_{1n} atom. The tubes are aligned along the b axis and pack with no specific intermolecular interactions between them, Fig. 4. A distinctive crystal packing pattern is noted in the Cc polymorph (Tan *et al.*, 2008*b*). Here, the inner N2–H_{2n} atom forms a hydrogen bond to a glide-related inner O1 atom, leading to a supramolecular layer that stacks along the a axis. The S1 atoms project to one side of the layer and the outer O2–H_{2o} atoms,

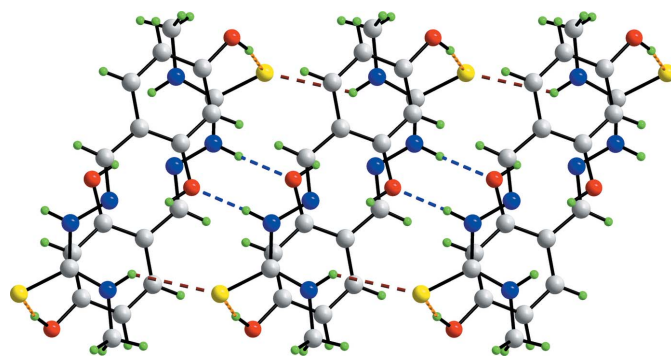


Figure 3
Supramolecular tube along the b axis in the structure of the $P2_1/c$ polymorph sustained by N–H···O, O–H···S and N–H···S hydrogen bonds, shown as blue, orange and brown dashed lines, respectively (see Table 1 for details).

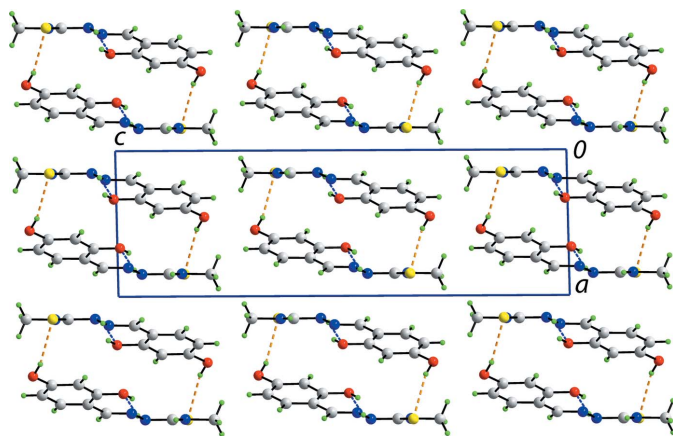


Figure 4
View in projection down the *b* axis of the unit-cell contents of the *P*₂₁/*c* polymorph, highlighting the packing of the supramolecular tubes.

with the *anti* disposition (see above), lie to the other. These form hydrogen bonds so that a three-dimensional architecture ensues, Fig. 5. In this scenario, the outer N1–H1_{*n*} atom only participates in an intramolecular hydrogen bond to the N3 atom, as does in the inner O1–H1_{*o*} atom.

4. Database survey

Given the interest in semithiocarbazones owing to their biological potential, it is not surprising that a search of Version 5.35 (plus May updates) of the Cambridge Crystallographic Database (Groom & Allen, 2014) revealed almost 100 hits for the CC(H)=NN(H)C(=S)N(H)C fragment. The only restriction in the search was that the heaviest atom be S. In the

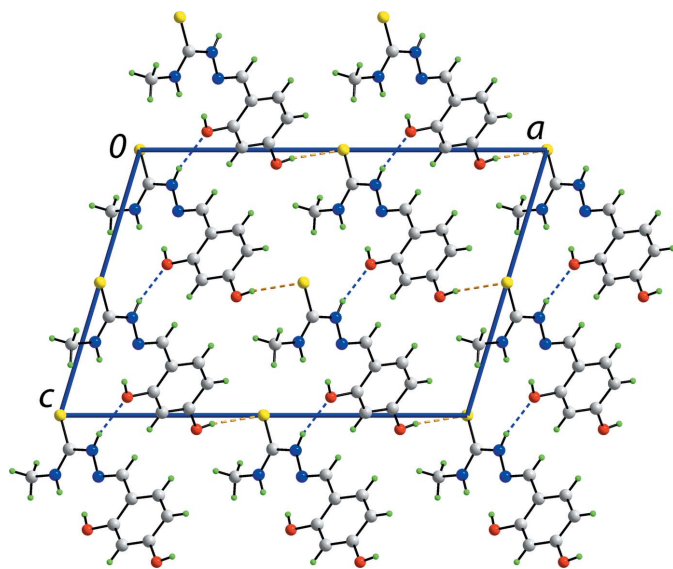


Figure 5
View in projection down the *b* axis of the unit-cell contents of the *C*_{*c*} polymorph, highlighting the the stacking of the layers along the *a* axis, sustained by N–H⋯O hydrogen bonds (blue dashed lines), and their connection by O–H⋯S hydrogen bonds (orange dashed lines).

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₉ H ₁₁ N ₃ O ₂ S
<i>M_r</i>	225.27
Crystal system, space group	Monoclinic, <i>P</i> ₂₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3058 (2), 6.0582 (1), 22.6041 (6)
β (°)	91.100 (2)
<i>V</i> (Å ³)	1000.27 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.31
Crystal size (mm)	0.48 × 0.19 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T_{min}</i> , <i>T_{max}</i>	0.866, 0.957
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	9696, 2302, 1950
<i>R_{int}</i>	0.027
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.086, 1.06
No. of reflections	2302
No. of parameters	153
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.30, -0.31

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS2014* and *SHELXL2014* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

absence of this restriction there were nearly 400 hits. Of the smaller set of structures, there was only one pair of polymorphs, namely two triclinic (*P* $\bar{1}$) forms for salicylaldehyde 4-phenylthiosemicarbazone, one with *Z*' = 3 (Seena *et al.*, 2008) and the other with *Z*' = 2 (Rubčić *et al.*, 2008). The most closely related structure in the literature is the N-Et derivative, reported twice (Tan *et al.*, 2008*a*; Hussein *et al.*, 2014). This structure exhibits the same molecular attributes as described above for the N-Me polymorphs, *i.e.* conformation, relative disposition of key atoms and intramolecular hydrogen bonding.

5. Synthesis and crystallization

A solution of 2,4-dihydroxybenzaldehyde (0.65 g, 4.75 mmol) in ethanol (20 ml) was added to a solution of 4-methyl-3-thiosemicarbazide (0.5 g, 4.75 mmol) in ethanol (20 ml). The resulting brown solution was refluxed with stirring for 2 h, and then filtered, washed with ethanol and dried *in vacuo* over silica gel. The filtrate was left to stand at room temperature for two days after which colourless block-like crystals were obtained (yield 0.79 g, 74%). M.p: 471–473 K. FT-IR (KBr, cm⁻¹) ν_{max}: 3377 (*s*, OH), 3190 (*s*, NH), 1615 (*m*, C=N), 1558 (*s*, C–O), 1012 (*m*, N–N), 1360, 845 (*w*, C=S). Analysis calculated for C₉H₁₁N₃O₂S: C, 47.94; H, 4.88; N, 18.64%. Found: C, 48.0; H, 4.68; N, 18.52%.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon-bound H-atoms were placed in calculated positions ($C-H = 0.95-0.98 \text{ \AA}$) and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $= 1.2U_{eq}(C)$ for other H atoms. The O- and N-bound H-atoms were located in a difference Fourier map and freely refined.

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Crystal structure of a new monoclinic polymorph of 2,4-dihydroxybenzaldehyde 4-methylthiosemicarbazone

M. A. Salam, Mouayed A. Hussein and Edward R. T. Tiekink

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINTE* (Bruker, 2009); data reduction: *SAINTE* (Bruker, 2009); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

2,4-Dihydroxybenzaldehyde 4-methylthiosemicarbazone

Crystal data

C₉H₁₁N₃O₂S

$M_r = 225.27$

Monoclinic, $P2_1/c$

$a = 7.3058$ (2) Å

$b = 6.0582$ (1) Å

$c = 22.6041$ (6) Å

$\beta = 91.100$ (2)°

$V = 1000.27$ (4) Å³

$Z = 4$

$F(000) = 472$

$D_x = 1.496$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3917 reflections

$\theta = 3.3$ – 29.8 °

$\mu = 0.31$ mm⁻¹

$T = 100$ K

Block, colourless

$0.48 \times 0.19 \times 0.14$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.866$, $T_{\max} = 0.957$

9696 measured reflections

2302 independent reflections

1950 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 1.8$ °

$h = -9 \rightarrow 9$

$k = -7 \rightarrow 7$

$l = -29 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.086$

$S = 1.06$

2302 reflections

153 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.7405P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.30$ e Å⁻³

$\Delta\rho_{\min} = -0.31$ e Å⁻³

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.15271 (5)	1.11056 (7)	1.14702 (2)	0.01707 (12)
O1	0.33247 (16)	0.2527 (2)	1.00557 (5)	0.0174 (3)
H1o	0.301 (3)	0.362 (4)	1.0247 (11)	0.044 (7)*
O2	0.45517 (16)	0.0527 (2)	0.80619 (5)	0.0204 (3)
H2o	0.541 (3)	-0.033 (4)	0.8232 (11)	0.051 (7)*
N1	0.15573 (18)	0.6695 (2)	1.14178 (6)	0.0148 (3)
H1n	0.153 (3)	0.557 (3)	1.1220 (9)	0.019 (5)*
N2	0.15295 (18)	0.8552 (2)	1.05291 (6)	0.0152 (3)
H2n	0.183 (3)	0.984 (4)	1.0359 (9)	0.029 (5)*
N3	0.19726 (17)	0.6617 (2)	1.02301 (6)	0.0139 (3)
C1	0.1544 (2)	0.8599 (3)	1.11312 (7)	0.0135 (3)
C2	0.1526 (2)	0.6471 (3)	1.20604 (7)	0.0197 (4)
H2A	0.2699	0.6968	1.2231	0.030*
H2B	0.1326	0.4920	1.2164	0.030*
H2C	0.0534	0.7374	1.2217	0.030*
C3	0.1997 (2)	0.6841 (3)	0.96619 (7)	0.0141 (3)
H3	0.1592	0.8197	0.9494	0.017*
C4	0.2616 (2)	0.5119 (3)	0.92679 (7)	0.0137 (3)
C5	0.3302 (2)	0.3078 (3)	0.94674 (7)	0.0135 (3)
C6	0.3978 (2)	0.1534 (3)	0.90734 (7)	0.0154 (3)
H6	0.4461	0.0173	0.9214	0.019*
C7	0.3941 (2)	0.1999 (3)	0.84699 (7)	0.0157 (3)
C8	0.3264 (2)	0.4006 (3)	0.82584 (7)	0.0177 (3)
H8	0.3239	0.4312	0.7846	0.021*
C9	0.2630 (2)	0.5540 (3)	0.86554 (7)	0.0168 (3)
H9	0.2192	0.6920	0.8512	0.020*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0239 (2)	0.0115 (2)	0.0158 (2)	0.00296 (15)	0.00059 (15)	-0.00209 (15)
O1	0.0274 (6)	0.0135 (6)	0.0114 (6)	0.0017 (5)	0.0029 (5)	0.0007 (5)
O2	0.0214 (6)	0.0243 (7)	0.0154 (6)	0.0041 (5)	0.0010 (5)	-0.0062 (5)
N1	0.0223 (7)	0.0099 (7)	0.0120 (7)	-0.0017 (5)	0.0015 (5)	-0.0019 (6)
N2	0.0215 (7)	0.0103 (7)	0.0137 (7)	0.0012 (5)	0.0019 (5)	-0.0007 (5)
N3	0.0163 (6)	0.0116 (6)	0.0139 (7)	-0.0005 (5)	0.0011 (5)	-0.0023 (5)
C1	0.0119 (7)	0.0145 (8)	0.0141 (8)	0.0005 (6)	0.0004 (6)	-0.0009 (6)
C2	0.0279 (9)	0.0177 (8)	0.0137 (8)	-0.0017 (7)	0.0020 (6)	0.0019 (7)
C3	0.0144 (7)	0.0125 (7)	0.0153 (8)	-0.0008 (6)	0.0001 (6)	0.0006 (6)

C4	0.0140 (7)	0.0143 (8)	0.0129 (7)	-0.0016 (6)	0.0011 (6)	0.0002 (6)
C5	0.0145 (7)	0.0150 (8)	0.0110 (7)	-0.0036 (6)	0.0004 (5)	0.0005 (6)
C6	0.0150 (7)	0.0136 (8)	0.0177 (8)	-0.0006 (6)	0.0018 (6)	0.0009 (6)
C7	0.0139 (7)	0.0180 (8)	0.0152 (8)	-0.0016 (6)	0.0025 (6)	-0.0043 (6)
C8	0.0184 (7)	0.0240 (9)	0.0106 (7)	0.0022 (6)	0.0006 (6)	0.0008 (7)
C9	0.0163 (7)	0.0187 (8)	0.0153 (8)	0.0008 (6)	0.0005 (6)	0.0027 (7)

Geometric parameters (Å, °)

S1—C1	1.7011 (16)	C2—H2B	0.9800
O1—C5	1.3707 (19)	C2—H2C	0.9800
O1—H1o	0.83 (3)	C3—C4	1.449 (2)
O2—C7	1.3640 (19)	C3—H3	0.9500
O2—H2o	0.90 (3)	C4—C5	1.405 (2)
N1—C1	1.323 (2)	C4—C9	1.408 (2)
N1—C2	1.459 (2)	C5—C6	1.389 (2)
N1—H1n	0.81 (2)	C6—C7	1.393 (2)
N2—C1	1.361 (2)	C6—H6	0.9500
N2—N3	1.3945 (18)	C7—C8	1.394 (2)
N2—H2n	0.90 (2)	C8—C9	1.378 (2)
N3—C3	1.292 (2)	C8—H8	0.9500
C2—H2A	0.9800	C9—H9	0.9500
C5—O1—H1o	108.3 (17)	C4—C3—H3	118.5
C7—O2—H2o	108.9 (16)	C5—C4—C9	117.76 (14)
C1—N1—C2	124.63 (14)	C5—C4—C3	123.32 (14)
C1—N1—H1n	117.4 (14)	C9—C4—C3	118.82 (14)
C2—N1—H1n	117.9 (14)	O1—C5—C6	117.41 (14)
C1—N2—N3	120.33 (13)	O1—C5—C4	121.55 (14)
C1—N2—H2n	114.2 (13)	C6—C5—C4	121.04 (14)
N3—N2—H2n	117.6 (13)	C5—C6—C7	119.46 (15)
C3—N3—N2	113.67 (13)	C5—C6—H6	120.3
N1—C1—N2	118.11 (14)	C7—C6—H6	120.3
N1—C1—S1	123.91 (12)	O2—C7—C6	122.00 (15)
N2—C1—S1	117.98 (12)	O2—C7—C8	117.19 (14)
N1—C2—H2A	109.5	C6—C7—C8	120.81 (14)
N1—C2—H2B	109.5	C9—C8—C7	119.10 (15)
H2A—C2—H2B	109.5	C9—C8—H8	120.4
N1—C2—H2C	109.5	C7—C8—H8	120.4
H2A—C2—H2C	109.5	C8—C9—C4	121.80 (15)
H2B—C2—H2C	109.5	C8—C9—H9	119.1
N3—C3—C4	123.08 (15)	C4—C9—H9	119.1
N3—C3—H3	118.5		
C1—N2—N3—C3	-176.54 (14)	C3—C4—C5—C6	-176.13 (14)
C2—N1—C1—N2	-178.35 (14)	O1—C5—C6—C7	178.45 (13)
C2—N1—C1—S1	1.2 (2)	C4—C5—C6—C7	-1.3 (2)
N3—N2—C1—N1	-15.6 (2)	C5—C6—C7—O2	-178.64 (14)

N3—N2—C1—S1	164.83 (11)	C5—C6—C7—C8	1.1 (2)
N2—N3—C3—C4	173.05 (13)	O2—C7—C8—C9	179.92 (14)
N3—C3—C4—C5	-2.2 (2)	C6—C7—C8—C9	0.2 (2)
N3—C3—C4—C9	-178.56 (14)	C7—C8—C9—C4	-1.3 (2)
C9—C4—C5—O1	-179.49 (14)	C5—C4—C9—C8	1.0 (2)
C3—C4—C5—O1	4.1 (2)	C3—C4—C9—C8	177.60 (14)
C9—C4—C5—C6	0.3 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 o \cdots N3	0.83 (2)	1.97 (2)	2.6992 (17)	147 (2)
N1—H1 n \cdots N3	0.815 (19)	2.35 (2)	2.7080 (19)	107.1 (16)
O2—H2 o \cdots S1 ⁱ	0.90 (2)	2.37 (2)	3.1918 (12)	152 (2)
N1—H1 n \cdots S1 ⁱⁱ	0.815 (19)	2.763 (18)	3.3883 (13)	134.9 (17)
N2—H2 n \cdots O1 ⁱⁱⁱ	0.90 (2)	2.08 (2)	2.9527 (17)	162 (2)

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