

Crystal structure of 2'-hydroxyacetophenone 4-methylthiosemicarbazide

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In the organic molecule of the title hydrate, C₁₁H₁₅N₃OS·H₂O, {systematic name: 3-ethyl-1-[(E)-[1-(2-hydroxyphenyl)ethylidene]amino]thiourea monohydrate}, a dihedral angle of 5.39 (2)° is formed between the hydroxybenzene ring and the non-H atoms comprising the side chain (r.m.s. deviation = 0.0625 Å), with the major deviation from planarity noted for the terminal ethyl group [the C–N–C–C torsion angle = –172.17 (13)°]. The N–H H atoms are *syn* and an intramolecular hydroxy–imine O–H···N hydrogen bond is noted. In the crystal, the N-bonded H atoms form hydrogen bonds to symmetry-related water molecules, and the latter form donor interactions with the hydroxy O atom and with a hydroxybenzene ring, forming a O–H···π interaction. The hydrogen bonding leads to supramolecular tubes aligned along the *b* axis. The tubes are connected into layers *via* C–H···O interactions, and these stack along the *c* axis with no directional interactions between them.

Keywords: crystal structure; thiosemicarbazide; hydrogen bonding; O–H···π interactions.

CCDC reference: 1053189

1. Related literature

For background to thiosemicarbazones and their coordination chemistry, see: Mazlan *et al.* (2014). The conformational flexibility in these molecules is reflected in the structure of the 4-methyl derivative where one molecule comprising the asymmetric unit is approximately planar and the other exhibits a clear twist between the hydroxybenzene and side chain, and in the structure of the 6-methoxy derivative where these residues are almost normal to each other, see: Anderson *et al.* (2012, 2014). For synthesis and methodology, see: Omar *et al.* (2014).

2. Experimental

2.1. Crystal data

C₁₁H₁₅N₃OS·H₂O
M_r = 255.33
 Triclinic, *P* $\bar{1}$
a = 6.7947 (5) Å
b = 8.5169 (8) Å
c = 11.1199 (9) Å
 α = 84.948 (7)°
 β = 81.825 (6)°

γ = 84.084 (7)°
V = 631.81 (9) Å³
Z = 2
 Cu *K*α radiation
 μ = 2.25 mm^{−1}
T = 100 K
 0.30 × 0.20 × 0.10 mm

2.2. Data collection

Oxford Diffraction Xcaliber Eos
 Gemini diffractometer
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.923, *T_{max}* = 1.000

8119 measured reflections
 2408 independent reflections
 2187 reflections with *I* > 2σ(*I*)
R_{int} = 0.026

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.035
wR(*F*²) = 0.095
S = 1.03
 2408 reflections
 171 parameters
 6 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max}$ = 0.33 e Å^{−3}
 $\Delta\rho_{\min}$ = −0.25 e Å^{−3}

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C3–C8 ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1O···N2	0.84 (1)	1.76 (1)	2.5292 (16)	150 (2)
N1–H1N···O1W ⁱ	0.86 (2)	2.09 (2)	2.8918 (17)	156 (2)
N3–H3N···O1W ⁱ	0.87 (2)	2.16 (2)	2.9625 (18)	154 (2)
O1W–H1W···O1	0.84 (2)	1.96 (2)	2.7894 (16)	174 (2)
O1W–H2W···Cg1 ⁱⁱⁱ	0.83 (1)	2.86 (1)	3.4165 (13)	127 (1)
C5–H5···O1 ⁱⁱⁱ	0.95	2.56	3.3702 (18)	143

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7380).

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supporting information

Acta Cryst. (2015). E71, o244–o245 [doi:10.1107/S2056989015004958]

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S1. Experimental

4-Methyl-3-thiosemicarbazide (0.02 mol) was dissolved in hot ethanol (95%; 40 ml). A solution of 0.02 mol of 2'-hydroxyacetophenone was added drop-wise into the first solution. The mixture was heated and stirred to reduce the volume to half of its initial volume. Then, it was allowed to stand at room temperature until a white crystalline precipitate formed. The precipitate was then collected and recrystallized from ethanol and dried over silica gel. Colourless crystals were obtained from the ethanolic solution. Yield: 92%. *M*.pt: 116 °C. Anal. Found (Calc): C: 56.1 (55.7); H: 5.9 (6.4); N: 18.5 (17.7).

S2. Refinement

Carbon-bound H-atoms were placed in calculated positions ($C-H = 0.95$ to 0.99 Å) and were included in the refinement in the riding model approximation with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$. The O—H H atoms were refined with $O-H = 0.84 \pm 0.01$ Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$. The N—H H atoms were refined similarly with $N-H = 0.88 \pm 0.01$ Å, and with $U_{iso}(H) = 1.2U_{eq}(N)$.

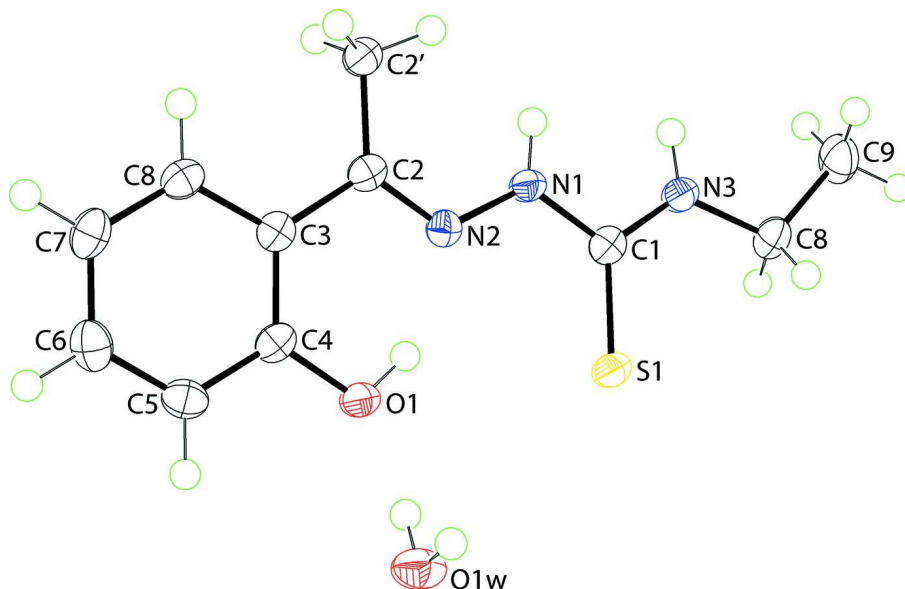


Figure 1

The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

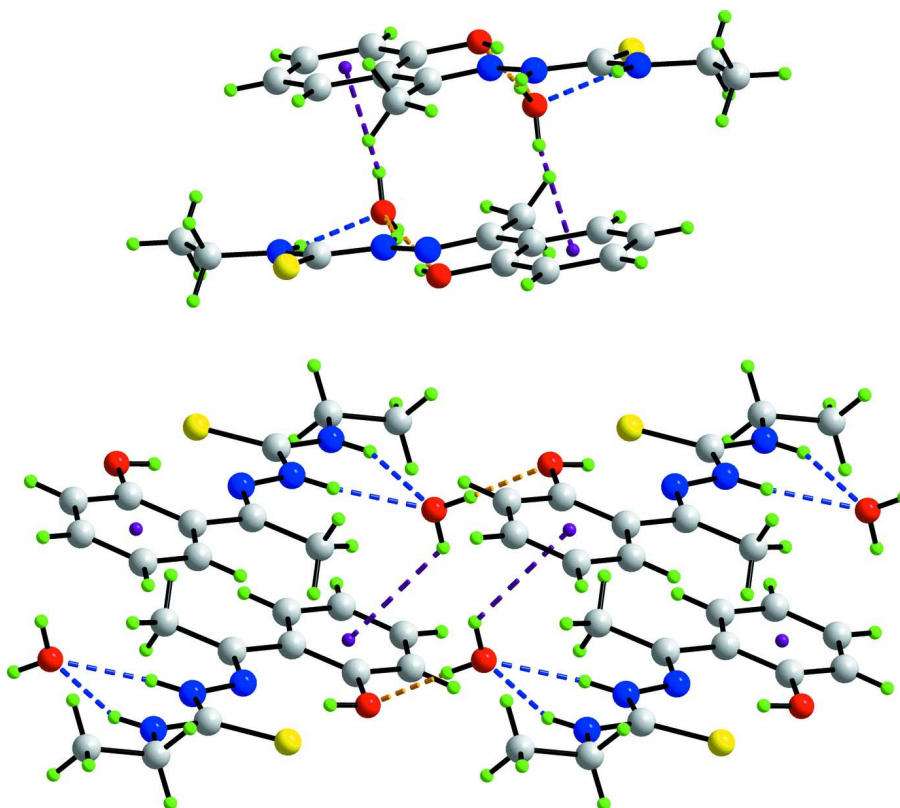


Figure 2

Two views of the supramolecular tube along the b axis sustained by $\text{O—H}\cdots\text{O}$, $\text{N—H}\cdots\text{O}$ and $\text{O—H}\cdots\pi$ hydrogen bonding, shown as orange, blue and purple dashed lines, respectively.

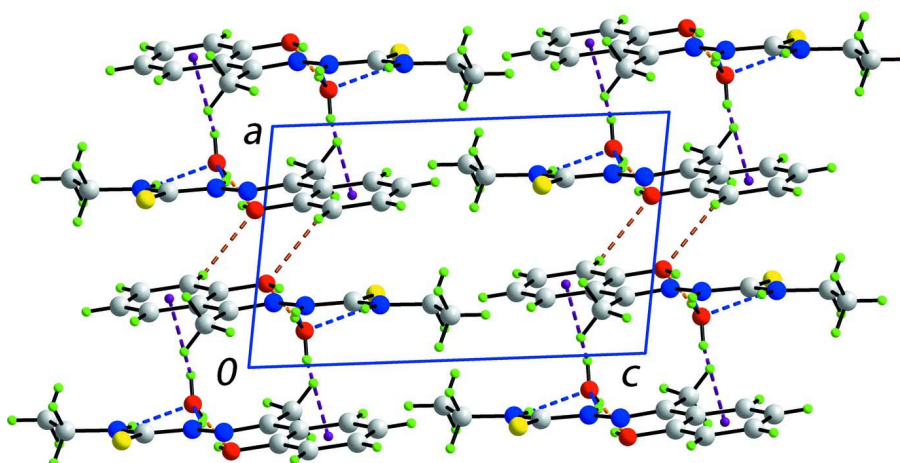


Figure 3

A view of the unit-cell contents in projection down the b axis. The $\text{O—H}\cdots\text{O}$, $\text{N—H}\cdots\text{O}$, $\text{O—H}\cdots\pi$ and $\text{C—H}\cdots\text{O}$ interactions are shown as orange, blue, purple and brown dashed lines, respectively.

3-Ethyl-1-[(E)-[1-(2-hydroxyphenyl)ethylidene]amino]thiourea monohydrate

Crystal data

$C_{11}H_{15}N_3OS \cdot H_2O$
 $M_r = 255.33$
 Triclinic, $P\bar{1}$
 $a = 6.7947$ (5) Å
 $b = 8.5169$ (8) Å
 $c = 11.1199$ (9) Å
 $\alpha = 84.948$ (7)°
 $\beta = 81.825$ (6)°
 $\gamma = 84.084$ (7)°
 $V = 631.81$ (9) Å³

$Z = 2$
 $F(000) = 272$
 $D_x = 1.342$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
 Cell parameters from 4230 reflections
 $\theta = 4.0$ – 71.4 °
 $\mu = 2.25$ mm⁻¹
 $T = 100$ K
 Prism, pale-yellow
 $0.30 \times 0.20 \times 0.10$ mm

Data collection

Oxford Diffraction Xcaliber Eos Gemini diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: 16.1952 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2011)
 $T_{\min} = 0.923$, $T_{\max} = 1.000$

8119 measured reflections
 2408 independent reflections
 2187 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 71.5$ °, $\theta_{\min} = 4.0$ °
 $h = -8 \rightarrow 8$
 $k = -10 \rightarrow 9$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.095$
 $S = 1.03$
 2408 reflections
 171 parameters
 6 restraints

Hydrogen site location: mixed
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0593P)^2 + 0.1686P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33$ e Å⁻³
 $\Delta\rho_{\min} = -0.25$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.28553 (5)	0.84923 (4)	0.30332 (3)	0.01932 (14)
O1	0.34603 (16)	0.67711 (12)	0.02373 (9)	0.0193 (2)
H1O	0.325 (3)	0.7637 (15)	0.0568 (16)	0.029*
N1	0.24861 (18)	1.08372 (15)	0.12735 (11)	0.0163 (3)
H1N	0.224 (3)	1.1825 (17)	0.1053 (16)	0.020*
N2	0.26593 (17)	0.97046 (14)	0.04679 (11)	0.0150 (3)
N3	0.24119 (18)	1.16243 (16)	0.31656 (11)	0.0174 (3)
H3N	0.227 (3)	1.2558 (18)	0.2795 (15)	0.021*
C1	0.2583 (2)	1.03944 (18)	0.24810 (13)	0.0160 (3)

C2	0.2391 (2)	1.00570 (18)	-0.06558 (13)	0.0153 (3)
C2'	0.1872 (2)	1.16980 (18)	-0.12094 (13)	0.0192 (3)
H2'1	0.1497	1.2423	-0.0561	0.029*
H2'2	0.0750	1.1686	-0.1672	0.029*
H2'3	0.3030	1.2053	-0.1755	0.029*
C3	0.2674 (2)	0.86995 (18)	-0.14260 (13)	0.0154 (3)
C4	0.3216 (2)	0.71390 (18)	-0.09556 (13)	0.0164 (3)
C5	0.3532 (2)	0.58929 (18)	-0.17128 (14)	0.0193 (3)
H5	0.3914	0.4854	-0.1391	0.023*
C6	0.3291 (2)	0.61601 (19)	-0.29349 (14)	0.0214 (3)
H6	0.3503	0.5303	-0.3445	0.026*
C7	0.2739 (2)	0.76788 (19)	-0.34155 (13)	0.0206 (3)
H7	0.2562	0.7863	-0.4250	0.025*
C8	0.2451 (2)	0.89188 (19)	-0.26665 (13)	0.0179 (3)
H8	0.2089	0.9955	-0.3004	0.021*
C9	0.2364 (2)	1.14844 (19)	0.44845 (13)	0.0202 (3)
H9A	0.3678	1.1022	0.4697	0.024*
H9B	0.1344	1.0773	0.4859	0.024*
C10	0.1872 (3)	1.3101 (2)	0.49712 (14)	0.0271 (4)
H10A	0.2892	1.3797	0.4605	0.041*
H10B	0.1840	1.3003	0.5858	0.041*
H10C	0.0563	1.3549	0.4766	0.041*
O1W	0.14391 (17)	0.42112 (13)	0.13237 (11)	0.0243 (3)
H1W	0.200 (3)	0.5018 (17)	0.1042 (17)	0.036*
H2W	0.0232 (16)	0.452 (2)	0.1447 (19)	0.036*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0267 (2)	0.0159 (2)	0.01519 (19)	-0.00163 (15)	-0.00399 (14)	0.00149 (14)
O1	0.0279 (6)	0.0139 (5)	0.0164 (5)	-0.0010 (4)	-0.0056 (4)	0.0005 (4)
N1	0.0221 (6)	0.0121 (6)	0.0147 (6)	-0.0017 (5)	-0.0036 (5)	0.0003 (5)
N2	0.0142 (6)	0.0156 (6)	0.0151 (6)	-0.0024 (5)	-0.0014 (4)	-0.0012 (5)
N3	0.0215 (6)	0.0155 (7)	0.0151 (6)	-0.0020 (5)	-0.0033 (5)	0.0005 (5)
C1	0.0126 (6)	0.0191 (8)	0.0166 (7)	-0.0030 (6)	-0.0022 (5)	-0.0002 (6)
C2	0.0126 (6)	0.0168 (8)	0.0165 (7)	-0.0037 (5)	-0.0014 (5)	0.0014 (6)
C2'	0.0239 (7)	0.0174 (8)	0.0164 (7)	-0.0017 (6)	-0.0036 (6)	-0.0003 (6)
C3	0.0120 (6)	0.0179 (8)	0.0164 (7)	-0.0034 (5)	-0.0016 (5)	-0.0007 (6)
C4	0.0146 (6)	0.0187 (8)	0.0162 (7)	-0.0045 (6)	-0.0028 (5)	0.0017 (6)
C5	0.0191 (7)	0.0152 (8)	0.0239 (7)	-0.0037 (6)	-0.0032 (6)	-0.0006 (6)
C6	0.0202 (7)	0.0235 (9)	0.0218 (7)	-0.0070 (6)	-0.0013 (6)	-0.0066 (6)
C7	0.0198 (7)	0.0276 (9)	0.0156 (7)	-0.0063 (6)	-0.0036 (5)	-0.0014 (6)
C8	0.0162 (7)	0.0194 (8)	0.0179 (7)	-0.0027 (6)	-0.0027 (5)	0.0021 (6)
C9	0.0232 (7)	0.0228 (8)	0.0151 (7)	-0.0049 (6)	-0.0028 (5)	-0.0006 (6)
C10	0.0361 (9)	0.0257 (9)	0.0204 (8)	-0.0072 (7)	-0.0004 (6)	-0.0072 (6)
O1W	0.0227 (6)	0.0173 (6)	0.0314 (6)	-0.0025 (5)	-0.0014 (5)	0.0029 (5)

Geometric parameters (Å, °)

S1—C1	1.6825 (16)	C4—C5	1.393 (2)
O1—C4	1.3653 (17)	C5—C6	1.388 (2)
O1—H1O	0.843 (9)	C5—H5	0.9500
N1—N2	1.3586 (17)	C6—C7	1.391 (2)
N1—C1	1.3713 (18)	C6—H6	0.9500
N1—H1N	0.862 (14)	C7—C8	1.383 (2)
N2—C2	1.2931 (18)	C7—H7	0.9500
N3—C1	1.3344 (19)	C8—H8	0.9500
N3—C9	1.4569 (18)	C9—C10	1.511 (2)
N3—H3N	0.865 (14)	C9—H9A	0.9900
C2—C3	1.480 (2)	C9—H9B	0.9900
C2—C2'	1.505 (2)	C10—H10A	0.9800
C2'—H2'1	0.9800	C10—H10B	0.9800
C2'—H2'2	0.9800	C10—H10C	0.9800
C2'—H2'3	0.9800	O1W—H1W	0.834 (9)
C3—C8	1.403 (2)	O1W—H2W	0.831 (9)
C3—C4	1.417 (2)		
C4—O1—H1O	105.5 (13)	C6—C5—C4	120.42 (14)
N2—N1—C1	119.33 (12)	C6—C5—H5	119.8
N2—N1—H1N	121.6 (12)	C4—C5—H5	119.8
C1—N1—H1N	119.0 (12)	C5—C6—C7	120.19 (14)
C2—N2—N1	121.39 (13)	C5—C6—H6	119.9
C1—N3—C9	124.21 (13)	C7—C6—H6	119.9
C1—N3—H3N	116.9 (12)	C8—C7—C6	119.35 (13)
C9—N3—H3N	118.8 (12)	C8—C7—H7	120.3
N3—C1—N1	112.99 (13)	C6—C7—H7	120.3
N3—C1—S1	123.95 (11)	C7—C8—C3	122.27 (14)
N1—C1—S1	123.06 (11)	C7—C8—H8	118.9
N2—C2—C3	115.00 (13)	C3—C8—H8	118.9
N2—C2—C2'	125.29 (13)	N3—C9—C10	109.63 (13)
C3—C2—C2'	119.70 (12)	N3—C9—H9A	109.7
C2—C2'—H2'1	109.5	C10—C9—H9A	109.7
C2—C2'—H2'2	109.5	N3—C9—H9B	109.7
H2'1—C2'—H2'2	109.5	C10—C9—H9B	109.7
C2—C2'—H2'3	109.5	H9A—C9—H9B	108.2
H2'1—C2'—H2'3	109.5	C9—C10—H10A	109.5
H2'2—C2'—H2'3	109.5	C9—C10—H10B	109.5
C8—C3—C4	117.28 (13)	H10A—C10—H10B	109.5
C8—C3—C2	120.87 (13)	C9—C10—H10C	109.5
C4—C3—C2	121.84 (13)	H10A—C10—H10C	109.5
O1—C4—C5	116.68 (13)	H10B—C10—H10C	109.5
O1—C4—C3	122.84 (13)	H1W—O1W—H2W	105 (2)
C5—C4—C3	120.48 (13)		
C1—N1—N2—C2	173.45 (12)	C2—C3—C4—O1	1.8 (2)

C9—N3—C1—N1	176.76 (12)	C8—C3—C4—C5	0.8 (2)
C9—N3—C1—S1	-2.4 (2)	C2—C3—C4—C5	-177.99 (12)
N2—N1—C1—N3	179.36 (12)	O1—C4—C5—C6	179.21 (12)
N2—N1—C1—S1	-1.51 (19)	C3—C4—C5—C6	-1.0 (2)
N1—N2—C2—C3	178.75 (11)	C4—C5—C6—C7	0.3 (2)
N1—N2—C2—C2'	0.0 (2)	C5—C6—C7—C8	0.6 (2)
N2—C2—C3—C8	-179.27 (12)	C6—C7—C8—C3	-0.7 (2)
C2'—C2—C3—C8	-0.4 (2)	C4—C3—C8—C7	0.1 (2)
N2—C2—C3—C4	-0.5 (2)	C2—C3—C8—C7	178.85 (13)
C2'—C2—C3—C4	178.29 (12)	C1—N3—C9—C10	-172.17 (13)
C8—C3—C4—O1	-179.39 (12)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C3–C8 ring.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O...N2	0.84 (1)	1.76 (1)	2.5292 (16)	150 (2)
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O1W—H1W...O1	0.84 (2)	1.96 (2)	2.7894 (16)	174 (2)
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