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Resorcinol ninhydrin complex: 1,5,9-trihydroxy-8-oxatetracyclo[7.7.0.0^{2,7}.0^{10,15}]-hexadeca-2,4,6,10(15),11,13-hexaen-16-one

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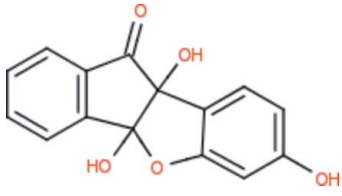
Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.106; data-to-parameter ratio = 12.2.

In the title compound, $C_{15}H_{10}O_5$, the cyclopentanone (r.m.s. deviation = 0.049 Å) and oxolane (r.m.s. deviation = 0.048 Å) rings make a dihedral angle of 67.91 (4)°. An intramolecular O—H···O hydrogen bond is observed. In the crystal, molecules associate *via* O—H···O hydrogen bonds, forming a three-dimensional network.

Related literature

For general background to ninhydrin derivatives, see: Hansen & Joullie (2005); Leane *et al.* (2004). For general background to resorcinol derivatives, see: Chen *et al.* (2011); Bao *et al.* (2010); Zheng & Wu (2007).



Experimental

Crystal data

$C_{15}H_{10}O_5$
M_r = 270.23
Monoclinic, $P2_1/c$
a = 9.1117 (5) Å
b = 12.2995 (7) Å
c = 10.1177 (5) Å
β = 91.837 (1)°
V = 1133.30 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 292 K
0.22 × 0.20 × 0.19 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
12939 measured reflections
2699 independent reflections
2468 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.05
2699 reflections
221 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4A···O3^{i}	0.90 (2)	2.02 (2)	2.877 (1)	158 (2)
O3—H3A···O4^{ii}	0.89 (2)	2.18 (2)	3.013 (1)	157 (2)
O2—H2A···O1^{iii}	0.87 (2)	1.92 (2)	2.746 (1)	159 (2)
O3—H3A···O2	0.89 (2)	2.33 (2)	2.667 (1)	102 (1)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON*.

SS acknowledges the Department of Science and Technology (DST), India, for providing computing facilities under the DST-Fast Track Scheme.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5867).

References

Bao, L., Wang, M., Zhao, F., Zhao, Y. & Liu, H. (2010). *Chem. Biodivers.* **7**, 2901–2907.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, L. P., Zhao, F., Wang, Y., Zhao, L. L., Li, Q. P. & Liu, H. W. (2011). *J. Asian. Nat. Prod. Res.* **13**, 734–743.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Hansen, D. B. & Joullie, M. M. (2005). *Chem. Soc. Rev.* **34**, 408–417.
Leane, M. M., Nankervis, R., Smith, A. & Illum, L. (2004). *Int. J. Pharm.* **271**, 241–249.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Zheng, Y. & Wu, F. E. (2007). *J. Asian. Nat. Prod. Res.* **9**, 545–549.

supporting information

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Resorcinol ninhydrin complex: 1,5,9-trihydroxy-8-oxatetracyclo-[7.7.0.0^{2,7}.0^{10,15}]hexadeca-2,4,6,10(15),11,13-hexaen-16-one

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S1. Comment

Resorcinol derivatives posses cytotoxity (Zheng & Wu, 2007; Bao *et al.*, 2010) and antitumor activities (Chen *et al.*, 2011). Ninhydrin analogue was found to be an important reagent to develop finger prints on porous surface (Hansen & Joullie, 2005). Ninhydrin assay is an essential aid in the design and testing of solid dosage forms with different chitosan-drug release profiles (Leane *et al.*, 2004).In view of these importance on ninhydrin and resorcinol derivatives, we have undertaken the crystal structure determination of the present complex, and the results are presented here.

The X-ray study confirmed the molecular structure and atomic connectivity for (I), as illustrated in Fig. 1.

The plane calculation revealed that the benzene, cyclopentanone, oxolane and phenyl rings are in planar. Atoms O1, O2 and O3 deviate by 0.235 (1), 0.916 (1) and 1.166 (1) Å, respectively with respect to the fused rings of benzene and cyclopentanone. Atoms O2, O3 and O4 deviate by -1.127 (1), -0.801 (1) and 0.091 (1) Å, respectively with respect to the fused rings of oxolane and phenyl rings. The dihedral angle between the two half of the molecule with respect to C8-C9 bond is 1.5 (1)°.

The molecular structure is influenced by an intramolecular O—H···O hydrogen bonds. In the molecular packing, O—H···O hydrogen bonds involving atoms O3 and O4 link inversion-related molecules to form R_2^2 (16) graph-set dimer. (Fig. 2 and Table 1). In addition to this atoms, O2 and C11 form a $R_2^2(10)$ graph-set motif in the unit cell with the help of intermolecular hydrogen bonds (Fig.3). A C(8) chain motif is formed in the unit cell with the help of O—H···O hydrogen bonds involving atoms O4 and O3 which results the helical shape arrangement along bc plane of the unit cell (Fig. 4).

S2. Experimental

A mixture of ninhydrin and resorcinol in molar ratio 1:1 were dissolved in dilute acetic medium and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which yielded a crystalline adduct. Single crystals were grown by slow evaporation from ethanol.

S3. Refinement

All H atoms were located from a difference Fourier map and refined isotropically.

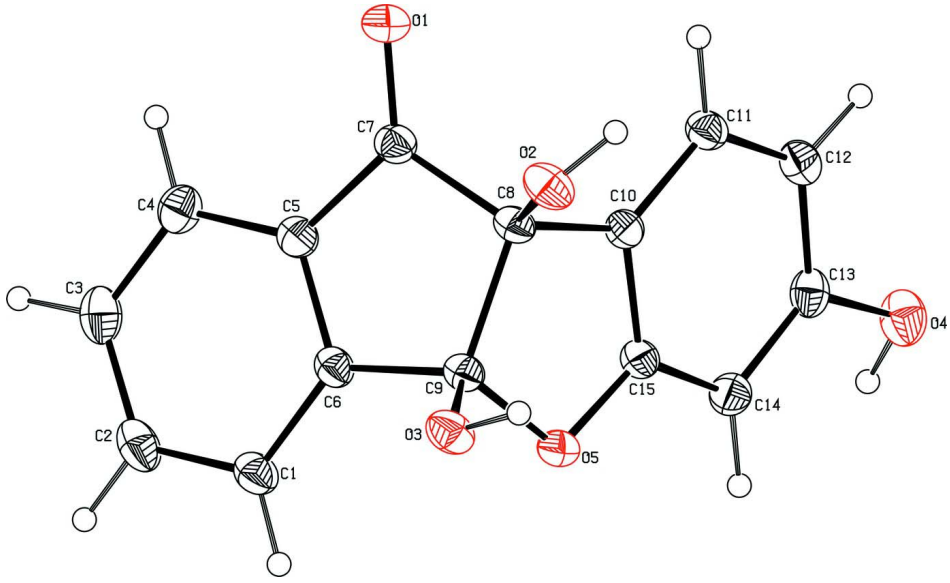

Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level

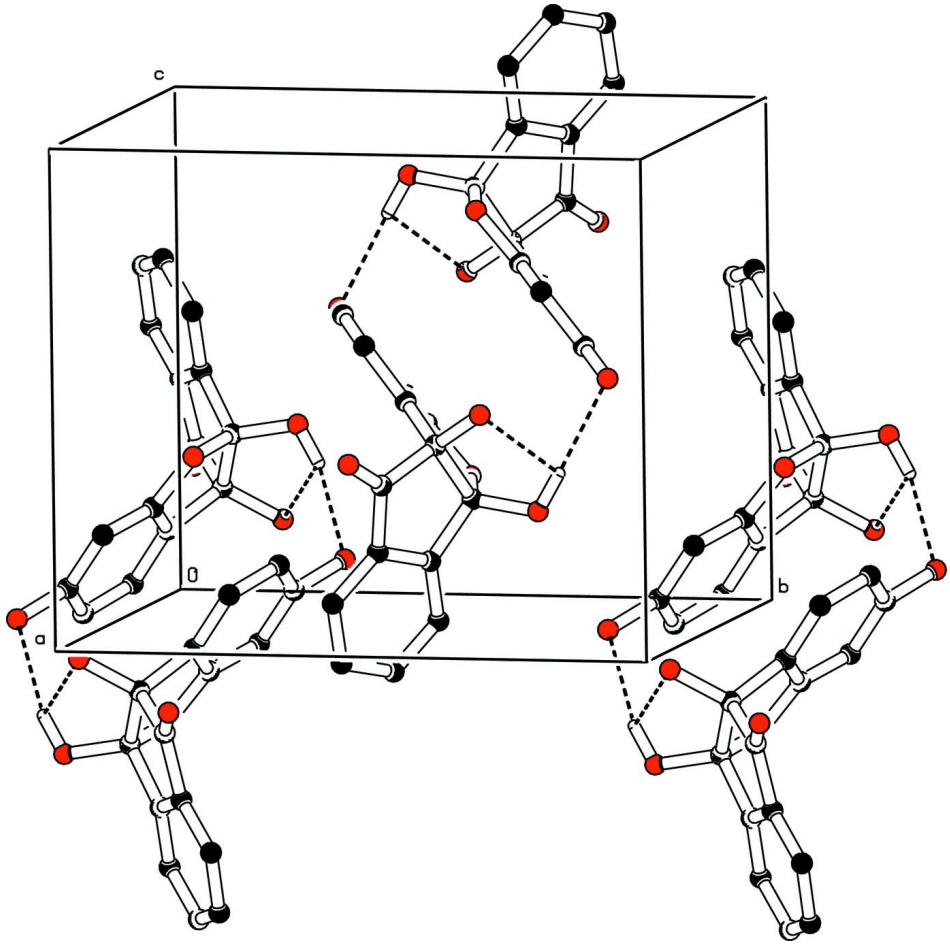

Figure 2

Molecular packing of the title compound, viewed along the *a* axis; H-bonds are shown as dashed lines forms a $R_2^2(16)$ dimers in unit cell. For the sake of clarity, H atoms, not involved in hydrogen bonds, have been omitted

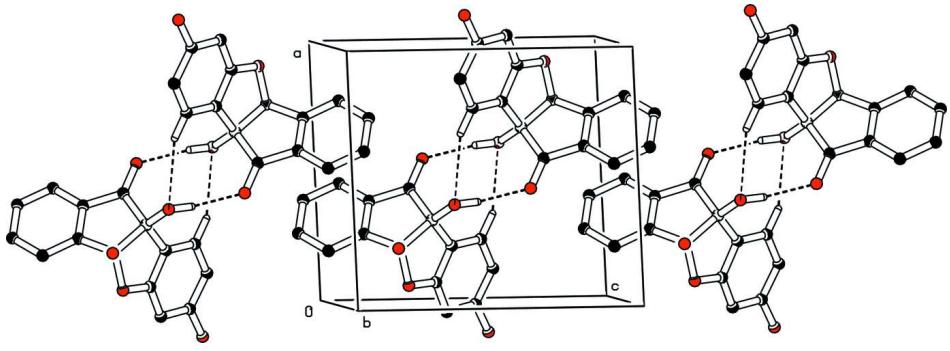

Figure 3

Molecular packing of the title compound, viewed along the *b* axis; H-bonds are shown as dashed lines forms a $R_2^2(10)$ dimers in unit cell. For the sake of clarity, H atoms, not involved in hydrogen bonds, have been omitted

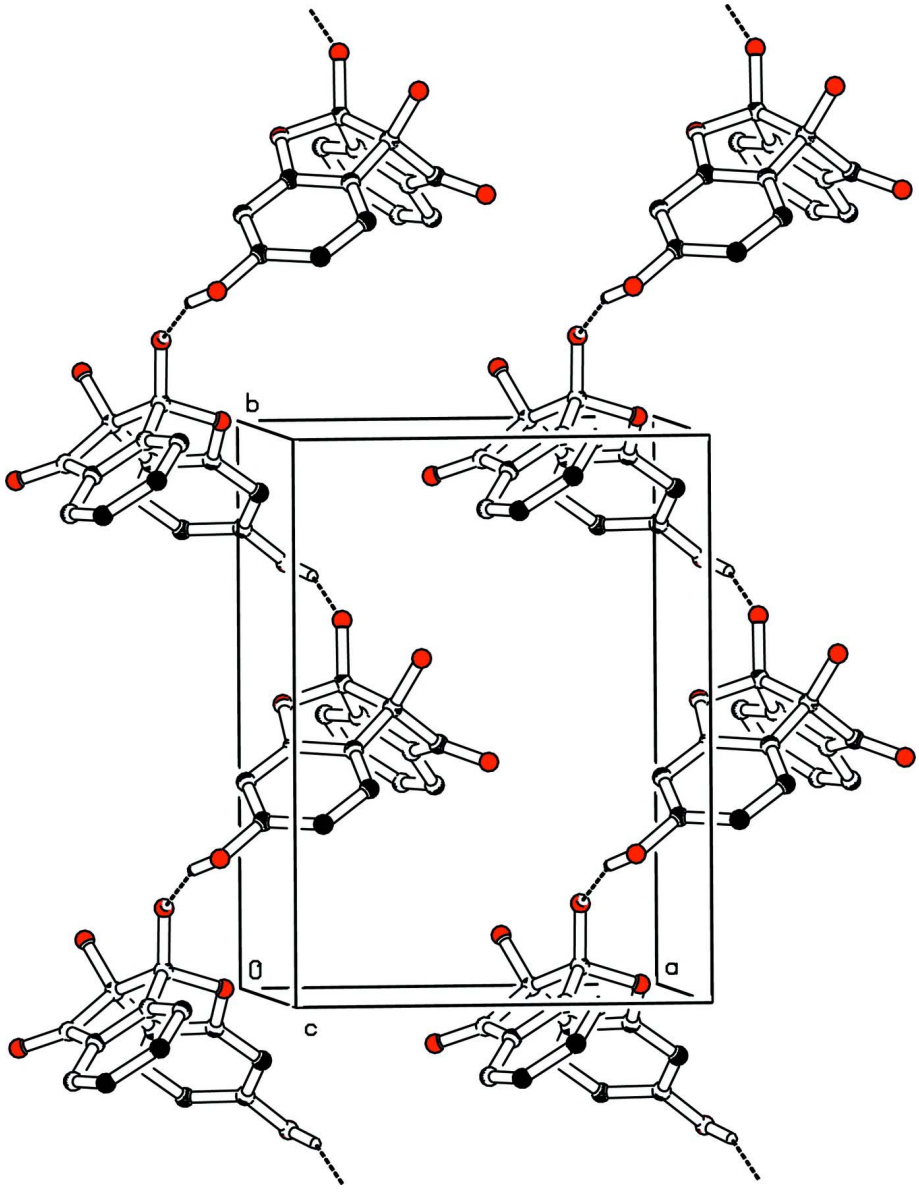

Figure 4

Molecular packing of the title compound, viewed along the *c* axis; H-bonds are shown as dashed lines forms a C(8) chain-motif in unit cell. For the sake of clarity, H atoms, not involved in hydrogen bonds, have been omitted

1,5,9-trihydroxy-8-oxatetracyclo[7.7.0.0^{2,7}.0^{10,15}]hexadeca- 2,4,6,10 (15),11,13-hexaen-16-one

Crystal data

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b = 12.2995 (7) Å
c = 10.1177 (5) Å
β = 91.837 (1)°
V = 1133.30 (11) Å^3
Z = 4
F(000) = 560
D_x = 1.584 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8468 reflections
θ = 2.2–27.1°
μ = 0.12 mm^{-1}

T = 292 K
Block, colourless

0.22 × 0.20 × 0.19 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
12939 measured reflections
2699 independent reflections

2468 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 28.0°, θ_{min} = 2.2°
h = −12→11
k = −16→16
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.05
2699 reflections
221 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.3056P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 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.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
O1	0.55633 (10)	0.40497 (9)	0.32526 (9)	0.0416 (2)
O2	0.38544 (11)	0.59167 (7)	0.40684 (9)	0.0382 (2)
H2A	0.394 (2)	0.5760 (16)	0.490 (2)	0.058 (5)*
O3	0.22262 (11)	0.65338 (7)	0.19634 (9)	0.0369 (2)
H3A	0.219 (2)	0.689 (2)	0.272 (2)	0.080 (7)*
O4	−0.12067 (11)	0.24783 (9)	0.55006 (10)	0.0444 (3)
H4A	−0.175 (2)	0.2263 (19)	0.479 (2)	0.076 (6)*
O5	0.07320 (9)	0.50826 (7)	0.24520 (8)	0.0336 (2)
C1	0.21080 (14)	0.48007 (11)	−0.02647 (12)	0.0345 (3)
H1	0.1252 (19)	0.5225 (14)	−0.0506 (16)	0.042 (4)*
C2	0.27738 (16)	0.41740 (12)	−0.12105 (13)	0.0409 (3)
H2	0.2341 (19)	0.4179 (14)	−0.2090 (18)	0.049 (4)*
C3	0.40256 (16)	0.35623 (11)	−0.09057 (14)	0.0418 (3)
H3	0.4472 (19)	0.3140 (14)	−0.1582 (17)	0.048 (4)*
C4	0.46396 (14)	0.35571 (10)	0.03612 (13)	0.0366 (3)

H4	0.5509 (18)	0.3132 (14)	0.0606 (15)	0.041 (4)*
C5	0.39742 (12)	0.41873 (10)	0.13132 (11)	0.0301 (2)
C6	0.27356 (12)	0.48078 (9)	0.10008 (11)	0.0285 (2)
C7	0.44307 (12)	0.43593 (10)	0.27024 (11)	0.0302 (2)
C8	0.32381 (12)	0.50301 (9)	0.33703 (11)	0.0283 (2)
C9	0.22170 (12)	0.54241 (9)	0.21795 (11)	0.0289 (2)
C10	0.22056 (12)	0.43138 (9)	0.41014 (11)	0.0278 (2)
C11	0.24218 (13)	0.36685 (10)	0.52153 (11)	0.0310 (2)
H11	0.3393 (17)	0.3619 (12)	0.5676 (15)	0.036 (4)*
C12	0.12568 (14)	0.30692 (10)	0.56731 (12)	0.0336 (3)
H12	0.1362 (17)	0.2601 (13)	0.6454 (16)	0.043 (4)*
C13	−0.01040 (13)	0.31088 (10)	0.50070 (12)	0.0328 (3)
C14	−0.03552 (13)	0.37657 (10)	0.39052 (12)	0.0331 (3)
H14	−0.1314 (18)	0.3805 (13)	0.3462 (15)	0.041 (4)*
C15	0.08212 (12)	0.43688 (10)	0.34892 (11)	0.0290 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0309 (4)	0.0562 (6)	0.0373 (5)	0.0065 (4)	−0.0056 (4)	0.0060 (4)
O2	0.0455 (5)	0.0369 (5)	0.0315 (5)	−0.0098 (4)	−0.0097 (4)	−0.0017 (4)
O3	0.0480 (5)	0.0302 (4)	0.0321 (5)	0.0039 (4)	−0.0046 (4)	0.0019 (3)
O4	0.0441 (5)	0.0478 (6)	0.0416 (5)	−0.0145 (4)	0.0066 (4)	−0.0008 (4)
O5	0.0264 (4)	0.0455 (5)	0.0288 (4)	0.0020 (3)	−0.0033 (3)	0.0050 (3)
C1	0.0349 (6)	0.0402 (6)	0.0281 (6)	−0.0044 (5)	−0.0046 (4)	0.0013 (5)
C2	0.0495 (7)	0.0471 (7)	0.0261 (6)	−0.0107 (6)	−0.0005 (5)	−0.0029 (5)
C3	0.0504 (8)	0.0396 (7)	0.0360 (7)	−0.0074 (6)	0.0106 (6)	−0.0079 (5)
C4	0.0357 (6)	0.0338 (6)	0.0408 (7)	−0.0013 (5)	0.0063 (5)	−0.0008 (5)
C5	0.0292 (5)	0.0319 (6)	0.0293 (6)	−0.0039 (4)	−0.0003 (4)	0.0019 (4)
C6	0.0293 (5)	0.0311 (5)	0.0250 (5)	−0.0044 (4)	−0.0006 (4)	0.0009 (4)
C7	0.0269 (5)	0.0333 (5)	0.0304 (6)	−0.0031 (4)	−0.0015 (4)	0.0047 (4)
C8	0.0288 (5)	0.0309 (5)	0.0249 (5)	−0.0016 (4)	−0.0051 (4)	0.0006 (4)
C9	0.0292 (5)	0.0316 (5)	0.0258 (5)	0.0004 (4)	−0.0031 (4)	0.0009 (4)
C10	0.0277 (5)	0.0310 (5)	0.0247 (5)	0.0002 (4)	−0.0006 (4)	−0.0026 (4)
C11	0.0322 (6)	0.0333 (6)	0.0272 (5)	0.0015 (4)	−0.0031 (4)	−0.0013 (4)
C12	0.0404 (6)	0.0321 (6)	0.0282 (6)	0.0005 (5)	0.0011 (5)	−0.0002 (4)
C13	0.0354 (6)	0.0323 (6)	0.0310 (6)	−0.0049 (5)	0.0061 (4)	−0.0067 (4)
C14	0.0284 (5)	0.0397 (6)	0.0310 (6)	−0.0016 (5)	−0.0011 (4)	−0.0055 (5)
C15	0.0297 (5)	0.0334 (6)	0.0239 (5)	0.0022 (4)	−0.0013 (4)	−0.0032 (4)

Geometric parameters (Å, º)

O1—C7	1.2178 (14)	C4—H4	0.975 (17)
O2—C8	1.4063 (14)	C5—C6	1.3904 (16)
O2—H2A	0.87 (2)	C5—C7	1.4683 (16)
O3—C9	1.3823 (14)	C6—C9	1.5021 (16)
O3—H3A	0.89 (2)	C7—C8	1.5379 (16)
O4—C13	1.3756 (15)	C8—C10	1.5011 (16)

O4—H4A	0.90 (2)	C8—C9	1.5749 (15)
O5—C15	1.3686 (14)	C10—C11	1.3873 (16)
O5—C9	1.4516 (14)	C10—C15	1.3890 (15)
C1—C2	1.3839 (19)	C11—C12	1.3843 (17)
C1—C6	1.3855 (16)	C11—H11	0.989 (16)
C1—H1	0.964 (17)	C12—C13	1.3930 (18)
C2—C3	1.393 (2)	C12—H12	0.979 (17)
C2—H2	0.962 (18)	C13—C14	1.3899 (18)
C3—C4	1.382 (2)	C14—C15	1.3803 (17)
C3—H3	0.960 (17)	C14—H14	0.970 (16)
C4—C5	1.3907 (17)		

C8—O2—H2A	109.8 (13)	O2—C8—C9	111.24 (9)
C9—O3—H3A	110.3 (15)	C10—C8—C9	101.15 (9)
C13—O4—H4A	105.4 (14)	C7—C8—C9	103.73 (9)
C15—O5—C9	107.37 (8)	O3—C9—O5	109.04 (9)
C2—C1—C6	117.74 (12)	O3—C9—C6	111.66 (9)
C2—C1—H1	119.7 (10)	O5—C9—C6	108.88 (9)
C6—C1—H1	122.5 (10)	O3—C9—C8	114.73 (9)
C1—C2—C3	121.46 (12)	O5—C9—C8	107.28 (9)
C1—C2—H2	117.4 (10)	C6—C9—C8	105.01 (9)
C3—C2—H2	121.1 (10)	C11—C10—C15	119.57 (11)
C4—C3—C2	120.81 (12)	C11—C10—C8	131.39 (10)
C4—C3—H3	119.4 (10)	C15—C10—C8	109.04 (10)
C2—C3—H3	119.8 (10)	C12—C11—C10	119.08 (11)
C3—C4—C5	117.86 (12)	C12—C11—H11	119.6 (9)
C3—C4—H4	122.6 (9)	C10—C11—H11	121.3 (9)
C5—C4—H4	119.5 (9)	C11—C12—C13	119.98 (11)
C6—C5—C4	121.15 (11)	C11—C12—H12	121.8 (9)
C6—C5—C7	109.97 (10)	C13—C12—H12	118.2 (9)
C4—C5—C7	128.83 (11)	O4—C13—C14	121.03 (11)
C1—C6—C5	120.97 (11)	O4—C13—C12	116.99 (11)
C1—C6—C9	127.29 (11)	C14—C13—C12	121.97 (11)
C5—C6—C9	111.73 (10)	C15—C14—C13	116.58 (11)
O1—C7—C5	127.04 (11)	C15—C14—H14	121.9 (9)
O1—C7—C8	124.56 (11)	C13—C14—H14	121.5 (9)
C5—C7—C8	108.39 (9)	O5—C15—C14	123.43 (10)
O2—C8—C10	117.01 (9)	O5—C15—C10	113.82 (10)
O2—C8—C7	111.12 (9)	C14—C15—C10	122.74 (11)
C10—C8—C7	111.37 (9)		

C6—C1—C2—C3	0.49 (19)	O2—C8—C9—O3	5.95 (14)
C1—C2—C3—C4	0.4 (2)	C10—C8—C9—O3	130.92 (10)
C2—C3—C4—C5	−0.50 (19)	C7—C8—C9—O3	−113.58 (10)
C3—C4—C5—C6	−0.34 (18)	O2—C8—C9—O5	−115.34 (10)
C3—C4—C5—C7	−177.34 (12)	C10—C8—C9—O5	9.63 (11)
C2—C1—C6—C5	−1.33 (18)	C7—C8—C9—O5	125.13 (9)
C2—C1—C6—C9	179.74 (11)	O2—C8—C9—C6	128.92 (10)

C4—C5—C6—C1	1.28 (18)	C10—C8—C9—C6	−106.11 (10)
C7—C5—C6—C1	178.80 (10)	C7—C8—C9—C6	9.39 (11)
C4—C5—C6—C9	−179.63 (10)	O2—C8—C10—C11	−62.49 (17)
C7—C5—C6—C9	−2.12 (13)	C7—C8—C10—C11	66.83 (15)
C6—C5—C7—O1	−170.36 (12)	C9—C8—C10—C11	176.52 (12)
C4—C5—C7—O1	6.9 (2)	O2—C8—C10—C15	116.84 (11)
C6—C5—C7—C8	8.49 (13)	C7—C8—C10—C15	−113.83 (10)
C4—C5—C7—C8	−174.24 (11)	C9—C8—C10—C15	−4.14 (12)
O1—C7—C8—O2	48.37 (15)	C15—C10—C11—C12	1.69 (17)
C5—C7—C8—O2	−130.52 (10)	C8—C10—C11—C12	−179.04 (11)
O1—C7—C8—C10	−84.00 (14)	C10—C11—C12—C13	0.81 (18)
C5—C7—C8—C10	97.11 (10)	C11—C12—C13—O4	178.84 (11)
O1—C7—C8—C9	167.98 (11)	C11—C12—C13—C14	−2.16 (18)
C5—C7—C8—C9	−10.91 (11)	O4—C13—C14—C15	179.85 (11)
C15—O5—C9—O3	−136.72 (9)	C12—C13—C14—C15	0.90 (18)
C15—O5—C9—C6	101.24 (10)	C9—O5—C15—C14	−170.98 (11)
C15—O5—C9—C8	−11.91 (12)	C9—O5—C15—C10	9.76 (13)
C1—C6—C9—O3	−60.94 (15)	C13—C14—C15—O5	−177.48 (10)
C5—C6—C9—O3	120.05 (11)	C13—C14—C15—C10	1.71 (17)
C1—C6—C9—O5	59.51 (15)	C11—C10—C15—O5	176.22 (10)
C5—C6—C9—O5	−119.51 (10)	C8—C10—C15—O5	−3.20 (13)
C1—C6—C9—C8	174.14 (11)	C11—C10—C15—C14	−3.04 (18)
C5—C6—C9—C8	−4.88 (12)	C8—C10—C15—C14	177.54 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O3^{i}	0.90 (2)	2.02 (2)	2.877 (1)	158 (2)
O3—H3*A*···O4^{ii}	0.89 (2)	2.18 (2)	3.013 (1)	157 (2)
O2—H2*A*···O1^{iii}	0.87 (2)	1.92 (2)	2.746 (1)	159 (2)
O3—H3*A*···O2	0.89 (2)	2.33 (2)	2.667 (1)	102 (1)

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