Crystal structures of 1-hydroxy-4-propyloxy-9,10-anthraquinone and its acetyl derivative

Hidemi Nakagawa and Chitoshi Kitamura*

Department of Materials Science, School of Engineering, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone, Shiga 522-8533, Japan. *Correspondence e-mail: kitamura.c@mat.usp.ac.jp

1-Hydroxy-4-propyloxy-9,10-anthraquinone, $C_{17}H_{14}O_4$, (I), and its acetyl derivative, 4-acetyloxy-4-propyloxy-9,10-anthraquinone, $C_{19}H_{16}O_5$, (II), were synthesized from the commercially available dye quinizarin. In both compounds, the anthraquinone frameworks are close to planarity. There is a large difference in the conformation of the propyloxy group; the molecule of (I) adopts a *gauche* conformation [O—C—C—C = −64.4 (2)°], although the molecule of (II) takes a *trans*-planar conformation (zigzag) [O—C—C—C = 176.1 (3)°]. In the molecule of (I), there is an intramolecular O—H$\cdots$O hydrogen bond. In both crystals, the molecules are linked by C—H $\cdots$ O hydrogen bonds. A difference in the molecular arrangements of (I) and (II) is found along the stacking directions.

1. Chemical context

9,10-Anthraquinone and its derivatives are important molecules as dyes and pigments. As a part of a project on the study of the substitution effects of the anthraquinone ring on optical properties in solution as well as in the solid state, we have been synthesizing new anthraquinone derivatives. Recently, we found that the recrystallization of 1,4-dipropyloxy-9,10-anthaquinone from hexane solution afforded two polymorphs, red prisms and yellow needles, whose crystal structures were different from each other (Kitamura *et al.*, 2015*b*). Then we became interested in the effect of the asymmetric substitution pattern of 9,10-anthraquinone because 1,4-dipropyloxy-9,10-anthraquinone is a symmetric molecule along the direction of the molecular short axis. We thought that mono-alkoxylation from quinizarin (1,4-dihydroxy-9,10-anthraquinone) should be effective to gain asymmetric 9,10-anthraquinones along the molecular short axis. We report herein the synthesis and crystal structures of 1-hydroxy-4-propyloxy-9,10-anthraquinone (I) and its acetyl derivative, 1-acetyloxy-4-propyloxy-9,10-anthraquinone (II).
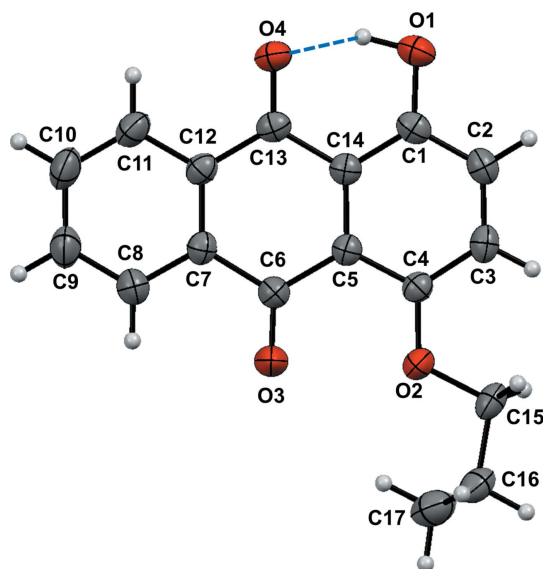

(I) (II)

1845
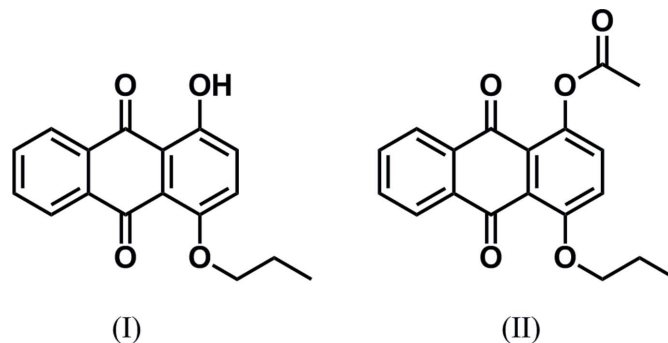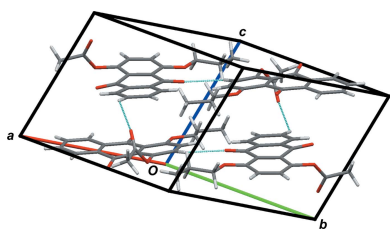
Figure 1
Molecular structure of compound (I), showing the atom labelling and 50% probability displacement ellipsoids. The intramolecular hydrogen bond is indicated by a dashed line.

2. Structural commentary

The molecular structures of the title compounds, (I) and (II), are illustrated in Figs. 1 and 2, respectively. In both molecules, the anthraquinone frameworks are nearly planar. However, there is a large difference in the conformation of the propyloxy group; in compound (I), the the propyloxy moiety adopts a *gauche* conformation [O2—C15—C16—C17 torsion angle = 64.4 (2)°], and in compound (II), it has a *trans*-planar (zigzag) conformation [O2—C17—C18—C19 = 176.1 (3)°]. In (I), there is an intramolecular O—H···O hydrogen bond
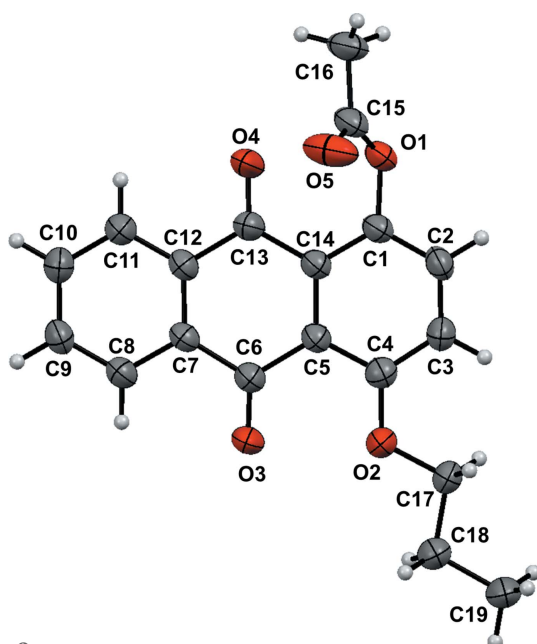

Figure 2
Molecular structure of compound (II), showing the atom labelling and 50% probability displacement ellipsoids.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4	0.98 (3)	1.61 (3)	2.525 (2)	153 (2)
C8—H8···O3^i	0.95	2.51	3.270 (2)	137
C15—H15A···O1^{ii}	0.99	2.88	3.359 (2)	111

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

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O3^i	0.95	2.6	3.384 (4)	140
C10—H10···O5^{ii}	0.95	2.57	3.180 (4)	123

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

forming an $S(6)$ ring motif (Fig. 1 and Table 1). In compound (II), the acetyl group plane (O1/O5/C15/C16) is inclined to the anthraquinone ring system by 71.87 (12)°.

3. Supramolecular features

The crystal packing structures of the title compounds, (I) and (II), are shown in Figs. 3 and 4, respectively. In both crystals, molecules are linked by intermolecular C—H···O hydrogen bonds. For compound (I), C—H···O hydrogen bonds along the lateral direction of the molecules are found (Fig. 3 and Table 1): C8—H8···O3^i, C15—H15A···O1^{ii} [symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x - \frac{3}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$]. In contrast, in compound (II) C—H···O interactions are formed along all directions (Fig. 4 and Table 2): C2—H2···O3^{iii}, C10—H10···O5^{iv} [symmetry codes: (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]. To understand the solid-state optical properties of dyes, revealing the characteristics of the stacking patterns of neighboring molecules is important. In both crystals, the anthraquinone ring systems are arranged nearly parallel, although there is a difference in the molecular arrangement of two neighboring molecules along the stacking directions (Figs. 5–8). As shown in Figs. 5 and 6, a small π overlap of the
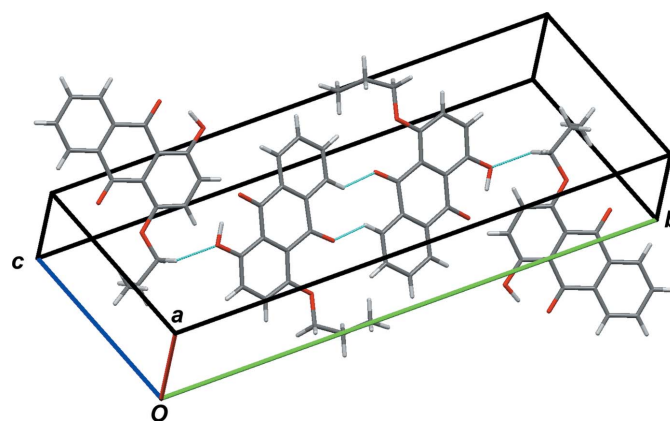

Figure 3
Packing of the unit cell of (I), showing short C—H···O contacts as blue lines.
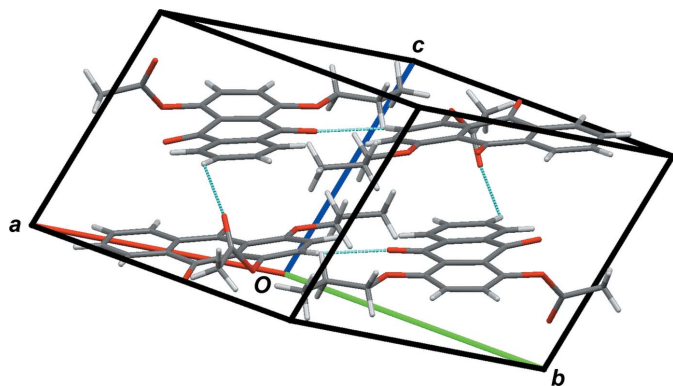
Figure 4
Packing of the unit cell of (II), showing short C—H⋯O contacts as blue lines.

Figure 6
Top view of two neighboring molecules of compound (II) along the stacking direction.

anthraquinone ring systems is observed for compound (II), on the other hand, compound (I) scarcely shows any π overlap. Regarding the overlap of the anthraquinone ring systems, in compound (I) there is a translational slip, while in compound (II) there is a rotational slip. The shortest distances for overlapping non-bonded atoms in the anthraquinone frameworks are 3.297 (2) Å (C11⋯C6^{v}) and 3.558 (2) Å (C13⋯C4^{v}) in compound (I), and 3.363 (4) Å (C8⋯C4^{iv}), 3.423 (4) Å (C11⋯C6^{iv}) and 3.523 (4) Å (C10⋯C14^{iv}) in compound (II) [symmetry code: (v) $x + 1, y, z$]. As shown in Figs. 7 and 8, the interplanar distances between the anthraquinone planes [3.3895 (12) Å for compound (I) and 3.396 (3) Å for compound (II)] are almost identical. The degree of overlap and the interplanar distance between two chromophores are considered to be the two factors essential for evaluating

intermolecular interactions. Therefore compound (II) would have stronger intermolecular interactions than compound (I).

4. Database survey

A literature search found no reports of crystal structures of 1-hydroxy-4-propyloxy-9,10-anthraquinone (I) and 1-acetyloxy-4-propyloxy-9,10-anthraquinone (II). Other hydroxy- or alkoxy-substituted anthraquinone compounds have been reported: 4-(3-bromopropyloxy)-1-hydroxy-9,10-anthraquinone (Ohira *et al.*, 2016), 1,4-dipropyloxy-9,10-anthraquinone
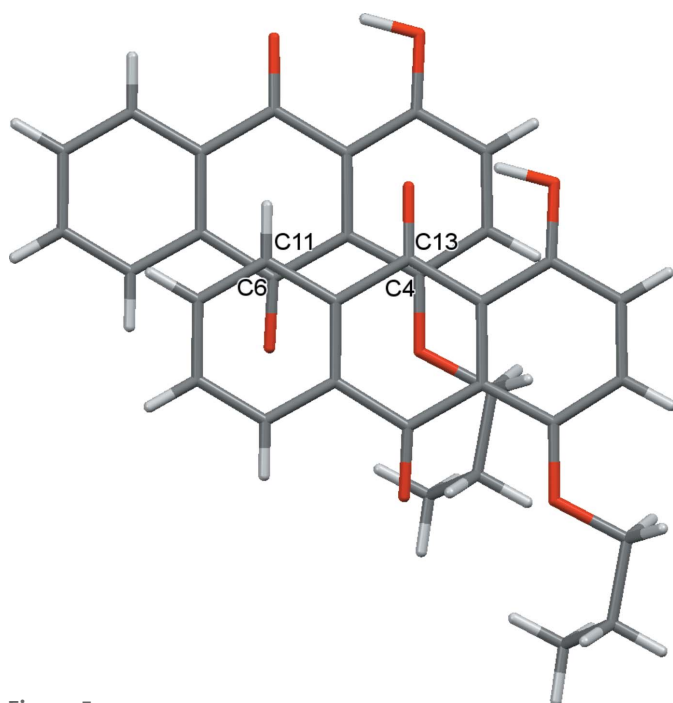

Figure 5
Top view of two neighboring molecules of compound (I) along the stacking direction.

Figure 7
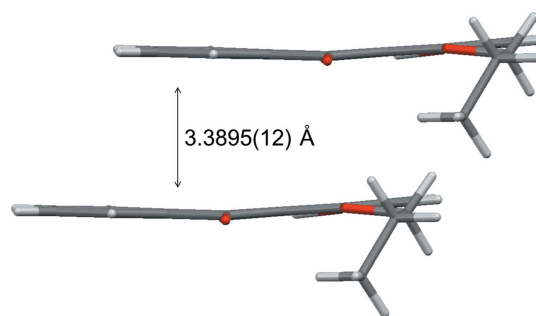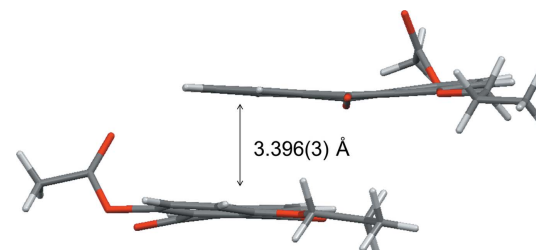Side view of two neighboring molecules of compound (I).

Figure 8
Side view of two neighboring molecules of compound (II).

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{17}H_{14}O_4$	$C_{19}H_{16}O_5$
M_r	282.28	324.32
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	200	200
a, b, c (Å)	4.7354 (3), 25.9882 (17), 11.0671 (9)	11.7730 (12), 15.514 (2), 8.9609 (10)
β (°)	102.268 (7)	111.153 (8)
V (Å^3)	1330.87 (17)	1526.4 (3)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.1	0.10
Crystal size (mm)	$0.5 \times 0.13 \times 0.05$	$0.55 \times 0.1 \times 0.05$
Data collection		
Diffractometer	R-AXIS RAPID	R-AXIS RAPID
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12176, 3029, 2035	13902, 3439, 1649
R_{int}	0.039	0.127
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.123, 1.02	0.070, 0.180, 0.96
No. of reflections	3029	3439
No. of parameters	195	219
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.20	0.20, −0.24

Computer programs: *PROCESS-AUTO* (Rigaku, 1998), *SIR2004* (Burla *et al.*, 2005), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

(Kitamura *et al.*, 2015*b*), 1,4-dihydroxy-2,3-dinitro-9,10-anthraquinone (Furukawa *et al.*, 2016), 1,4-diethoxy-9,10-anthraquinone (Kitamura *et al.*, 2015*a*), 2-bromo-1,4-dihydroxy-9,10-anthraquinone (Furukawa *et al.*, 2014), 2,6-dimethoxy-9,10-anthraquinone (Ohta *et al.*, 2012*a*), 2,6-dipropyloxy-9,10-anthraquinone (Ohta *et al.*, 2012*b*), 2,3,6,7-tetrapropyloxy-9,10-anthraquinone (Ohta *et al.*, 2012*b*).

5. Synthesis and crystallization

The title compounds, (I) and (II), were synthesized starting from quinizarin (1,4-dihydroxy-9,10-anthraquinone), as shown in Fig. 9

Compound (I): A mixture of quinizarin (289 mg, 1.20 mmol), 1-bromopropane (675 mg, 5.49 mmol), K$_2$CO$_3$ (185 mg, 1.34 mmol) in DMF (5 mL) was stirred at 353 K for 3 h under N$_2$. After cooling to room temperature, water (60 mL) was added to the reaction mixture. The brown solid that precipitated was filtered off. The resulting solid was solubilized with CH$_2$Cl$_2$. The organic layer was washed with 1 *M* NaOH to remove the unreacted quinizarin, then washed sequentially with brine, dried over Na$_2$SO$_4$, and evaporated under reduced pressure. The residual brown solid was purified by chromatography on silica gel with an eluent of CH$_2$Cl$_2$. The title compound (I) was obtained as an orange solid (132 mg, 46%). m.p. 387.5–389 K. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.14 (*t*, *J* = 7.4 Hz, 3H, CH$_3$), 1.91–2.00 (*m*, 2H, CH$_2$), 4.11 (*t*, *J* = 6.6 Hz, 2H, CH$_2$), 7.28–7.32 (*m*, 1H, ArH), 7.39–7.41 (*m*, 1H, ArH), 7.73–7.82 (*m*, 2H, ArH), 8.27–8.31 (*m*, 2H, ArH), 13.03

(*s*, 1H, OH). Crystals suitable for X-ray diffraction were grown by slow evaporation of an AcOEt–hexane (>*v*:*v* = 1:10) solution.

Compound (II): A mixture of compound (I) (132 mg, 0.47 mmol), K$_2$CO$_3$ (137 mg, 0.99 mmol) in acetic anhydride (5 mL) was stirred at 383 K for 3 h under air. After cooling to room temperature, water (50 mL) was added into the resulting mixture, then the mixture was stirred for 20 min at room temperature. The mixture was extracted with CH$_2$Cl$_2$. The
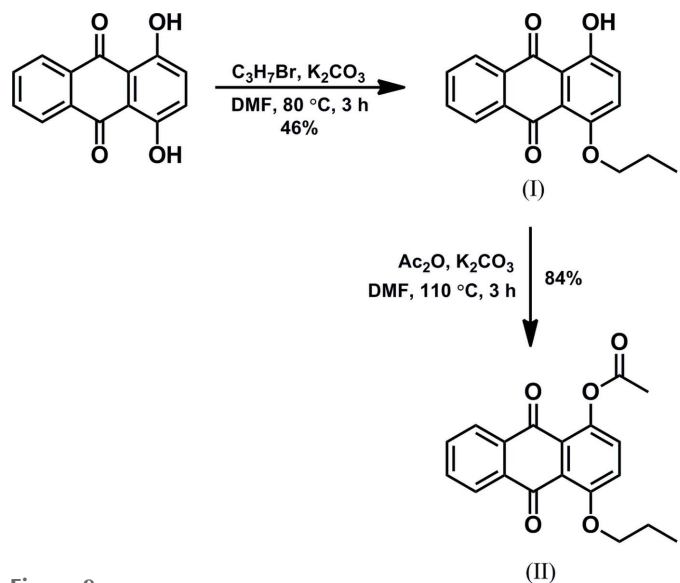
Figure 9
Reaction scheme for the synthesis of compounds (I) and (II).

organic layer was washed with 10% $NaHCO_3$ solution and then brine, and dried over Na_2SO_4, and evaporated under reduced pressure. The residual yellow solid was purified by recrystallization from a hexane–toluene ($>v:v$ = 3:1) solution to provide title compound (II) as a yellow solid (128 mg, 84%). m.p. 401–403 K. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.146 (t, J = 7.3 Hz, 3H, CH$_3$), 1.93–2.02 (m, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$), 4.13 (t, J = 6.4 Hz, 2H, CH$_2$), 7.32–7.36 (m, 2H, ArH), 7.68–7.76 (m, 2H, ArH), 8.12–8.22 (m, 2H, ArH). Crystals suitable for X-ray diffraction were grown by slow evaporation of a hexane-toluene ($>v:v$ = 18:1) solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The hydroxyl H atom, H1 of compound (I), was refined isotropically. All other H atoms were positioned geometrically and treated as riding atoms: C—H = 0.95–0.99 Å with U_{iso}(H) = 1.5U_{eq}(C) for CH$_3$ and 1.2U_{eq}(C) for CH$_2$ and aromatic C—H.

Funding information

References

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.

Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Furukawa, W., Takehara, M., Inoue, Y. & Kitamura, C. (2014). *Acta Cryst.* E**70**, o1130.

Furukawa, W., Takehara, M., Inoue, Y. & Kitamura, C. (2016). *IUCrData*, **1**, x160906.

Kitamura, C., Li, S., Takehara, M., Inoue, Y., Ono, K. & Kawase, T. (2015a). *Acta Cryst.* E**71**, o504–o505.

Kitamura, C., Li, S., Takehara, M., Inoue, Y., Ono, K., Kawase, T. & Fujimoto, K. J. (2015b). *Bull. Chem. Soc. Jpn*, **88**, 713–715.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Ohira, N., Takehara, M., Inoue, Y. & Kitamura, C. (2016). *IUCrData*, **1**, x160753.

Ohta, A., Hattori, K., Kobayashi, T., Naito, H., Kawase, T. & Kitamura, C. (2012a). *Acta Cryst.* E**68**, o2843.

Ohta, A., Hattori, K., Kusumoto, Y., Kawase, T., Kobayashi, T., Naito, H. & Kitamura, C. (2012b). *Chem. Lett.* **41**, 674–676.

Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Crystal structures of 1-hydroxy-4-propyloxy-9,10-anthraquinone and its acetyl derivative

Hidemi Nakagawa and Chitoshi Kitamura

Computing details

For both structures, data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO* (Rigaku, 1998); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

1-Hydroxy-4-propyloxy-9,10-anthraquinone (I)

Crystal data

$C_{17}H_{14}O_4$	$F(000) = 592$
$M_r = 282.28$	$D_x = 1.409$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 8070 reflections
$a = 4.7354$ (3) Å	$\theta = 3.0–27.4°$
$b = 25.9882$ (17) Å	$\mu = 0.1$ mm^{-1}
$c = 11.0671$ (9) Å	$T = 200$ K
$\beta = 102.268$ (7)°	Needle, orange
$V = 1330.87$ (17) Å^3	$0.5 \times 0.13 \times 0.05$ mm
$Z = 4$	

Data collection

R-AXIS RAPID diffractometer	3029 independent reflections
Radiation source: normal sealed x-ray tube	2035 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.039$
Detector resolution: 10 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
ω scans	$h = -6 \rightarrow 5$
12176 measured reflections	$k = -33 \rightarrow 32$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: mixed
$wR(F^2) = 0.123$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.02$	
3029 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.1583P]$ where $P = (F_o^2 + 2F_c^2)/3$
195 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
0 constraints	$\Delta\rho_{max} = 0.17$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.20$ 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_{iso}*/U_{eq}
C1	0.5957 (3)	0.24895 (6)	0.42197 (15)	0.0330 (4)
C2	0.3444 (4)	0.23736 (6)	0.33536 (16)	0.0358 (4)
H2	0.2979	0.2025	0.314	0.043*
C3	0.1644 (3)	0.27569 (6)	0.28092 (15)	0.0350 (4)
H3	−0.0048	0.267	0.2214	0.042*
C4	0.2236 (3)	0.32769 (6)	0.31091 (15)	0.0304 (3)
C5	0.4712 (3)	0.34058 (6)	0.40077 (14)	0.0288 (3)
C6	0.5450 (3)	0.39481 (6)	0.43736 (16)	0.0334 (4)
C7	0.7983 (3)	0.40429 (6)	0.54037 (15)	0.0319 (4)
C8	0.8576 (4)	0.45434 (7)	0.58305 (17)	0.0409 (4)
H8	0.7373	0.4819	0.5465	0.049*
C9	1.0910 (4)	0.46402 (8)	0.67839 (18)	0.0497 (5)
H9	1.1314	0.4983	0.7065	0.06*
C10	1.2665 (4)	0.42437 (8)	0.73352 (19)	0.0512 (5)
H10	1.4256	0.4314	0.7996	0.061*
C11	1.2107 (4)	0.37463 (7)	0.69259 (17)	0.0434 (4)
H11	1.3308	0.3473	0.7306	0.052*
C12	0.9770 (3)	0.36437 (6)	0.59508 (15)	0.0321 (4)
C13	0.9209 (3)	0.31127 (6)	0.55027 (15)	0.0315 (4)
C14	0.6585 (3)	0.30036 (6)	0.45649 (14)	0.0296 (3)
C15	−0.1815 (3)	0.35323 (7)	0.15327 (15)	0.0375 (4)
H15A	−0.3207	0.3296	0.1798	0.045*
H15B	−0.1016	0.336	0.0881	0.045*
C16	−0.3300 (4)	0.40232 (7)	0.10439 (17)	0.0445 (4)
H16A	−0.3997	0.4198	0.172	0.053*
H16B	−0.5009	0.3939	0.0388	0.053*
C17	−0.1379 (4)	0.43891 (8)	0.0523 (2)	0.0580 (5)
H17A	−0.0718	0.4222	−0.0161	0.087*
H17B	0.0296	0.4481	0.1172	0.087*
H17C	−0.2469	0.4701	0.0221	0.087*
O1	0.7687 (3)	0.20912 (4)	0.46962 (12)	0.0422 (3)
O2	0.0480 (2)	0.36605 (4)	0.25698 (11)	0.0374 (3)
O3	0.4064 (3)	0.43123 (4)	0.38701 (13)	0.0522 (4)
O4	1.0922 (2)	0.27624 (4)	0.59342 (11)	0.0396 (3)
H1	0.930 (6)	0.2263 (10)	0.525 (2)	0.086 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0370 (8)	0.0307 (8)	0.0344 (9)	0.0001 (7)	0.0146 (7)	0.0027 (6)
C2	0.0412 (9)	0.0306 (8)	0.0372 (10)	−0.0049 (7)	0.0122 (7)	−0.0038 (7)
C3	0.0325 (8)	0.0403 (9)	0.0326 (9)	−0.0083 (7)	0.0076 (7)	−0.0063 (7)
C4	0.0279 (7)	0.0336 (8)	0.0299 (9)	−0.0001 (7)	0.0066 (6)	0.0004 (6)
C5	0.0283 (7)	0.0311 (7)	0.0276 (8)	−0.0018 (6)	0.0073 (6)	−0.0001 (6)
C6	0.0332 (8)	0.0307 (8)	0.0352 (9)	0.0002 (7)	0.0049 (7)	−0.0006 (7)
C7	0.0314 (8)	0.0344 (8)	0.0300 (9)	−0.0035 (7)	0.0068 (7)	−0.0012 (7)
C8	0.0418 (9)	0.0356 (8)	0.0436 (11)	−0.0034 (8)	0.0051 (8)	−0.0033 (7)
C9	0.0521 (11)	0.0469 (10)	0.0457 (12)	−0.0109 (9)	0.0003 (9)	−0.0103 (8)
C10	0.0474 (10)	0.0597 (11)	0.0396 (11)	−0.0105 (10)	−0.0059 (8)	−0.0062 (9)
C11	0.0381 (9)	0.0520 (10)	0.0354 (10)	−0.0002 (8)	−0.0026 (7)	0.0033 (8)
C12	0.0305 (8)	0.0371 (8)	0.0283 (9)	−0.0009 (7)	0.0056 (6)	0.0028 (7)
C13	0.0310 (8)	0.0357 (8)	0.0290 (9)	0.0006 (7)	0.0095 (6)	0.0058 (6)
C14	0.0301 (7)	0.0316 (7)	0.0286 (8)	−0.0008 (7)	0.0099 (6)	0.0017 (6)
C15	0.0286 (8)	0.0520 (10)	0.0294 (9)	−0.0023 (8)	0.0003 (7)	−0.0052 (7)
C16	0.0337 (9)	0.0589 (11)	0.0376 (11)	0.0077 (9)	0.0002 (7)	−0.0031 (8)
C17	0.0502 (11)	0.0622 (12)	0.0572 (14)	0.0067 (10)	0.0019 (10)	0.0147 (10)
O1	0.0472 (7)	0.0307 (6)	0.0489 (8)	0.0055 (6)	0.0106 (6)	0.0054 (5)
O2	0.0331 (6)	0.0388 (6)	0.0357 (7)	0.0023 (5)	−0.0028 (5)	−0.0018 (5)
O3	0.0524 (8)	0.0329 (6)	0.0595 (9)	0.0053 (6)	−0.0150 (6)	−0.0012 (6)
O4	0.0382 (6)	0.0392 (6)	0.0394 (7)	0.0067 (5)	0.0038 (5)	0.0076 (5)

Geometric parameters (Å, º)

C1—O1	1.3552 (19)	C10—C11	1.376 (3)
C1—C2	1.393 (2)	C10—H10	0.95
C1—C14	1.404 (2)	C11—C12	1.397 (2)
C2—C3	1.365 (2)	C11—H11	0.95
C2—H2	0.95	C12—C13	1.471 (2)
C3—C4	1.406 (2)	C13—O4	1.2449 (18)
C3—H3	0.95	C13—C14	1.468 (2)
C4—O2	1.3531 (18)	C15—O2	1.4422 (19)
C4—C5	1.407 (2)	C15—C16	1.501 (2)
C5—C14	1.424 (2)	C15—H15A	0.99
C5—C6	1.487 (2)	C15—H15B	0.99
C6—O3	1.2172 (19)	C16—C17	1.512 (3)
C6—C7	1.489 (2)	C16—H16A	0.99
C7—C8	1.392 (2)	C16—H16B	0.99
C7—C12	1.393 (2)	C17—H17A	0.98
C8—C9	1.379 (3)	C17—H17B	0.98
C8—H8	0.95	C17—H17C	0.98
C9—C10	1.382 (3)	O1—H1	0.98 (3)
C9—H9	0.95		
O1—C1—C2	117.38 (14)	C10—C11—H11	120

O1—C1—C14	123.06 (15)	C12—C11—H11	120
C2—C1—C14	119.56 (15)	C7—C12—C11	120.12 (15)
C3—C2—C1	120.52 (15)	C7—C12—C13	120.16 (14)
C3—C2—H2	119.7	C11—C12—C13	119.72 (15)
C1—C2—H2	119.7	O4—C13—C14	120.98 (14)
C2—C3—C4	121.52 (15)	O4—C13—C12	120.02 (14)
C2—C3—H3	119.2	C14—C13—C12	118.98 (14)
C4—C3—H3	119.2	C1—C14—C5	120.30 (14)
O2—C4—C3	122.08 (14)	C1—C14—C13	118.34 (14)
O2—C4—C5	118.55 (13)	C5—C14—C13	121.36 (13)
C3—C4—C5	119.36 (15)	O2—C15—C16	107.86 (14)
C4—C5—C14	118.68 (13)	O2—C15—H15A	110.1
C4—C5—C6	122.03 (14)	C16—C15—H15A	110.1
C14—C5—C6	119.28 (14)	O2—C15—H15B	110.1
O3—C6—C5	122.65 (15)	C16—C15—H15B	110.1
O3—C6—C7	119.34 (14)	H15A—C15—H15B	108.4
C5—C6—C7	118.00 (14)	C15—C16—C17	113.45 (15)
C8—C7—C12	119.21 (15)	C15—C16—H16A	108.9
C8—C7—C6	119.08 (15)	C17—C16—H16A	108.9
C12—C7—C6	121.71 (14)	C15—C16—H16B	108.9
C9—C8—C7	120.09 (17)	C17—C16—H16B	108.9
C9—C8—H8	120	H16A—C16—H16B	107.7
C7—C8—H8	120	C16—C17—H17A	109.5
C8—C9—C10	120.70 (17)	C16—C17—H17B	109.5
C8—C9—H9	119.6	H17A—C17—H17B	109.5
C10—C9—H9	119.6	C16—C17—H17C	109.5
C11—C10—C9	119.97 (18)	H17A—C17—H17C	109.5
C11—C10—H10	120	H17B—C17—H17C	109.5
C9—C10—H10	120	C1—O1—H1	102.8 (14)
C10—C11—C12	119.90 (17)	C4—O2—C15	118.00 (12)
O1—C1—C2—C3	−178.11 (14)	C8—C7—C12—C13	−179.10 (14)
C14—C1—C2—C3	2.2 (2)	C6—C7—C12—C13	0.9 (2)
C1—C2—C3—C4	−0.7 (2)	C10—C11—C12—C7	−0.9 (3)
C2—C3—C4—O2	179.53 (15)	C10—C11—C12—C13	179.01 (16)
C2—C3—C4—C5	−1.2 (2)	C7—C12—C13—O4	175.01 (14)
O2—C4—C5—C14	−179.17 (13)	C11—C12—C13—O4	−4.9 (2)
C3—C4—C5—C14	1.5 (2)	C7—C12—C13—C14	−6.2 (2)
O2—C4—C5—C6	−0.3 (2)	C11—C12—C13—C14	173.89 (15)
C3—C4—C5—C6	−179.55 (14)	O1—C1—C14—C5	178.51 (14)
C4—C5—C6—O3	−4.5 (3)	C2—C1—C14—C5	−1.9 (2)
C14—C5—C6—O3	174.43 (16)	O1—C1—C14—C13	−1.2 (2)
C4—C5—C6—C7	175.19 (14)	C2—C1—C14—C13	178.45 (14)
C14—C5—C6—C7	−5.9 (2)	C4—C5—C14—C1	0.0 (2)
O3—C6—C7—C8	4.9 (2)	C6—C5—C14—C1	−178.97 (14)
C5—C6—C7—C8	−174.80 (14)	C4—C5—C14—C13	179.65 (14)
O3—C6—C7—C12	−175.16 (16)	C6—C5—C14—C13	0.7 (2)
C5—C6—C7—C12	5.2 (2)	O4—C13—C14—C1	3.8 (2)

C12—C7—C8—C9	0.0 (3)	C12—C13—C14—C1	−174.90 (13)
C6—C7—C8—C9	179.96 (16)	O4—C13—C14—C5	−175.84 (14)
C7—C8—C9—C10	−0.7 (3)	C12—C13—C14—C5	5.4 (2)
C8—C9—C10—C11	0.6 (3)	O2—C15—C16—C17	64.4 (2)
C9—C10—C11—C12	0.2 (3)	C3—C4—O2—C15	−9.3 (2)
C8—C7—C12—C11	0.8 (2)	C5—C4—O2—C15	171.45 (14)
C6—C7—C12—C11	−179.20 (15)	C16—C15—O2—C4	−175.86 (13)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4	0.98 (3)	1.61 (3)	2.5249 (18)	153 (2)
C8—H8···O3[i]	0.95	2.51	3.270 (2)	137
C15—H15A···O1[ii]	0.99	2.88	3.359 (2)	111

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

1-Acetyloxy-4-propyloxy-9,10-anthraquinone (II)

Crystal data

$C_{19}H_{16}O_5$
$M_r = 324.32$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.7730 (12)$ Å
$b = 15.514 (2)$ Å
$c = 8.9609 (10)$ Å
$\beta = 111.153 (8)°$
$V = 1526.4 (3)$ Å^3
$Z = 4$

$F(000) = 680$
$D_x = 1.411$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6030 reflections
$\theta = 3.2–27.5°$
$\mu = 0.10$ mm^{-1}
$T = 200$ K
Needle, yellow
$0.55 \times 0.1 \times 0.05$ mm

Data collection

R-AXIS RAPID
   diffractometer
Radiation source: normal sealed x-ray tube
Graphite monochromator
Detector resolution: 10 pixels mm^{-1}
ω scans
13902 measured reflections

3439 independent reflections
1649 reflections with $I > 2\sigma(I)$
$R_{int} = 0.127$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
$h = −15\rightarrow15$
$k = −20\rightarrow20$
$l = −10\rightarrow11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.180$
$S = 0.96$
3439 reflections
219 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant
   direct methods

Secondary atom site location: structure-
   invariant direct methods
Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0805P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = −0.24$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.73574 (17)	−0.04963 (13)	0.5929 (3)	0.0468 (6)
O2	0.42969 (17)	0.16690 (14)	0.7620 (3)	0.0483 (6)
O3	0.53107 (19)	0.29687 (14)	0.6807 (3)	0.0540 (6)
O4	0.8033 (2)	0.08785 (16)	0.4753 (3)	0.0702 (8)
O5	0.9066 (2)	−0.0077 (2)	0.7902 (3)	0.0765 (9)
C1	0.6653 (2)	0.0082 (2)	0.6418 (4)	0.0408 (7)
C2	0.5870 (2)	−0.0265 (2)	0.7073 (4)	0.0442 (8)
H2	0.5871	−0.0869	0.7251	0.053*
C3	0.5088 (3)	0.0255 (2)	0.7471 (4)	0.0455 (8)
H3	0.4543	0.0004	0.7912	0.055*
C4	0.5070 (2)	0.1141 (2)	0.7248 (4)	0.0422 (8)
C5	0.5900 (2)	0.1519 (2)	0.6615 (3)	0.0372 (7)
C6	0.5986 (2)	0.2472 (2)	0.6488 (3)	0.0402 (7)
C7	0.6959 (2)	0.2810 (2)	0.5962 (3)	0.0377 (7)
C8	0.7145 (3)	0.3696 (2)	0.5977 (4)	0.0444 (8)
H8	0.6651	0.4071	0.6323	0.053*
C9	0.8044 (3)	0.4036 (2)	0.5493 (4)	0.0468 (8)
H9	0.8158	0.4642	0.5501	0.056*
C10	0.8774 (3)	0.3499 (2)	0.4999 (4)	0.0485 (8)
H10	0.9396	0.3733	0.468	0.058*
C11	0.8596 (3)	0.2620 (2)	0.4971 (4)	0.0447 (8)
H11	0.909	0.225	0.4616	0.054*
C12	0.7697 (2)	0.2272 (2)	0.5461 (4)	0.0388 (7)
C13	0.7508 (3)	0.1335 (2)	0.5408 (4)	0.0426 (8)
C14	0.6682 (2)	0.0963 (2)	0.6175 (3)	0.0379 (7)
C15	0.8571 (3)	−0.0477 (2)	0.6697 (5)	0.0495 (8)
C16	0.9202 (3)	−0.1012 (2)	0.5859 (4)	0.0603 (10)
H16A	0.9495	−0.0642	0.5187	0.09*
H16B	0.8633	−0.144	0.5187	0.09*
H16C	0.9894	−0.1308	0.6649	0.09*
C17	0.3442 (3)	0.1282 (2)	0.8232 (4)	0.0472 (8)
H17A	0.3879	0.1001	0.9274	0.057*
H17B	0.2949	0.0841	0.7476	0.057*
C18	0.2633 (3)	0.1994 (2)	0.8430 (4)	0.0536 (9)
H18A	0.2249	0.2301	0.7402	0.064*
H18B	0.3126	0.2413	0.9236	0.064*
C19	0.1645 (3)	0.1607 (2)	0.8970 (5)	0.0711 (12)
H19A	0.1176	0.1178	0.8186	0.107*
H19B	0.1099	0.2066	0.9055	0.107*

H19C	0.2028	0.1329	1.0015	0.107*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0506 (11)	0.0288 (13)	0.0650 (15)	0.0007 (9)	0.0258 (12)	−0.0081 (10)
O2	0.0496 (12)	0.0379 (14)	0.0699 (15)	0.0019 (10)	0.0365 (12)	0.0032 (11)
O3	0.0596 (12)	0.0321 (14)	0.0861 (17)	0.0101 (11)	0.0454 (13)	0.0047 (12)
O4	0.1004 (18)	0.0341 (15)	0.109 (2)	0.0120 (13)	0.0781 (18)	0.0053 (14)
O5	0.0604 (14)	0.077 (2)	0.080 (2)	0.0213 (14)	0.0106 (15)	−0.0307 (17)
C1	0.0420 (15)	0.0303 (18)	0.0516 (19)	0.0030 (13)	0.0187 (16)	−0.0029 (15)
C2	0.0465 (15)	0.0286 (19)	0.057 (2)	−0.0033 (13)	0.0179 (17)	0.0010 (14)
C3	0.0460 (16)	0.038 (2)	0.059 (2)	−0.0036 (14)	0.0260 (17)	0.0047 (15)
C4	0.0385 (15)	0.041 (2)	0.0477 (19)	0.0008 (14)	0.0166 (16)	0.0000 (15)
C5	0.0378 (14)	0.0309 (18)	0.0437 (18)	0.0024 (12)	0.0159 (15)	0.0034 (13)
C6	0.0415 (15)	0.0325 (19)	0.049 (2)	0.0023 (14)	0.0195 (16)	0.0016 (14)
C7	0.0410 (15)	0.0293 (18)	0.0436 (18)	0.0054 (13)	0.0163 (15)	0.0024 (13)
C8	0.0529 (17)	0.0319 (19)	0.053 (2)	0.0041 (14)	0.0251 (17)	0.0013 (15)
C9	0.0514 (17)	0.0310 (19)	0.060 (2)	−0.0044 (14)	0.0222 (17)	0.0013 (15)
C10	0.0493 (17)	0.041 (2)	0.061 (2)	−0.0054 (15)	0.0267 (18)	0.0030 (16)
C11	0.0459 (16)	0.037 (2)	0.056 (2)	0.0022 (14)	0.0250 (17)	0.0027 (15)
C12	0.0427 (15)	0.0307 (19)	0.0438 (18)	0.0034 (13)	0.0166 (15)	0.0037 (14)
C13	0.0493 (16)	0.0350 (19)	0.050 (2)	0.0052 (14)	0.0261 (17)	0.0005 (15)
C14	0.0401 (14)	0.0304 (18)	0.0435 (18)	0.0024 (13)	0.0155 (15)	0.0003 (13)
C15	0.0510 (18)	0.032 (2)	0.066 (2)	0.0078 (15)	0.0228 (19)	−0.0013 (17)
C16	0.060 (2)	0.047 (3)	0.080 (3)	0.0102 (17)	0.033 (2)	−0.0139 (19)
C17	0.0456 (16)	0.041 (2)	0.064 (2)	−0.0031 (14)	0.0316 (17)	0.0025 (16)
C18	0.0505 (17)	0.045 (2)	0.077 (2)	0.0002 (15)	0.0368 (19)	−0.0024 (17)
C19	0.071 (2)	0.047 (3)	0.122 (3)	0.0025 (18)	0.067 (3)	−0.004 (2)

Geometric parameters (Å, º)

O1—C15	1.344 (4)	C9—C10	1.380 (4)
O1—C1	1.396 (3)	C9—H9	0.95
O2—C4	1.353 (3)	C10—C11	1.378 (4)
O2—C17	1.440 (3)	C10—H10	0.95
O3—C6	1.213 (3)	C11—C12	1.393 (4)
O4—C13	1.220 (3)	C11—H11	0.95
O5—C15	1.198 (4)	C12—C13	1.469 (4)
C1—C2	1.370 (4)	C13—C14	1.494 (4)
C1—C14	1.387 (4)	C15—C16	1.486 (4)
C2—C3	1.364 (4)	C16—H16A	0.98
C2—H2	0.95	C16—H16B	0.98
C3—C4	1.389 (4)	C16—H16C	0.98
C3—H3	0.95	C17—C18	1.510 (4)
C4—C5	1.421 (4)	C17—H17A	0.99
C5—C14	1.417 (4)	C17—H17B	0.99
C5—C6	1.488 (4)	C18—C19	1.535 (4)

C6—C7	1.484 (4)	C18—H18A	0.99
C7—C8	1.390 (4)	C18—H18B	0.99
C7—C12	1.390 (4)	C19—H19A	0.98
C8—C9	1.385 (4)	C19—H19B	0.98
C8—H8	0.95	C19—H19C	0.98
C15—O1—C1	117.9 (2)	C7—C12—C13	120.0 (3)
C4—O2—C17	117.8 (3)	C11—C12—C13	119.8 (3)
C2—C1—C14	121.0 (3)	O4—C13—C12	119.5 (3)
C2—C1—O1	116.7 (3)	O4—C13—C14	121.6 (3)
C14—C1—O1	122.2 (2)	C12—C13—C14	118.9 (2)
C3—C2—C1	120.0 (3)	C1—C14—C5	120.1 (3)
C3—C2—H2	120	C1—C14—C13	120.6 (3)
C1—C2—H2	120	C5—C14—C13	119.3 (3)
C2—C3—C4	121.6 (3)	O5—C15—O1	123.7 (3)
C2—C3—H3	119.2	O5—C15—C16	125.1 (3)
C4—C3—H3	119.2	O1—C15—C16	111.2 (3)
O2—C4—C3	122.7 (3)	C15—C16—H16A	109.5
O2—C4—C5	118.0 (3)	C15—C16—H16B	109.5
C3—C4—C5	119.3 (3)	H16A—C16—H16B	109.5
C14—C5—C4	117.9 (3)	C15—C16—H16C	109.5
C14—C5—C6	121.0 (2)	H16A—C16—H16C	109.5
C4—C5—C6	121.0 (3)	H16B—C16—H16C	109.5
O3—C6—C7	119.8 (3)	O2—C17—C18	107.3 (3)
O3—C6—C5	123.0 (3)	O2—C17—H17A	110.3
C7—C6—C5	117.2 (2)	C18—C17—H17A	110.3
C8—C7—C12	118.8 (3)	O2—C17—H17B	110.3
C8—C7—C6	118.9 (3)	C18—C17—H17B	110.3
C12—C7—C6	122.3 (3)	H17A—C17—H17B	108.5
C9—C8—C7	120.6 (3)	C17—C18—C19	109.5 (3)
C9—C8—H8	119.7	C17—C18—H18A	109.8
C7—C8—H8	119.7	C19—C18—H18A	109.8
C10—C9—C8	120.3 (3)	C17—C18—H18B	109.8
C10—C9—H9	119.8	C19—C18—H18B	109.8
C8—C9—H9	119.8	H18A—C18—H18B	108.2
C11—C10—C9	119.7 (3)	C18—C19—H19A	109.5
C11—C10—H10	120.1	C18—C19—H19B	109.5
C9—C10—H10	120.1	H19A—C19—H19B	109.5
C10—C11—C12	120.3 (3)	C18—C19—H19C	109.5
C10—C11—H11	119.8	H19A—C19—H19C	109.5
C12—C11—H11	119.8	H19B—C19—H19C	109.5
C7—C12—C11	120.2 (3)		
C15—O1—C1—C2	−115.1 (3)	C8—C7—C12—C11	−0.6 (4)
C15—O1—C1—C14	68.5 (4)	C6—C7—C12—C11	179.7 (3)
C14—C1—C2—C3	1.2 (5)	C8—C7—C12—C13	−179.0 (3)
O1—C1—C2—C3	−175.2 (3)	C6—C7—C12—C13	1.3 (4)
C1—C2—C3—C4	−0.8 (5)	C10—C11—C12—C7	0.9 (5)

C17—O2—C4—C3	−1.7 (4)	C10—C11—C12—C13	179.3 (3)
C17—O2—C4—C5	178.8 (3)	C7—C12—C13—O4	169.4 (3)
C2—C3—C4—O2	179.4 (3)	C11—C12—C13—O4	−9.0 (5)
C2—C3—C4—C5	−1.1 (5)	C7—C12—C13—C14	−11.2 (4)
O2—C4—C5—C14	−177.9 (3)	C11—C12—C13—C14	170.4 (3)
C3—C4—C5—C14	2.6 (4)	C2—C1—C14—C5	0.3 (5)
O2—C4—C5—C6	4.8 (4)	O1—C1—C14—C5	176.6 (3)
C3—C4—C5—C6	−174.7 (3)	C2—C1—C14—C13	−177.9 (3)
C14—C5—C6—O3	177.8 (3)	O1—C1—C14—C13	−1.7 (5)
C4—C5—C6—O3	−5.1 (5)	C4—C5—C14—C1	−2.2 (4)
C14—C5—C6—C7	−3.0 (4)	C6—C5—C14—C1	175.0 (3)
C4—C5—C6—C7	174.2 (3)	C4—C5—C14—C13	176.1 (3)
O3—C6—C7—C8	5.4 (4)	C6—C5—C14—C13	−6.7 (4)
C5—C6—C7—C8	−173.8 (3)	O4—C13—C14—C1	11.5 (5)
O3—C6—C7—C12	−174.8 (3)	C12—C13—C14—C1	−167.9 (3)
C5—C6—C7—C12	5.9 (4)	O4—C13—C14—C5	−166.7 (3)
C12—C7—C8—C9	0.4 (5)	C12—C13—C14—C5	13.9 (4)
C6—C7—C8—C9	−179.9 (3)	C1—O1—C15—O5	10.3 (5)
C7—C8—C9—C10	−0.5 (5)	C1—O1—C15—C16	−169.8 (3)
C8—C9—C10—C11	0.7 (5)	C4—O2—C17—C18	−175.8 (3)
C9—C10—C11—C12	−0.9 (5)	O2—C17—C18—C19	176.1 (3)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C2—H2⋯O3[i]	0.95	2.6	3.384 (4)	140
C10—H10⋯O5[ii]	0.95	2.57	3.180 (4)	123

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