CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and crystal structures of two purpurin derivatives: 1,4-dihydroxy-2-propoxyanthraquinone and 2-butoxy-1,4-dihydroxyanthraquinone

Eric Bosch* and Emily N. McClain

Department of Chemistry, Missouri State University, Springfield, MO 65897, USA. *Correspondence e-mail: ericbosch@missouristate.edu

Received 11 August 2017
Accepted 11 October 2017

Edited by S. Parkin, University of Kentucky, USA

Keywords: crystal structure; purpurin; anthraquinone; hydrogen bonding.

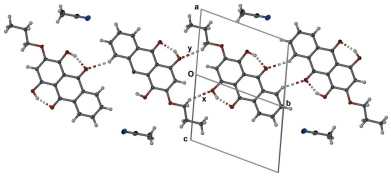
CCDC references: 1579381; 1579380

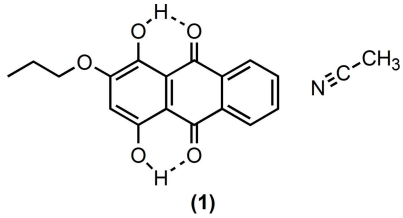
Supporting information: this article has supporting information at journals.iucr.org/e

The title compounds were obtained by deprotonation of 1,2,4-trihydroxyanthraquinone (purpurin) using sodium hydride followed by reaction with either 1-bromopropane or 1-bromobutane. 1,4-Dihydroxy-2-propoxyanthraquinone crystallizes as a 1:1 solvate from acetonitrile, $C_{17}H_{14}O_5\cdot CH_3CN$. The anthraquinone core of the molecule is essentially planar and both hydroxy groups participate in intramolecular O—H···O (carbonyl) hydrogen bonds. The propyl chain is angled slightly above the plane of the anthraquinone moiety with a maximum deviation of 0.247 (2) Å above the plane for the terminal carbon atom. In contrast, 2-butoxy-1,4-dihydroxyanthraquinone, $C_{18}H_{16}O_5$, crystallizes from nitromethane with two independent molecules in the asymmetric unit. The anthraquinone core of each independent molecule is essentially planar and both hydroxy groups on both molecules participate in intramolecular O—H···O(carbonyl) hydrogen bonds. The butyl chain in one molecule is also angled slightly above the plane of the anthraquinone moiety, with a maximum deviation of 0.833 (5) Å above the plane for the terminal carbon atom. In contrast, the butyl group on the second molecule is twisted out of the plane of the anthraquinone core with a torsion angle of 65.1 (3)°, resulting in a maximum deviation of 1.631 (5) Å above the plane for the terminal carbon atom.

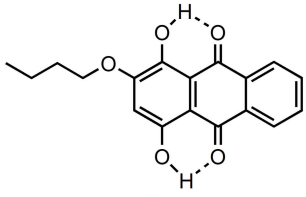
1. Chemical context

Purpurin, 1,2,4-trihydroxy anthraquinone, is a major component of the dye extracted from madder root (Schweppe & Winter, 1997). The extract from madder root has been used to dye wool and other fabrics since antiquity. Purpurin is commercially available and we here report two derivatives, 1,4-dihydroxy-2-propoxy anthraquinone and 2-butoxy-1,4-dihydroxy anthraquinone, prepared by selective deprotonation of purpurin followed by alkylation with the either 1-bromopropane or 1-bromobutane.





(1)



(2)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O5	0.88 (1)	1.75 (1)	2.5537 (13)	152 (2)
O3—H3*O*···O4	0.87 (1)	1.75 (1)	2.5578 (13)	153 (2)
C10—H10···N1	0.95	2.73	3.4009 (19)	128
C15—H15*A*···O3^{i}	0.99	2.57	3.2179 (16)	123
C11—H11···O5^{ii}	0.95	2.47	3.2446 (17)	138

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O5	0.85 (2)	1.78 (2)	2.564 (3)	153 (3)
O3—H3*O*···O4	0.87 (2)	1.74 (2)	2.536 (3)	151 (3)
O6—H6*O*···O10	0.86 (2)	1.72 (2)	2.542 (3)	158 (3)
O8—H8*O*···O9	0.87 (2)	1.73 (2)	2.554 (3)	155 (3)
C3—H3···O10	0.95	2.55	3.494 (3)	173
C29—H29···O3	0.95	2.41	3.231 (4)	144
C15—H15*B*···O6^{i}	0.99	2.52	3.485 (3)	164
C21—H21···O8^{ii}	0.95	2.55	3.502 (3)	180
C33—H33*A*···O9^{iii}	0.99	2.56	3.547 (4)	172

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+3, -y+1, -z+1$; (iii) $-x+2, -y+1, -z+1$.

2. Structural commentary

The asymmetric unit of 1,4-dihydroxy-2-propoxy anthraquinone (1), crystallized from acetonitrile solvent, contains a single anthraquinone molecule and one acetonitrile solvate molecule as shown in Fig. 1. The two intramolecular hydrogen bonds (Table 1) are typical for the 1,4-dihydroxy anthraquinones and 1-hydroxyanthraquinones. These hydrogen bonds are maintained in chloroform solution, as shown by the chemical shift of 13.47 and 13.56 ppm for the two hydroxyl protons. The anthraquinone moiety is planar, with an average root mean square (r.m.s.) deviation of atoms C1 to C14 of 0.021 Å, in which the maximum deviation from the plane defined by atoms C1 to C14 is 0.044 (1) Å for C9. The propyl chain is angled slightly above the plane of the anthraquinone moiety, with deviations of 0.043 (2), 0.143 (2) and 0.247 (2) Å for atoms C15, C16 and C17, respectively, from the plane defined by atoms C1–C14. The acetonitrile is angled towards H10 with a N1···C10 distance of 3.401 (2) Å. The final difference map shows several peaks of 0.2 to 0.7 e Å^{-3} in the anthraquinone plane that suggest the presence of minor whole-molecule disorder in which the anthraquinone is translated in the plane and/or flipped over.

In contrast, the asymmetric unit of 2-butoxy-1,4-dihydroxy anthraquinone (2) crystallized from nitromethane solvent, contains two unique anthraquinone molecules as shown in Fig. 2. Both molecules feature two intramolecular hydrogen bonds (Table 2) similar to those observed in (1). These hydrogen bonds are also maintained in chloroform solution, as shown by the chemical shift of 13.46 and 13.55 ppm for the two hydroxyl protons. The anthraquinone moieties in both molecules are planar. The r.m.s deviation of atoms C1 to C14 is 0.006 Å, with a maximum deviation from the plane defined by atoms C1 to C14 of 0.011 (2) Å for C13. The r.m.s. deviation from the plane defined by atoms C19 to C32 is 0.025 Å, with a maximum deviation of 0.048 (2) Å for C31. The butyl chain attached to O2 is twisted out of the C1–C14 anthraquinone plane with a O2—C15—C16—C17 torsion angle of −65.1 (3)°. The butyl chain has an *anti*-conformation, the C15—C16—C17—C18 torsion angle being −173.1 (2)°. The deviations of the butyl carbon atoms from the anthraquinone plane defined by atoms C1 to C14 are 0.101 (4), 0.194 (4), 1.467 (4) and 1.631 (5) Å for atoms C15, C16, C17 and C18, respectively. The butyl chain in the second unique molecule, attached to O7, is tilted slightly out of the plane of the anthraquinone with a C20—O7—C33—C34 torsion angle of −167.3 (2)°. This butyl chain also adopts an *anti*-conformation, the C33—C34—C35—C36 torsion angle being −175.2 (3)°. The resultant deviations of the butyl carbon atoms from the plane defined by atoms C19–C32 are 0.077 (4), 0.428 (4), 0.356 (4) and 0.833 (5) Å for atoms C33, C34, C35 and C36, respectively. There is a close intermolecular contact between phenyl hydrogen atom H3 and carbonyl oxygen atom O10, with a C3···O10 distance of 3.494 (3) Å (labelled X in Fig. 2). A second close intermolecular contact, between phenyl hydrogen atom H29 and hydroxyl oxygen atom O3 gives a C29···O3 distance of 3.231 (4) Å (labelled Y in Fig. 2).

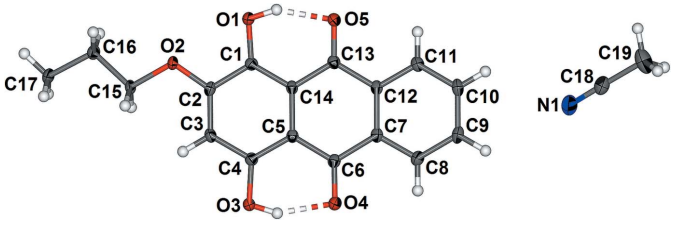


Figure 1
Molecular structure of (1) with the included acetonitrile. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary size.

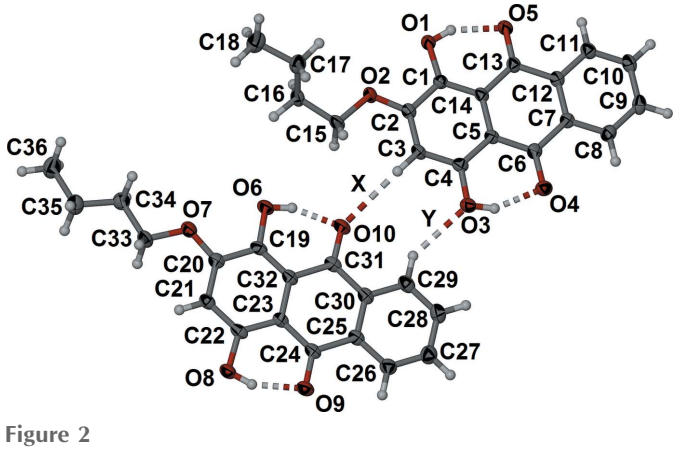


Figure 2
Asymmetric unit of (2) showing the close intermolecular C—H···O contacts X and Y (see text). Displacement ellipsoids of non-H atoms are drawn at the 50% probability level and H atoms are shown as circles of arbitrary size.

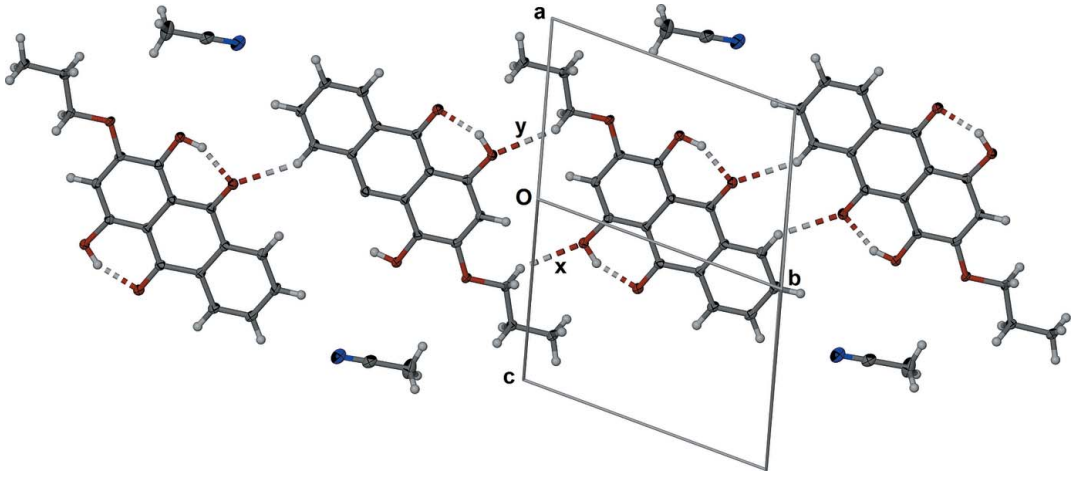


Figure 3
Structure of (1) viewed along the [101] direction, with close C—H···O contacts labelled x and y (see text).

3. Supramolecular features

In the crystal, molecules of (1) form planes that incorporate the acetonitrile molecule, as shown in Fig. 3. The acetonitrile molecule is almost coplanar with the anthraquinone moiety, with deviations of 0.401 (2), 0.536 (2) and 0.722 (2) Å for atoms N1, C18, and C19, respectively, from the plane defined by atoms C1–C14. There is a close C—H···O interaction (Table 1) between a phenyl hydrogen atom and an adjacent carbonyl oxygen atom of an inversion-related molecule of (1). The C11···O5#2 distance is 3.245 (2) Å [symmetry code: (#2) $2-x, 2-y, 1-z$] and the interaction is labelled x in Fig. 3. The methylene hydrogen H15*A* is close to the carbonyl oxygen O3 of a second inversion-related molecule of (1). The C15···O3#1 distance is 3.218 (2) Å [symmetry code: (#1) $1-x, -y, 1-z$], and the interaction is labelled y in Fig. 3. The anthraquinone units of (1) alternately π-stack in pairs as shown in Fig. 4. Each π-stacked pair (A and B in Fig. 4) has significant overlap of the anthraquinone moiety with *Cg*1···*Cg*3#3, *Cg*2···*Cg*2#3 [symmetry code: (#3) $1-x, 1-y, 1-z$; *Cg*1, *Cg*2 and *Cg*3 are the centroids of the six-membered rings C1–C5/C14, C5–C7/C12–C14 and C7–C12, respectively] distances of 3.607 (1) and 3.569 (1) Å, respectively, with slippages of 1.304 and 1.331 Å, respectively. The pairs of π-stacked molecules of (1) are offset π-stacked and the alkyl chain has a C—H···π interaction with one end of the anthraquinone unit, as shown in Fig. 4 (molecules labelled A and C). The C16···*Cg*3#4 distance is 3.587 (2) Å [symmetry code: (#4) $2-x, 1-y, 1-z$].

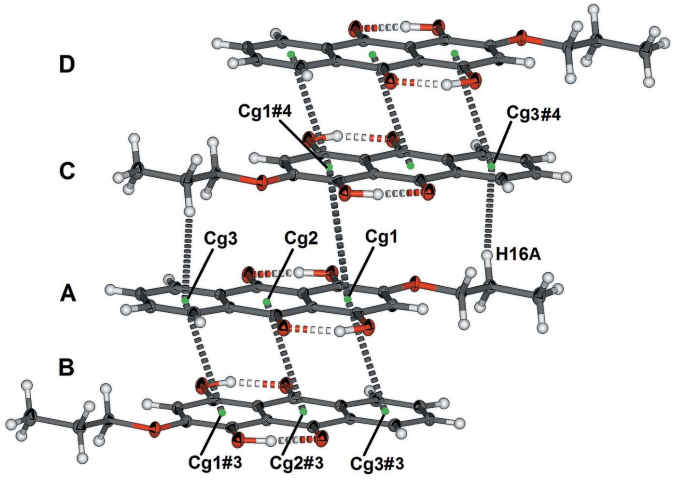


Figure 4
Repetitive π-stacking of (1). Displacement ellipsoids of non-H atoms are drawn at the 50% probability level [symmetry codes: (#1) $-x, -y, 1-z$; (#2) $2-x, 2-y, 2-z$; (#3) $1-x, 1-y, 1-z$; (#4) $2-x, 1-y, 1-z$].

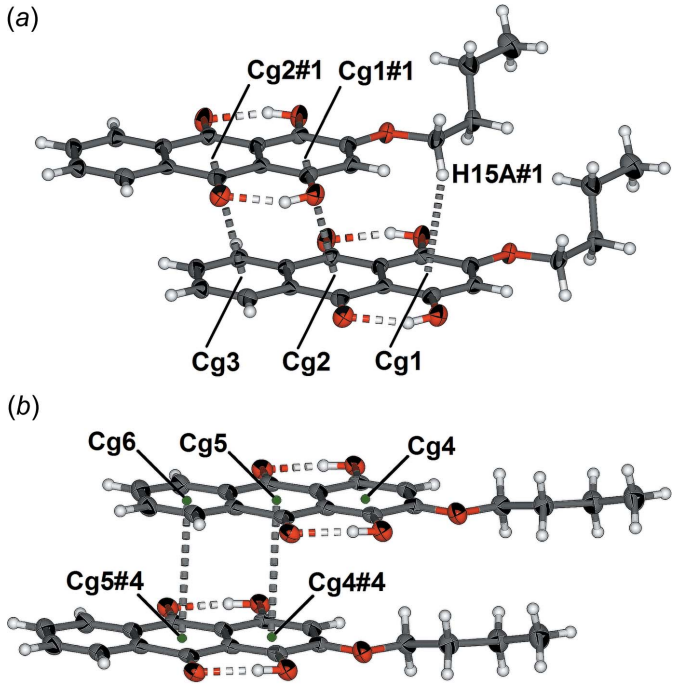


Figure 5
π-Stacking of the two unique molecules of (2) showing the C—H···π and π–π interactions as grey dashed lines. Part (*a*) shows the C1–C14 anthraquinone unit and (*b*) the C19–C32 anthraquinone unit. Displacement ellipsoids drawn at the 50% probability level [symmetry codes: (#1) $x-1, y, z$; (#2) $3-x, 1-y, 1-z$; (#3) $2-x, 1-y, 1-z$; (#4) $1+x, y, z$].

The two unique anthraquinone molecules in the asymmetric unit of (2) offset π-stack in individual columns. There are three close C—H···O contacts (Table 2) between these offset π-stacked columns. The C···O distances are 3.485 (3), 3.502 (3) and 3.548 (4) Å for C15···O6#1, C21···O8#2, and C33···O9#3. respectively [symmetry codes: (#1) $x-1, y, z$; (#2) $3-x, 1-y, 1-z$; (#3) $2-x, 1-y, 1-z$]. The interactions within each of the two unique sets of π-stacked molecules are shown in Fig. 5. For the anthraquinone unit defined by C1–C14 (Fig. 5*a*), the centroid-to-centroid distances *Cg*2···*Cg*1#1 and *Cg*3···*Cg*2#1 are 3.521 (2) and 3.517 (2) Å, with slippages of 0.960 and 0.948 Å, respectively, where *Cg*1, *Cg*2 and *Cg*3 are the centroids of the six-membered rings C1–C5/C14, C5–C7/C12–C14 and C7–C12, respectively. The methylene hydrogen atom H15*A*#1 is positioned above centroid *Cg*1 with a C15···*Cg*1 distance of 3.690 (3) Å. For the anthraquinone unit defined by C19–C32 (Fig. 5*b*), the centroid-to-centroid distances *Cg*5···*Cg*4#4 and *Cg*6···*Cg*5#4 [symmetry code: (#4) $1+x, y, z$; *Cg*4, *Cg*5 and *Cg*6 are the centroids of the C19–C23/C32, C23—C25/C30-C32 and C25–C30 rings, respectively] are 3.520 (1) and 4.009 (1) Å with slippages of 0.960 and 2.145 Å, respectively.

4. Database survey

A search of the Cambridge Crystallographic Database (Version 5.38, Nov. 2016; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for the anthraquinone ring system with oxygen atoms at positions 1, 2 and 4 without restriction on substitution of the other aromatic position, revealed 15 structures. Database entries not including atomic coordinates were excluded. The structure of the parent compound, 1,2,4-trihydroxy anthraquinone monohydrate has been reported (refcode QEGNEV; Yatsenko *et al.*, 2000). In addition, structures have been determined for several organic derivatives that were isolated from natural sources. For example, the derivative most closely related to the structures reported here, 1,4-dihydroxy-2-methoxy-7-methylanthracene-9,10-dione, has been isolated from two different fungi and the structure reported [refcodes GEPCOU (She *et al.*, 2006) and GEPCOU01 (Muangsin *et al.*, 2008)]. Complexes of purpurin with rhenium (refcodes CEVNIB, CEVNOH and AVABEF; Sathiyendiran, *et al.*, 2006, 2011), copper [refcode ZOMSEB; Das, *et al.*, 2014), tin (refcodes MOQTAO and MOQTES; de Sousa *et al.*, 2009), calcium and aluminum (refcode LAYBAO; Bergerhoff & Wunderlich, 1993) have been reported. In each of the reported structures, those compounds with a free hydroxyl group flanking the anthraquinone carbonyl also exhibit the intramolecular hydrogen bond reported for (1) and (2).

5. Synthesis and crystallization

Synthesis of 1,4-dihydroxy-2-propoxy anthraquinone (1). In a flask under an atmosphere of argon, a dark red–orange solution of purpurin (0.26 g) in dimethylformamide (10 mL) and tetrahydrofuran (20 mL) was cooled in an ice–salt bath. Sodium hydride (0.081 g, 1 eq.) was added and the resultant violet solution was stirred in the ice bath for 20 minutes. Excess 1-bromopropane (1 mL) was added, a water condenser attached, and the flask was removed from the cooling bath and heated to 353 K for 24 h. The flask was cooled to room temperature and the solvents evaporated. The crude product was purified by column chromatography with silica gel (0.65–0.40 mm) and mixtures of hexane and ethyl acetate of increasing polarity. The eluant was monitored by TLC with a 5:1 mixture of hexane and ethyl acetate. The solvent was evaporated and the product obtained as a red–orange solid (0.15 g). ^{1}H NMR: (400MHz, $CDCl_3$) δ 13.56 (*s*, 1H), 13.47 (*s*, 1H), 8.33 (*dd*, J = 2.0, 7.0 Hz, 2H), 7.84–7.77 (*m*, 2H), 6.67 (*s*, 1H), 4.09 (*t*, J = 8.0 Hz, 2H), 1.97 (*s*, J = 7.0 Hz, 2H), 1.11 (*t*, J = 7.4 Hz, 3H). ^{13}C NMR: 189.87, 186.98, 163.64, 159.97, 153.30, 137.17, 136.78, 136.41, 135.95, 129.63, 129.47, 115.07, 110.03, 108.64, 73.84, 24.68, 13.02. Compound (1) crystallized from acetonitrile as large dark-red blocks that included an acetonitrile molecule as a 1:1 solvate. When these blocks were cut to small individual pieces or ground with a mortar and pestle they appeared orange. The crystals lost luster after removal from the mother liquor, presumably due to loss of the acetonitrile.

Synthesis of 4-butoxy-1,2-dihydroxyanthraquinone (2). The same procedure was used with 1 mL of 1-bromobutane. The compound was isolated as a dark red–purple solid. ^{1}H NMR: (400MHz, $CDCl_3$) δ 13.55 (*s*, 1H), 13.46 (*s*,1H), 8.33 (*dd*, J = 2.0, 7.0 Hz, 2H), 7.84–7.76 (*m*, 2H), 6.66 (*s*, 1H), 4.13 (*t*, J = 6.6 Hz, 2H), 1.92 (*m*, 2H), 1.56 (*m*, 2H), 1.02 (*t*, J = 7.4 Hz, 3H). ^{13}C NMR: 187.40, 184.50, 161.22, 157.56, 150.87, 134.72, 134.33, 133.96, 133.51, 107.57, 106.18, 69.73, 30.85, 19.37, 13.98. Compound (2) was recrystallized from nitromethane as dark red–black blocks. When these blocks were cut to small individual pieces or ground with a mortar and pestle they appeared orange–red.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms potentially involved in hydrogen-bonding interactions were located by difference methods and initially restrained in the refinement with O—H = 0.84 (2) Å and with U_{iso}(H) = 1.2U_{eq}(O). Other H atoms were included in the refinement at calculated positions, C—H = 0.95 Å for aromatic, C—H = 0.99 Å for methylene and C—H = 0.98 Å for methyl hydrogens with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methylene H atoms and 1.5U_{eq}(C) for methyl H atoms.

Acknowledgements

We thank the Missouri State University Provost Incentive Fund that funded the purchase of the X-ray diffractometer.

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bergerhoff, G. & Wunderlich, C. H. (1993). *Z. Kristallogr.* **207**, 189–192.

Table 3
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$C_{17}H_{14}O_5 \cdot C_2H_3N$	$C_{18}H_{16}O_5$
M_r	339.33	312.31
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$
Temperature (K)	100	100
a, b, c (Å)	8.2160 (11), 9.8605 (13), 10.7410 (14)	4.7730 (9), 44.272 (8), 13.807 (3)
α, β, γ (°)	95.999 (2), 90.181 (2), 113.774 (2)	90, 95.164 (2), 90
V (Å^3)	790.99 (18)	2905.8 (9)
Z	2	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.10	0.10
Crystal size (mm)	0.45 × 0.18 × 0.09	0.48 × 0.10 × 0.03
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.869, 1.000	0.854, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10216, 3548, 2718	36901, 6456, 3747
R_{int}	0.022	0.104
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.644	0.643
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.153, 1.06	0.063, 0.166, 1.04
No. of reflections	3548	6456
No. of parameters	234	429
No. of restraints	2	4
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})	0.71, −0.27	0.26, −0.27

Computer programs: *SMART* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *X-SEED* (Barbour, 2001).

Bruker (2014). *SMART*, *SAINT*, and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Das, P., Jain, C. K., Dey, S. K., Saha, R., Chowdhury, A. D., Roychoudhury, S., Kumar, S., Majumder, H. K. & Das, S. (2014). *RSC Adv.* **4**, 59344–59357.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Muangsin, N., Wisetsakdakorn, W., Chaichit, N., Sihanonth, P., Petsom, A. & Sangvanich, P. (2008). *Dyes Pigments*, **77**, 653–656.

Sathiyendiran, M., Liao, R. T., Thanasekaran, P., Luo, T. T., Venkataramanan, N. S., Lee, G. H., Peng, S. M. & Lu, K. L. (2006). *Inorg. Chem.* **45**, 10052–10054.

Sathiyendiran, M., Tsai, C. C., Thanasekaran, P., Luo, T. T., Yang, C. I., Lee, G. H., Peng, S. M. & Lu, K. L. (2011). *Chem. Eur. J.* **17**, 3343–3346.

Schweppe, H. & Winter, J. (1997). *Artists Pigments*, **3**, edited by E. W. Fitzhugh, pp. 109–142. New York: Oxford University Press.

She, Z.-G., Huang, H.-R., Lin, Y.-C., Vrijmoed, L. L. P. & Jones, E. B. G. (2006). *Acta Cryst.* E**62**, o3737–o3738.

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

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

Sousa, A. T. de, Bessler, K. E., Lemos, S. S., Ellena, J. & Gatto, C. C. (2009). *Z. Anorg. Allg. Chem.* **635**, 106–111.

Yatsenko, A. V., Chernyshev, V. V., Popov, S. I., Sonneveld, E. J. & Schenk, H. (2000). *Dyes Pigments*, **45**, 169–176.

supporting information

Acta Cryst. (2017). E**73**, 1687-1691 [https://doi.org/10.1107/S2056989017014724]

Synthesis and crystal structures of two purpurin derivatives: 1,4-dihydroxy-2-propoxyanthraquinone and 2-butoxy-1,4-dihydroxyanthraquinone

Eric Bosch and Emily N. McClain

Computing details

For both structures, data collection: *SMART* (Bruker, 2014); cell refinement: *SMART* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015b); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED* (Barbour, 2001).

1,4-Dihydroxy-2-propoxyanthraquinone acetonitrile monosolvate (1)

Crystal data

$C_{17}H_{14}O_5 \cdot C_2H_3N$
$M_r = 339.33$
Triclinic, $P\overline{1}$
$a = 8.2160$ (11) Å
$b = 9.8605$ (13) Å
$c = 10.7410$ (14) Å
$\alpha = 95.999$ (2)°
$\beta = 90.181$ (2)°
$\gamma = 113.774$ (2)°
$V = 790.99$ (18) Å^3
$Z = 2$
$F(000) = 356$
$D_x = 1.425$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3016 reflections
$\theta = 2.7$–27.2°
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Cut irregular block, orange
0.45 × 0.18 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.869$, $T_{max} = 1.000$
10216 measured reflections
3548 independent reflections
2718 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.3°$, $\theta_{min} = 1.9°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.153$
$S = 1.06$
3548 reflections
234 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 0.0684P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ 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	0.93351 (13)	0.54640 (11)	0.31245 (9)	0.0224 (2)
H1O	0.943 (2)	0.6376 (15)	0.3329 (15)	0.027*
N1	0.69308 (19)	1.25060 (16)	0.93564 (13)	0.0376 (4)
C1	0.83016 (17)	0.46925 (15)	0.39909 (12)	0.0179 (3)
O2	0.85708 (12)	0.26110 (10)	0.29025 (9)	0.0216 (2)
C2	0.78580 (17)	0.31187 (15)	0.38774 (12)	0.0186 (3)
O3	0.50110 (13)	0.19718 (10)	0.64607 (9)	0.0231 (3)
H3O	0.471 (2)	0.2555 (17)	0.6993 (14)	0.028*
C3	0.67840 (17)	0.22550 (15)	0.47188 (12)	0.0190 (3)
H3	0.650425	0.121543	0.464073	0.023*
O4	0.48044 (13)	0.42907 (11)	0.76272 (9)	0.0236 (2)
C4	0.60915 (17)	0.28978 (15)	0.56995 (12)	0.0184 (3)
O5	0.90743 (13)	0.77360 (10)	0.43289 (9)	0.0237 (3)
C5	0.65148 (17)	0.44303 (14)	0.58446 (12)	0.0168 (3)
C6	0.58069 (17)	0.50732 (15)	0.68671 (12)	0.0186 (3)
C7	0.63155 (17)	0.67078 (15)	0.70039 (12)	0.0182 (3)
C8	0.57026 (18)	0.73660 (16)	0.80017 (12)	0.0215 (3)
H8	0.496307	0.676508	0.858499	0.026*
C9	0.61668 (18)	0.88946 (16)	0.81480 (13)	0.0230 (3)
H9	0.577257	0.934122	0.884204	0.028*
C10	0.72114 (18)	0.97713 (15)	0.72752 (13)	0.0232 (3)
H10	0.750414	1.081320	0.736488	0.028*
C11	0.78274 (18)	0.91324 (15)	0.62752 (13)	0.0211 (3)
H11	0.854261	0.973685	0.568420	0.025*
C12	0.73939 (17)	0.75953 (14)	0.61376 (12)	0.0175 (3)
C13	0.80994 (17)	0.69324 (15)	0.50858 (12)	0.0185 (3)
C14	0.76399 (17)	0.53320 (14)	0.49710 (12)	0.0171 (3)
C15	0.80376 (18)	0.10079 (14)	0.26995 (12)	0.0197 (3)
H15A	0.672284	0.048972	0.262662	0.024*
H15B	0.847744	0.066928	0.341400	0.024*
C16	0.88231 (18)	0.06548 (15)	0.15066 (12)	0.0216 (3)
H16A	1.013724	0.117694	0.158502	0.026*
H16B	0.839009	0.100713	0.079785	0.026*
C17	0.8285 (2)	−0.10258 (15)	0.12525 (13)	0.0259 (3)
H17A	0.864454	−0.138135	0.198037	0.039*
H17B	0.887518	−0.124293	0.051405	0.039*
H17C	0.699127	−0.153202	0.110002	0.039*
C18	0.7439 (2)	1.37684 (18)	0.95263 (14)	0.0300 (3)
C19	0.8085 (2)	1.53842 (19)	0.97699 (19)	0.0451 (5)

H19A	0.707605	1.567300	0.974361	0.068*
H19B	0.891236	1.584642	0.913041	0.068*
H19C	0.870055	1.572114	1.059963	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0257 (5)	0.0171 (5)	0.0230 (5)	0.0076 (4)	0.0075 (4)	0.0008 (4)
N1	0.0451 (8)	0.0342 (8)	0.0356 (8)	0.0199 (7)	0.0016 (6)	−0.0023 (6)
C1	0.0159 (6)	0.0174 (6)	0.0186 (6)	0.0052 (5)	0.0005 (5)	0.0013 (5)
O2	0.0243 (5)	0.0157 (5)	0.0244 (5)	0.0086 (4)	0.0078 (4)	−0.0012 (4)
C2	0.0173 (6)	0.0200 (7)	0.0190 (6)	0.0092 (5)	0.0005 (5)	−0.0026 (5)
O3	0.0278 (5)	0.0164 (5)	0.0249 (5)	0.0086 (4)	0.0091 (4)	0.0029 (4)
C3	0.0188 (6)	0.0151 (6)	0.0230 (7)	0.0071 (5)	0.0002 (5)	0.0003 (5)
O4	0.0263 (5)	0.0202 (5)	0.0239 (5)	0.0092 (4)	0.0069 (4)	0.0018 (4)
C4	0.0176 (6)	0.0184 (6)	0.0194 (6)	0.0076 (5)	0.0011 (5)	0.0021 (5)
O5	0.0271 (5)	0.0170 (5)	0.0247 (5)	0.0066 (4)	0.0067 (4)	0.0018 (4)
C5	0.0165 (6)	0.0167 (6)	0.0170 (6)	0.0071 (5)	−0.0007 (5)	0.0000 (5)
C6	0.0178 (6)	0.0193 (7)	0.0193 (6)	0.0086 (5)	0.0004 (5)	0.0007 (5)
C7	0.0168 (6)	0.0182 (7)	0.0195 (6)	0.0078 (5)	−0.0019 (5)	−0.0012 (5)
C8	0.0225 (7)	0.0233 (7)	0.0192 (6)	0.0106 (6)	0.0007 (5)	−0.0004 (5)
C9	0.0228 (7)	0.0245 (7)	0.0230 (7)	0.0131 (6)	−0.0025 (5)	−0.0056 (5)
C10	0.0235 (7)	0.0183 (7)	0.0282 (7)	0.0107 (6)	−0.0037 (6)	−0.0042 (5)
C11	0.0207 (7)	0.0189 (6)	0.0236 (7)	0.0084 (5)	−0.0014 (5)	0.0008 (5)
C12	0.0167 (6)	0.0173 (7)	0.0180 (6)	0.0073 (5)	−0.0029 (5)	−0.0018 (5)
C13	0.0175 (6)	0.0170 (7)	0.0201 (6)	0.0065 (5)	−0.0009 (5)	0.0006 (5)
C14	0.0161 (6)	0.0156 (7)	0.0185 (6)	0.0061 (5)	−0.0015 (5)	−0.0012 (5)
C15	0.0206 (7)	0.0139 (6)	0.0233 (7)	0.0065 (5)	0.0030 (5)	−0.0017 (5)
C16	0.0223 (7)	0.0212 (7)	0.0208 (7)	0.0089 (5)	0.0021 (5)	−0.0006 (5)
C17	0.0319 (8)	0.0222 (7)	0.0228 (7)	0.0113 (6)	0.0068 (6)	−0.0028 (5)
C18	0.0311 (8)	0.0349 (9)	0.0271 (7)	0.0178 (7)	−0.0004 (6)	−0.0015 (6)
C19	0.0445 (10)	0.0300 (9)	0.0596 (11)	0.0163 (8)	−0.0157 (9)	−0.0045 (8)

Geometric parameters (Å, º)

O1—C1	1.3410 (15)	C9—C10	1.392 (2)
O1—H1O	0.875 (13)	C9—H9	0.9500
N1—C18	1.136 (2)	C10—C11	1.3877 (19)
C1—C14	1.3938 (19)	C10—H10	0.9500
C1—C2	1.4353 (19)	C11—C12	1.4013 (18)
O2—C2	1.3493 (16)	C11—H11	0.9500
O2—C15	1.4516 (15)	C12—C13	1.4814 (19)
C2—C3	1.3714 (19)	C13—C14	1.4584 (19)
O3—C4	1.3407 (15)	C15—C16	1.5075 (18)
O3—H3O	0.874 (14)	C15—H15A	0.9900
C3—C4	1.4106 (18)	C15—H15B	0.9900
C3—H3	0.9500	C16—C17	1.5265 (18)
O4—C6	1.2505 (16)	C16—H16A	0.9900

C4—C5	1.3983 (18)	C16—H16B	0.9900
O5—C13	1.2480 (16)	C17—H17A	0.9800
C5—C14	1.4292 (19)	C17—H17B	0.9800
C5—C6	1.4498 (18)	C17—H17C	0.9800
C6—C7	1.4836 (18)	C18—C19	1.456 (2)
C7—C8	1.3947 (18)	C19—H19A	0.9800
C7—C12	1.4025 (18)	C19—H19B	0.9800
C8—C9	1.3887 (19)	C19—H19C	0.9800
C8—H8	0.9500		

C1—O1—H1O	104.0 (11)	C12—C11—H11	120.0
O1—C1—C14	123.72 (12)	C11—C12—C7	119.64 (12)
O1—C1—C2	117.06 (11)	C11—C12—C13	119.48 (12)
C14—C1—C2	119.22 (12)	C7—C12—C13	120.88 (12)
C2—O2—C15	116.12 (10)	O5—C13—C14	121.35 (12)
O2—C2—C3	125.11 (12)	O5—C13—C12	120.31 (12)
O2—C2—C1	114.62 (12)	C14—C13—C12	118.33 (12)
C3—C2—C1	120.27 (12)	C1—C14—C5	120.48 (12)
C4—O3—H3O	104.0 (11)	C1—C14—C13	119.04 (12)
C2—C3—C4	120.53 (12)	C5—C14—C13	120.47 (12)
C2—C3—H3	119.7	O2—C15—C16	107.99 (10)
C4—C3—H3	119.7	O2—C15—H15A	110.1
O3—C4—C5	122.48 (11)	C16—C15—H15A	110.1
O3—C4—C3	116.90 (12)	O2—C15—H15B	110.1
C5—C4—C3	120.61 (12)	C16—C15—H15B	110.1
C4—C5—C14	118.88 (12)	H15A—C15—H15B	108.4
C4—C5—C6	119.80 (12)	C15—C16—C17	109.75 (11)
C14—C5—C6	121.32 (12)	C15—C16—H16A	109.7
O4—C6—C5	121.78 (12)	C17—C16—H16A	109.7
O4—C6—C7	120.05 (11)	C15—C16—H16B	109.7
C5—C6—C7	118.17 (12)	C17—C16—H16B	109.7
C8—C7—C12	119.70 (12)	H16A—C16—H16B	108.2
C8—C7—C6	119.52 (12)	C16—C17—H17A	109.5
C12—C7—C6	120.79 (12)	C16—C17—H17B	109.5
C9—C8—C7	120.41 (13)	H17A—C17—H17B	109.5
C9—C8—H8	119.8	C16—C17—H17C	109.5
C7—C8—H8	119.8	H17A—C17—H17C	109.5
C8—C9—C10	119.86 (12)	H17B—C17—H17C	109.5
C8—C9—H9	120.1	N1—C18—C19	178.89 (17)
C10—C9—H9	120.1	C18—C19—H19A	109.5
C11—C10—C9	120.40 (12)	C18—C19—H19B	109.5
C11—C10—H10	119.8	H19A—C19—H19B	109.5
C9—C10—H10	119.8	C18—C19—H19C	109.5
C10—C11—C12	119.97 (13)	H19A—C19—H19C	109.5
C10—C11—H11	120.0	H19B—C19—H19C	109.5

C15—O2—C2—C3	4.50 (19)	C9—C10—C11—C12	0.2 (2)
C15—O2—C2—C1	−175.30 (10)	C10—C11—C12—C7	0.9 (2)

O1—C1—C2—O2	0.80 (18)	C10—C11—C12—C13	−178.36 (11)
C14—C1—C2—O2	−179.69 (11)	C8—C7—C12—C11	−0.8 (2)
O1—C1—C2—C3	−179.01 (11)	C6—C7—C12—C11	178.81 (11)
C14—C1—C2—C3	0.5 (2)	C8—C7—C12—C13	178.54 (11)
O2—C2—C3—C4	−179.31 (12)	C6—C7—C12—C13	−1.9 (2)
C1—C2—C3—C4	0.5 (2)	C11—C12—C13—O5	0.1 (2)
C2—C3—C4—O3	178.11 (11)	C7—C12—C13—O5	−179.19 (11)
C2—C3—C4—C5	−1.2 (2)	C11—C12—C13—C14	179.48 (11)
O3—C4—C5—C14	−178.34 (11)	C7—C12—C13—C14	0.19 (19)
C3—C4—C5—C14	0.9 (2)	O1—C1—C14—C5	178.71 (11)
O3—C4—C5—C6	1.4 (2)	C2—C1—C14—C5	−0.8 (2)
C3—C4—C5—C6	−179.28 (11)	O1—C1—C14—C13	−0.8 (2)
C4—C5—C6—O4	−0.6 (2)	C2—C1—C14—C13	179.77 (11)
C14—C5—C6—O4	179.13 (11)	C4—C5—C14—C1	0.1 (2)
C4—C5—C6—C7	178.82 (11)	C6—C5—C14—C1	−179.73 (11)
C14—C5—C6—C7	−1.4 (2)	C4—C5—C14—C13	179.51 (11)
O4—C6—C7—C8	1.5 (2)	C6—C5—C14—C13	−0.3 (2)
C5—C6—C7—C8	−177.94 (11)	O5—C13—C14—C1	−0.3 (2)
O4—C6—C7—C12	−178.03 (11)	C12—C13—C14—C1	−179.62 (11)
C5—C6—C7—C12	2.49 (19)	O5—C13—C14—C5	−179.72 (11)
C12—C7—C8—C9	−0.6 (2)	C12—C13—C14—C5	0.91 (19)
C6—C7—C8—C9	179.85 (11)	C2—O2—C15—C16	174.51 (10)
C7—C8—C9—C10	1.7 (2)	O2—C15—C16—C17	−179.69 (10)
C8—C9—C10—C11	−1.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O5	0.88 (1)	1.75 (1)	2.5537 (13)	152 (2)
O3—H3*O*···O4	0.87 (1)	1.75 (1)	2.5578 (13)	153 (2)
C10—H10···N1	0.95	2.73	3.4009 (19)	128
C15—H15*A*···O3^{i}	0.99	2.57	3.2179 (16)	123
C11—H11···O5^{ii}	0.95	2.47	3.2446 (17)	138

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

2-Butoxy-1,4-dihydroxyanthraquinone (2)

Crystal data

$C_{18}H_{16}O_5$
M_r = 312.31
Monoclinic, $P2_1/n$
a = 4.7730 (9) Å
b = 44.272 (8) Å
c = 13.807 (3) Å
β = 95.164 (2)°
V = 2905.8 (9) Å^3
Z = 8

$F(000)$ = 1312
D_x = 1.428 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2921 reflections
θ = 2.4–23.8°
μ = 0.10 mm^{-1}
T = 100 K
Cut irregular block, orange-red
0.48 × 0.10 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.854, T_{max} = 1.000
36901 measured reflections
6456 independent reflections
3747 reflections with $I > 2\sigma(I)$
R_{int} = 0.104
θ_{max} = 27.2°, θ_{min} = 1.6°
h = −6→6
k = −56→56
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.166
S = 1.04
6456 reflections
429 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 2.0816P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 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	−0.3186 (4)	0.27290 (4)	0.38526 (14)	0.0341 (5)
H1O	−0.448 (5)	0.2616 (6)	0.359 (2)	0.041*
C1	−0.3234 (6)	0.29688 (6)	0.32535 (19)	0.0272 (6)
O2	0.0428 (4)	0.31529 (4)	0.43337 (13)	0.0312 (5)
C2	−0.1245 (6)	0.32043 (6)	0.3504 (2)	0.0275 (6)
O3	−0.2823 (4)	0.37359 (4)	0.15477 (15)	0.0350 (5)
H3O	−0.399 (6)	0.3708 (7)	0.1034 (17)	0.042*
C3	−0.1160 (6)	0.34561 (6)	0.2928 (2)	0.0287 (6)
H3	0.017152	0.361103	0.309821	0.034*
O4	−0.6827 (4)	0.35220 (4)	0.04208 (14)	0.0367 (5)
C4	−0.3032 (6)	0.34858 (6)	0.2089 (2)	0.0286 (6)
O5	−0.7188 (4)	0.25237 (4)	0.26716 (15)	0.0375 (5)
C5	−0.5023 (5)	0.32611 (6)	0.18344 (19)	0.0254 (6)
O6	0.7609 (4)	0.39771 (4)	0.48700 (15)	0.0355 (5)
H6O	0.636 (6)	0.3937 (7)	0.4395 (17)	0.043*
C6	−0.6920 (6)	0.32954 (6)	0.0958 (2)	0.0293 (6)
O7	1.1866 (4)	0.42067 (4)	0.59154 (14)	0.0367 (5)
C7	−0.9003 (5)	0.30521 (6)	0.07061 (19)	0.0266 (6)
O8	1.2269 (4)	0.50371 (4)	0.37289 (15)	0.0341 (5)
H8O	1.123 (6)	0.5094 (7)	0.3208 (16)	0.041*
C8	−1.0870 (6)	0.30801 (6)	−0.0124 (2)	0.0328 (7)

H8	−1.081236	0.325412	−0.052455	0.039*
O9	0.8632 (4)	0.50517 (4)	0.22553 (14)	0.0359 (5)
C9	−1.2818 (6)	0.28529 (7)	−0.0366 (2)	0.0349 (7)
H9	−1.410599	0.287331	−0.092840	0.042*
O10	0.4078 (4)	0.40025 (4)	0.33801 (14)	0.0346 (5)
C10	−1.2893 (6)	0.25958 (6)	0.0210 (2)	0.0340 (7)
H10	−1.419875	0.243897	0.003368	0.041*
C11	−1.1065 (6)	0.25689 (6)	0.1040 (2)	0.0321 (7)
H11	−1.114821	0.239564	0.144244	0.038*
C12	−0.9090 (6)	0.27958 (6)	0.12909 (19)	0.0274 (6)
C13	−0.7114 (6)	0.27581 (6)	0.2171 (2)	0.0286 (6)
C14	−0.5100 (5)	0.29996 (6)	0.2427 (2)	0.0264 (6)
C15	0.2386 (6)	0.33909 (6)	0.4653 (2)	0.0313 (6)
H15B	0.136313	0.358244	0.473426	0.038*
H15A	0.375876	0.342303	0.416602	0.038*
C16	0.3885 (6)	0.32930 (6)	0.5611 (2)	0.0339 (7)
H16A	0.538850	0.344065	0.580570	0.041*
H16B	0.479215	0.309504	0.552161	0.041*
C17	0.1962 (7)	0.32659 (7)	0.6425 (2)	0.0402 (7)
H17A	0.060155	0.310046	0.626768	0.048*
H17B	0.088094	0.345572	0.646233	0.048*
C18	0.3532 (8)	0.32039 (7)	0.7413 (2)	0.0488 (9)
H18A	0.475930	0.302797	0.736548	0.073*
H18B	0.217716	0.316330	0.788912	0.073*
H18C	0.467288	0.338036	0.761934	0.073*
C19	0.8649 (6)	0.42371 (6)	0.4540 (2)	0.0296 (6)
C20	1.0975 (6)	0.43683 (6)	0.5119 (2)	0.0301 (6)
C21	1.2100 (6)	0.46359 (6)	0.4840 (2)	0.0302 (6)
H21	1.362242	0.472501	0.522992	0.036*
C22	1.1009 (6)	0.47784 (6)	0.3981 (2)	0.0300 (6)
C23	0.8739 (6)	0.46552 (6)	0.3399 (2)	0.0278 (6)
C24	0.7634 (6)	0.48070 (6)	0.2524 (2)	0.0293 (6)
C25	0.5272 (6)	0.46627 (6)	0.1918 (2)	0.0300 (6)
C26	0.4175 (6)	0.48005 (7)	0.1061 (2)	0.0365 (7)
H26	0.489850	0.498971	0.087551	0.044*
C27	0.2030 (7)	0.46627 (7)	0.0475 (2)	0.0413 (8)
H27	0.132225	0.475545	−0.011761	0.050*
C28	0.0917 (6)	0.43906 (7)	0.0752 (2)	0.0394 (7)
H28	−0.057104	0.429841	0.035422	0.047*
C29	0.1970 (6)	0.42527 (6)	0.1608 (2)	0.0354 (7)
H29	0.120415	0.406580	0.179632	0.042*
C30	0.4146 (6)	0.43869 (6)	0.2195 (2)	0.0305 (6)
C31	0.5203 (6)	0.42406 (6)	0.3111 (2)	0.0296 (6)
C32	0.7571 (6)	0.43774 (6)	0.3698 (2)	0.0290 (6)
C33	1.4201 (6)	0.43232 (6)	0.6555 (2)	0.0354 (7)
H33A	1.359002	0.449853	0.692861	0.042*
H33B	1.575349	0.438816	0.617335	0.042*
C34	1.5157 (7)	0.40682 (7)	0.7235 (2)	0.0392 (7)

H34A	1.589349	0.390176	0.685154	0.047*
H34B	1.351732	0.398995	0.754780	0.047*
C35	1.7415 (7)	0.41641 (7)	0.8018 (2)	0.0449 (8)
H35A	1.663659	0.431719	0.844235	0.054*
H35B	1.900044	0.425732	0.771114	0.054*
C36	1.8488 (8)	0.38931 (8)	0.8632 (2)	0.0525 (9)
H36A	1.695632	0.381183	0.898166	0.079*
H36B	2.003713	0.395739	0.910094	0.079*
H36C	1.915812	0.373660	0.820721	0.079*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0317 (11)	0.0275 (11)	0.0412 (12)	−0.0051 (9)	−0.0072 (9)	0.0049 (9)
C1	0.0237 (14)	0.0243 (14)	0.0334 (15)	0.0016 (11)	0.0025 (12)	0.0025 (12)
O2	0.0262 (10)	0.0271 (10)	0.0389 (11)	−0.0023 (8)	−0.0038 (9)	−0.0001 (8)
C2	0.0236 (14)	0.0239 (14)	0.0350 (15)	0.0027 (11)	0.0020 (12)	−0.0028 (11)
O3	0.0343 (12)	0.0276 (11)	0.0423 (12)	−0.0038 (9)	−0.0007 (9)	0.0058 (9)
C3	0.0229 (14)	0.0232 (14)	0.0400 (16)	−0.0018 (11)	0.0033 (12)	−0.0031 (12)
O4	0.0353 (12)	0.0298 (11)	0.0446 (12)	0.0010 (9)	0.0009 (9)	0.0078 (9)
C4	0.0251 (15)	0.0226 (14)	0.0387 (16)	0.0024 (11)	0.0057 (12)	0.0020 (12)
O5	0.0347 (12)	0.0297 (11)	0.0464 (12)	−0.0070 (9)	−0.0060 (9)	0.0081 (9)
C5	0.0211 (14)	0.0233 (13)	0.0325 (15)	0.0019 (11)	0.0059 (11)	−0.0008 (11)
O6	0.0331 (12)	0.0261 (10)	0.0468 (13)	−0.0057 (9)	0.0015 (9)	0.0027 (9)
C6	0.0236 (14)	0.0279 (15)	0.0364 (16)	0.0066 (11)	0.0024 (12)	0.0021 (12)
O7	0.0321 (11)	0.0302 (11)	0.0467 (12)	−0.0039 (9)	−0.0022 (9)	0.0032 (9)
C7	0.0224 (14)	0.0272 (14)	0.0306 (15)	0.0048 (11)	0.0048 (12)	−0.0013 (11)
O8	0.0304 (11)	0.0261 (10)	0.0456 (12)	−0.0053 (9)	0.0028 (9)	0.0013 (9)
C8	0.0322 (16)	0.0337 (16)	0.0324 (16)	0.0068 (13)	0.0024 (13)	0.0022 (12)
O9	0.0342 (12)	0.0263 (11)	0.0474 (12)	−0.0037 (9)	0.0047 (9)	0.0027 (9)
C9	0.0273 (16)	0.0401 (17)	0.0360 (17)	0.0071 (13)	−0.0035 (13)	−0.0072 (13)
O10	0.0291 (11)	0.0263 (11)	0.0487 (12)	−0.0046 (8)	0.0049 (9)	−0.0003 (9)
C10	0.0279 (16)	0.0323 (16)	0.0411 (17)	−0.0001 (12)	−0.0006 (13)	−0.0099 (13)
C11	0.0292 (16)	0.0276 (15)	0.0394 (16)	−0.0003 (12)	0.0030 (13)	−0.0039 (12)
C12	0.0235 (14)	0.0266 (14)	0.0323 (15)	0.0036 (11)	0.0029 (12)	−0.0039 (12)
C13	0.0239 (14)	0.0282 (15)	0.0335 (15)	0.0013 (12)	0.0008 (12)	−0.0015 (12)
C14	0.0207 (13)	0.0232 (14)	0.0355 (15)	0.0006 (11)	0.0033 (11)	−0.0004 (11)
C15	0.0266 (15)	0.0225 (14)	0.0443 (17)	−0.0034 (11)	0.0009 (13)	−0.0019 (12)
C16	0.0295 (16)	0.0277 (15)	0.0427 (17)	−0.0001 (12)	−0.0065 (13)	−0.0047 (13)
C17	0.0374 (18)	0.0405 (18)	0.0415 (18)	0.0057 (14)	−0.0024 (14)	−0.0005 (14)
C18	0.061 (2)	0.0373 (19)	0.0463 (19)	0.0090 (16)	−0.0058 (17)	−0.0034 (15)
C19	0.0277 (15)	0.0196 (13)	0.0425 (17)	−0.0021 (11)	0.0083 (13)	−0.0014 (12)
C20	0.0263 (15)	0.0263 (14)	0.0382 (16)	0.0031 (12)	0.0058 (13)	−0.0011 (12)
C21	0.0243 (15)	0.0255 (14)	0.0412 (17)	−0.0009 (11)	0.0058 (13)	−0.0041 (12)
C22	0.0265 (15)	0.0216 (14)	0.0432 (17)	−0.0018 (11)	0.0107 (13)	−0.0056 (12)
C23	0.0235 (14)	0.0217 (14)	0.0386 (16)	0.0013 (11)	0.0058 (12)	−0.0025 (12)
C24	0.0236 (14)	0.0238 (14)	0.0413 (16)	0.0001 (11)	0.0069 (12)	−0.0037 (12)
C25	0.0247 (15)	0.0257 (14)	0.0404 (16)	0.0012 (11)	0.0064 (12)	−0.0027 (12)

C26	0.0330 (17)	0.0319 (16)	0.0445 (18)	−0.0002 (13)	0.0029 (14)	0.0034 (13)
C27	0.0371 (18)	0.0395 (18)	0.0462 (19)	0.0042 (14)	−0.0024 (15)	0.0013 (14)
C28	0.0311 (17)	0.0384 (17)	0.0475 (19)	0.0008 (13)	−0.0022 (14)	−0.0066 (14)
C29	0.0277 (16)	0.0303 (16)	0.0483 (18)	−0.0006 (12)	0.0049 (14)	−0.0055 (13)
C30	0.0240 (15)	0.0278 (15)	0.0401 (17)	0.0020 (11)	0.0055 (13)	−0.0051 (12)
C31	0.0250 (15)	0.0234 (14)	0.0416 (17)	0.0023 (11)	0.0095 (13)	−0.0047 (12)
C32	0.0227 (14)	0.0242 (14)	0.0405 (16)	0.0004 (11)	0.0059 (12)	−0.0039 (12)
C33	0.0313 (16)	0.0294 (15)	0.0446 (18)	−0.0043 (13)	−0.0009 (13)	−0.0040 (13)
C34	0.0383 (18)	0.0347 (17)	0.0440 (18)	0.0003 (14)	−0.0001 (14)	0.0010 (14)
C35	0.046 (2)	0.0380 (18)	0.0495 (19)	0.0035 (15)	−0.0053 (16)	−0.0038 (15)
C36	0.056 (2)	0.047 (2)	0.052 (2)	0.0065 (17)	−0.0088 (17)	−0.0009 (16)

Geometric parameters (Å, º)

O1—C1	1.345 (3)	C16—H16A	0.9900
O1—H1O	0.848 (18)	C16—H16B	0.9900
C1—C14	1.390 (4)	C17—C18	1.520 (4)
C1—C2	1.431 (4)	C17—H17A	0.9900
O2—C2	1.356 (3)	C17—H17B	0.9900
O2—C15	1.450 (3)	C18—H18A	0.9800
C2—C3	1.372 (4)	C18—H18B	0.9800
O3—C4	1.344 (3)	C18—H18C	0.9800
O3—H3O	0.870 (17)	C19—C32	1.377 (4)
C3—C4	1.404 (4)	C19—C20	1.432 (4)
C3—H3	0.9500	C20—C21	1.370 (4)
O4—C6	1.251 (3)	C21—C22	1.402 (4)
C4—C5	1.399 (4)	C21—H21	0.9500
O5—C13	1.249 (3)	C22—C23	1.400 (4)
C5—C14	1.420 (4)	C23—C32	1.426 (4)
C5—C6	1.453 (4)	C23—C24	1.441 (4)
O6—C19	1.349 (3)	C24—C25	1.486 (4)
O6—H6O	0.863 (18)	C25—C26	1.392 (4)
C6—C7	1.485 (4)	C25—C30	1.401 (4)
O7—C20	1.348 (3)	C26—C27	1.388 (4)
O7—C33	1.453 (3)	C26—H26	0.9500
C7—C8	1.393 (4)	C27—C28	1.384 (4)
C7—C12	1.396 (4)	C27—H27	0.9500
O8—C22	1.354 (3)	C28—C29	1.384 (4)
O8—H8O	0.874 (17)	C28—H28	0.9500
C8—C9	1.390 (4)	C29—C30	1.392 (4)
C8—H8	0.9500	C29—H29	0.9500
O9—C24	1.253 (3)	C30—C31	1.469 (4)
C9—C10	1.391 (4)	C31—C32	1.462 (4)
C9—H9	0.9500	C33—C34	1.512 (4)
O10—C31	1.254 (3)	C33—H33A	0.9900
C10—C11	1.381 (4)	C33—H33B	0.9900
C10—H10	0.9500	C34—C35	1.517 (4)
C11—C12	1.399 (4)	C34—H34A	0.9900

C11—H11	0.9500	C34—H34B	0.9900
C12—C13	1.479 (4)	C35—C36	1.531 (4)
C13—C14	1.460 (4)	C35—H35A	0.9900
C15—C16	1.510 (4)	C35—H35B	0.9900
C15—H15B	0.9900	C36—H36A	0.9800
C15—H15A	0.9900	C36—H36B	0.9800
C16—C17	1.518 (4)	C36—H36C	0.9800

C1—O1—H1O	103 (2)	C17—C18—H18C	109.5
O1—C1—C14	123.8 (2)	H18A—C18—H18C	109.5
O1—C1—C2	116.9 (2)	H18B—C18—H18C	109.5
C14—C1—C2	119.3 (2)	O6—C19—C32	123.3 (2)
C2—O2—C15	116.7 (2)	O6—C19—C20	116.6 (2)
O2—C2—C3	125.4 (2)	C32—C19—C20	120.1 (2)
O2—C2—C1	114.2 (2)	O7—C20—C21	125.8 (3)
C3—C2—C1	120.4 (2)	O7—C20—C19	114.4 (2)
C4—O3—H3O	105 (2)	C21—C20—C19	119.9 (3)
C2—C3—C4	120.3 (2)	C20—C21—C22	120.1 (3)
C2—C3—H3	119.9	C20—C21—H21	120.0
C4—C3—H3	119.9	C22—C21—H21	120.0
O3—C4—C5	121.9 (2)	O8—C22—C23	121.4 (3)
O3—C4—C3	117.5 (2)	O8—C22—C21	117.3 (2)
C5—C4—C3	120.5 (2)	C23—C22—C21	121.3 (2)
C4—C5—C14	119.2 (2)	C22—C23—C32	118.2 (2)
C4—C5—C6	119.6 (2)	C22—C23—C24	120.4 (2)
C14—C5—C6	121.2 (2)	C32—C23—C24	121.4 (2)
C19—O6—H6O	100 (2)	O9—C24—C23	122.1 (3)
O4—C6—C5	121.7 (2)	O9—C24—C25	119.7 (3)
O4—C6—C7	120.1 (2)	C23—C24—C25	118.2 (2)
C5—C6—C7	118.2 (2)	C26—C25—C30	119.3 (3)
C20—O7—C33	118.4 (2)	C26—C25—C24	119.9 (3)
C8—C7—C12	119.9 (3)	C30—C25—C24	120.8 (3)
C8—C7—C6	119.6 (2)	C27—C26—C25	120.3 (3)
C12—C7—C6	120.6 (2)	C27—C26—H26	119.8
C22—O8—H8O	103 (2)	C25—C26—H26	119.8
C9—C8—C7	119.9 (3)	C28—C27—C26	120.2 (3)
C9—C8—H8	120.1	C28—C27—H27	119.9
C7—C8—H8	120.1	C26—C27—H27	119.9
C8—C9—C10	120.4 (3)	C27—C28—C29	120.1 (3)
C8—C9—H9	119.8	C27—C28—H28	120.0
C10—C9—H9	119.8	C29—C28—H28	120.0
C11—C10—C9	119.9 (3)	C28—C29—C30	120.2 (3)
C11—C10—H10	120.1	C28—C29—H29	119.9
C9—C10—H10	120.1	C30—C29—H29	119.9
C10—C11—C12	120.3 (3)	C29—C30—C25	119.9 (3)
C10—C11—H11	119.9	C29—C30—C31	119.5 (3)
C12—C11—H11	119.9	C25—C30—C31	120.6 (3)
C7—C12—C11	119.7 (2)	O10—C31—C32	121.0 (3)

C7—C12—C13	121.1 (2)	O10—C31—C30	120.2 (2)
C11—C12—C13	119.2 (2)	C32—C31—C30	118.9 (2)
O5—C13—C14	121.7 (2)	C19—C32—C23	120.5 (2)
O5—C13—C12	120.0 (2)	C19—C32—C31	119.5 (2)
C14—C13—C12	118.2 (2)	C23—C32—C31	120.0 (2)
C1—C14—C5	120.3 (2)	O7—C33—C34	106.5 (2)
C1—C14—C13	119.1 (2)	O7—C33—H33A	110.4
C5—C14—C13	120.6 (2)	C34—C33—H33A	110.4
O2—C15—C16	107.4 (2)	O7—C33—H33B	110.4
O2—C15—H15B	110.2	C34—C33—H33B	110.4
C16—C15—H15B	110.2	H33A—C33—H33B	108.6
O2—C15—H15A	110.2	C33—C34—C35	112.9 (2)
C16—C15—H15A	110.2	C33—C34—H34A	109.0
H15B—C15—H15A	108.5	C35—C34—H34A	109.0
C15—C16—C17	113.7 (2)	C33—C34—H34B	109.0
C15—C16—H16A	108.8	C35—C34—H34B	109.0
C17—C16—H16A	108.8	H34A—C34—H34B	107.8
C15—C16—H16B	108.8	C34—C35—C36	110.9 (3)
C17—C16—H16B	108.8	C34—C35—H35A	109.5
H16A—C16—H16B	107.7	C36—C35—H35A	109.5
C16—C17—C18	113.3 (3)	C34—C35—H35B	109.5
C16—C17—H17A	108.9	C36—C35—H35B	109.5
C18—C17—H17A	108.9	H35A—C35—H35B	108.1
C16—C17—H17B	108.9	C35—C36—H36A	109.5
C18—C17—H17B	108.9	C35—C36—H36B	109.5
H17A—C17—H17B	107.7	H36A—C36—H36B	109.5
C17—C18—H18A	109.5	C35—C36—H36C	109.5
C17—C18—H18B	109.5	H36A—C36—H36C	109.5
H18A—C18—H18B	109.5	H36B—C36—H36C	109.5

C15—O2—C2—C3	2.6 (4)	C33—O7—C20—C21	0.9 (4)
C15—O2—C2—C1	−176.8 (2)	C33—O7—C20—C19	−179.4 (2)
O1—C1—C2—O2	−0.6 (3)	O6—C19—C20—O7	1.7 (4)
C14—C1—C2—O2	178.7 (2)	C32—C19—C20—O7	−178.9 (2)
O1—C1—C2—C3	179.9 (2)	O6—C19—C20—C21	−178.5 (2)
C14—C1—C2—C3	−0.7 (4)	C32—C19—C20—C21	0.8 (4)
O2—C2—C3—C4	−179.2 (2)	O7—C20—C21—C22	178.6 (3)
C1—C2—C3—C4	0.2 (4)	C19—C20—C21—C22	−1.1 (4)
C2—C3—C4—O3	−179.2 (2)	C20—C21—C22—O8	−177.9 (2)
C2—C3—C4—C5	0.6 (4)	C20—C21—C22—C23	1.0 (4)
O3—C4—C5—C14	178.8 (2)	O8—C22—C23—C32	178.2 (2)
C3—C4—C5—C14	−1.0 (4)	C21—C22—C23—C32	−0.7 (4)
O3—C4—C5—C6	0.4 (4)	O8—C22—C23—C24	−1.7 (4)
C3—C4—C5—C6	−179.4 (2)	C21—C22—C23—C24	179.4 (3)
C4—C5—C6—O4	−0.1 (4)	C22—C23—C24—O9	−0.4 (4)
C14—C5—C6—O4	−178.5 (3)	C32—C23—C24—O9	179.7 (3)
C4—C5—C6—C7	179.8 (2)	C22—C23—C24—C25	178.4 (3)
C14—C5—C6—C7	1.4 (4)	C32—C23—C24—C25	−1.5 (4)

O4—C6—C7—C8	−0.8 (4)	O9—C24—C25—C26	−0.3 (4)
C5—C6—C7—C8	179.3 (2)	C23—C24—C25—C26	−179.1 (3)
O4—C6—C7—C12	178.8 (3)	O9—C24—C25—C30	179.0 (3)
C5—C6—C7—C12	−1.0 (4)	C23—C24—C25—C30	0.2 (4)
C12—C7—C8—C9	0.1 (4)	C30—C25—C26—C27	−1.4 (4)
C6—C7—C8—C9	179.8 (3)	C24—C25—C26—C27	178.0 (3)
C7—C8—C9—C10	−0.8 (4)	C25—C26—C27—C28	1.6 (5)
C8—C9—C10—C11	1.5 (4)	C26—C27—C28—C29	−0.9 (5)
C9—C10—C11—C12	−1.6 (4)	C27—C28—C29—C30	0.1 (4)
C8—C7—C12—C11	−0.2 (4)	C28—C29—C30—C25	0.1 (4)
C6—C7—C12—C11	−179.9 (2)	C28—C29—C30—C31	178.8 (3)
C8—C7—C12—C13	179.3 (2)	C26—C25—C30—C29	0.6 (4)
C6—C7—C12—C13	−0.3 (4)	C24—C25—C30—C29	−178.8 (3)
C10—C11—C12—C7	1.0 (4)	C26—C25—C30—C31	−178.2 (3)
C10—C11—C12—C13	−178.6 (2)	C24—C25—C30—C31	2.5 (4)
C7—C12—C13—O5	−178.4 (3)	C29—C30—C31—O10	−2.8 (4)
C11—C12—C13—O5	1.2 (4)	C25—C30—C31—O10	176.0 (2)
C7—C12—C13—C14	1.3 (4)	C29—C30—C31—C32	177.3 (3)
C11—C12—C13—C14	−179.1 (2)	C25—C30—C31—C32	−3.9 (4)
O1—C1—C14—C5	179.7 (2)	O6—C19—C32—C23	178.8 (2)
C2—C1—C14—C5	0.4 (4)	C20—C19—C32—C23	−0.5 (4)
O1—C1—C14—C13	−1.0 (4)	O6—C19—C32—C31	−0.9 (4)
C2—C1—C14—C13	179.6 (2)	C20—C19—C32—C31	179.8 (2)
C4—C5—C14—C1	0.5 (4)	C22—C23—C32—C19	0.5 (4)
C6—C5—C14—C1	178.9 (2)	C24—C23—C32—C19	−179.6 (3)
C4—C5—C14—C13	−178.8 (2)	C22—C23—C32—C31	−179.9 (2)
C6—C5—C14—C13	−0.4 (4)	C24—C23—C32—C31	0.0 (4)
O5—C13—C14—C1	−0.6 (4)	O10—C31—C32—C19	2.4 (4)
C12—C13—C14—C1	179.7 (2)	C30—C31—C32—C19	−177.7 (2)
O5—C13—C14—C5	178.7 (3)	O10—C31—C32—C23	−177.2 (2)
C12—C13—C14—C5	−1.0 (4)	C30—C31—C32—C23	2.7 (4)
C2—O2—C15—C16	176.7 (2)	C20—O7—C33—C34	−167.3 (2)
O2—C15—C16—C17	−65.1 (3)	O7—C33—C34—C35	−174.3 (3)
C15—C16—C17—C18	−173.1 (2)	C33—C34—C35—C36	−175.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O5	0.85 (2)	1.78 (2)	2.564 (3)	153 (3)
O3—H3*O*···O4	0.87 (2)	1.74 (2)	2.536 (3)	151 (3)
O6—H6*O*···O10	0.86 (2)	1.72 (2)	2.542 (3)	158 (3)
O8—H8*O*···O9	0.87 (2)	1.73 (2)	2.554 (3)	155 (3)
C3—H3···O10	0.95	2.55	3.494 (3)	173
C29—H29···O3	0.95	2.41	3.231 (4)	144
C15—H15*B*···O6^{i}	0.99	2.52	3.485 (3)	164

C21—H21···O8^{ii}	0.95	2.55	3.502 (3)	180
C33—H33*A*···O9^{iii}	0.99	2.56	3.547 (4)	172

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