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2-Hydroxy-1,6,7,8-tetramethoxy-3-methylanthraquinone

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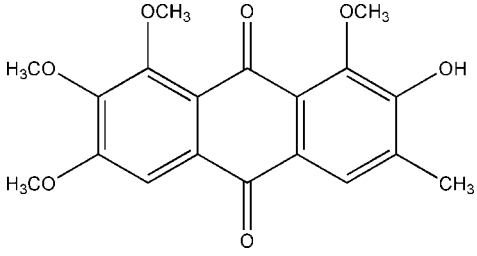
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.046; wR factor = 0.133; data-to-parameter ratio = 16.1.

The title compound, $C_{19}H_{18}O_7$, also known as chrysoobtusin, was isolated from *Cassia tora* L. (Leguminosae). The anthraquinone ring system is almost planar, the dihedral angle between the two benzene rings being 4.27 (4)°. The structure is stabilized by intra- and intermolecular O—H···O and C—H···O hydrogen bonds, and by weak π–π stacking interactions along the b axis, with a centroid–centroid distance between related benzene rings of 3.800 (4) Å.

Related literature

For related literature, see: Boonnak *et al.* (2005); Hao *et al.* (1995); Jia *et al.* (2007); Ng *et al.* (2005); Patil *et al.* (2004); Wu & Yen (2004); Allen *et al.* (1987).



Experimental

Crystal data

$C_{19}H_{18}O_7$
M_r = 358.33
Monoclinic, $P2_1/n$
a = 12.2960 (3) Å
b = 7.8545 (2) Å
c = 18.3361 (5) Å
β = 106.581 (2)°
V = 1697.24 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 (2) K
0.30 × 0.28 × 0.26 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: none
13295 measured reflections
3871 independent reflections
2527 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.02
3871 reflections
241 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C18—H18A···O4	0.96	2.53	3.074 (3)	116
C17—H17A···O4	0.96	2.60	3.046 (3)	109
C16—H16A···O1	0.96	2.50	3.049 (3)	116
O7—H7···O6	0.82	2.19	2.6482 (17)	116
O7—H7···O3^{i}	0.82	2.02	2.7221 (16)	144

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2185).

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supporting information

Acta Cryst. (2008). E**64**, o371 [doi:10.1107/S1600536807067864]

2-Hydroxy-1,6,7,8-tetramethoxy-3-methylanthraquinone

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S1. Comment

Anthraquinone derivatives extracted from the seeds of *Cassia tora L*. (most common familiar name in China: Juemingzi) have been used traditionally to improve visual acuity. Recent studies have demonstrated that they have multiple pharmacological actions such as antimicrobial, diuretic, antidiarrhoic, antioxidant, antihepatotoxic and antimutagenic activities (Wu & Yen, 2004). One component found in *Cassia tora L*., 2-hydroxy-1,6,7,8-tetramethoxy-3-methylanthraquinone, is known as chrysoobusin and exhibits a variety of potent biological effects such as suppression of mutagenicity of mycotoxins (Hao *et al.*, 1995), antioxidant activity (Jia *et al.*, 2007) and hypolipidemic activity (Patil *et al.*, 2004). We report here the structure of the title compound.

In the title compound (Fig. 1), the C—C bond lengths show normal values (Allen *et al.*, 1987), and the C—O and C=O bond lengths are comparable to those observed in similar structures (Ng *et al.*, 2005; Boonnak *et al.*, 2005). The anthraquinone ring system is substantially planar, the dihedral angle between the two benzene rings being 4.27 (4)°. The molecules are self-assembled by intra- and intermolecular C—H···O and O—H···.O hydrogen bonding interactions (Table 1) into a superamolecular network. The crystal structure is further stabilized by weak π-π stacking interactions along the *b* axis (Fig. 2) occurring between centrosymmetrically related anthraquinone ring systems. The centroid-to-centriod distances between related benzene rings of the stacked molecules is 3.800 (4) Å.

S2. Experimental

The seeds of *Cassia tora L*. (800 g) were shattered to powder (about 30 mesh) and extracted with 60% ethanol (3000 ml) for 40 min by microwave irradiation at 333 K. The extraction procedure was repeated three times. The extracts were combined and evaporated to dryness under reduced pressure at 333 K, the residue was redissolved in water (600 ml) and was added 400 ml light petroleum to remove low-polar substaces three times. Then the enriched extracts were extracted with chloroform four times (500 ml for each time), the chlorofrom solution were combined and evaporated to dryness under reduced pressure at 333 K, 4.52 g crude extracts was obtained. The crude extracts were separated with n-hexane-ethyl acetate-methanol-water (11: 90: 10: 10, *v*/*v*) using high-speed counter-current chromatography (HSCCC) to obtain 2-hydroxy-1,6,7,8-tetramethoxy-3-methylanthraquinone (yield 46.2 mg). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

S3. Refinement

All H atoms were placed at calculated positions and were treated as riding on the parent C atoms with C—H = 0.93–0.97 and O—H = 0.82 Å, and with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C, O).

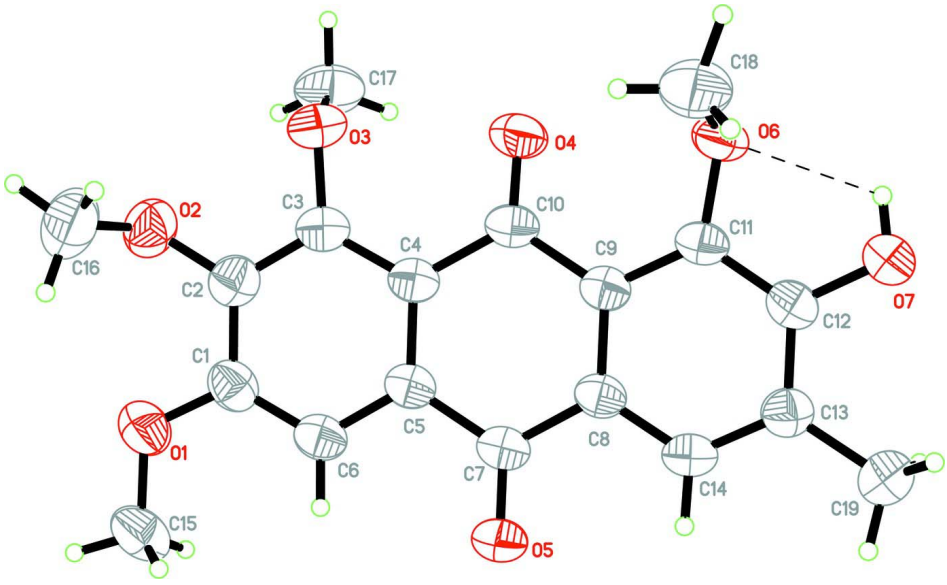

Figure 1

The molecular structure of the title compound showing the atomic-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

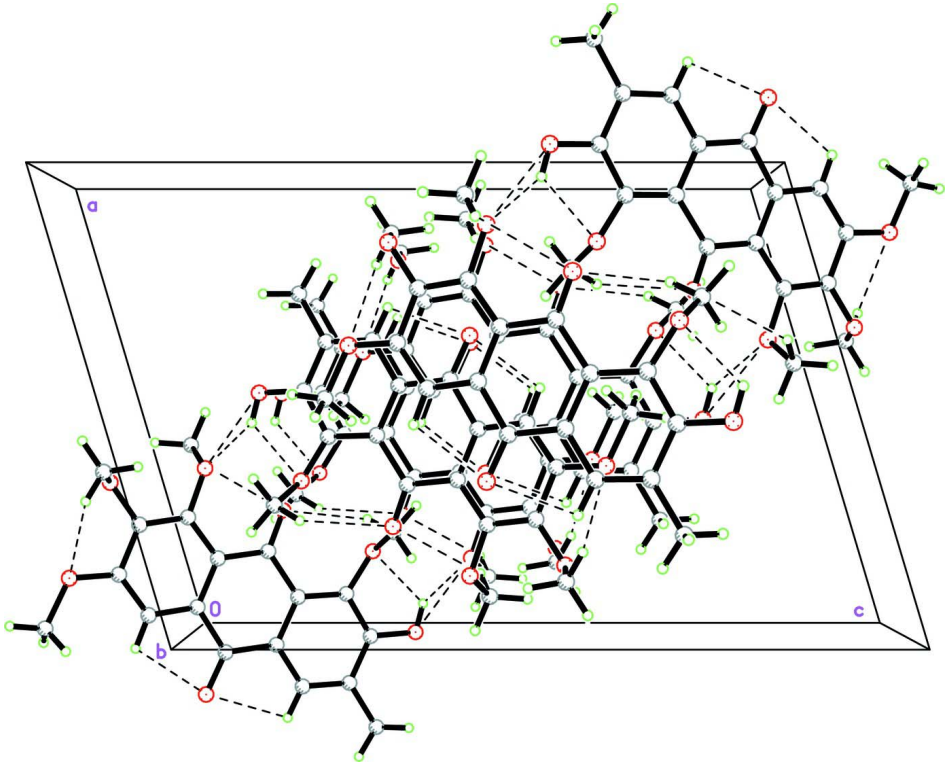

Figure 2

The molecular packing of the title compound showing the intra- and intermolecular hydrogen bonding interactions as broken lines.

2-Hydroxy-1,6,7,8-tetramethoxy-3-methylanthraquinone

Crystal data

$C_{19}H_{18}O_7$
$M_r = 358.33$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 12.2960$ (3) Å
$b = 7.8545$ (2) Å
$c = 18.3361$ (5) Å
$\beta = 106.581$ (2)°
$V = 1697.24$ (8) Å^3
$Z = 4$
$F(000) = 752$
$D_x = 1.402$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3645 reflections
$\theta = 1.4$–$28.0°$
$\mu = 0.11$ mm^{-1}
$T = 296$ K
Block, yellow
0.30 × 0.28 × 0.26 mm

Data collection

Bruker APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
f and ω scans
13295 measured reflections
3871 independent reflections
2527 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.8°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.133$
$S = 1.02$
3871 reflections
241 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
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.2883P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

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

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.12772 (16)	0.3847 (2)	−0.08053 (10)	0.0478 (4)
C2	0.23670 (15)	0.3514 (2)	−0.03234 (10)	0.0479 (4)
C3	0.25066 (14)	0.2624 (2)	0.03525 (9)	0.0417 (4)
C4	0.15663 (13)	0.2073 (2)	0.05800 (9)	0.0391 (4)
C5	0.04861 (13)	0.2443 (2)	0.00932 (9)	0.0394 (4)

C6	0.03506 (15)	0.3313 (2)	−0.05891 (9)	0.0452 (4)
H6	−0.0376	0.3536	−0.0902	0.054*
C7	−0.05610 (14)	0.1888 (2)	0.02762 (9)	0.0419 (4)
C8	−0.04420 (13)	0.10489 (19)	0.10100 (9)	0.0391 (4)
C9	0.06335 (13)	0.07377 (19)	0.15239 (9)	0.0385 (4)
C10	0.16909 (14)	0.1101 (2)	0.12996 (9)	0.0420 (4)
C11	0.06680 (13)	−0.0001 (2)	0.22235 (9)	0.0404 (4)
C12	−0.03346 (14)	−0.0496 (2)	0.23820 (9)	0.0447 (4)
C13	−0.14001 (14)	−0.0222 (2)	0.18680 (9)	0.0459 (4)
C14	−0.14247 (14)	0.0570 (2)	0.11918 (9)	0.0444 (4)
H14	−0.2124	0.0793	0.0844	0.053*
C15	0.01444 (17)	0.4980 (3)	−0.19883 (11)	0.0645 (5)
H15A	−0.0223	0.3913	−0.2157	0.097*
H15B	0.0236	0.5600	−0.2418	0.097*
H15C	−0.0311	0.5634	−0.1744	0.097*
C16	0.3571 (2)	0.5740 (3)	−0.04686 (16)	0.0795 (7)
H16A	0.2951	0.6370	−0.0794	0.119*
H16B	0.4246	0.5946	−0.0619	0.119*
H16C	0.3690	0.6098	0.0049	0.119*
C17	0.41092 (17)	0.0855 (3)	0.06199 (13)	0.0682 (6)
H17A	0.3652	−0.0108	0.0666	0.102*
H17B	0.4855	0.0729	0.0967	0.102*
H17C	0.4163	0.0920	0.0109	0.102*
C18	0.21311 (19)	0.1135 (3)	0.32189 (12)	0.0727 (6)
H18A	0.2443	0.1858	0.2907	0.109*
H18B	0.2723	0.0790	0.3660	0.109*
H18C	0.1559	0.1745	0.3375	0.109*
C19	−0.24641 (16)	−0.0758 (3)	0.20556 (12)	0.0666 (6)
H19A	−0.3114	−0.0311	0.1680	0.100*
H19B	−0.2450	−0.0327	0.2548	0.100*
H19C	−0.2507	−0.1978	0.2058	0.100*
O1	0.12327 (11)	0.46722 (18)	−0.14620 (7)	0.0641 (4)
O2	0.33123 (11)	0.39758 (17)	−0.05315 (8)	0.0617 (4)
O3	0.36000 (9)	0.23760 (15)	0.07962 (6)	0.0495 (3)
O4	0.26068 (10)	0.05769 (19)	0.16791 (7)	0.0642 (4)
O5	−0.14949 (10)	0.21417 (18)	−0.01744 (7)	0.0581 (4)
O6	0.16389 (10)	−0.03329 (16)	0.27947 (6)	0.0510 (3)
O7	−0.02886 (10)	−0.12633 (19)	0.30522 (7)	0.0599 (4)
H7	0.0376	−0.1434	0.3291	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0551 (11)	0.0446 (9)	0.0446 (9)	0.0084 (8)	0.0161 (8)	0.0035 (8)
C2	0.0478 (10)	0.0460 (9)	0.0522 (10)	0.0032 (8)	0.0180 (8)	−0.0028 (8)
C3	0.0395 (9)	0.0421 (9)	0.0407 (9)	0.0039 (7)	0.0069 (7)	−0.0082 (7)
C4	0.0396 (9)	0.0387 (8)	0.0363 (8)	0.0037 (7)	0.0064 (7)	−0.0053 (7)
C5	0.0412 (9)	0.0371 (8)	0.0367 (8)	0.0034 (7)	0.0061 (7)	−0.0039 (7)

C6	0.0450 (9)	0.0420 (9)	0.0455 (9)	0.0075 (7)	0.0080 (7)	0.0007 (8)
C7	0.0409 (9)	0.0399 (9)	0.0401 (8)	0.0051 (7)	0.0038 (7)	−0.0022 (7)
C8	0.0399 (9)	0.0369 (8)	0.0368 (8)	0.0029 (7)	0.0047 (7)	−0.0036 (7)
C9	0.0396 (8)	0.0349 (8)	0.0376 (8)	0.0017 (7)	0.0056 (7)	−0.0034 (7)
C10	0.0388 (9)	0.0431 (9)	0.0392 (9)	0.0036 (7)	0.0032 (7)	−0.0049 (7)
C11	0.0386 (8)	0.0389 (8)	0.0379 (8)	0.0025 (7)	0.0017 (7)	−0.0031 (7)
C12	0.0474 (10)	0.0459 (9)	0.0379 (8)	0.0022 (8)	0.0078 (7)	0.0005 (7)
C13	0.0426 (9)	0.0484 (10)	0.0450 (9)	0.0006 (8)	0.0098 (7)	−0.0017 (8)
C14	0.0368 (8)	0.0475 (9)	0.0435 (9)	0.0043 (7)	0.0026 (7)	−0.0019 (8)
C15	0.0741 (14)	0.0684 (13)	0.0482 (10)	0.0172 (11)	0.0129 (10)	0.0118 (10)
C16	0.0717 (15)	0.0681 (14)	0.1065 (19)	−0.0097 (12)	0.0382 (14)	0.0046 (14)
C17	0.0536 (11)	0.0765 (14)	0.0700 (13)	0.0212 (10)	0.0104 (10)	−0.0125 (11)
C18	0.0665 (13)	0.0868 (16)	0.0526 (11)	−0.0165 (12)	−0.0026 (10)	−0.0160 (11)
C19	0.0477 (11)	0.0890 (15)	0.0636 (12)	−0.0002 (10)	0.0165 (9)	0.0115 (11)
O1	0.0621 (8)	0.0764 (9)	0.0543 (8)	0.0081 (7)	0.0177 (7)	0.0207 (7)
O2	0.0554 (8)	0.0657 (9)	0.0712 (9)	0.0024 (7)	0.0298 (7)	0.0041 (7)
O3	0.0375 (6)	0.0581 (7)	0.0487 (7)	0.0028 (5)	0.0056 (5)	−0.0093 (6)
O4	0.0424 (7)	0.0934 (11)	0.0526 (7)	0.0150 (7)	0.0069 (6)	0.0189 (7)
O5	0.0399 (7)	0.0773 (9)	0.0495 (7)	0.0038 (6)	0.0005 (6)	0.0141 (7)
O6	0.0447 (7)	0.0585 (7)	0.0411 (6)	−0.0002 (6)	−0.0016 (5)	0.0051 (6)
O7	0.0489 (7)	0.0822 (10)	0.0461 (7)	0.0018 (7)	0.0096 (6)	0.0156 (7)

Geometric parameters (Å, º)

C1—O1	1.355 (2)	C13—C14	1.380 (2)
C1—C6	1.374 (2)	C13—C19	1.505 (2)
C1—C2	1.403 (2)	C14—H14	0.9300
C2—O2	1.372 (2)	C15—O1	1.429 (2)
C2—C3	1.390 (2)	C15—H15A	0.9600
C3—O3	1.3723 (19)	C15—H15B	0.9600
C3—C4	1.405 (2)	C15—H15C	0.9600
C4—C5	1.403 (2)	C16—O2	1.419 (2)
C4—C10	1.494 (2)	C16—H16A	0.9600
C5—C6	1.393 (2)	C16—H16B	0.9600
C5—C7	1.485 (2)	C16—H16C	0.9600
C6—H6	0.9300	C17—O3	1.428 (2)
C7—O5	1.2245 (19)	C17—H17A	0.9600
C7—C8	1.468 (2)	C17—H17B	0.9600
C8—C14	1.394 (2)	C17—H17C	0.9600
C8—C9	1.409 (2)	C18—O6	1.425 (2)
C9—C11	1.397 (2)	C18—H18A	0.9600
C9—C10	1.499 (2)	C18—H18B	0.9600
C10—O4	1.2144 (19)	C18—H18C	0.9600
C11—O6	1.3699 (18)	C19—H19A	0.9600
C11—C12	1.400 (2)	C19—H19B	0.9600
C12—O7	1.355 (2)	C19—H19C	0.9600
C12—C13	1.395 (2)	O7—H7	0.8200

O1—C1—C6	125.14 (16)	C13—C14—C8	122.57 (15)
O1—C1—C2	115.97 (16)	C13—C14—H14	118.7
C6—C1—C2	118.88 (16)	C8—C14—H14	118.7
O2—C2—C3	118.82 (16)	O1—C15—H15A	109.5
O2—C2—C1	120.56 (16)	O1—C15—H15B	109.5
C3—C2—C1	120.52 (16)	H15A—C15—H15B	109.5
O3—C3—C2	116.80 (15)	O1—C15—H15C	109.5
O3—C3—C4	122.02 (15)	H15A—C15—H15C	109.5
C2—C3—C4	121.13 (15)	H15B—C15—H15C	109.5
C5—C4—C3	117.20 (15)	O2—C16—H16A	109.5
C5—C4—C10	120.50 (14)	O2—C16—H16B	109.5
C3—C4—C10	122.29 (14)	H16A—C16—H16B	109.5
C6—C5—C4	121.45 (15)	O2—C16—H16C	109.5
C6—C5—C7	117.22 (14)	H16A—C16—H16C	109.5
C4—C5—C7	121.32 (15)	H16B—C16—H16C	109.5
C1—C6—C5	120.80 (16)	O3—C17—H17A	109.5
C1—C6—H6	119.6	O3—C17—H17B	109.5
C5—C6—H6	119.6	H17A—C17—H17B	109.5
O5—C7—C8	121.37 (16)	O3—C17—H17C	109.5
O5—C7—C5	120.42 (15)	H17A—C17—H17C	109.5
C8—C7—C5	118.21 (14)	H17B—C17—H17C	109.5
C14—C8—C9	120.37 (15)	O6—C18—H18A	109.5
C14—C8—C7	118.30 (14)	O6—C18—H18B	109.5
C9—C8—C7	121.33 (15)	H18A—C18—H18B	109.5
C11—C9—C8	117.57 (15)	O6—C18—H18C	109.5
C11—C9—C10	121.97 (14)	H18A—C18—H18C	109.5
C8—C9—C10	120.37 (14)	H18B—C18—H18C	109.5
O4—C10—C4	121.60 (15)	C13—C19—H19A	109.5
O4—C10—C9	120.89 (15)	C13—C19—H19B	109.5
C4—C10—C9	117.48 (13)	H19A—C19—H19B	109.5
O6—C11—C9	124.92 (15)	C13—C19—H19C	109.5
O6—C11—C12	114.54 (14)	H19A—C19—H19C	109.5
C9—C11—C12	120.53 (14)	H19B—C19—H19C	109.5
O7—C12—C13	118.00 (15)	C1—O1—C15	118.27 (15)
O7—C12—C11	120.03 (14)	C2—O2—C16	115.05 (15)
C13—C12—C11	121.98 (15)	C3—O3—C17	113.79 (13)
C14—C13—C12	116.89 (15)	C11—O6—C18	113.88 (14)
C14—C13—C19	122.28 (16)	C12—O7—H7	109.5
C12—C13—C19	120.83 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18*A*···O4	0.96	2.53	3.074 (3)	116
C17—H17*A*···O4	0.96	2.60	3.046 (3)	109
C16—H16*A*···O1	0.96	2.50	3.049 (3)	116

O7—H7···O6	0.82	2.19	2.6482 (17)	116
O7—H7···O3^{i}	0.82	2.02	2.7221 (16)	144

Symmetry code: (i) $-x+1/2, y-1/2, -z+1/2$.