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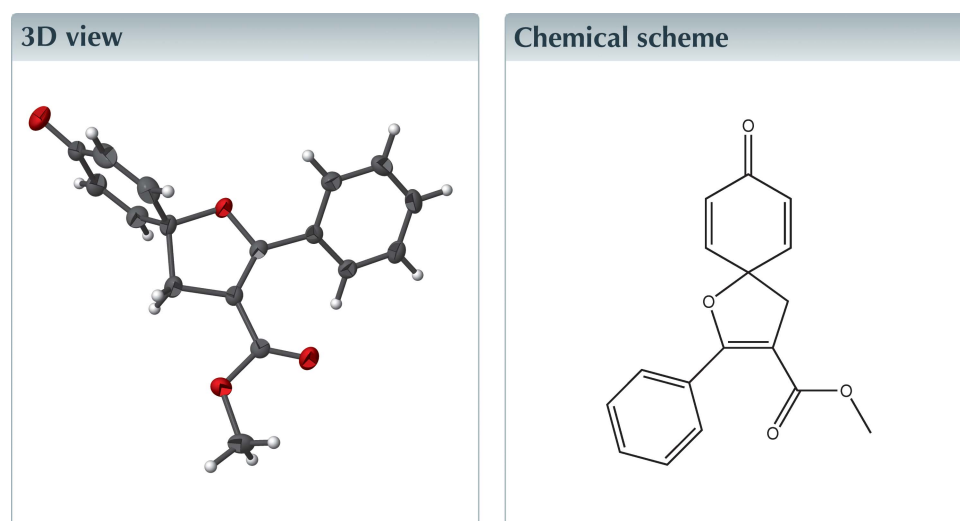
Structural data: full structural data are available from iucrdata.iucr.org

Methyl 8-oxo-2-phenyl-1-oxaspiro[4.5]deca-2,6,9-triene-3-carboxylate

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The title compound, C₁₇H₁₄O₄, is a 5/6 spiro-ring fused system, where the five- and six-membered rings are inclined to one another by 89.79 (5)° at the spiro-carbon. In the crystal, non-classical C—H···O hydrogen bonds form inversion dimers and connect the molecules into chains along [001].



Structure description

Compounds with spiro ring systems, when compared to planar aromatic compounds, have greater three-dimensionality and different physical properties. This has been shown to increase their potential effectiveness as drugs (Winkler *et al.*, 2015; Zheng *et al.*, 2014). The title compound is a 5/6 spiro-ring fused system, in which the six-membered ring is a cyclohexadienone moiety where the carbonyl group and the two double bonds constitute a highly conjugated system, making it an efficient Michael acceptor. This chemical property is normally associated with biological activity (Pirovani *et al.*, 2009). Good evidence of the pharmacophoric properties of the cyclohexadienone moiety is the loss of antimalarial activity of *aculeatin A* when this group is reduced to the corresponding ketone analogue. Furthermore, construction of an *aculeatin A* analogue with two spirocyclohexadienone units led to improved antimalarial potency (Winkler *et al.*, 2015).

In the title compound, Fig. 1, the five-membered and the six-membered rings of the spiro system are almost planar, with r.m.s. deviations 0.021 and 0.008 Å, respectively. The hexadienone ring is rotated by 89.79 (5)° with respect to the five-membered ring. This is similar to the values found in related 5/6 spiro-ring fused systems containing the cyclohexadienone moiety that have been reported previously (Lou, 2012; Martins *et al.*, 2014; Rønneest *et al.*, 2011). The phenyl ring is inclined to the five-membered ring by 35.88 (6)°, while the planar methyl carboxylate substituent, C3/C16/O4/C17, is inclined to this ring by only 6.61 (13)°. The torsion angles C4—C3—C16—O4, 5.93 (17)°, C15—C1—C2—O2,

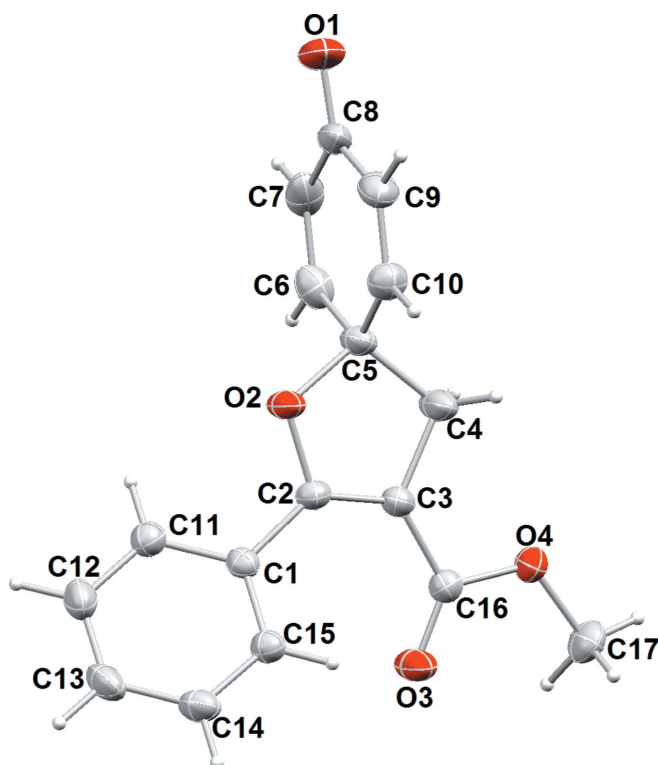


Figure 1
The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids.

$-141.12(12)^\circ$, and $C1-C2-C3-C16$, $4.3(2)^\circ$ are close to those found in an analogous 5/6 spiro-system containing a dibrominated cyclohexadienone ring (Martins *et al.*, 2014).

In the crystal, molecules form pairs of inversion dimers *via* non-classical hydrogen bonds ($C4-H4A \cdots O1$ and $C14-H14 \cdots O3$, Table 1), building up head-to-tail chains along $[001]$ (Fig. 2).

Synthesis and crystallization

The title compound was obtained by a synthetic protocol whose first step is the Heck reaction of a Morita–Baylis–Hillman adduct with 4-iodophenol, in the presence of a Nájera

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C4-H4A \cdots O1^i$	0.99	2.58	3.2504 (19)	125
$C14-H14 \cdots O3^{ii}$	0.95	2.52	3.3884 (17)	153

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{14}O_4$
M_r	282.28
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (\AA)	8.0416 (8), 9.4577 (10), 9.7397 (10)
α, β, γ ($^\circ$)	74.168 (2), 84.636 (2), 78.731 (2)
V (\AA^3)	698.28 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	$0.37 \times 0.21 \times 0.21$
Data collection	
Diffractometer	Bruker APEX CCD detector
Absorption correction	Multi-scan (SADABS; Bruker, 2010)
T_{\min}, T_{\max}	0.680, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30763, 2846, 2638
R_{int}	0.020
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.099, 1.05
No. of reflections	2846
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{\AA}^{-3}$)	0.49, -0.37

Computer programs: APEX2 and SAINT (Bruker, 2010), SHELXS97 (Sheldrick, 2008), SHELXL2014/7 (Sheldrick, 2015), Mercury (Macrae *et al.*, 2006) and publCIF (Westrip, 2010).

N-oxime-derived palladacycle as catalyst, to give the corresponding α -aryl- β -keto ester (83% yield for the isolated and purified product). Next, the α -aryl- β -keto ester was treated with [bis(trifluoroacetoxy)iodo]benzene, in anhydrous acetonitrile, to furnish the desired spiro-hexadienone (75% yield for the isolated and purified product). The compound was re-

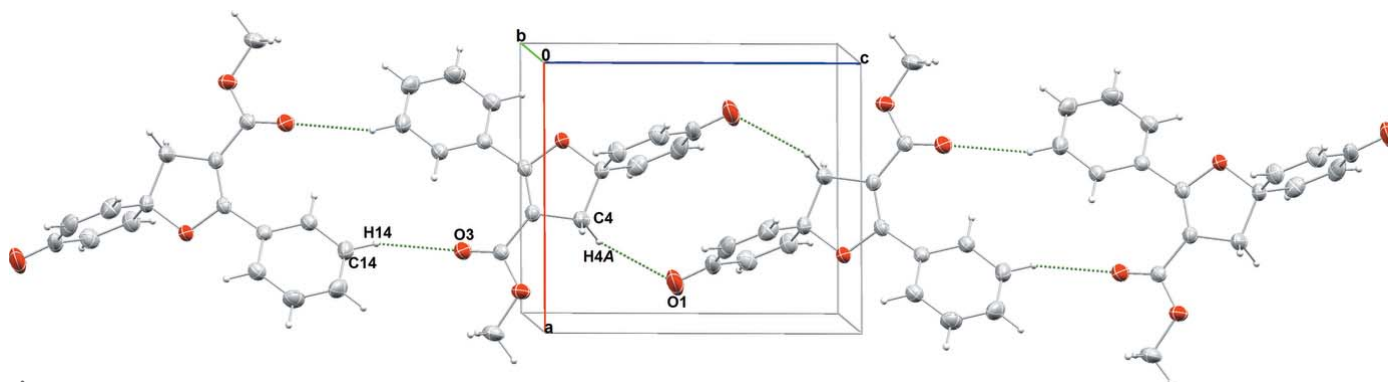


Figure 2
Crystal packing of the title compound, showing the dimers formed by non-classical intermolecular $C-H \cdots O$ hydrogen bonds (dashed lines).

dissolved in dichloromethane and light-yellow block-like crystals were obtained by slow evaporation of the solvent at room temperature. For a detailed description of this synthesis, see Pirovani *et al.* (2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Methyl 8-oxo-2-phenyl-1-oxaspiro[4.5]deca-2,6,9-triene-3-carboxylate

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Crystal data

$C_{17}H_{14}O_4$	$Z = 2$
$M_r = 282.28$	$F(000) = 296$
Triclinic, $P\bar{1}$	$D_x = 1.343 \text{ Mg m}^{-3}$
$a = 8.0416 (8) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 9.4577 (10) \text{ \AA}$	Cell parameters from 93 reflections
$c = 9.7397 (10) \text{ \AA}$	$\theta = 3.3\text{--}26.7^\circ$
$\alpha = 74.168 (2)^\circ$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 84.636 (2)^\circ$	$T = 150 \text{ K}$
$\gamma = 78.731 (2)^\circ$	Block, light yellow
$V = 698.28 (12) \text{ \AA}^3$	$0.37 \times 0.21 \times 0.21 \text{ mm}$

Data collection

Bruker APEX CCD detector	30763 measured reflections
diffractometer	2846 independent reflections
Radiation source: fine-focus sealed tube	2638 reflections with $I > 2\sigma(I)$
Detector resolution: $8.3333 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.020$
phi and ω scans	$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan	$h = -10 \rightarrow 10$
(SADABS; Bruker, 2010)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.680$, $T_{\text{max}} = 0.746$	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.3344P]$
$wR(F^2) = 0.099$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2846 reflections	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$
191 parameters	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$
0 restraints	

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.18597 (17)	0.00818 (15)	0.58977 (12)	0.0594 (4)
O2	0.30998 (11)	0.27812 (11)	0.07753 (10)	0.0320 (2)
O3	0.72621 (12)	0.36813 (12)	-0.23114 (10)	0.0381 (3)
O4	0.86312 (11)	0.18240 (10)	-0.06200 (10)	0.0300 (2)
C1	0.32385 (15)	0.43009 (13)	-0.15731 (13)	0.0220 (3)
C2	0.41536 (15)	0.32065 (13)	-0.03849 (13)	0.0225 (3)
C3	0.57777 (16)	0.25242 (13)	-0.01880 (13)	0.0233 (3)
C4	0.59324 (17)	0.14561 (17)	0.12760 (15)	0.0360 (3)
H4A	0.6756	0.1694	0.1836	0.043*
H4B	0.6284	0.0411	0.1217	0.043*
C5	0.41077 (16)	0.17208 (14)	0.19365 (13)	0.0266 (3)
C6	0.39846 (19)	0.24628 (15)	0.31205 (16)	0.0339 (3)
H6	0.4411	0.3367	0.2950	0.041*
C7	0.3303 (2)	0.19091 (17)	0.44045 (15)	0.0380 (3)
H7	0.3293	0.2411	0.5128	0.046*
C8	0.25653 (18)	0.05505 (17)	0.47397 (14)	0.0357 (3)
C9	0.26682 (18)	-0.02037 (15)	0.36014 (16)	0.0349 (3)
H9	0.2242	-0.1109	0.3785	0.042*
C10	0.33392 (18)	0.03464 (15)	0.23263 (14)	0.0311 (3)
H10	0.3332	-0.0165	0.1612	0.037*
C11	0.18775 (17)	0.53458 (14)	-0.12597 (14)	0.0285 (3)
H11	0.1596	0.5370	-0.0296	0.034*
C12	0.09371 (18)	0.63454 (16)	-0.23470 (17)	0.0371 (3)
H12	0.0026	0.7069	-0.2131	0.045*
C13	0.13212 (18)	0.62930 (17)	-0.37493 (16)	0.0382 (3)
H13	0.0664	0.6973	-0.4493	0.046*
C14	0.26596 (18)	0.52542 (16)	-0.40708 (14)	0.0325 (3)
H14	0.2918	0.5221	-0.5035	0.039*
C15	0.36248 (16)	0.42623 (14)	-0.29899 (13)	0.0255 (3)
H15	0.4550	0.3556	-0.3214	0.031*
C16	0.72412 (15)	0.27742 (13)	-0.11712 (13)	0.0231 (3)
C17	1.01867 (17)	0.19418 (18)	-0.14803 (17)	0.0376 (3)
H17A	1.0201	0.1452	-0.2249	0.056*
H17B	1.1158	0.1456	-0.0881	0.056*
H17C	1.0256	0.2997	-0.1894	0.056*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0608 (8)	0.0683 (8)	0.0271 (6)	0.0076 (6)	0.0145 (5)	0.0055 (5)
O2	0.0230 (5)	0.0425 (6)	0.0217 (5)	-0.0041 (4)	0.0019 (3)	0.0043 (4)
O3	0.0268 (5)	0.0483 (6)	0.0291 (5)	-0.0070 (4)	0.0014 (4)	0.0063 (4)
O4	0.0217 (4)	0.0317 (5)	0.0320 (5)	-0.0012 (4)	0.0011 (4)	-0.0042 (4)
C1	0.0210 (6)	0.0215 (6)	0.0236 (6)	-0.0075 (4)	-0.0007 (4)	-0.0034 (5)
C2	0.0247 (6)	0.0241 (6)	0.0197 (6)	-0.0085 (5)	0.0019 (5)	-0.0056 (5)

C3	0.0251 (6)	0.0235 (6)	0.0204 (6)	-0.0055 (5)	-0.0011 (5)	-0.0037 (5)
C4	0.0268 (7)	0.0433 (8)	0.0266 (7)	-0.0026 (6)	0.0010 (5)	0.0063 (6)
C5	0.0275 (6)	0.0291 (6)	0.0199 (6)	-0.0058 (5)	-0.0012 (5)	-0.0001 (5)
C6	0.0392 (8)	0.0260 (6)	0.0391 (8)	-0.0070 (6)	-0.0107 (6)	-0.0087 (6)
C7	0.0470 (8)	0.0408 (8)	0.0276 (7)	0.0060 (6)	-0.0102 (6)	-0.0184 (6)
C8	0.0345 (7)	0.0388 (8)	0.0217 (7)	0.0071 (6)	0.0022 (5)	0.0014 (6)
C9	0.0366 (7)	0.0278 (7)	0.0370 (8)	-0.0099 (6)	0.0035 (6)	-0.0019 (6)
C10	0.0373 (7)	0.0309 (7)	0.0289 (7)	-0.0091 (6)	0.0003 (5)	-0.0124 (5)
C11	0.0281 (6)	0.0276 (6)	0.0292 (7)	-0.0053 (5)	0.0027 (5)	-0.0070 (5)
C12	0.0297 (7)	0.0294 (7)	0.0439 (8)	0.0022 (5)	0.0013 (6)	-0.0018 (6)
C13	0.0316 (7)	0.0358 (7)	0.0360 (8)	-0.0031 (6)	-0.0066 (6)	0.0090 (6)
C14	0.0323 (7)	0.0388 (7)	0.0235 (6)	-0.0099 (6)	-0.0019 (5)	-0.0004 (5)
C15	0.0243 (6)	0.0277 (6)	0.0242 (6)	-0.0062 (5)	0.0003 (5)	-0.0056 (5)
C16	0.0230 (6)	0.0244 (6)	0.0234 (6)	-0.0058 (5)	-0.0014 (5)	-0.0076 (5)
C17	0.0214 (6)	0.0457 (8)	0.0436 (8)	-0.0038 (6)	0.0040 (6)	-0.0113 (7)

Geometric parameters (Å, °)

O1—C8	1.2233 (17)	C7—C8	1.463 (2)
O2—C2	1.3649 (14)	C7—H7	0.9500
O2—C5	1.4753 (15)	C8—C9	1.462 (2)
O3—C16	1.2049 (16)	C9—C10	1.3176 (19)
O4—C16	1.3422 (15)	C9—H9	0.9500
O4—C17	1.4445 (16)	C10—H10	0.9500
C1—C15	1.3947 (17)	C11—C12	1.382 (2)
C1—C11	1.3954 (18)	C11—H11	0.9500
C1—C2	1.4697 (17)	C12—C13	1.384 (2)
C2—C3	1.3450 (18)	C12—H12	0.9500
C3—C16	1.4603 (17)	C13—C14	1.383 (2)
C3—C4	1.5058 (17)	C13—H13	0.9500
C4—C5	1.5484 (18)	C14—C15	1.3857 (18)
C4—H4A	0.9900	C14—H14	0.9500
C4—H4B	0.9900	C15—H15	0.9500
C5—C10	1.4889 (18)	C17—H17A	0.9800
C5—C6	1.4916 (19)	C17—H17B	0.9800
C6—C7	1.329 (2)	C17—H17C	0.9800
C6—H6	0.9500		
C2—O2—C5	109.13 (9)	C9—C8—C7	116.56 (12)
C16—O4—C17	116.00 (10)	C10—C9—C8	121.37 (13)
C15—C1—C11	119.37 (11)	C10—C9—H9	119.3
C15—C1—C2	121.86 (11)	C8—C9—H9	119.3
C11—C1—C2	118.65 (11)	C9—C10—C5	123.96 (12)
C3—C2—O2	113.21 (11)	C9—C10—H10	118.0
C3—C2—C1	134.71 (11)	C5—C10—H10	118.0
O2—C2—C1	112.08 (10)	C12—C11—C1	120.20 (12)
C2—C3—C16	127.59 (11)	C12—C11—H11	119.9
C2—C3—C4	109.82 (11)	C1—C11—H11	119.9

C16—C3—C4	122.55 (11)	C11—C12—C13	120.06 (13)
C3—C4—C5	102.63 (11)	C11—C12—H12	120.0
C3—C4—H4A	111.2	C13—C12—H12	120.0
C5—C4—H4A	111.2	C14—C13—C12	120.20 (13)
C3—C4—H4B	111.2	C14—C13—H13	119.9
C5—C4—H4B	111.2	C12—C13—H13	119.9
H4A—C4—H4B	109.2	C13—C14—C15	120.14 (13)
O2—C5—C10	106.01 (10)	C13—C14—H14	119.9
O2—C5—C6	106.60 (10)	C15—C14—H14	119.9
C10—C5—C6	113.32 (11)	C14—C15—C1	120.01 (12)
O2—C5—C4	104.99 (9)	C14—C15—H15	120.0
C10—C5—C4	112.35 (12)	C1—C15—H15	120.0
C6—C5—C4	112.79 (12)	O3—C16—O4	123.01 (11)
C7—C6—C5	122.59 (13)	O3—C16—C3	127.24 (12)
C7—C6—H6	118.7	O4—C16—C3	109.75 (10)
C5—C6—H6	118.7	O4—C17—H17A	109.5
C6—C7—C8	122.11 (13)	O4—C17—H17B	109.5
C6—C7—H7	118.9	H17A—C17—H17B	109.5
C8—C7—H7	118.9	O4—C17—H17C	109.5
O1—C8—C9	121.24 (15)	H17A—C17—H17C	109.5
O1—C8—C7	122.17 (15)	H17B—C17—H17C	109.5
C5—O2—C2—C3	2.26 (14)	C6—C7—C8—O1	-176.17 (15)
C5—O2—C2—C1	-178.33 (10)	C6—C7—C8—C9	2.1 (2)
C15—C1—C2—C3	38.1 (2)	O1—C8—C9—C10	175.99 (15)
C11—C1—C2—C3	-145.95 (14)	C7—C8—C9—C10	-2.3 (2)
C15—C1—C2—O2	-141.12 (12)	C8—C9—C10—C5	2.6 (2)
C11—C1—C2—O2	34.81 (15)	O2—C5—C10—C9	-118.93 (15)
O2—C2—C3—C16	-176.46 (11)	C6—C5—C10—C9	-2.3 (2)
C1—C2—C3—C16	4.3 (2)	C4—C5—C10—C9	126.94 (15)
O2—C2—C3—C4	1.02 (15)	C15—C1—C11—C12	-0.87 (19)
C1—C2—C3—C4	-178.22 (13)	C2—C1—C11—C12	-176.89 (12)
C2—C3—C4—C5	-3.59 (15)	C1—C11—C12—C13	1.3 (2)
C16—C3—C4—C5	174.03 (11)	C11—C12—C13—C14	-0.8 (2)
C2—O2—C5—C10	-123.48 (11)	C12—C13—C14—C15	-0.1 (2)
C2—O2—C5—C6	115.50 (11)	C13—C14—C15—C1	0.6 (2)
C2—O2—C5—C4	-4.38 (14)	C11—C1—C15—C14	-0.08 (18)
C3—C4—C5—O2	4.65 (14)	C2—C1—C15—C14	175.81 (11)
C3—C4—C5—C10	119.40 (12)	C17—O4—C16—O3	-0.14 (18)
C3—C4—C5—C6	-111.02 (13)	C17—O4—C16—C3	179.99 (11)
O2—C5—C6—C7	118.32 (14)	C2—C3—C16—O3	3.3 (2)
C10—C5—C6—C7	2.09 (19)	C4—C3—C16—O3	-173.93 (14)
C4—C5—C6—C7	-126.98 (15)	C2—C3—C16—O4	-176.89 (12)
C5—C6—C7—C8	-2.1 (2)	C4—C3—C16—O4	5.93 (17)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C4—H4 <i>A</i> \cdots O1 ⁱ	0.99	2.58	3.2504 (19)	125
C14—H14 \cdots O3 ⁱⁱ	0.95	2.52	3.3884 (17)	153

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