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Crystal structure of 2-oxo-2*H*-chromen-3-yl propanoate

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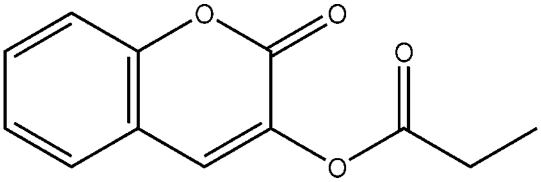
In the title compound, $C_{12}H_{10}O_4$, the dihedral angle between the coumarin ring system [maximum deviation = 0.033 (8) Å] and the propionate side chain is 78.48 (8)°. In the crystal, weak C—H$\cdots$O hydrogen bonds generate inversion dimers and and C—H$\cdots\pi$ and π–π interactions link the dimers into a three-dimensional network. A quantum chemical calculation is in good agreement with the observed structure.

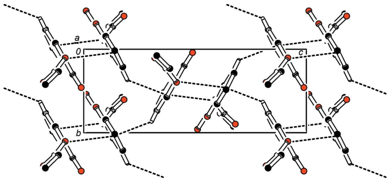
1. Chemical context

Coumarin and its derivatives are widely recognized for their multiple biological activities, including anticancer (Lacy *et al.*, 2004; Kostova, 2005), anti-inflammatory (Todeschini *et al.*, 1998), antiviral (Borges *et al.*, 2005), antimalarial (Agarwal *et al.*, 2005) and anticoagulant (Maurer *et al.*, 1998) properties. As part of our studies in this area, we now describe the synthesis and crystal structure of the title compound, (I).



2. Structural commentary

In compound (I) (Fig. 1), the coumarin ring system is almost planar [maximum deviation = 0.033 (1)Å] and is oriented at an angle of 70.84 (8)° with respect to the plane formed by the



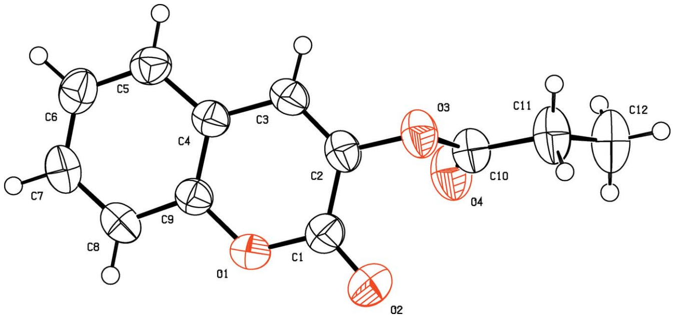


Figure 1
The molecular structure of compound (I), with displacement ellipsoids drawn at the 50% probability level.

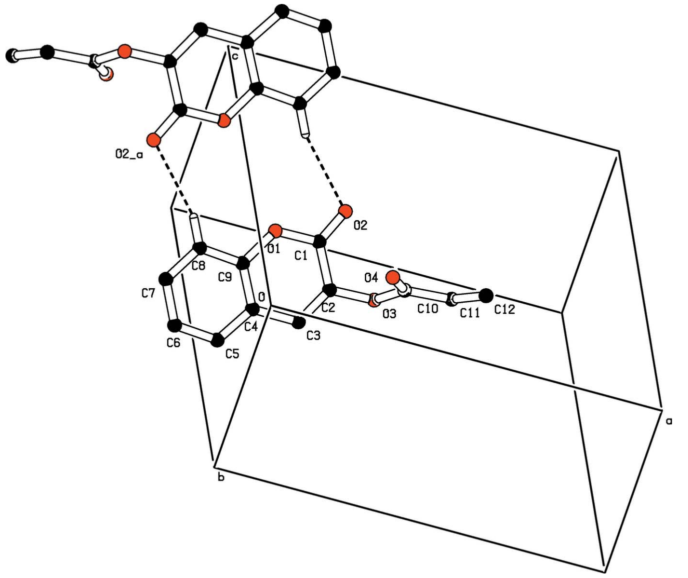


Figure 2
View of an inversion dimer linked by a pair of C8—H8$\cdots$O2 ($-x$, $-y$, $-z + 1$) interactions, generating an $R_2^2(12)$ loop. This dimers stack by unit translation along the *c* axis. H atoms not involved in hydrogen bonding have been omitted.

propanoate group. An inspection of the bond lengths shows that there is a slight asymmetry of the electronic distribution around the coumarin ring: the C2—C3 [1.329 (2) Å] and C2—C1 [1.460 (2) Å] bond lengths are shorter and longer, respectively, than those expected for a $C_{ar}—C_{ar}$ bond. This suggests that the electron density is preferentially located in the C2—C3 bond at the pyrone ring, as seen in other coumarin-3-carboxamide derivatives (Gomes *et al.*, 2016).

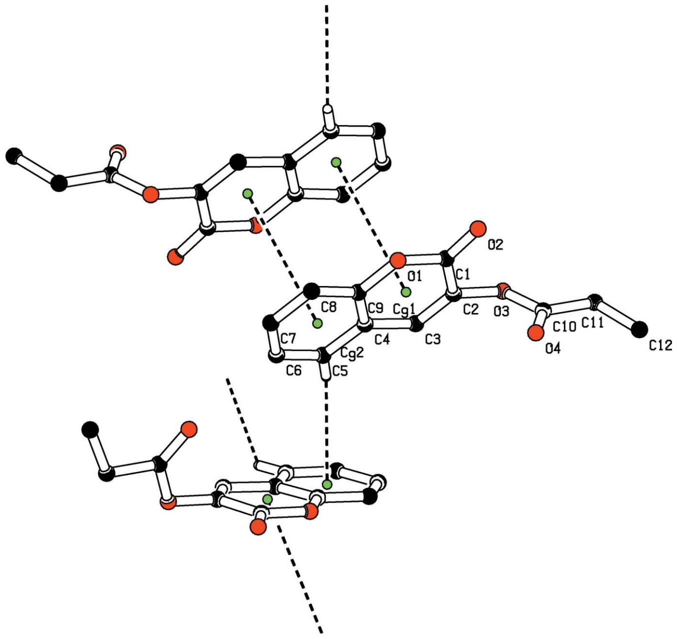


Figure 3
A view of the crystal packing, showing the π–π stacking and C—H$\cdots\pi$ interactions (dashed lines). The green dots are ring centroids. H atoms not involved in the C—H$\cdots\pi$ interactions have been omitted for clarity.

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

*Cg*2 is the centroid of the C4–C9 ring.

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C8—H8$\cdots$O2^{i}	0.93	2.59	3.4783 (19)	161
C5—H5$\cdots$*Cg*2^{ii}	0.93	2.78	3.4959 (16)	134

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

3. Supramolecular features

In the crystal, the molecules are linked by pairs of C8—H8$\cdots$O2(x, $-y$, $1 - z$) weak hydrogen bonds to form $R_2^2(12)$ loops, which lie in a chain running along the *c* axis direction (Fig. 2). Weak aromatic π–π stacking interactions of 3.7956 (8) Å (Janiak, 2000) are present between the coumarin pyran ring (centroid *Cg*1) and benzene ring (centroid *Cg*2) of symmetry-related ($-x$, $1 - y$, $1 - z$) molecules, thus forming a three-dimensional supramolecular network. A weak C—H$\cdots$*Cg* (π–ring) interaction is also present (Figs. 3 and 4, and Table 1).

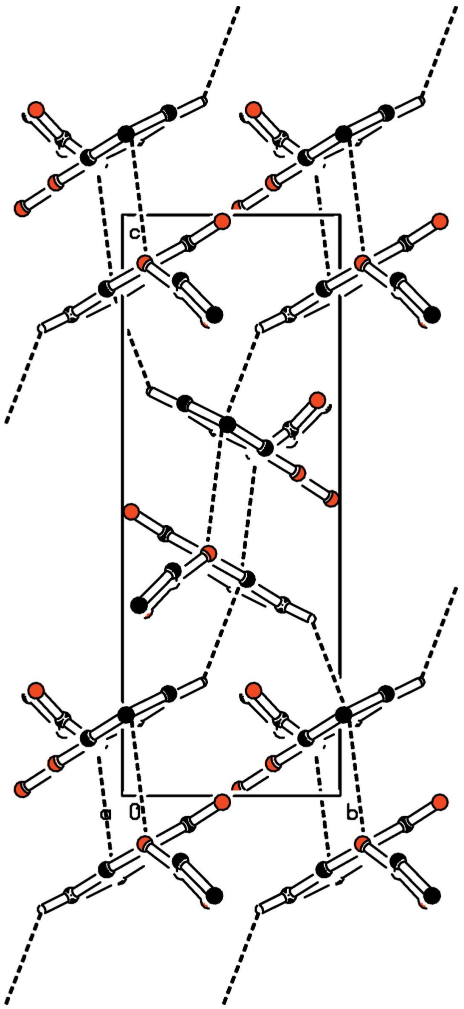


Figure 4
Part of the crystal structure of (I), showing C—H$\cdots\pi$ and π–π interactions as dashed lines. H atoms have been omitted for clarity.

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Table 2
Experimental and calculated bond lengths (Å).

Bond	X-ray	HF(6–31G)
O1—C1	1.3628 (17)	1.371
O1—C9	1.3769 (17)	1.378
O2—C1	1.2004 (18)	1.227
O3—C10	1.3713 (18)	1.359
O3—C2	1.3893 (17)	1.381
O4—C10	1.1932 (19)	1.21
C1—C2	1.460 (2)	1.468
C2—C3	1.329 (2)	1.355
C3—C4	1.4403 (19)	1.441
C4—C5	1.401 (2)	1.406
C4—C9	1.3928 (18)	1.407
C5—C6	1.370 (2)	1.387
C6—C7	1.386 (2)	1.395
C7—C8	1.379 (2)	1.383
C8—C9	1.3842 (19)	1.408
C10—C11	1.495 (2)	1.497
C11—C12	1.491 (3)	1.525

4. Theoretical calculations

Quantum-chemical calculations were performed to compare with the experimental analysis. An *ab-initio* Hartree–Fock (HF) method was used with the standard basis set of 6-31G using the *GAUSSIAN03* software package (Frisch *et al.*, 2004; Dennington *et al.*, 2007) to obtain the optimized molecular structure. The computational results are in good agreement with the experimental crystallographic data (Table 2).

5. Synthesis and crystallization

In a 100 ml round-necked flask topped with a water condenser were introduced successively 25 ml of dried diethyl ether, 6.17 $\times 10^{-3}$ mol ($\simeq$ 0.8 ml) of propionic anhydride and 2.35 ml (4.7 molar equivalents) of dried pyridine. While stirring strongly, 6.17 $\times$ 10^{-3} mol (1 g) of 3-hydroxycoumarin was added in small portions over 30 min. The reaction mixture was left under agitation at room temperature for 3 h. The mixture was then poured in a separating funnel containing 40 ml of chloroform and washed with diluted hydrochloric acid solution until the pH was 2–3. The organic layer was extracted, washed with water to neutrality, dried over $MgSO_4$ and the solvent removed. The resulting precipitate (crude product) was filtered off with petroleum ether and recrystallized from a solvent mixture of chloroform–hexane (1/3, *v*/*v*). Colourless prisms of the title compound were obtained in a yield of 65%, m. p. = 351–353 K.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were placed in calculated positions [C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene)] and refined using a riding-model approximation with U_{iso}(H) constrained to 1.2 (aromatic and methylene group) or 1.5 (methyl group) times U_{eq} of the respective parent atom.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{10}O_4$
M_r	218.20
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	12.1179 (4), 5.7243 (2), 15.3275 (5)
β (°)	94.881 (3)
V (Å^3)	1059.36 (6)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.87
Crystal size (mm)	0.46 × 0.16 × 0.08
Data collection	
Diffractometer	Agilent SuperNova Dual (Cu at zero) Source diffractometer with an AtlasS2 detector
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.778, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6028, 1930, 1655
R_{int}	0.020
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.605
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.117, 1.06
No. of reflections	1930
No. of parameters	145
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.16

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

2-Oxo-2*H*-chromen-3-yl propanoate

Crystal data

$C_{12}H_{10}O_4$
$M_r = 218.20$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 12.1179$ (4) Å
$b = 5.7243$ (2) Å
$c = 15.3275$ (5) Å
$\beta = 94.881$ (3)°
$V = 1059.36$ (6) Å^3
$Z = 4$
$F(000) = 456$
$D_x = 1.368$ Mg m^{-3}
Melting point: 351 K
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 3028 reflections
$\theta = 5.8$–68.6°
$\mu = 0.87$ mm^{-1}
$T = 293$ K
Prism, colourless
0.46 × 0.16 × 0.08 mm

Data collection

Agilent SuperNova Dual (Cu at zero) Source diffractometer with an AtlasS2 detector
Radiation source: sealed X-ray tube
Mirror monochromator
Detector resolution: 5.3048 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min} = 0.778$, $T_{max} = 1.000$
6028 measured reflections
1930 independent reflections
1655 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 68.9$°, $\theta_{min} = 3.7$°
$h = -14 \rightarrow 14$
$k = -6 \rightarrow 6$
$l = -15 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.117$
$S = 1.06$
1930 reflections
145 parameters
0 restraints
40 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 0.1085P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.16$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ 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}
O1	0.08845 (8)	0.19504 (17)	0.44462 (6)	0.0505 (3)
O3	0.36752 (8)	0.39585 (19)	0.41680 (7)	0.0567 (3)
C9	0.02550 (11)	0.3708 (2)	0.40435 (8)	0.0426 (3)
C2	0.25245 (11)	0.3964 (2)	0.40998 (9)	0.0466 (3)
C3	0.19407 (11)	0.5719 (2)	0.37284 (8)	0.0455 (3)
H3	0.2298	0.6985	0.3497	0.055*
C4	0.07494 (11)	0.5644 (2)	0.36879 (8)	0.0420 (3)
C8	−0.08834 (12)	0.3450 (3)	0.40123 (9)	0.0521 (3)
H8	−0.1198	0.2150	0.4258	0.063*
C1	0.20130 (12)	0.1982 (2)	0.45088 (9)	0.0492 (3)
O4	0.36176 (9)	0.1032 (2)	0.31915 (8)	0.0683 (3)
O2	0.24985 (10)	0.0406 (2)	0.48893 (8)	0.0695 (3)
C5	0.00553 (12)	0.7361 (2)	0.32863 (9)	0.0497 (3)
H5	0.0362	0.8676	0.3045	0.060*
C6	−0.10727 (13)	0.7114 (3)	0.32463 (10)	0.0566 (4)
H6	−0.1527	0.8257	0.2975	0.068*
C7	−0.15398 (12)	0.5169 (3)	0.36080 (10)	0.0567 (4)
H7	−0.2306	0.5022	0.3578	0.068*
C10	0.41542 (12)	0.2272 (3)	0.36892 (10)	0.0530 (3)
C11	0.53858 (13)	0.2315 (4)	0.38698 (13)	0.0728 (5)
H11A	0.5644	0.3905	0.3808	0.087*
H11B	0.5576	0.1839	0.4471	0.087*
C12	0.59736 (16)	0.0768 (5)	0.32791 (15)	0.0858 (6)
H12A	0.6758	0.0871	0.3428	0.129*
H12B	0.5806	0.1252	0.2683	0.129*
H12C	0.5736	−0.0817	0.3346	0.129*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0500 (5)	0.0463 (5)	0.0557 (5)	−0.0037 (4)	0.0068 (4)	0.0091 (4)
O3	0.0398 (5)	0.0614 (6)	0.0686 (6)	−0.0025 (4)	0.0019 (4)	−0.0145 (5)
C9	0.0453 (7)	0.0438 (6)	0.0394 (6)	−0.0015 (5)	0.0069 (5)	−0.0014 (5)
C2	0.0395 (7)	0.0505 (7)	0.0499 (7)	−0.0036 (5)	0.0052 (5)	−0.0083 (5)
C3	0.0468 (7)	0.0425 (7)	0.0485 (7)	−0.0072 (5)	0.0109 (5)	−0.0037 (5)
C4	0.0459 (7)	0.0411 (6)	0.0398 (6)	−0.0018 (5)	0.0083 (5)	−0.0037 (5)
C8	0.0473 (7)	0.0570 (8)	0.0535 (7)	−0.0083 (6)	0.0125 (6)	−0.0022 (6)

C1	0.0506 (7)	0.0490 (7)	0.0479 (7)	0.0031 (6)	0.0034 (5)	0.0009 (6)
O4	0.0510 (6)	0.0805 (8)	0.0730 (7)	−0.0006 (5)	0.0025 (5)	−0.0238 (6)
O2	0.0665 (7)	0.0669 (7)	0.0749 (7)	0.0122 (6)	0.0041 (6)	0.0197 (6)
C5	0.0575 (8)	0.0450 (7)	0.0474 (7)	0.0025 (6)	0.0100 (6)	0.0013 (5)
C6	0.0548 (8)	0.0611 (9)	0.0540 (7)	0.0145 (7)	0.0065 (6)	−0.0010 (6)
C7	0.0411 (7)	0.0715 (9)	0.0584 (8)	0.0027 (6)	0.0097 (6)	−0.0069 (7)
C10	0.0450 (8)	0.0594 (8)	0.0545 (7)	0.0007 (6)	0.0038 (6)	−0.0053 (6)
C11	0.0430 (8)	0.0917 (13)	0.0829 (11)	0.0053 (8)	−0.0003 (7)	−0.0168 (10)
C12	0.0526 (10)	0.1094 (16)	0.0951 (13)	0.0179 (10)	0.0050 (9)	−0.0168 (12)

Geometric parameters (Å, º)

O1—C1	1.3628 (17)	O4—C10	1.1932 (19)
O1—C9	1.3769 (17)	C5—C6	1.370 (2)
O3—C10	1.3713 (18)	C5—H5	0.9300
O3—C2	1.3893 (17)	C6—C7	1.386 (2)
C9—C8	1.3842 (19)	C6—H6	0.9300
C9—C4	1.3926 (18)	C7—H7	0.9300
C2—C3	1.329 (2)	C10—C11	1.495 (2)
C2—C1	1.460 (2)	C11—C12	1.491 (3)
C3—C4	1.4403 (19)	C11—H11A	0.9700
C3—H3	0.9300	C11—H11B	0.9700
C4—C5	1.401 (2)	C12—H12A	0.9600
C8—C7	1.379 (2)	C12—H12B	0.9600
C8—H8	0.9300	C12—H12C	0.9600
C1—O2	1.2004 (18)		
C1—O1—C9	122.43 (10)	C4—C5—H5	119.8
C10—O3—C2	115.41 (11)	C5—C6—C7	120.31 (14)
O1—C9—C8	116.74 (12)	C5—C6—H6	119.8
O1—C9—C4	121.11 (12)	C7—C6—H6	119.8
C8—C9—C4	122.15 (13)	C8—C7—C6	120.90 (14)
C3—C2—O3	121.88 (12)	C8—C7—H7	119.6
C3—C2—C1	122.80 (12)	C6—C7—H7	119.6
O3—C2—C1	115.22 (12)	O4—C10—O3	121.89 (13)
C2—C3—C4	119.40 (12)	O4—C10—C11	127.56 (15)
C2—C3—H3	120.3	O3—C10—C11	110.52 (13)
C4—C3—H3	120.3	C12—C11—C10	113.50 (15)
C9—C4—C5	117.88 (12)	C12—C11—H11A	108.9
C9—C4—C3	118.03 (12)	C10—C11—H11A	108.9
C5—C4—C3	124.05 (12)	C12—C11—H11B	108.9
C7—C8—C9	118.32 (13)	C10—C11—H11B	108.9
C7—C8—H8	120.8	H11A—C11—H11B	107.7
C9—C8—H8	120.8	C11—C12—H12A	109.5
O2—C1—O1	118.14 (13)	C11—C12—H12B	109.5
O2—C1—C2	125.74 (14)	H12A—C12—H12B	109.5
O1—C1—C2	116.12 (12)	C11—C12—H12C	109.5
C6—C5—C4	120.43 (13)	H12A—C12—H12C	109.5

C6—C5—H5	119.8	H12B—C12—H12C	109.5

C1—O1—C9—C8	179.07 (12)	C9—O1—C1—C2	−1.73 (18)
C1—O1—C9—C4	−0.99 (18)	C3—C2—C1—O2	−176.26 (14)
C10—O3—C2—C3	−113.91 (15)	O3—C2—C1—O2	0.3 (2)
C10—O3—C2—C1	69.53 (17)	C3—C2—C1—O1	3.69 (19)
O3—C2—C3—C4	−179.09 (11)	O3—C2—C1—O1	−179.78 (10)
C1—C2—C3—C4	−2.8 (2)	C9—C4—C5—C6	−0.27 (19)
O1—C9—C4—C5	179.85 (11)	C3—C4—C5—C6	177.46 (12)
C8—C9—C4—C5	−0.21 (19)	C4—C5—C6—C7	0.4 (2)
O1—C9—C4—C3	1.98 (17)	C9—C8—C7—C6	−0.4 (2)
C8—C9—C4—C3	−178.08 (12)	C5—C6—C7—C8	−0.1 (2)
C2—C3—C4—C9	−0.08 (18)	C2—O3—C10—O4	6.2 (2)
C2—C3—C4—C5	−177.81 (12)	C2—O3—C10—C11	−175.47 (14)
O1—C9—C8—C7	−179.53 (12)	O4—C10—C11—C12	6.5 (3)
C4—C9—C8—C7	0.5 (2)	O3—C10—C11—C12	−171.65 (17)
C9—O1—C1—O2	178.23 (13)		

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C4–C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O2^{i}	0.93	2.59	3.4783 (19)	161
C5—H5···*Cg*2^{ii}	0.93	2.78	3.4959 (16)	134

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