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Methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate

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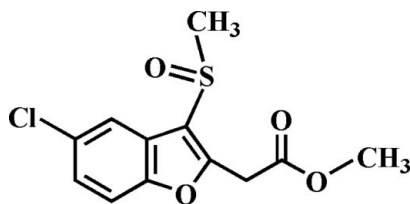
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.035; wR factor = 0.101; data-to-parameter ratio = 14.9.

The title compound, $\text{C}_{12}\text{H}_{11}\text{ClO}_4\text{S}$, was prepared by the oxidation of methyl 2-(5-chloro-3-methylsulfonyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid. The O atom and the methyl group of the methylsulfonyl substituent lie on opposite sides of the plane of the benzofuran fragment. The crystal structure is stabilized by aromatic π - π interactions between the benzene rings of neighbouring molecules [centroid-to-centroid distance = 3.809 (2) Å], and by C-H... π interactions between a methyl H atom and the furan ring of an adjacent molecule. In addition, the crystal structure exhibits intermolecular C-H...O hydrogen bonds.

Related literature

For details of the pharmacological activities of benzofuran compounds, see: Ward (1999). For the crystal structures of similar 2-(3-methylsulfonyl-1-benzofuran-2-yl)acetic acid derivatives, see: Choi *et al.* (2007, 2008).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{11}\text{ClO}_4\text{S}$
 $M_r = 286.72$
 Triclinic, $P\bar{1}$
 $a = 7.8910$ (5) Å
 $b = 8.9416$ (6) Å
 $c = 10.4048$ (7) Å
 $\alpha = 73.774$ (1)°
 $\beta = 78.743$ (1)°
 $\gamma = 68.559$ (1)°
 $V = 652.55$ (7) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.46$ mm⁻¹
 $T = 298$ (2) K
 $0.40 \times 0.40 \times 0.20$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1999)
 $T_{\min} = 0.827$, $T_{\max} = 0.907$
 3753 measured reflections
 2525 independent reflections
 2123 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.101$
 $S = 1.06$
 2525 reflections
 169 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1/C2/C7/O1/C8 furan ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C11-H11C...Cg1 ⁱ	0.96	2.92	3.858 (2)	165
C3-H3...O4 ⁱⁱ	0.94 (2)	2.41 (2)	3.320 (3)	162.7 (17)
C9-H9B...O1 ⁱⁱⁱ	0.97	2.59	3.550 (2)	172
C9-H9A...O4 ^{iv}	0.97	2.23	3.183 (3)	169

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 1998); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2153).

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supporting information

Acta Cryst. (2008). E64, o2139 [doi:10.1107/S1600536808033503]

Methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate

Hong Dae Choi, Pil Ja Seo, Byeng Wha Son and Uk Lee

S1. Comment

Benzofuran derivatives occur widely in natural products and show a variety of interesting pharmacological activities such as antimicrobial, fungicidal, insecticidal and antioxidant properties (Ward, 1999). As a part of our ongoing studies on the synthesis and structure of 2-(3-methylsulfinyl-1-benzofuran-2-yl)acetic acid analogues, the crystal structure of ethyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2007) and methyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008) have been described in the literature. Here we report the crystal structure of the title compound, methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.011 (2) Å from the least-squares plane defined by the nine constituent atoms. The molecular packing (Fig. 2) is stabilized by aromatic π - π stacking interactions between the benzene rings of adjacent molecules. The $Cg2 \cdots Cg2^{ii}$ distance is 3.809 (2) Å ($Cg2$ is the centroid of the C2–C7 benzene ring; symmetry code as in Fig. 2). The molecular packing is further stabilized by C—H \cdots π interactions between a methyl H atom and the furan ring of the benzofuran unit, with a C11—H11C \cdots Cg1ⁱ separation of 2.92 Å (Fig. 2 and Table 1; $Cg1$ is the centroid of the C1/C2/C7/O1/C8 furan ring). Additionally, intermolecular C—H \cdots O hydrogen bonds in the structure were observed (Table 1).

S2. Experimental

77% 3-Chloroperoxybenzoic acid (292 mg, 1.3 mmol) was added in small portions to a stirred solution of methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate (325 mg, 1.2 mmol) in dichloromethane (40 ml) at 273 K. After being stirred for 3 h at room temperature, the mixture was washed with saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was purified by column chromatography (ethyl acetate) to afford the title compound as a colorless solid [yield 77%, m.p. 415–416 K; R_f = 0.72 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by evaporation of a solution of the title compound in benzene at room temperature. Spectroscopic analysis: ^1H NMR (CDCl_3 , 400 MHz) δ 3.07 (s, 3H), 3.75 (s, 3H), 4.05 (s, 2H), 7.34 (dd, J = 8.76 Hz and J = 1.80 Hz, 1H), 7.44 (d, J = 8.80 Hz, 1H), 7.90 (d, J = 1.80 Hz, 1H); EI-MS 288 [$M+2$], 286 [M^+].

S3. Refinement

All H atoms were geometrically positioned and refined using a riding model, with C—H = 0.93 Å (aromatic), 0.97 Å (methylene), and 0.96 Å (methyl) H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (aromatic & methylene), and 1.5 $U_{\text{eq}}(\text{C})$ (methyl) H atoms.

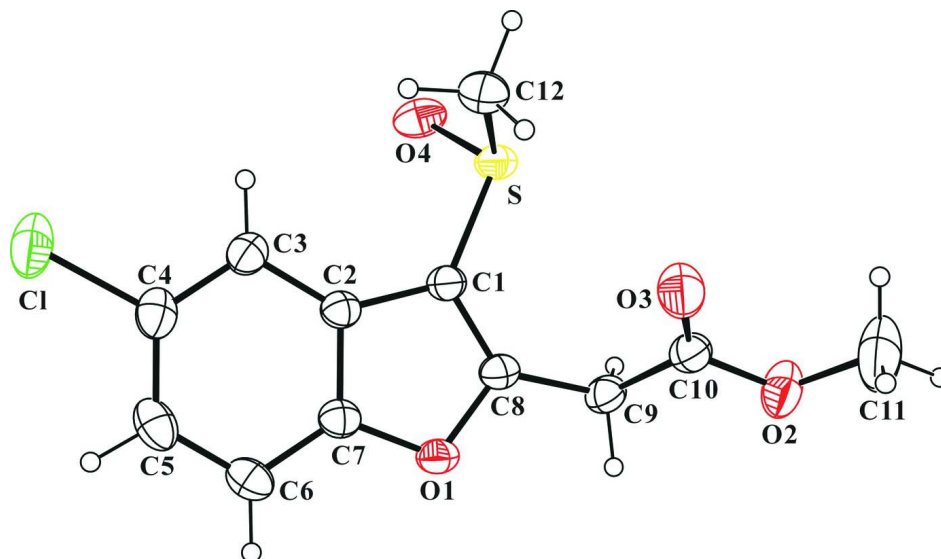


Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

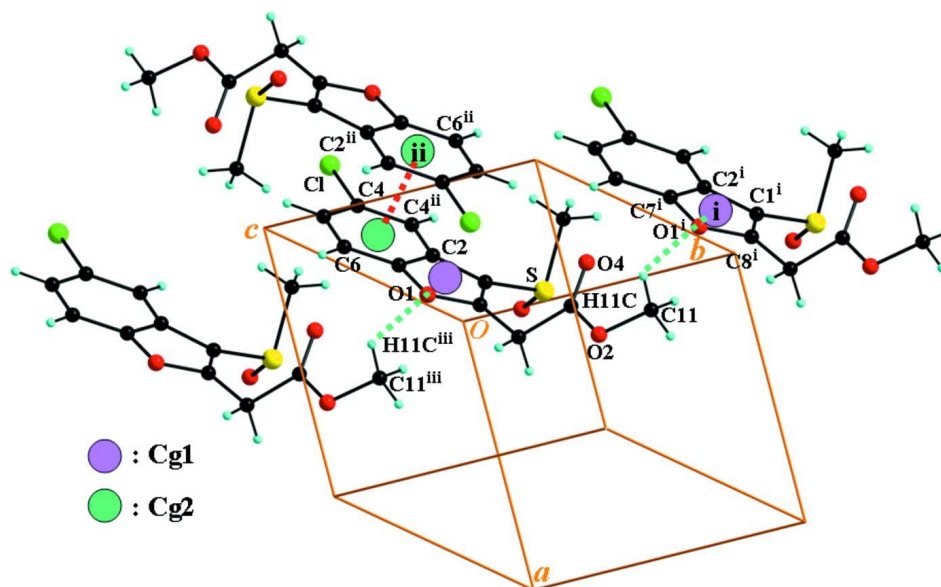


Figure 2

π - π and C—H... π interactions (dotted lines) in the title compound. Cg denotes the ring centroid. [Symmetry code: (i) $x, y + 1, z$; (ii) $-x, -y + 1, -z + 2$; (iii) $x, y - 1, z$.]

Methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate

Crystal data

$C_{12}H_{11}ClO_4S$

$M_r = 286.72$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.8910(5)\text{ \AA}$

$b = 8.9416(6)\text{ \AA}$

$c = 10.4048(7)\text{ \AA}$

$\alpha = 73.774(1)^\circ$

$\beta = 78.743(1)^\circ$

$\gamma = 68.559(1)^\circ$

$V = 652.55(7)\text{ \AA}^3$

$Z = 2$

$F(000) = 296$
 $D_x = 1.459 \text{ Mg m}^{-3}$
 Melting point = 415–416 K
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 2313 reflections

$\theta = 2.8\text{--}28.2^\circ$
 $\mu = 0.46 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Block, colourless
 $0.40 \times 0.40 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: $10.0 \text{ pixels mm}^{-1}$
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1999)
 $T_{\min} = 0.827$, $T_{\max} = 0.907$

3753 measured reflections
 2525 independent reflections
 2123 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -11 \rightarrow 7$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.101$
 $S = 1.06$
 2525 reflections
 169 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 atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.2053P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl	-0.22541 (8)	0.20560 (7)	0.87139 (8)	0.0834 (2)
S	0.23616 (7)	0.63233 (7)	0.54121 (5)	0.05176 (17)
O1	0.33659 (17)	0.45642 (16)	0.92043 (12)	0.0468 (3)
O2	0.5278 (2)	0.89402 (19)	0.72451 (19)	0.0728 (5)
O3	0.2521 (2)	0.9006 (2)	0.69823 (19)	0.0748 (5)
O4	0.2462 (2)	0.4995 (2)	0.47609 (15)	0.0688 (4)
C1	0.2400 (2)	0.5423 (2)	0.71481 (17)	0.0429 (4)
C2	0.1418 (2)	0.4347 (2)	0.79676 (17)	0.0424 (4)
C3	0.0067 (3)	0.3789 (2)	0.7780 (2)	0.0489 (4)
H3	-0.040 (3)	0.409 (3)	0.694 (2)	0.053 (6)*

C4	-0.0519 (3)	0.2747 (2)	0.8878 (2)	0.0555 (5)
C5	0.0180 (3)	0.2229 (3)	1.0116 (2)	0.0596 (5)
H5	-0.0254	0.1511	1.0818	0.072*
C6	0.1517 (3)	0.2778 (2)	1.0307 (2)	0.0556 (5)
H6	0.2007	0.2447	1.1124	0.067*
C7	0.2087 (2)	0.3845 (2)	0.92181 (19)	0.0450 (4)
C8	0.3537 (2)	0.5507 (2)	0.79220 (18)	0.0433 (4)
C9	0.4870 (3)	0.6396 (2)	0.7667 (2)	0.0494 (4)
H9A	0.5801	0.6024	0.6959	0.059*
H9B	0.5470	0.6105	0.8475	0.059*
C10	0.4045 (3)	0.8245 (3)	0.72678 (19)	0.0489 (4)
C11	0.4682 (5)	1.0733 (3)	0.6855 (4)	0.1092 (12)
H11A	0.4158	1.1104	0.6016	0.164*
H11B	0.5713	1.1098	0.6754	0.164*
H11C	0.3782	1.1180	0.7537	0.164*
C12	0.0024 (3)	0.7661 (3)	0.5437 (2)	0.0661 (6)
H12A	-0.0223	0.8297	0.4543	0.099*
H12B	-0.0183	0.8390	0.6018	0.099*
H12C	-0.0772	0.7011	0.5764	0.099*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0594 (4)	0.0550 (3)	0.1360 (6)	-0.0274 (3)	-0.0214 (4)	-0.0029 (4)
S	0.0541 (3)	0.0652 (3)	0.0390 (3)	-0.0251 (2)	-0.0121 (2)	-0.0044 (2)
O1	0.0496 (7)	0.0499 (7)	0.0406 (7)	-0.0133 (6)	-0.0141 (5)	-0.0075 (5)
O2	0.0579 (9)	0.0575 (9)	0.1130 (14)	-0.0244 (7)	-0.0186 (9)	-0.0208 (9)
O3	0.0557 (9)	0.0564 (9)	0.1072 (13)	-0.0179 (7)	-0.0286 (9)	0.0023 (9)
O4	0.0751 (10)	0.0872 (11)	0.0505 (8)	-0.0219 (9)	-0.0140 (7)	-0.0269 (8)
C1	0.0460 (9)	0.0439 (10)	0.0394 (9)	-0.0139 (8)	-0.0101 (7)	-0.0081 (7)
C2	0.0436 (9)	0.0383 (9)	0.0431 (9)	-0.0087 (7)	-0.0086 (7)	-0.0096 (7)
C3	0.0465 (10)	0.0432 (10)	0.0584 (12)	-0.0125 (8)	-0.0119 (9)	-0.0123 (9)
C4	0.0449 (10)	0.0376 (10)	0.0800 (14)	-0.0101 (8)	-0.0095 (10)	-0.0100 (9)
C5	0.0537 (12)	0.0419 (10)	0.0671 (13)	-0.0109 (9)	0.0000 (10)	0.0018 (9)
C6	0.0564 (12)	0.0489 (11)	0.0489 (11)	-0.0091 (9)	-0.0087 (9)	-0.0009 (9)
C7	0.0437 (9)	0.0416 (10)	0.0455 (10)	-0.0078 (8)	-0.0086 (7)	-0.0093 (8)
C8	0.0428 (9)	0.0448 (10)	0.0417 (9)	-0.0107 (8)	-0.0107 (7)	-0.0093 (7)
C9	0.0449 (10)	0.0534 (11)	0.0534 (11)	-0.0163 (8)	-0.0143 (8)	-0.0115 (9)
C10	0.0472 (10)	0.0557 (11)	0.0468 (10)	-0.0193 (9)	-0.0064 (8)	-0.0124 (8)
C11	0.095 (2)	0.0580 (16)	0.186 (4)	-0.0338 (16)	-0.030 (2)	-0.0244 (19)
C12	0.0659 (13)	0.0603 (13)	0.0673 (14)	-0.0152 (11)	-0.0275 (11)	-0.0009 (11)

Geometric parameters (Å, °)

Cl—C4	1.748 (2)	C4—C5	1.391 (3)
S—O4	1.4950 (17)	C5—C6	1.381 (3)
S—C1	1.7613 (18)	C5—H5	0.9300
S—C12	1.794 (2)	C6—C7	1.380 (3)

O1—C8	1.376 (2)	C6—H6	0.9300
O1—C7	1.377 (2)	C8—C9	1.482 (3)
O2—C10	1.327 (2)	C9—C10	1.504 (3)
O2—C11	1.454 (3)	C9—H9A	0.9700
O3—C10	1.194 (2)	C9—H9B	0.9700
C1—C8	1.350 (2)	C11—H11A	0.9600
C1—C2	1.443 (3)	C11—H11B	0.9600
C2—C7	1.394 (3)	C11—H11C	0.9600
C2—C3	1.396 (3)	C12—H12A	0.9600
C3—C4	1.378 (3)	C12—H12B	0.9600
C3—H3	0.94 (2)	C12—H12C	0.9600
O4—S—C1	105.98 (9)	C6—C7—C2	123.72 (18)
O4—S—C12	106.01 (11)	C1—C8—O1	110.86 (16)
C1—S—C12	98.50 (10)	C1—C8—C9	133.29 (17)
C8—O1—C7	106.35 (13)	O1—C8—C9	115.85 (15)
C10—O2—C11	116.4 (2)	C8—C9—C10	114.36 (15)
C8—C1—C2	107.57 (15)	C8—C9—H9A	108.7
C8—C1—S	124.18 (15)	C10—C9—H9A	108.7
C2—C1—S	127.95 (14)	C8—C9—H9B	108.7
C7—C2—C3	119.64 (17)	C10—C9—H9B	108.7
C7—C2—C1	104.63 (16)	H9A—C9—H9B	107.6
C3—C2—C1	135.72 (17)	O3—C10—O2	123.6 (2)
C4—C3—C2	116.31 (19)	O3—C10—C9	126.28 (19)
C4—C3—H3	121.9 (13)	O2—C10—C9	110.06 (16)
C2—C3—H3	121.8 (13)	O2—C11—H11A	109.5
C3—C4—C5	123.7 (2)	O2—C11—H11B	109.5
C3—C4—C1	118.25 (17)	H11A—C11—H11B	109.5
C5—C4—C1	118.09 (16)	O2—C11—H11C	109.5
C6—C5—C4	120.25 (19)	H11A—C11—H11C	109.5
C6—C5—H5	119.9	H11B—C11—H11C	109.5
C4—C5—H5	119.9	S—C12—H12A	109.5
C7—C6—C5	116.40 (19)	S—C12—H12B	109.5
C7—C6—H6	121.8	H12A—C12—H12B	109.5
C5—C6—H6	121.8	S—C12—H12C	109.5
O1—C7—C6	125.70 (17)	H12A—C12—H12C	109.5
O1—C7—C2	110.58 (15)	H12B—C12—H12C	109.5
O4—S—C1—C8	129.68 (17)	C5—C6—C7—C2	-1.4 (3)
C12—S—C1—C8	-120.88 (18)	C3—C2—C7—O1	-178.32 (15)
O4—S—C1—C2	-43.19 (19)	C1—C2—C7—O1	1.0 (2)
C12—S—C1—C2	66.26 (19)	C3—C2—C7—C6	1.4 (3)
C8—C1—C2—C7	-0.4 (2)	C1—C2—C7—C6	-179.31 (18)
S—C1—C2—C7	173.45 (14)	C2—C1—C8—O1	-0.4 (2)
C8—C1—C2—C3	178.8 (2)	S—C1—C8—O1	-174.49 (13)
S—C1—C2—C3	-7.4 (3)	C2—C1—C8—C9	-179.77 (19)
C7—C2—C3—C4	-0.2 (3)	S—C1—C8—C9	6.1 (3)
C1—C2—C3—C4	-179.2 (2)	C7—O1—C8—C1	1.0 (2)

C2—C3—C4—C5	-1.0 (3)	C7—O1—C8—C9	-179.52 (15)
C2—C3—C4—C1	178.26 (14)	C1—C8—C9—C10	60.7 (3)
C3—C4—C5—C6	1.0 (3)	O1—C8—C9—C10	-118.61 (18)
C1—C4—C5—C6	-178.22 (16)	C11—O2—C10—O3	0.5 (4)
C4—C5—C6—C7	0.2 (3)	C11—O2—C10—C9	179.1 (2)
C8—O1—C7—C6	179.08 (18)	C8—C9—C10—O3	-10.1 (3)
C8—O1—C7—C2	-1.22 (19)	C8—C9—C10—O2	171.31 (17)
C5—C6—C7—O1	178.32 (18)		

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>
C11—H11C \cdots Cg1 ⁱ	0.96	2.92	3.858 (2)	165
C3—H3 \cdots O4 ⁱⁱ	0.94 (2)	2.41 (2)	3.320 (3)	162.7 (17)
C9—H9B \cdots O1 ⁱⁱⁱ	0.97	2.59	3.550 (2)	172
C9—H9A \cdots O4 ^{iv}	0.97	2.23	3.183 (3)	169

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