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ISSN 2056-9890

Crystal structure of [(2*R*,3*R*,4*S*)-3,4-bis(acetyloxy)-5-iodo-3,4-dihydro-2*H*-pyran-2-yl]methyl acetate

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Received 21 November 2014; accepted 24 November 2014

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

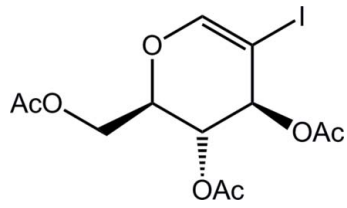
In the title compound, $C_{12}H_{15}IO_7$, the 3,4-dihydro-2*H*-pyran ring is in a distorted half-boat conformation with the atom bearing the acetyloxy group adjacent to the C atom bearing the methylacetate group lying 0.633 (6) Å above the plane of the remaining ring atoms (r.m.s. deviation = 0.0907 Å). In the crystal, molecules are linked into a supramolecular chain along the *a* axis through two C—H···O interactions to the same acceptor carbonyl O atom; these chains pack with no specific intermolecular interactions between them.

Keywords: Crystal structure; carbohydrate; conformation; C—H···O interactions; crystal structure.

CCDC reference: 1035669

1. Related literature

For the structure of the unsubstituted parent compound, determined three times, and having a distorted half-boat conformation, see: Vangehr *et al.* (1979); Krajewski *et al.* (1979); Voelter *et al.* (1981).



2. Experimental

2.1. Crystal data

$C_{12}H_{15}IO_7$
M_r = 398.14
Orthorhombic, $P2_12_12_1$
a = 7.9048 (2) Å
b = 8.7521 (2) Å
c = 22.7094 (5) Å
V = 1571.12 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.06 mm^{-1}
T = 293 K
0.35 × 0.24 × 0.11 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.601, T_{max} = 0.745
6116 measured reflections
2818 independent reflections
2456 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.071
S = 1.04
2818 reflections
184 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.58 e Å^{-3}
Absolute structure: Flack x determined using 925 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.000 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O6^{i}	0.93	2.58	3.448 (7)	156
C3—H3···O6^{ii}	0.98	2.55	3.383 (6)	143

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SIR* (Burla *et al.*, 2014; program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *MarvinSketch* (ChemAxon, 2010) and *publCIF* (Westrip, 2010).

Acknowledgements

We thank Professor Regina H. A. Santos from IQSC–USP for the X-ray data collection. The Brazilian agencies CNPq (305626/2013–2 to JZS; 306121/2013-2 to IC; 308320/2010-7 to HAS) and FAPESP are acknowledged for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7323).

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supporting information

Acta Cryst. (2015). E**71**, o53–o54 [https://doi.org/10.1107/S205698901402564X]

Crystal structure of [(2*R*,3*R*,4*S*)-3,4-bis(acetyloxy)-5-iodo-3,4-dihydro-2*H*-pyran-2-yl]methyl acetate

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S1. Experimental

S1.1. Synthesis and crystallization

To a solution of 3,4,6-tri-oxoacetyl-D-Glucal (3 mmol) in acetonitrile (9 mL) at 373 K under a N_2 atmosphere was added N-iodosuccinimide (3.6 mmol) and silver nitrate (0.6 mmol) as catalyst followed by stirring for 4 h. After consumption of the starting material (TLC monitoring), the reaction mixture was filtered through a sintered funnel (using Celite) and the filtrate was then evaporated giving a crude product which was purified by silica gel column chromatography (20-30% of EtOAc/hexane) to obtain the title compound. Suitable crystals were obtained by keeping the EtOAc solution of the product at 277 K for 48 h.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.73 (s, 1H), 5.44 (d, J = 5.1 Hz, 1H), 5.18 (dd, J = 5.1, 7.0 Hz, 1>H), 4.37-4.30 (m, 2H), 4.08-4.18 (m, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 170.5, 170.3, 169.4, 149.4, 74.0, 70.6, 67.6, 66.3, 61.0, 20.9, 20.8, 20.7 ppm. HRMS: calcd. for $C_{12}H_{15}IO_7$ $[M + H]^+$ 397.9862; found: 397.9863.

S1.2. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H = 0.93 to 0.98 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) = 1.2–1.5U_{eq}(C).

S2. Results and discussion

The 3,4-dihydro-2*H*-pyran ring in the title compound, Fig. 1, is in a distorted half-boat conformation as reflected in the conformational parameters: the puckering amplitude (Q) = 0.497 (5) Å, θ = 52.6 (6)° and φ = 268.6 (7)°. In this conformation, the C4 atom lies 0.633 (6) Å above the plane of the remaining ring atoms which have a r.m.s. of 0.0907 Å. The substituents at the C3 and C4 sites occupy equatorial positions while that at atom C5 is bisectional. The crystal structure of the unsubstituted parent compound has been reported three times and also adopts a distorted half-boat conformation (Vangehr *et al.*, 1979; Krajewski *et al.*, 1979; Voelter *et al.*, 1981).

In the crystal , the molecules are linked *via* two independent C—H···O interactions, Table 1, involving the same carbonyl-O6 atom as acceptor. The resulting supramolecular architecture is a chain parallel to the *a* axis, Fig. 2. These chains pack with no specific intermolecular interactions between them, Fig. 3.

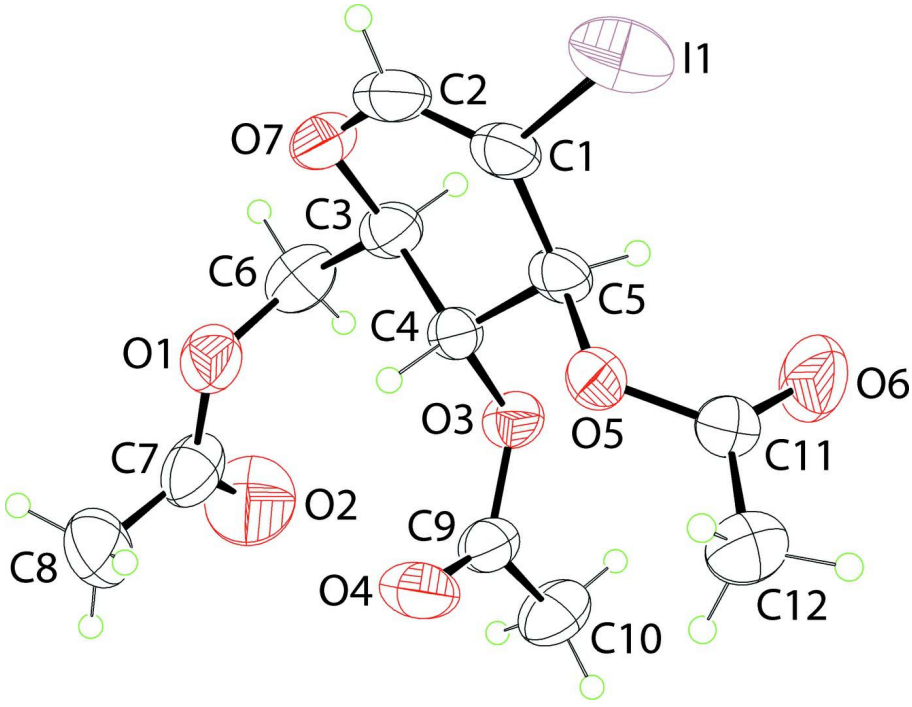

Figure 1

The molecular structure of the title compound showing displacement ellipsoids at the 35% probability level.

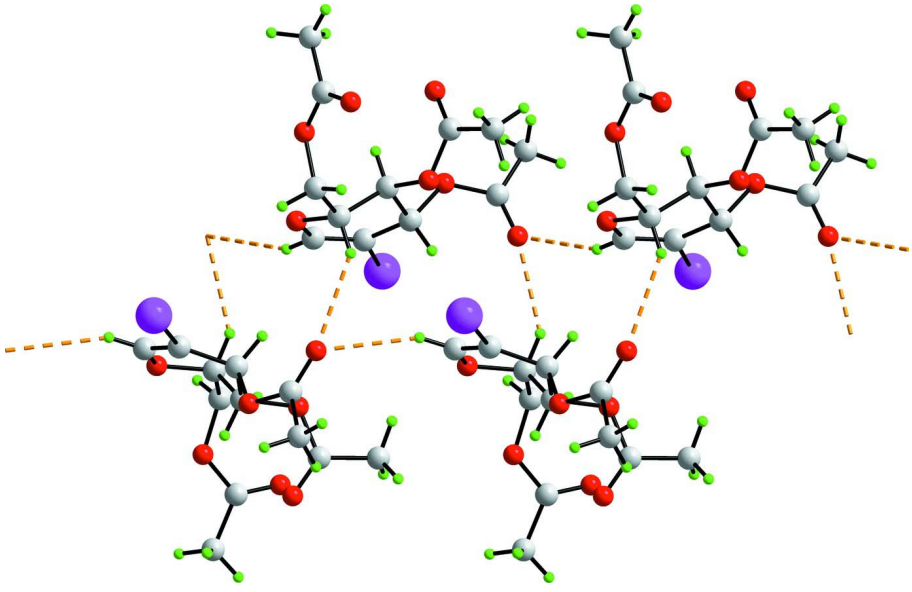

Figure 2

A view of the supramolecular chain along the *a* axis mediated by C—H···O interactions (orange dashed lines).

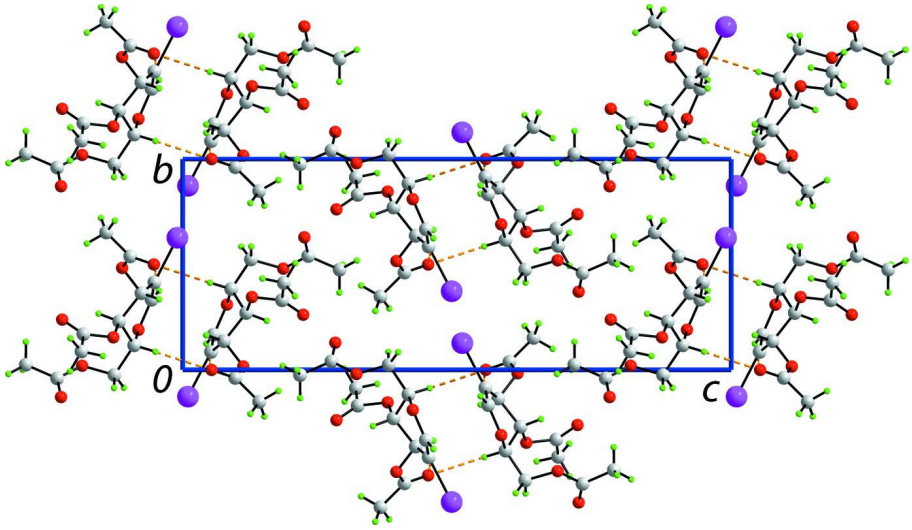

Figure 3

A view in projection down the *a* axis of the unit-cell contents. The C—H···O interactions are shown as orange dashed lines.

[(2*R*,3*R*,4*S*)-3,4-Bis(acetyloxy)-5-iodo-3,4-dihydro-2*H*-pyran-2-yl]methyl acetate

Crystal data

$C_{12}H_{15}IO_7$
$M_r = 398.14$
Orthorhombic, $P2_12_12_1$
$a = 7.9048$ (2) Å
$b = 8.7521$ (2) Å
$c = 22.7094$ (5) Å
$V = 1571.12$ (6) Å^3
$Z = 4$
$F(000) = 784$
$D_x = 1.683$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3256 reflections
$\theta = 2.7$–25.1°
$\mu = 2.06$ mm^{-1}
$T = 293$ K
Irregular, colourless
0.35 × 0.24 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.601$, $T_{max} = 0.745$
6116 measured reflections
2818 independent reflections
2456 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25.4°$, $\theta_{min} = 1.8°$
$h = -9\rightarrow5$
$k = -7\rightarrow10$
$l = -27\rightarrow27$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 1.04$
2818 reflections
184 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
$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2 + 0.3563P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.58$ e Å^{-3}

Absolute structure: Flack *x* determined using 925 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.000 (11)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
I	0.55529 (6)	0.37319 (5)	0.49032 (2)	0.1044 (2)
O1	0.5090 (4)	0.9803 (5)	0.31664 (17)	0.0798 (10)
O2	0.7080 (7)	1.1290 (7)	0.2782 (3)	0.141 (2)
O3	0.8630 (3)	0.8456 (4)	0.37365 (13)	0.0609 (8)
O4	0.8637 (5)	0.7615 (5)	0.28034 (15)	0.0839 (11)
O5	0.8078 (4)	0.5163 (4)	0.38956 (12)	0.0603 (8)
O6	1.0344 (5)	0.4998 (6)	0.44747 (19)	0.1042 (14)
O7	0.4218 (4)	0.8098 (5)	0.41934 (15)	0.0749 (9)
C1	0.5672 (6)	0.5851 (6)	0.44833 (17)	0.0637 (11)
C2	0.4291 (6)	0.6670 (7)	0.44323 (19)	0.0728 (14)
H2	0.3287	0.6246	0.4569	0.087*
C3	0.5830 (5)	0.8834 (6)	0.41154 (19)	0.0653 (12)
H3	0.6264	0.9136	0.4502	0.078*
C4	0.7049 (5)	0.7701 (5)	0.38426 (17)	0.0514 (10)
H4	0.6585	0.7334	0.3468	0.062*
C5	0.7335 (5)	0.6361 (6)	0.42476 (16)	0.0576 (10)
H5	0.8095	0.6647	0.4570	0.069*
C6	0.5543 (7)	1.0241 (6)	0.3756 (3)	0.0825 (14)
H6A	0.4643	1.0846	0.3929	0.099*
H6B	0.6564	1.0855	0.3749	0.099*
C7	0.5931 (7)	1.0403 (7)	0.2711 (3)	0.0887 (18)
C8	0.5349 (9)	0.9756 (11)	0.2140 (3)	0.121 (3)
H8A	0.5497	0.8667	0.2143	0.181*
H8B	0.6000	1.0190	0.1824	0.181*
H8C	0.4174	0.9993	0.2083	0.181*
C9	0.9308 (6)	0.8302 (5)	0.3190 (2)	0.0607 (11)
C10	1.0949 (6)	0.9124 (7)	0.3156 (3)	0.0869 (16)
H10A	1.0799	1.0066	0.2946	0.130*
H10B	1.1762	0.8500	0.2954	0.130*
H10C	1.1348	0.9338	0.3547	0.130*
C11	0.9611 (6)	0.4617 (6)	0.4043 (2)	0.0653 (11)
C12	1.0198 (7)	0.3483 (8)	0.3605 (3)	0.0952 (19)
H12A	1.1130	0.2915	0.3766	0.143*
H12B	1.0556	0.4002	0.3254	0.143*
H12C	0.9290	0.2796	0.3512	0.143*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I	0.1334 (4)	0.0973 (3)	0.0825 (3)	−0.0195 (3)	0.0270 (2)	0.0107 (2)
O1	0.0605 (18)	0.092 (3)	0.087 (2)	−0.0091 (16)	−0.0051 (16)	0.015 (2)
O2	0.126 (4)	0.127 (4)	0.169 (5)	−0.048 (4)	0.012 (3)	0.045 (4)
O3	0.0480 (14)	0.074 (2)	0.0606 (16)	−0.0122 (14)	0.0004 (12)	−0.0116 (16)
O4	0.080 (2)	0.114 (3)	0.058 (2)	−0.022 (2)	0.0163 (18)	−0.013 (2)
O5	0.0586 (16)	0.076 (2)	0.0461 (15)	0.0052 (15)	−0.0067 (13)	−0.0102 (15)
O6	0.075 (2)	0.146 (4)	0.092 (3)	0.021 (3)	−0.030 (2)	−0.026 (3)
O7	0.0491 (16)	0.105 (3)	0.0702 (19)	0.0004 (17)	0.0113 (15)	−0.0053 (19)
C1	0.069 (3)	0.081 (3)	0.0416 (19)	−0.010 (3)	0.0058 (19)	−0.006 (2)
C2	0.066 (3)	0.102 (4)	0.050 (2)	−0.018 (3)	0.017 (2)	−0.014 (3)
C3	0.056 (2)	0.085 (3)	0.055 (2)	−0.006 (3)	0.0020 (18)	−0.020 (3)
C4	0.0427 (19)	0.069 (3)	0.042 (2)	−0.0070 (19)	−0.0024 (17)	−0.011 (2)
C5	0.059 (2)	0.077 (3)	0.0368 (18)	−0.011 (2)	−0.0018 (16)	−0.011 (2)
C6	0.068 (3)	0.073 (3)	0.107 (4)	0.001 (3)	0.008 (3)	−0.011 (3)
C7	0.063 (3)	0.086 (4)	0.118 (5)	0.007 (3)	0.004 (3)	0.041 (4)
C8	0.102 (4)	0.174 (8)	0.086 (4)	0.001 (5)	−0.008 (4)	0.057 (5)
C9	0.052 (2)	0.065 (3)	0.065 (3)	0.002 (2)	0.010 (2)	0.002 (2)
C10	0.059 (3)	0.092 (4)	0.109 (4)	−0.010 (3)	0.017 (3)	0.007 (3)
C11	0.058 (2)	0.084 (3)	0.055 (2)	0.001 (3)	0.003 (2)	0.005 (2)
C12	0.086 (4)	0.116 (5)	0.084 (4)	0.023 (4)	0.010 (3)	−0.013 (4)

Geometric parameters (Å, º)

I—C1	2.087 (5)	C4—C5	1.507 (6)
O1—C7	1.336 (7)	C4—H4	0.9800
O1—C6	1.438 (7)	C5—H5	0.9800
O2—C7	1.205 (8)	C6—H6A	0.9700
O3—C9	1.359 (5)	C6—H6B	0.9700
O3—C4	1.434 (5)	C7—C8	1.490 (10)
O4—C9	1.188 (6)	C8—H8A	0.9600
O5—C11	1.345 (6)	C8—H8B	0.9600
O5—C5	1.444 (5)	C8—H8C	0.9600
O6—C11	1.186 (6)	C9—C10	1.486 (7)
O7—C2	1.364 (7)	C10—H10A	0.9600
O7—C3	1.439 (5)	C10—H10B	0.9600
C1—C2	1.311 (7)	C10—H10C	0.9600
C1—C5	1.488 (6)	C11—C12	1.479 (7)
C2—H2	0.9300	C12—H12A	0.9600
C3—C6	1.495 (8)	C12—H12B	0.9600
C3—C4	1.515 (6)	C12—H12C	0.9600
C3—H3	0.9800		
C7—O1—C6	119.4 (5)	O1—C6—H6B	109.9
C9—O3—C4	116.8 (3)	C3—C6—H6B	109.9
C11—O5—C5	119.1 (3)	H6A—C6—H6B	108.3

C2—O7—C3	114.9 (4)	O2—C7—O1	121.7 (7)
C2—C1—C5	122.6 (5)	O2—C7—C8	126.4 (6)
C2—C1—I	119.3 (4)	O1—C7—C8	111.8 (5)
C5—C1—I	118.1 (4)	C7—C8—H8A	109.5
C1—C2—O7	124.9 (4)	C7—C8—H8B	109.5
C1—C2—H2	117.6	H8A—C8—H8B	109.5
O7—C2—H2	117.6	C7—C8—H8C	109.5
O7—C3—C6	107.6 (4)	H8A—C8—H8C	109.5
O7—C3—C4	108.7 (4)	H8B—C8—H8C	109.5
C6—C3—C4	114.3 (4)	O4—C9—O3	123.3 (4)
O7—C3—H3	108.7	O4—C9—C10	126.6 (4)
C6—C3—H3	108.7	O3—C9—C10	110.1 (4)
C4—C3—H3	108.7	C9—C10—H10A	109.5
O3—C4—C5	109.3 (3)	C9—C10—H10B	109.5
O3—C4—C3	108.7 (3)	H10A—C10—H10B	109.5
C5—C4—C3	110.8 (4)	C9—C10—H10C	109.5
O3—C4—H4	109.3	H10A—C10—H10C	109.5
C5—C4—H4	109.3	H10B—C10—H10C	109.5
C3—C4—H4	109.3	O6—C11—O5	123.1 (5)
O5—C5—C1	109.9 (4)	O6—C11—C12	126.2 (5)
O5—C5—C4	106.8 (3)	O5—C11—C12	110.7 (4)
C1—C5—C4	108.7 (4)	C11—C12—H12A	109.5
O5—C5—H5	110.5	C11—C12—H12B	109.5
C1—C5—H5	110.5	H12A—C12—H12B	109.5
C4—C5—H5	110.5	C11—C12—H12C	109.5
O1—C6—C3	109.1 (4)	H12A—C12—H12C	109.5
O1—C6—H6A	109.9	H12B—C12—H12C	109.5
C3—C6—H6A	109.9		

C5—C1—C2—O7	−3.9 (7)	C2—C1—C5—C4	−13.0 (6)
I—C1—C2—O7	176.7 (3)	I—C1—C5—C4	166.4 (3)
C3—O7—C2—C1	−13.7 (6)	O3—C4—C5—O5	−76.7 (4)
C2—O7—C3—C6	170.0 (4)	C3—C4—C5—O5	163.5 (3)
C2—O7—C3—C4	45.7 (5)	O3—C4—C5—C1	164.8 (3)
C9—O3—C4—C5	108.8 (4)	C3—C4—C5—C1	45.0 (4)
C9—O3—C4—C3	−130.1 (4)	C7—O1—C6—C3	−128.3 (5)
O7—C3—C4—O3	177.0 (3)	O7—C3—C6—O1	−68.9 (5)
C6—C3—C4—O3	56.8 (5)	C4—C3—C6—O1	51.9 (5)
O7—C3—C4—C5	−62.8 (4)	C6—O1—C7—O2	1.0 (8)
C6—C3—C4—C5	177.0 (4)	C6—O1—C7—C8	177.0 (5)
C11—O5—C5—C1	−121.9 (4)	C4—O3—C9—O4	1.9 (6)
C11—O5—C5—C4	120.4 (4)	C4—O3—C9—C10	−179.0 (4)
C2—C1—C5—O5	−129.5 (5)	C5—O5—C11—O6	5.3 (7)
I—C1—C5—O5	49.9 (4)	C5—O5—C11—C12	−175.9 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O6^{i}	0.93	2.58	3.448 (7)	156
C3—H3···O6^{ii}	0.98	2.55	3.383 (6)	143

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