



Crystal structure of (–)-(S)-4-[(2S,3S,4S,Z)-3-hydroxy-4-methylhept-5-en-2-yl]-1,3-dioxolan-2-one

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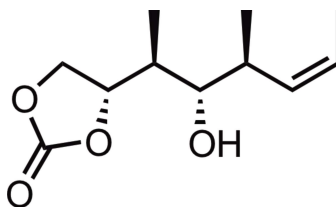
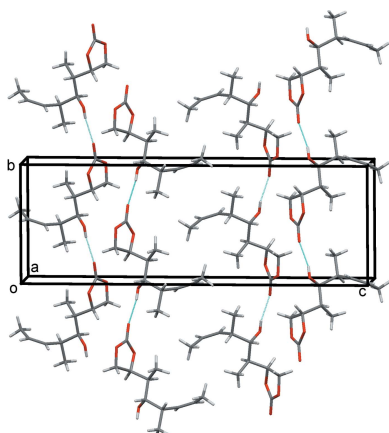
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Keywords: crystal structure; polypropionate; 1,2-carbonate; stereotetrads; O—H...O hydrogen bonding.**CCDC reference:** 1548935**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound, C₁₁H₁₈O₄, consists of an *anti,anti,anti*-stereotetrad with a 1,2-carbonate and an alkene motif. The molecule displays a common zigzag conformation. The five-membered ring has a twisted conformation on the C—C bond. In the crystal, a strong intermolecular hydrogen bond between the hydroxy group and the carboxylate moiety from an adjacent molecule forms chains propagating along the *b*-axis direction. The absolute structure of the molecule in the crystal was determined by resonant scattering [Fleck parameter = 0.05 (6)].

1. Chemical context

The title compound was obtained as part of our studies toward the synthesis of (–)-dolabriferol and (–)-dolabriferol B (Ciavatta *et al.*, 1996; Jiménez-Romero *et al.*, 2012), using an epoxide-based approach for the stereotetrad construction. Polypropionate chains are structural motifs consisting of alternating methyl and hydroxy groups within an aliphatic framework (Torres *et al.*, 2004, 2009; Tirado *et al.*, 2005, Rodríguez *et al.*, 2006). Their structure is found in various natural products, many of them possessing a wide range of biological activity, typically antibiotic, antitumor, antifungal, antiparasitic, among others (Rohr, 2000). Different methodologies for the synthesis of polypropionates have been developed, with aldol and aldol-related chemistry being the most used (Schetter & Mahrwald, 2006).



In our laboratory, we have developed an epoxide-based methodology for the construction of polypropionates, consisting of a reiterative sequence of three steps. Our approach involves a regioselective epoxide cleavage with an alkynyl aluminium reagent (Torres *et al.*, 2005) or Grignard reagent (Rodríguez *et al.*, 2006), *cis* or *trans* reduction of the alkyne (if needed), and the stereoselective epoxidation of the resulting alkenol for the elaboration of each propionate unit. In this approach, the configuration of the hydroxyl group is derived from the absolute configuration of the epoxide precursor, while the *syn/anti* relative configuration of the

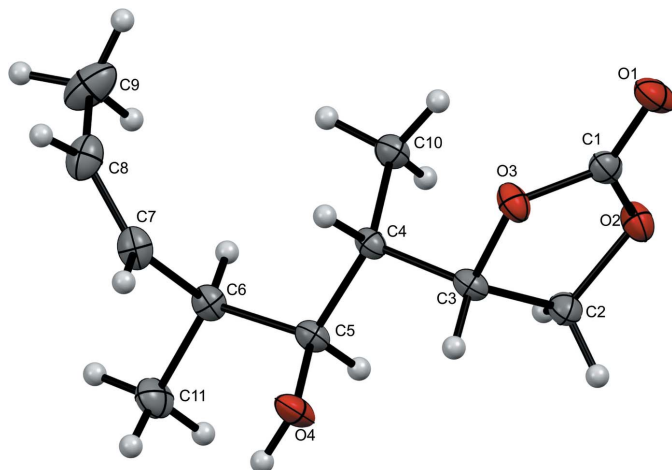


Figure 1
The molecular structure of the title compound, with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

methyl and hydroxyl groups is derived from the epoxide geometry. One of the advantages of this methodology is that it is a substrate-controlled synthesis; the only enantiomeric step in this sequence is the first epoxidation (Katsuki & Sharpless, 1980).

2. Structural commentary

The molecular structure of the title compound is illustrated in Fig. 1. The alkyl back bone has a typical zigzag conformation with two of the three methyl groups, those located on C4 and C6, *anti* to one another. Likewise, the hydroxy group located on C5 is in an *anti* relative conformation with respect to the methyl groups. The five-membered ring (O2/O3/C1–C3) has a twisted conformation on bond C2–C3 [puckering parameters $Q(2) = 0.137(2) \text{ \AA}$ and $\varphi(2) = 307.4(10)^\circ$].

3. Supramolecular features

The conformational distance between the hydroxyl group and the carbonyl moiety does not allow intramolecular hydrogen-bond formation, therefore, hydrogen bonding is observed through intermolecular interactions alone (Table 1). In the crystal, neighbouring molecules are linked by the O4–H4...O1ⁱ hydrogen bond, forming chains along [010]; see Fig. 2 and Table 1.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, updated May 2017; Groom *et al.*, 2016) revealed no related compounds with the 3-hydroxy-2-methyl-1,2-carbonate substructure. However, a search for the 2,4-dimethylhex-5-en-3-ol fragment revealed more than 120 hits. Many of these involve reactants for the synthesis of natural products, such as superotolide A (Yakelis & Roush, 2003) and erythronolides A and B (Lynch *et al.*, 1989a; 1989b).

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4–H4...O1 ⁱ	0.82	2.05	2.811 (2)	155

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

5. Synthesis and crystallization

The synthesis of the title compound, illustrated in Fig. 3, was performed through the selective protection of the 1,2-diol of (+)-(2*S*,3*S*,4*S*,5*S*,*Z*)-3,5-dimethyloct-6-ene-1,2,4-triol with a carbonate using *N,N'*-carbonyldiimidazole (CDI) in CH_2Cl_2 as solvent, favouring formation of the 1,2-carbonate over the 1,3-carbonate. This reaction afforded the optically active *anti,anti,anti*-polypropionate unit with the correct absolute configuration. To a dry round-bottom flask containing the 1,2-diol of (+)-(2*S*,3*S*,4*S*,5*S*,*Z*)-3,5-dimethyloct-6-ene-1,2,4-triol (0.04 g, 0.212 mmol) in dry CH_2Cl_2 (1.07 ml, 0.2 M) was added *N,N'*-carbonyldiimidazole (0.048 g, 0.30 mmol). The reaction mixture was stirred at 298 K for 2.5 h, then saturated aqueous NaCl was added. The resulting mixture was then extracted with ethyl acetate (three times). The combined organic layer was dried over MgSO_4 and concentrated at reduced pressure. The crude product was purified by flash chromatography (2:1, ethyl acetate:hexane) to yield 0.027 g (62%) of the pure title carbonate product as a white solid (m.p. 360–363 K). Block-like clear crystals suitable for X-ray diffraction, were obtained by slow diffusion of a 1:1 (*v:v*) ethyl

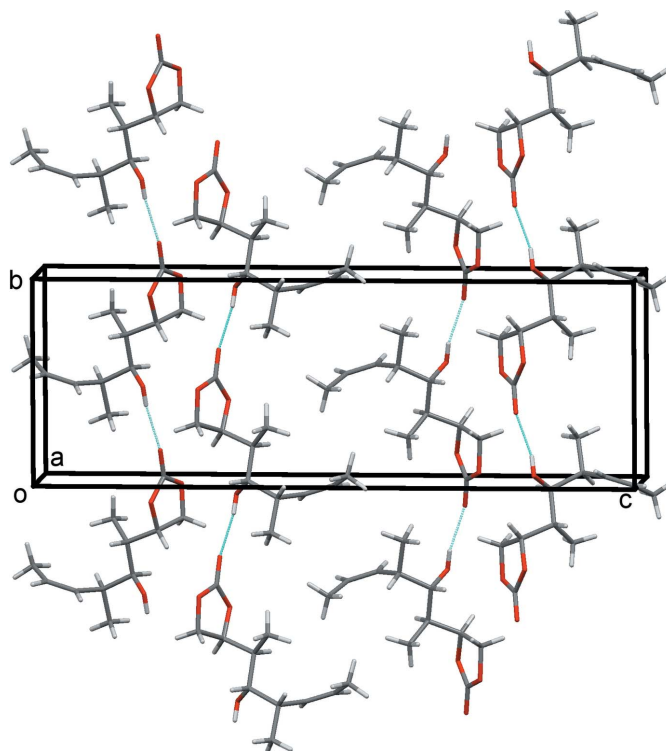


Figure 2
A view along the *a* axis of crystal packing of the title compound, with hydrogen bonds shown as dashed lines (see Table 1).

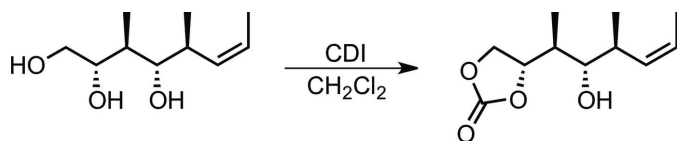


Figure 3
Reaction scheme

acetate:hexanes solution of the title compound at room temperature over a period of two days. NMR analyses were performed on a Bruker AV-500 spectrometer using Chloroform-*d* as solvent (CDCl₃). The solvent signal at 7.26 and 77.00 ppm were used as internal standards for proton and carbon respectively. ¹H NMR (500 MHz, CDCl₃) δ 5.69 (*dq*, *J* = 10.9, 6.8 Hz, 1H), 5.23 (*ddt*, *J* = 11.2, 9.8, 1.8 Hz, 1H), 4.99 (*td*, *J* = 8.2, 5.0 Hz, 1H), 4.44 (*t*, *J* = 8.6 Hz, 1H), 4.37 (*t*, *J* = 8.6 Hz, 1H), 3.26 (*dd*, *J* = 7.5, 4.2 Hz, 1H), 2.72 (*ddq*, *J* = 6.9, 6.7, 3.1 Hz, 1H), 2.29 (*ddq*, *J* = 6.6, 4.5, 2.4 Hz, 1H), 2.00 (*s*, 1H, -OH), 1.65 (*dd*, *J* = 6.8, 1.9 Hz, 3H), 1.05 (*d*, *J* = 6.9 Hz, 3H), 1.00 (*d*, *J* = 6.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 155.3, 131.3, 127.4, 77.5, 77.3, 66.9, 36.8, 35.3, 17.1, 13.3, 11.7. [α]_D²⁰ = -2.0 (*c* = 1.0, CHCl₃). Analysis calculated for C₁₁H₁₈O₄: C, 61.66, H, 8.47%. Found: C, 61.74, H, 8.44%. IR data: C=O: 1761.32 cm⁻¹, C—O: 1061.01 cm⁻¹.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were included in geometrically calculated positions and refined as riding: O—H = 0.82 Å, C—H = 0.93–0.98 Å with *U*_{iso}(H) = 1.5*U*_{eq}(O-hydroxyl and C-methyl) and 1.2*U*_{eq}(C) for other H atoms.

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₁ H ₁₈ O ₄
<i>M</i> _r	214.25
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.0968 (1), 8.8153 (1), 25.6052 (3)
<i>V</i> (Å ³)	1150.44 (3)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	0.77
Crystal size (mm)	0.23 × 0.13 × 0.06
Data collection	
Diffractometer	Rigaku OD SuperNova, single source at offset/far, HyPix3000
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2016)
<i>T</i> _{min} , <i>T</i> _{max}	0.739, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	17757, 2131, 2081
<i>R</i> _{int}	0.030
(sin θ/λ) _{max} (Å ⁻¹)	0.606
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.094, 1.26
No. of reflections	2131
No. of parameters	141
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.23, -0.17
Absolute structure	Flack <i>x</i> determined using 812 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.05 (6)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2016* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008) and *OLEX2* (Dolomanov *et al.*, 2009).

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Crystal structure of (–)-(S)-4-[(2S,3S,4S,Z)-3-hydroxy-4-methylhept-5-en-2-yl]-1,3-dioxolan-2-one

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2016); cell refinement: *CrysAlis PRO* (Rigaku OD, 2016); data reduction: *CrysAlis PRO* (Rigaku OD, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

(–)-(S)-4-[(2S,3S,4S,Z)-3-hydroxy-4-methylhept-5-en-2-yl]-1,3-dioxolan-2-one

Crystal data

$C_{11}H_{18}O_4$	$D_x = 1.237 \text{ Mg m}^{-3}$
$M_r = 214.25$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
Orthorhombic, $P2_12_12_1$	Cell parameters from 12810 reflections
$a = 5.0968 (1) \text{ \AA}$	$\theta = 3.5\text{--}68.8^\circ$
$b = 8.8153 (1) \text{ \AA}$	$\mu = 0.77 \text{ mm}^{-1}$
$c = 25.6052 (3) \text{ \AA}$	$T = 100 \text{ K}$
$V = 1150.44 (3) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.23 \times 0.13 \times 0.06 \text{ mm}$
$F(000) = 464$	

Data collection

Rigaku OD SuperNova, Single source at offset/far, HyPix3000 diffractometer	$T_{\min} = 0.739$, $T_{\max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source	17757 measured reflections
Mirror monochromator	2131 independent reflections
ω scans	2081 reflections with $I > 2\sigma(I)$
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2016)	$R_{\text{int}} = 0.030$
	$\theta_{\max} = 69.0^\circ$, $\theta_{\min} = 3.5^\circ$
	$h = -6 \rightarrow 6$
	$k = -10 \rightarrow 10$
	$l = -30 \rightarrow 31$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.4414P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.26$	$(\Delta/\sigma)_{\max} < 0.001$
2131 reflections	$\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$
141 parameters	$\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

Extinction correction: (SHELXL2016;
Sheldrick, 2015b),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0032 (6)

Absolute structure: Flack x determined using
812 quotients $[(F^+) - (F^-)] / [(F^+) + (F^-)]$ (Parsons *et al.*,
2013)
Absolute structure parameter: 0.05 (6)

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	0.9031 (4)	-0.13807 (18)	0.69895 (7)	0.0267 (4)
O2	0.6220 (3)	0.03761 (19)	0.72821 (6)	0.0234 (4)
O3	0.9752 (3)	0.10820 (18)	0.68416 (6)	0.0214 (4)
O4	0.8749 (4)	0.55481 (18)	0.66999 (6)	0.0241 (4)
H4	0.838292	0.644582	0.674153	0.036*
C1	0.8397 (5)	-0.0079 (3)	0.70337 (9)	0.0196 (5)
C2	0.6171 (5)	0.2019 (3)	0.73034 (9)	0.0208 (5)
H2A	0.653581	0.237855	0.765407	0.025*
H2B	0.447987	0.240857	0.719285	0.025*
C3	0.8339 (5)	0.2503 (2)	0.69242 (9)	0.0182 (5)
H3	0.949859	0.323486	0.709691	0.022*
C4	0.7482 (5)	0.3135 (2)	0.63967 (8)	0.0164 (5)
H4A	0.904016	0.316110	0.617275	0.020*
C5	0.6564 (5)	0.4780 (2)	0.64684 (9)	0.0179 (5)
H5	0.509516	0.479338	0.671547	0.021*
C6	0.5674 (5)	0.5528 (3)	0.59550 (8)	0.0188 (5)
H6	0.418322	0.494773	0.581917	0.023*
C7	0.7832 (5)	0.5488 (3)	0.55492 (9)	0.0224 (5)
H7	0.947944	0.581376	0.565794	0.027*
C8	0.7641 (5)	0.5043 (3)	0.50573 (9)	0.0266 (5)
H8	0.916088	0.510563	0.485756	0.032*
C9	0.5243 (6)	0.4446 (4)	0.47858 (10)	0.0394 (7)
H9A	0.492138	0.503209	0.447625	0.059*
H9B	0.375977	0.452228	0.501530	0.059*
H9C	0.551540	0.340378	0.469213	0.059*
C10	0.5456 (5)	0.2129 (3)	0.61247 (9)	0.0208 (5)
H10A	0.379257	0.222893	0.629735	0.031*
H10B	0.601834	0.109062	0.613932	0.031*
H10C	0.528349	0.243598	0.576661	0.031*
C11	0.4749 (6)	0.7165 (3)	0.60482 (10)	0.0268 (6)
H11A	0.343748	0.717439	0.631719	0.040*
H11B	0.401916	0.756573	0.573128	0.040*
H11C	0.621298	0.777709	0.615420	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0337 (10)	0.0144 (8)	0.0319 (9)	0.0021 (7)	-0.0088 (8)	-0.0007 (7)
O2	0.0230 (8)	0.0183 (8)	0.0289 (8)	-0.0017 (7)	0.0033 (7)	0.0048 (7)
O3	0.0198 (8)	0.0151 (7)	0.0292 (8)	0.0029 (7)	0.0022 (7)	0.0037 (6)
O4	0.0278 (9)	0.0128 (7)	0.0316 (9)	0.0000 (7)	-0.0107 (7)	-0.0023 (7)
C1	0.0218 (11)	0.0181 (11)	0.0189 (10)	-0.0010 (10)	-0.0052 (9)	0.0004 (9)
C2	0.0244 (12)	0.0166 (11)	0.0215 (11)	0.0024 (11)	0.0028 (10)	0.0003 (9)
C3	0.0180 (11)	0.0134 (10)	0.0231 (11)	0.0004 (9)	-0.0006 (9)	-0.0017 (8)
C4	0.0159 (10)	0.0128 (10)	0.0205 (10)	0.0007 (9)	0.0012 (9)	-0.0006 (8)
C5	0.0175 (11)	0.0146 (10)	0.0214 (11)	-0.0010 (9)	-0.0012 (9)	-0.0014 (9)
C6	0.0158 (11)	0.0181 (11)	0.0224 (11)	-0.0002 (9)	-0.0019 (9)	0.0013 (9)
C7	0.0164 (11)	0.0230 (11)	0.0277 (11)	0.0002 (10)	-0.0008 (9)	0.0054 (10)
C8	0.0217 (12)	0.0331 (13)	0.0251 (11)	0.0042 (11)	0.0026 (10)	0.0053 (10)
C9	0.0310 (15)	0.0616 (19)	0.0258 (13)	-0.0003 (15)	-0.0020 (11)	-0.0064 (13)
C10	0.0218 (12)	0.0182 (11)	0.0224 (11)	-0.0015 (10)	-0.0008 (9)	-0.0013 (9)
C11	0.0314 (14)	0.0192 (12)	0.0299 (12)	0.0065 (11)	-0.0050 (11)	0.0029 (10)

Geometric parameters (Å, °)

O1—C1	1.198 (3)	C6—H6	0.9800
O2—C1	1.340 (3)	C6—C7	1.513 (3)
O2—C2	1.450 (3)	C6—C11	1.536 (3)
O3—C1	1.329 (3)	C7—H7	0.9300
O3—C3	1.461 (3)	C7—C8	1.323 (3)
O4—H4	0.8200	C8—H8	0.9300
O4—C5	1.432 (3)	C8—C9	1.501 (4)
C2—H2A	0.9700	C9—H9A	0.9600
C2—H2B	0.9700	C9—H9B	0.9600
C2—C3	1.532 (3)	C9—H9C	0.9600
C3—H3	0.9800	C10—H10A	0.9600
C3—C4	1.525 (3)	C10—H10B	0.9600
C4—H4A	0.9800	C10—H10C	0.9600
C4—C5	1.535 (3)	C11—H11A	0.9600
C4—C10	1.529 (3)	C11—H11B	0.9600
C5—H5	0.9800	C11—H11C	0.9600
C5—C6	1.539 (3)		
C1—O2—C2	109.32 (19)	C5—C6—H6	107.9
C1—O3—C3	110.52 (17)	C7—C6—C5	111.25 (19)
C5—O4—H4	109.5	C7—C6—H6	107.9
O1—C1—O2	123.7 (2)	C7—C6—C11	110.58 (19)
O1—C1—O3	124.2 (2)	C11—C6—C5	111.11 (18)
O3—C1—O2	112.07 (19)	C11—C6—H6	107.9
O2—C2—H2A	111.0	C6—C7—H7	116.3
O2—C2—H2B	111.0	C8—C7—C6	127.4 (2)
O2—C2—C3	104.01 (18)	C8—C7—H7	116.3

H2A—C2—H2B	109.0	C7—C8—H8	116.4
C3—C2—H2A	111.0	C7—C8—C9	127.2 (2)
C3—C2—H2B	111.0	C9—C8—H8	116.4
O3—C3—C2	102.04 (17)	C8—C9—H9A	109.5
O3—C3—H3	109.4	C8—C9—H9B	109.5
O3—C3—C4	109.03 (18)	C8—C9—H9C	109.5
C2—C3—H3	109.4	H9A—C9—H9B	109.5
C4—C3—C2	117.2 (2)	H9A—C9—H9C	109.5
C4—C3—H3	109.4	H9B—C9—H9C	109.5
C3—C4—H4A	107.1	C4—C10—H10A	109.5
C3—C4—C5	109.04 (18)	C4—C10—H10B	109.5
C3—C4—C10	112.68 (18)	C4—C10—H10C	109.5
C5—C4—H4A	107.1	H10A—C10—H10B	109.5
C10—C4—H4A	107.1	H10A—C10—H10C	109.5
C10—C4—C5	113.36 (19)	H10B—C10—H10C	109.5
O4—C5—C4	105.02 (18)	C6—C11—H11A	109.5
O4—C5—H5	108.7	C6—C11—H11B	109.5
O4—C5—C6	112.33 (18)	C6—C11—H11C	109.5
C4—C5—H5	108.7	H11A—C11—H11B	109.5
C4—C5—C6	113.11 (18)	H11A—C11—H11C	109.5
C6—C5—H5	108.7	H11B—C11—H11C	109.5
O2—C2—C3—O3	-13.8 (2)	C2—C3—C4—C10	-49.2 (3)
O2—C2—C3—C4	105.2 (2)	C3—O3—C1—O1	175.2 (2)
O3—C3—C4—C5	-167.31 (18)	C3—O3—C1—O2	-4.5 (2)
O3—C3—C4—C10	65.9 (2)	C3—C4—C5—O4	56.7 (2)
O4—C5—C6—C7	61.8 (2)	C3—C4—C5—C6	179.52 (19)
O4—C5—C6—C11	-61.9 (3)	C4—C5—C6—C7	-56.9 (3)
C1—O2—C2—C3	12.2 (2)	C4—C5—C6—C11	179.4 (2)
C1—O3—C3—C2	11.6 (2)	C5—C6—C7—C8	131.2 (3)
C1—O3—C3—C4	-113.0 (2)	C6—C7—C8—C9	-1.0 (4)
C2—O2—C1—O1	174.9 (2)	C10—C4—C5—O4	-176.93 (18)
C2—O2—C1—O3	-5.3 (2)	C10—C4—C5—C6	-54.1 (3)
C2—C3—C4—C5	77.5 (2)	C11—C6—C7—C8	-104.8 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 \cdots O1 ⁱ	0.82	2.05	2.811 (2)	155

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