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Hexamethyl 13,14-dioxapentacyclo-[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene-1,4,5,6,11,12-hexacarboxylate

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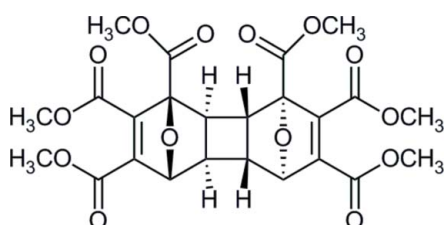
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 Key indicators: single-crystal X-ray study; $T = 147$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.035; wR factor = 0.098; data-to-parameter ratio = 15.9.

In the title compound, $\text{C}_{24}\text{H}_{24}\text{O}_{14}$, the stereochemistry at the cyclobutane ring is *cis-anti-cis* and the $-\text{COOMe}$ groups in the bicyclic rings are *syn* to each other. The molecule lies on a twofold rotation axis. In the crystal, weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds connect molecules into chains along $[001]$, forming $R_2^2(10)$ rings.

Related literature

For related structures, see: Lough *et al.* (2012*a,b*). For the synthetic background, see: Ballantine *et al.* (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_{24}\text{H}_{24}\text{O}_{14}$
 $M_r = 536.43$

 Monoclinic, $C2/c$
 $a = 25.1309$ (18) Å
 $b = 10.0840$ (7) Å
 $c = 9.5922$ (7) Å
 $\beta = 95.430$ (2)°
 $V = 2419.9$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 147$ K
 $0.15 \times 0.10 \times 0.07$ mm

Data collection

 Bruker Kappa APEX DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\min} = 0.711$, $T_{\max} = 0.746$

 11038 measured reflections
 2787 independent reflections
 2366 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.098$
 $S = 1.04$
 2787 reflections

 175 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C6}-\text{H6}\cdots\text{O1}^i$	1.00	2.38	3.2105 (13)	140

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT (Bruker, 2007); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6954).

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supporting information

Acta Cryst. (2012). E68, o2963 [https://doi.org/10.1107/S1600536812039232]

Hexamethyl 13,14-dioxapentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene-1,4,5,6,11,12-hexacarboxylate

Alan J. Lough, Kelsey Jack and William Tam

S1. Comment

We have recently investigated the Ru-catalyzed isomerization and dimerization reaction of oxanorbornadiene compounds (Ballantine *et al.*, 2009). When dissolved in 1,2-dichloroethane in the presence of Cp*Ru(COD)Cl, 1,2,3-trimethyl-7-oxabicyclo[2,2,1]hepta-2,5-diene-1,2,3-tricarboxylate will dimerize into (I) (Fig. 1). The desired product was resolved using fractional crystallization in methanol. The stereochemistry and regiochemistry of the product was determined by this single-crystal X-ray analysis. The only dimer product obtained was found to have a *cis*-anti-*cis* stereochemistry at the cyclobutane ring of the dimer, and the two COOMe groups in the bicyclic rings are *syn* to each other.

The molecular structure of (I) is shown in Fig. 2. The molecule lies on a twofold rotation axis. In the crystal, weak C—H···O hydrogen bonds connect molecules into one-dimensional chains (Fig. 3) along [001] forming $R^2_2(10)$ rings (Bernstein *et al.*, 1995).

For related structures, see the two preceding papers (Lough *et al.*, 2012*a,b*).

S2. Experimental

1,2,3-Trimethyl-7-oxabicyclo[2,2,1]hepta-2,5-diene-1,2,3-tricarboxylate (316 mg, 1.2 mmol) was weighed into an oven-dried vial, purged with nitrogen and transferred into a Dry Box. In the Dry Box, Cp*Ru(COD)Cl (10 mol%) was added to another oven dried vial and dissolved in 1,2-dichloroethane (2 ml). The Ru-catalyst was then transferred into the vial containing the 7-oxanorbornadiene. The vial was sealed with a screw cap and removed from the Dry Box. The reaction was heated at 333 K with stirring for 18 h. The crude product was purified by column chromatography (EtOAc:hexanes=2:3) followed by recrystallization in methanol to give the dimer (I). Colourless needles were grown by slow evaporation of a solution of (I) in methanol.

S3. Refinement

Hydrogen atoms were placed in calculated positions with C—H distances of 0.98 and 1.00 Å. They were included in the refinement in a riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

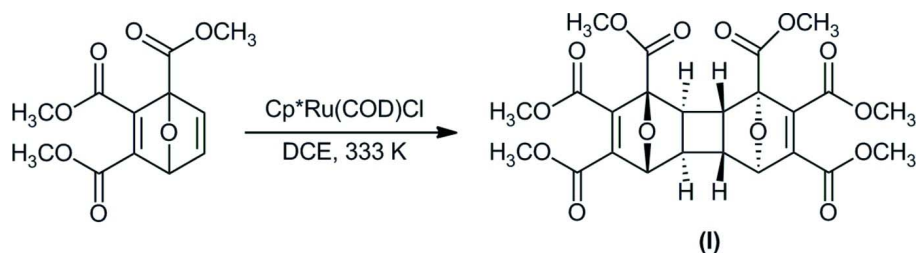


Figure 1
Reaction scheme

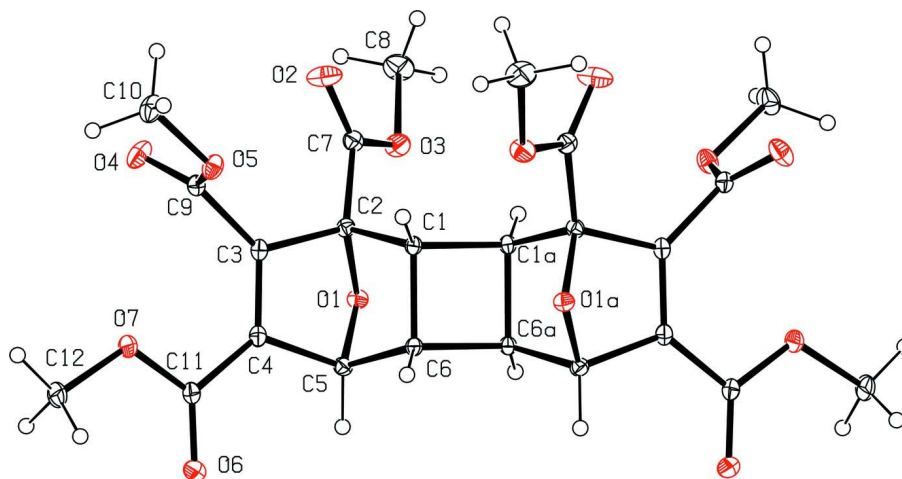


Figure 2
The molecular structure of (I) showing 30% probability ellipsoids (symmetry code (a): $-x + 2, y, -z + 1/2$).

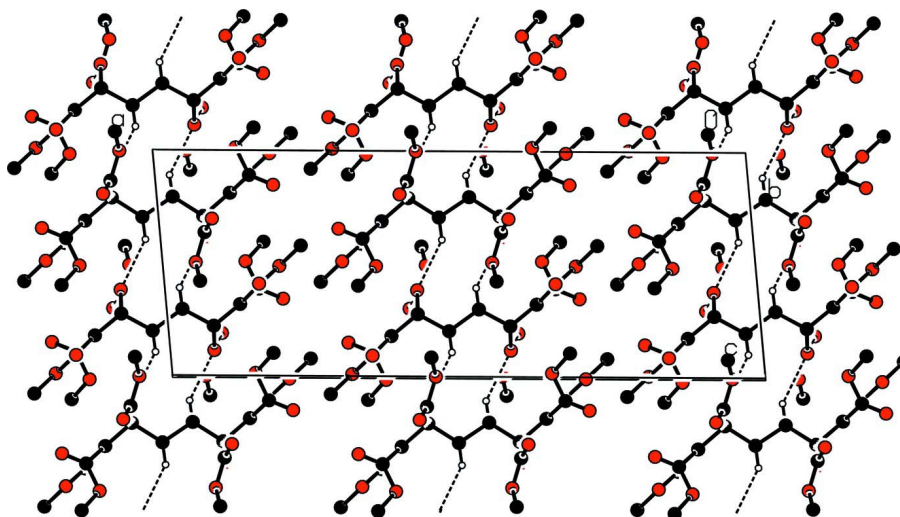


Figure 3
Part of the crystal structure showing weak hydrogen bonds as dashed lines.

Hexamethyl 13,14-dioxapentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca- 5,11-diene-1,4,5,6,11,12-hexacarboxylate

Crystal data

C₂₄H₂₄O₁₄ $M_r = 536.43$ Monoclinic, *C2/c*

Hall symbol: -C 2yc

 $a = 25.1309$ (18) Å $b = 10.0840$ (7) Å $c = 9.5922$ (7) Å $\beta = 95.430$ (2)° $V = 2419.9$ (3) Å³ $Z = 4$ $F(000) = 1120$ $D_x = 1.472$ Mg m⁻³Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 6078 reflections

 $\theta = 3.0$ – 27.5 ° $\mu = 0.12$ mm⁻¹ $T = 147$ K

Needle, colourless

 $0.15 \times 0.10 \times 0.07$ mm

Data collection

Bruker Kappa APEX DUO CCD

diffractometer

Radiation source: fine-focus sealed tube

Bruker Triumph monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2007)

 $T_{\min} = 0.711$, $T_{\max} = 0.746$

11038 measured reflections

2787 independent reflections

2366 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.028$ $\theta_{\max} = 27.5$ °, $\theta_{\min} = 1.6$ ° $h = -32 \rightarrow 32$ $k = -13 \rightarrow 12$ $l = -11 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.098$ $S = 1.04$

2787 reflections

175 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

 $w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 1.6228P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.42$ e Å⁻³ $\Delta\rho_{\min} = -0.25$ e Å⁻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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.92545 (3)	0.44122 (8)	0.38295 (8)	0.01527 (19)
O2	0.91010 (5)	0.09784 (10)	0.30367 (10)	0.0322 (3)
O3	0.94389 (4)	0.20695 (9)	0.49626 (9)	0.0237 (2)
O4	0.80179 (4)	0.21560 (10)	0.15093 (10)	0.0272 (2)

O5	0.85951 (3)	0.23192 (9)	-0.01412 (9)	0.0206 (2)
O6	0.84027 (4)	0.69996 (9)	0.08929 (10)	0.0250 (2)
O7	0.80331 (4)	0.50766 (9)	0.00853 (10)	0.0227 (2)
C1	0.97293 (4)	0.35610 (11)	0.20451 (11)	0.0133 (2)
H1	0.9723	0.3106	0.1117	0.016*
C2	0.92422 (4)	0.33021 (12)	0.28941 (11)	0.0141 (2)
C3	0.87579 (4)	0.36255 (12)	0.18620 (11)	0.0149 (2)
C4	0.87513 (5)	0.49467 (12)	0.17852 (12)	0.0157 (2)
C5	0.92285 (4)	0.54296 (12)	0.27571 (11)	0.0149 (2)
H5A	0.9202	0.6361	0.3103	0.018*
C6	0.97323 (4)	0.51140 (11)	0.20141 (11)	0.0134 (2)
H6	0.9748	0.5528	0.1071	0.016*
C7	0.92448 (5)	0.19809 (12)	0.36304 (12)	0.0171 (3)
C8	0.93932 (6)	0.08885 (15)	0.58051 (15)	0.0322 (3)
H8A	0.9590	0.1018	0.6726	0.048*
H8B	0.9543	0.0129	0.5338	0.048*
H8C	0.9016	0.0721	0.5920	0.048*
C9	0.84091 (5)	0.26211 (12)	0.10758 (12)	0.0165 (2)
C10	0.82628 (5)	0.14106 (15)	-0.10214 (14)	0.0263 (3)
H10A	0.8400	0.1345	-0.1942	0.039*
H10B	0.7895	0.1742	-0.1134	0.039*
H10C	0.8270	0.0533	-0.0582	0.039*
C11	0.83860 (4)	0.58061 (13)	0.08826 (12)	0.0170 (2)
C12	0.76407 (5)	0.58064 (14)	-0.08202 (15)	0.0266 (3)
H12A	0.7429	0.5185	-0.1433	0.040*
H12B	0.7824	0.6433	-0.1392	0.040*
H12C	0.7404	0.6294	-0.0247	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0186 (4)	0.0149 (4)	0.0123 (4)	0.0003 (3)	0.0013 (3)	-0.0014 (3)
O2	0.0547 (7)	0.0168 (5)	0.0246 (5)	-0.0047 (4)	0.0011 (4)	-0.0007 (4)
O3	0.0295 (5)	0.0222 (5)	0.0183 (4)	-0.0033 (4)	-0.0035 (4)	0.0069 (4)
O4	0.0228 (5)	0.0311 (6)	0.0287 (5)	-0.0110 (4)	0.0078 (4)	-0.0079 (4)
O5	0.0188 (4)	0.0252 (5)	0.0177 (4)	-0.0039 (3)	0.0015 (3)	-0.0053 (4)
O6	0.0227 (5)	0.0180 (5)	0.0329 (5)	0.0026 (3)	-0.0045 (4)	-0.0004 (4)
O7	0.0180 (4)	0.0207 (5)	0.0274 (5)	-0.0002 (3)	-0.0091 (4)	0.0033 (4)
C1	0.0127 (5)	0.0146 (6)	0.0120 (5)	-0.0002 (4)	-0.0012 (4)	-0.0003 (4)
C2	0.0143 (5)	0.0150 (6)	0.0127 (5)	-0.0004 (4)	-0.0001 (4)	-0.0018 (4)
C3	0.0116 (5)	0.0190 (6)	0.0142 (5)	-0.0004 (4)	0.0009 (4)	0.0002 (4)
C4	0.0121 (5)	0.0188 (6)	0.0160 (5)	0.0002 (4)	0.0002 (4)	-0.0011 (4)
C5	0.0154 (5)	0.0138 (6)	0.0153 (5)	0.0013 (4)	-0.0004 (4)	-0.0001 (4)
C6	0.0133 (5)	0.0138 (6)	0.0126 (5)	-0.0004 (4)	-0.0019 (4)	-0.0001 (4)
C7	0.0166 (6)	0.0179 (6)	0.0174 (6)	0.0007 (4)	0.0038 (4)	0.0013 (5)
C8	0.0412 (8)	0.0286 (8)	0.0263 (7)	0.0004 (6)	0.0011 (6)	0.0140 (6)
C9	0.0139 (5)	0.0180 (6)	0.0172 (5)	0.0004 (4)	-0.0007 (4)	0.0001 (5)
C10	0.0243 (7)	0.0316 (8)	0.0223 (6)	-0.0046 (5)	-0.0013 (5)	-0.0102 (6)

C11	0.0125 (5)	0.0196 (6)	0.0188 (5)	0.0009 (4)	0.0013 (4)	0.0003 (5)
C12	0.0193 (6)	0.0274 (7)	0.0306 (7)	0.0005 (5)	-0.0106 (5)	0.0074 (6)

Geometric parameters (Å, °)

O1—C2	1.4331 (14)	C3—C4	1.3343 (17)
O1—C5	1.4500 (14)	C3—C9	1.4960 (16)
O2—C7	1.1991 (16)	C4—C11	1.4808 (16)
O3—C7	1.3271 (15)	C4—C5	1.5275 (15)
O3—C8	1.4499 (16)	C5—C6	1.5435 (16)
O4—C9	1.1987 (15)	C5—H5A	1.0000
O5—C9	1.3331 (15)	C6—C6 ⁱ	1.563 (2)
O5—C10	1.4547 (15)	C6—H6	1.0000
O6—C11	1.2043 (16)	C8—H8A	0.9800
O7—C11	1.3358 (15)	C8—H8B	0.9800
O7—C12	1.4514 (14)	C8—H8C	0.9800
C1—C1 ⁱ	1.545 (2)	C10—H10A	0.9800
C1—C2	1.5553 (15)	C10—H10B	0.9800
C1—C6	1.5663 (16)	C10—H10C	0.9800
C1—H1	1.0000	C12—H12A	0.9800
C2—C7	1.5076 (16)	C12—H12B	0.9800
C2—C3	1.5295 (15)	C12—H12C	0.9800
C2—O1—C5	96.42 (8)	C5—C6—H6	115.8
C7—O3—C8	116.11 (11)	C6 ⁱ —C6—H6	115.8
C9—O5—C10	114.99 (10)	C1—C6—H6	115.8
C11—O7—C12	116.12 (10)	O2—C7—O3	125.51 (12)
C1 ⁱ —C1—C2	113.51 (11)	O2—C7—C2	122.33 (11)
C1 ⁱ —C1—C6	90.30 (5)	O3—C7—C2	112.12 (10)
C2—C1—C6	100.56 (9)	O3—C8—H8A	109.5
C1 ⁱ —C1—H1	116.2	O3—C8—H8B	109.5
C2—C1—H1	116.2	H8A—C8—H8B	109.5
C6—C1—H1	116.2	O3—C8—H8C	109.5
O1—C2—C7	113.46 (9)	H8A—C8—H8C	109.5
O1—C2—C3	101.97 (9)	H8B—C8—H8C	109.5
C7—C2—C3	117.36 (10)	O4—C9—O5	125.55 (11)
O1—C2—C1	103.01 (9)	O4—C9—C3	123.42 (11)
C7—C2—C1	115.14 (9)	O5—C9—C3	111.03 (10)
C3—C2—C1	104.05 (9)	O5—C10—H10A	109.5
C4—C3—C9	130.13 (11)	O5—C10—H10B	109.5
C4—C3—C2	104.70 (10)	H10A—C10—H10B	109.5
C9—C3—C2	125.05 (10)	O5—C10—H10C	109.5
C3—C4—C11	128.35 (11)	H10A—C10—H10C	109.5
C3—C4—C5	106.24 (10)	H10B—C10—H10C	109.5
C11—C4—C5	125.29 (11)	O6—C11—O7	125.15 (11)
O1—C5—C4	100.80 (9)	O6—C11—C4	124.12 (11)
O1—C5—C6	101.41 (9)	O7—C11—C4	110.72 (11)
C4—C5—C6	106.46 (9)	O7—C12—H12A	109.5

O1—C5—H5A	115.4	O7—C12—H12B	109.5
C4—C5—H5A	115.4	H12A—C12—H12B	109.5
C6—C5—H5A	115.4	O7—C12—H12C	109.5
C5—C6—C6 ⁱ	114.97 (11)	H12A—C12—H12C	109.5
C5—C6—C1	101.06 (9)	H12B—C12—H12C	109.5
C6 ⁱ —C6—C1	89.66 (5)		
C5—O1—C2—C7	-178.09 (9)	O1—C5—C6—C1	37.92 (10)
C5—O1—C2—C3	-50.92 (9)	C4—C5—C6—C1	-67.09 (10)
C5—O1—C2—C1	56.76 (9)	C1 ⁱ —C1—C6—C5	-117.62 (10)
C1 ⁱ —C1—C2—O1	62.75 (8)	C2—C1—C6—C5	-3.62 (10)
C6—C1—C2—O1	-32.23 (10)	C1 ⁱ —C1—C6—C6 ⁱ	-2.22 (12)
C1 ⁱ —C1—C2—C7	-61.30 (10)	C2—C1—C6—C6 ⁱ	111.78 (10)
C6—C1—C2—C7	-156.28 (9)	C8—O3—C7—O2	-10.06 (19)
C1 ⁱ —C1—C2—C3	168.84 (6)	C8—O3—C7—C2	172.22 (11)
C6—C1—C2—C3	73.86 (10)	O1—C2—C7—O2	160.49 (12)
O1—C2—C3—C4	32.45 (11)	C3—C2—C7—O2	41.86 (17)
C7—C2—C3—C4	157.06 (10)	C1—C2—C7—O2	-81.16 (15)
C1—C2—C3—C4	-74.43 (11)	O1—C2—C7—O3	-21.71 (14)
O1—C2—C3—C9	-151.28 (10)	C3—C2—C7—O3	-140.34 (10)
C7—C2—C3—C9	-26.67 (16)	C1—C2—C7—O3	96.65 (12)
C1—C2—C3—C9	101.85 (12)	C10—O5—C9—O4	4.24 (18)
C9—C3—C4—C11	0.3 (2)	C10—O5—C9—C3	-176.27 (10)
C2—C3—C4—C11	176.35 (11)	C4—C3—C9—O4	-94.36 (17)
C9—C3—C4—C5	-175.80 (11)	C2—C3—C9—O4	90.36 (16)
C2—C3—C4—C5	0.21 (12)	C4—C3—C9—O5	86.14 (16)
C2—O1—C5—C4	50.47 (9)	C2—C3—C9—O5	-89.15 (13)
C2—O1—C5—C6	-58.97 (9)	C12—O7—C11—O6	-0.57 (18)
C3—C4—C5—O1	-32.25 (12)	C12—O7—C11—C4	178.21 (10)
C11—C4—C5—O1	151.47 (11)	C3—C4—C11—O6	178.87 (13)
C3—C4—C5—C6	73.20 (12)	C5—C4—C11—O6	-5.68 (19)
C11—C4—C5—C6	-103.08 (12)	C3—C4—C11—O7	0.08 (18)
O1—C5—C6—C6 ⁱ	-56.92 (8)	C5—C4—C11—O7	175.53 (11)
C4—C5—C6—C6 ⁱ	-161.93 (7)		

Symmetry code: (i) $-x+2, y, -z+1/2$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots O1 ⁱⁱ	1.00	2.38	3.2105 (13)	140

Symmetry code: (ii) $x, -y+1, z-1/2$.