



(2*R*,3*R*)-1,4-Dioxaspiro[4.4]nonane-2,3-dicarboxylic and (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylic acids

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Received 11 June 2018

Accepted 4 July 2018

Edited by E. V. Boldyreva, Russian Academy of Sciences, Russia

Keywords: tartaric acid; 1,3-dioxolane; ketals; NMR; hydrogen bonding; crystal structure.

CCDC references: 1853435; 1853434

Supporting information: this article has supporting information at journals.iucr.org/e

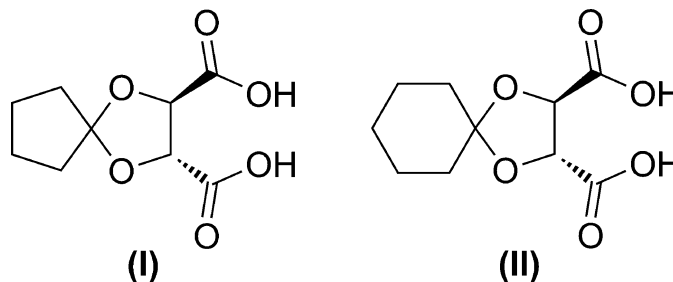
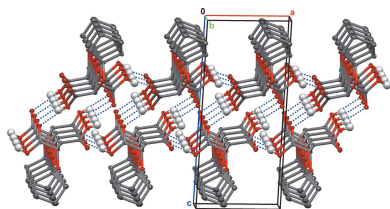
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The title compounds, C₉H₁₂O₆ and C₁₀H₁₄O₆, were formed by careful hydrolysis of the corresponding diethyl esters. Their single crystals were grown from an ethyl acetate/hexane mixture. Crystals of both compounds have monoclinic (*P*2₁) symmetry with a single molecule in the asymmetric unit. Both crystal structures are very similar and display four –CO–OH···O=C(OH)– hydrogen bonds, forming a two-dimensional double-layered framework.

1. Chemical context

Transition-metal catalysis has developed as a powerful tool to create a variety of carbon–carbon and carbon–heteroatom bonds. Enantioselective versions of these reactions are especially interesting in the light of the possible pharmaceutical applications. The general route to such processes supposes the use of transition metal complexes with chiral ligands (Yang *et al.*, 2017). Therefore, easily accessible ligands of this type are of great importance for homogenous catalysis. Chiral phosphine ligands and amino acids are the most popular in this respect (Crassous, 2009). Examples of chiral carboxylate ligands are also known (Saget *et al.*, 2012), which can be useful in the synthesis of chiral coordination compounds and materials derived from them (Lam *et al.*, 2011). Various tartaric acid derivatives, which are also used in organic synthesis as chiral auxiliary agents to create chiral building blocks (Kassai *et al.*, 2000; Seebach *et al.*, 2001), might be particularly useful in solving the stated problem. Herein we report the synthesis and structures of two tartaric acid derivatives that may potentially be used as synthetic precursors of chiral transition-metal catalysts.



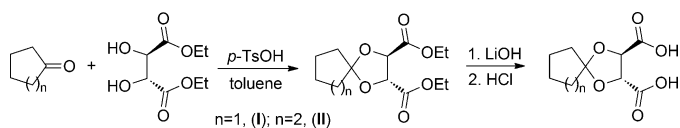


Figure 1
The synthesis of the title compounds (I) and (II).

Condensation of cyclopentanone or cyclohexanone with (2*R*,3*R*) diethyl tartrate led to the formation of the corresponding ketals, careful hydrolysis of which allowed us to prepare the title acids (Fig. 1).

2. Structural commentary

The structures of tartaric acid derivatives (I) and (II) were found as anticipated (Figs. 2 and 3, respectively), having a single molecule in the asymmetric unit. The 1,3-dioxolane, cyclopentane [in (I)] and cyclohexane [in (II)] fragments have the usual conformations. The C—C, C—O and C=O bond lengths are within regular distances (Tables 1 and 2). A detailed structural and conformational analysis for the crystal structures of some related acetals $R'C_3H_5O_2(COR)_2$ ($R = NH_2$, OAlkyl, OH; substituent R' is at the 2-position of the 1,3-dioxolane ring) was given by Eissmann *et al.* (2012). Although the absolute structures of (I) and (II) cannot be unambiguously determined using the Flack parameter (Flack, 1983; Parsons, *et al.*, 2013) with the *SHELXL* program (Sheldrick, 2015), the chirality at carbon atoms C2, C3 (2*R*,3*R*) is initially known from their synthetic precursor (diethyl L-tartrate), and has been also confirmed for (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate, and for (II) by optical rotation measurements (see the experimental section). The molecules of (I) and (II) have very similar positions in the unit cells, making the structures nearly isomorphous, but the *c* axis in (II) is elongated by almost 1.5 Å compared with that in (I)

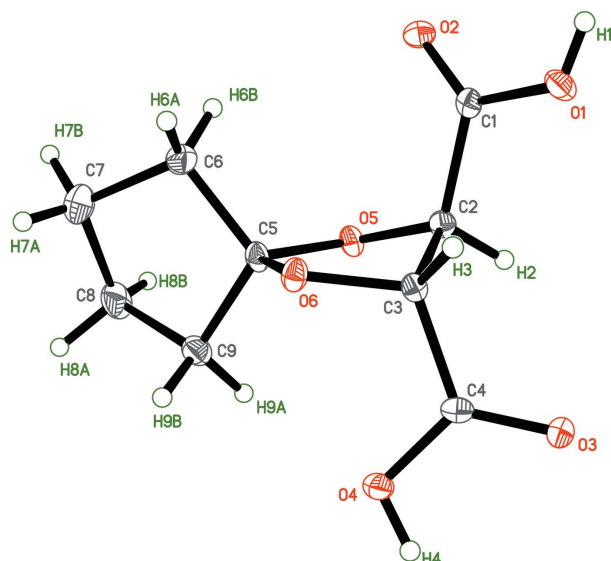


Figure 2
The structure of (2*R*,3*R*)-1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylic acid, (I). Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected bond lengths (Å) for (I).

O1—C1	1.325 (3)	C1—C2	1.521 (4)
O2—C1	1.208 (3)	C2—C3	1.541 (4)
O3—C4	1.222 (3)	C3—C4	1.519 (4)
O4—C4	1.314 (3)	C5—C9	1.529 (4)
O5—C2	1.409 (3)	C5—C6	1.539 (4)
O5—C5	1.443 (3)	C6—C7	1.533 (4)
O6—C3	1.409 (3)	C7—C8	1.529 (4)
O6—C5	1.439 (3)	C8—C9	1.522 (4)

Table 2
Selected bond lengths (Å) for (II).

O1—C1	1.322 (2)	C2—C3	1.541 (2)
O2—C1	1.208 (2)	C3—C4	1.532 (2)
O3—C4	1.2229 (19)	C5—C6	1.519 (2)
O4—C4	1.3135 (18)	C5—C10	1.525 (2)
O5—C2	1.4107 (18)	C6—C7	1.533 (2)
O5—C5	1.4398 (18)	C7—C8	1.526 (3)
O6—C3	1.4135 (17)	C8—C9	1.532 (2)
O6—C5	1.441 (2)	C9—C10	1.538 (2)
C1—C2	1.529 (2)		

(see Table 5 below) because of the presence of an additional —(CH₂)— unit in the cycloalkane fragment in (II) (see Fig. 4 for the alignment of the cycloalkane fragments in the unit cell).

3. Supramolecular features

The molecules of both structures are packed in two-dimensional frameworks by four —CO—OH...O=C(OH)— hydrogen bonds between neighboring carboxyl groups (Tables 3 and 4). The packing diagrams for (I) (Figs. 4, 5*a*) are nearly identical to those of (II) (not shown). The molecules form double layers parallel to the *ab* plane and sterically shielded from other layers by the cycloalkane fragments (Fig. 4). Hydrogen-bonded chains within the same layer are formed *via*

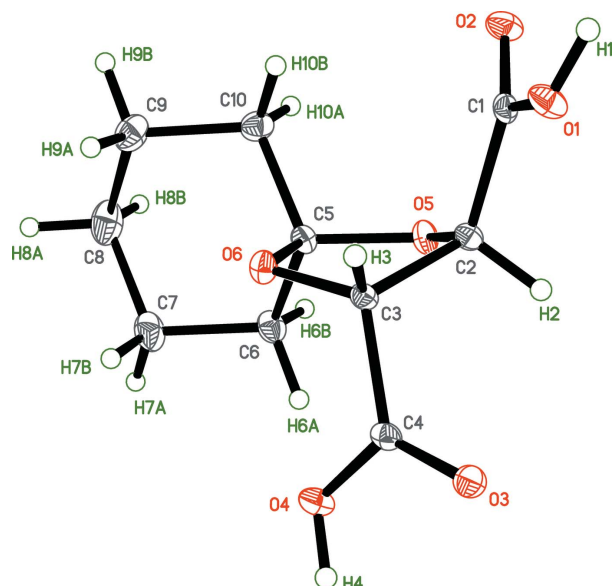
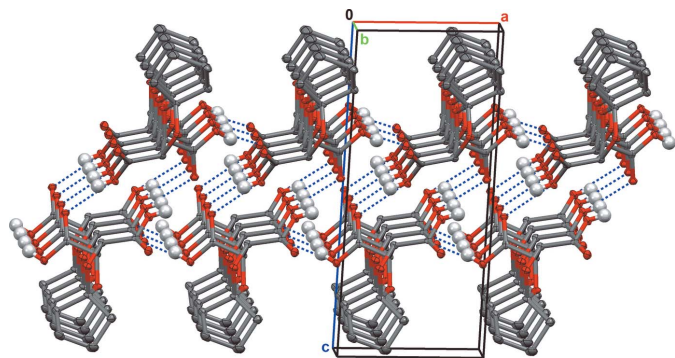


Figure 3
The structure of (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylic acid, (II). Displacement ellipsoids are drawn at the 50% probability level.


Figure 4

The packing of (I) parallel to (010). Two interacting molecular layers are shown. Only the H atoms involved in hydrogen bonding (blue dashed lines) have been included. Displacement ellipsoids are drawn at the 50% probability level.

two interactions involving the O1–H1 and O3 atoms of each molecule. These chains are interconnected into a two-dimensional hydrogen-bonded double-layered framework parallel to (001) by the O4–H4 and O2 atoms. The complicated structure of the two-dimensional double-layered framework is shown in Fig. 5*a*, but it can best be visualized in the simplified scheme in Fig. 5*b*. It might be noted that some weak C–H···O intermolecular interactions are also present (see the supporting information).

4. Database survey

Twenty crystal structures of tartaric acid ester derivatives possessing the 1,3-dioxolane cycle, $R'R''C_3H_2O_2(COOR)_2$, are

Table 3
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1···O3 ⁱ	0.78 (4)	1.87 (4)	2.620 (3)	159 (4)
O4–H4···O2 ⁱⁱ	0.84 (4)	1.92 (4)	2.723 (3)	159 (3)

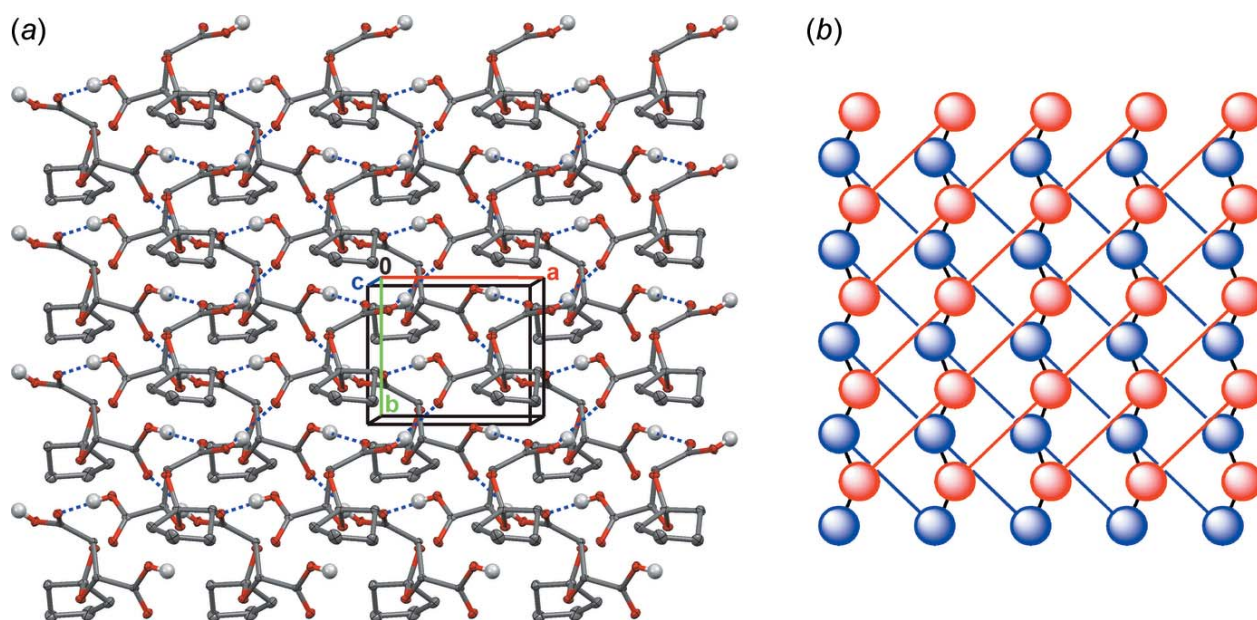
Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 1$; (ii) $x + 1, y - 1, z$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1···O3 ⁱ	0.84 (3)	1.80 (3)	2.6230 (16)	164 (3)
O4–H4···O2 ⁱⁱ	0.85 (3)	1.88 (3)	2.7116 (16)	164 (2)

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

known to date [Cambridge Structural Database (CSD) Version 5.39, latest update Feb 2018; Groom *et al.*, 2016]. There are 10 crystal structures of esters bearing one substituent R' ($R'' = H$) at the 2-position of the 1,3-dioxolane fragment (acetals): CSD refcodes DAZJET (Lee *et al.*, 1999), LACREM, LACRUC (Roush *et al.*, 1992), LEPHAR, LEPHEV (Eissmann *et al.*, 2012), OLEGAN (Karisalmi *et al.*, 2003), WEGXOW (Belokon' *et al.*, 2005), XEYSEA (Jiang *et al.*, 2007), YAXHIQ (Lv *et al.*, 2012) and YIVGUF (Barrett *et al.*, 1995). The crystal structures of esters with two substituents R' and R'' (ketals) are represented by GAGHAY, GUHGUL (Pelphrey *et al.*, 2004), KEMRID (Wink & Dewan, 1990), MIWDIF (Ates & Curran, 2001), NAFWEW (Mikołajczyk *et al.*, 1996), QOTVUQ (Maezaki *et al.*, 2000), VICXOU/VICXOU10 (Giordano *et al.*, 1990; Ianelli *et al.*, 1992), VIHVAL (Linker *et al.*, 2013) and VUCHAC, VUCHEG


Figure 5

(*a*) The packing of (I) parallel to (001). Two interacting molecular layers are shown. Only the H atoms involved in hydrogen bonding (blue dashed lines) have been included. Displacement ellipsoids are drawn at the 50% probability level. (*b*) The simplified structure of the two-dimensional double-layered framework. Molecules (circles) and hydrogen bonds (solid lines) within the same layers are shown in the same colour (blue or red). Hydrogen bonds between two layers are shown as solid black lines.

(Ianneli *et al.*, 1992). The crystal structures of 14 related amide derivatives $R'R''C_3H_2O_2(CONR_2)_2$ are also known (see the CSD and also Eissmann *et al.*, 2012 and references therein). However, established crystal structures of related acids, $R'R''C_3H_2O_2(COOH)_2$, are limited to only one structure with $R' = -C_6H_4-4-COOH$ and $R'' = H$ (LEPHIZ; Eissmann *et al.*, 2012). This fact can be explained by some subtle problems with the individual isolation of pure acid samples because of the facile hydrolysis of the 1,3-dioxolane fragment during their preparation. Therefore, the synthesis and especially the crystallization of $R'R''C_3H_2O_2(COOH)_2$ acids is a challenging task.

5. Synthesis and crystallization

5.1. General experimental remarks

(+)-Diethyl L-tartrate [Sigma–Aldrich, >99%, found $[\alpha]_D^{297K} = +12^\circ$ (acetone, 20.5 mg ml⁻¹); lit. data $[\alpha]_D^{293K} = +10^\circ$ (ethanol, 53 mg ml⁻¹), see Černý, 1977] was used as purchased. ¹H and ¹³C{¹H} NMR spectra were recorded with Bruker AM-300 and Bruker DRX-500 spectrometers in CDCl₃ (Cambridge Isotope Laboratories, Inc., 99.8% ²H) and in acetone-*d*₆ (Sigma–Aldrich, 99.9 atom % ²H).

5.2. Synthesis of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate

A 1000 ml round-bottomed flask equipped with a reflux condenser and a Dean–Stark trap was charged with diethyl L-tartrate (85.56 ml, 500 mmol), cyclohexanone (51.82 ml, 500 mmol), toluene (600 ml) and *p*-toluenesulfonic acid monohydrate (2.80 g, 147 mmol). The mixture was refluxed for 62 h. The resulting dark-brown mixture was washed with a saturated aqueous solution of NaHCO₃ (2 × 100 ml) and with water (2 × 100 ml). The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed on a rotary evaporator. The obtained dark-brown oil was distilled under reduced pressure (388–391 K, 250 Pa). The yield of the colourless liquid was 84% (120.25 g, 420 mmol). $\eta_D^{293K} = 1.4625$, $[\alpha]_D^{297K} = -28.7$ (acetone, 20.5 mg ml⁻¹) [Lit. data $\eta_D^{293K} = 1.4605$, $[\alpha]_D^{293K} = -35.57$ (Tsuzuki, 1937)]. ¹H NMR (CDCl₃) δ : 1.12 (*t*, 6H, CH₃–CH₂–O), 1.30–1.45 (*m*, 10H, –C₅H₁₀–), 4.10 (*quartet*, 4H, CH₃–CH₂–O), 4.55 (*s*, 2H, CH).

5.3. Synthesis of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylate

The synthesis of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylate was carried out analogously to that of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate, starting from 85.47 ml (500 mmol) of diethyl L-tartrate, 44.23 ml (500 mmol) of cyclopentanone, 600 ml of toluene and 2.80 g (14.7 mmol) of *p*-toluenesulfonic acid monohydrate. The yield of the colourless liquid after vacuum distillation (383–385 K, 265 Pa) was 78% (106.08 g, 390 mmol). ¹H NMR (CDCl₃) δ : 1.17 (*t*, 6H, CH₃–CH₂–O), 1.51–1.63 (*m*, 4H, –C₄H₈–), 1.64–1.77 (*m*, 2H, –C₄H₈–), 1.77–1.91 (*m*, 2H, –C₄H₈–), 4.12 (*quartet*, 4H, CH₃–CH₂–O), 4.57 (*s*, 2H, CH).

5.4. Synthesis and crystallization of (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylic acid, (II)

A 100 ml round-bottomed flask was charged with 2.130 g (7.52 mmol) of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate, 22.5 ml of THF, 22.5 ml of methanol and 22.5 ml of 2 *M* aqueous solution of LiOH. The reaction mixture was stirred for 6 h. It was then washed with diethyl ether (3 × 20 ml). The aqueous solution was acidified with a 2 *M* solution of HCl to pH \approx 1 at 273 K. The formed acid was extracted with ethyl acetate (3 × 20 ml). The organic layer was dried over Na₂SO₄. The solution was removed on a rotary evaporator. The yield of the resulting white powder was 72% (1.250 g, 5.43 mmol). M.p. = 413 K, $[\alpha]_D^{297K} = -27.3$ (acetone, 20.5 mg ml⁻¹) [Lit. data $[\alpha]_D^{20} = -24.0$, ethanol, 304 mg ml⁻¹ (Innis & Lamaty, 1977)]. ¹H NMR (acetone-*d*₆) δ : 1.36–1.44 (*m*, 2H, –C₅H₁₀–), 1.53–1.74 (*m*, 8H, –C₅H₁₀–), 4.82 (*s*, 2H, CH), 7.0 (*br.s*, 2H, –COOH). ¹³C{¹H} NMR (acetone-*d*₆) δ : 24.6, 25.6, 36.8, 77.7, 114.7, 171.7. Crystals of (II) were grown from an ethyl acetate/hexane (1:1 *v/v*) mixture.

5.5. Synthesis and crystallization of (2*R*,3*R*)-1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylic acid, (I)

The synthesis of (I) was carried out analogously to that of (II), starting from 2.723 g (10 mmol) of (2*R*,3*R*)-diethyl 1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylate, 22.5 ml of THF, 22.5 ml of methanol and 22.5 ml of 2 *M* aqueous solution of LiOH. The yield of the resulting white powder was 50% (1.081 g, 5 mmol). ¹H NMR (acetone-*d*₆) δ : 1.59–1.72 (*m*, 4H, –C₄H₈–), 1.74–1.87 (*m*, 2H, –C₄H₈–), 1.90–2.02 (*m*, 2H, –C₄H₈–), 4.78 (*s*, 2H, CH), 7.5 (*br.s*, 2H, –COOH). ¹³C{¹H} NMR (acetone-*d*₆) δ : 24.0, 37.4, 77.9, 123.6, 171.4. Crystals of (I) were grown from an ethyl acetate/hexane (1:1 *v/v*) mixture.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The positions of all non-H and the hydroxy H atoms were found from the electron difference density maps. These atoms were refined with individual anisotropic (non-H) or isotropic (hydroxy H) displacement parameters. The positions of the other H atoms were also found from the difference map but they were positioned geometrically (C–H distance = 0.99 Å for methylene, 1.00 Å for tertiary hydrogen atoms) and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Reflection (001) in (II) was affected by the beam stop, and was therefore omitted from the refinement.

Acknowledgements

Equipment from the collective exploitation center ‘New petrochemical processes, polymer composites and adhesives’ of TIPS RAS was used.

Funding information

Funding for this research was provided by: the TIPS RAS State Plan.

Table 5
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₉ H ₁₂ O ₆	C ₁₀ H ₁₄ O ₆
<i>M_r</i>	216.19	230.21
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁	Monoclinic, <i>P</i> ₂ ₁
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.2930 (8), 5.3712 (7), 14.0916 (17)	6.4272 (8), 5.2976 (6), 15.5678 (19)
β (°)	92.885 (2)	94.469 (2)
<i>V</i> (Å ³)	475.71 (10)	528.45 (11)
<i>Z</i>	2	2
Radiation type	Mo Kα	Mo Kα
μ (mm ⁻¹)	0.13	0.12
Crystal size (mm)	0.21 × 0.07 × 0.03	0.39 × 0.15 × 0.05
Data collection		
Diffractometer	Bruker SMART APEXII	Bruker SMART APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.827, 0.996	0.917, 0.995
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4142, 2455, 1914	4329, 2612, 2503
<i>R_{int}</i>	0.030	0.015
(sin θ/λ) _{max} (Å ⁻¹)	0.682	0.682
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.043, 0.083, 1.06	0.028, 0.072, 1.05
No. of reflections	2455	2612
No. of parameters	144	153
No. of restraints	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.29, -0.24	0.30, -0.20

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2017* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

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supporting information

Acta Cryst. (2018). E74, 1058-1062 [https://doi.org/10.1107/S2056989018009593]

(2*R*,3*R*)-1,4-Dioxaspiro[4.4]nonane-2,3-dicarboxylic and (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylic acids

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Computing details

For both structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2017* (Sheldrick, 2015) and *pubCIF* (Westrip, 2010).

(2*R*,3*R*)-1,4-Dioxaspiro[4.4]nonane-2,3-dicarboxylic acid (I)

Crystal data

C₉H₁₂O₆

M_r = 216.19

Monoclinic, *P*2₁

a = 6.2930 (8) Å

b = 5.3712 (7) Å

c = 14.0916 (17) Å

β = 92.885 (2)°

V = 475.71 (10) Å³

Z = 2

F(000) = 228

D_x = 1.509 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 621 reflections

θ = 3–29°

μ = 0.13 mm⁻¹

T = 100 K

Needle, colourless

0.21 × 0.07 × 0.03 mm

Data collection

Bruker SMART APEXII
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

T_{min} = 0.827, *T_{max}* = 0.996

4142 measured reflections

2455 independent reflections

1914 reflections with *I* > 2σ(*I*)

R_{int} = 0.030

θ_{max} = 29.0°, θ_{min} = 2.9°

h = -8→8

k = -7→7

l = -14→19

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.043

wR(*F*²) = 0.083

S = 1.06

2455 reflections

144 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

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.

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.3838 (4)	0.5521 (4)	0.45124 (15)	0.0153 (5)
H1	0.271 (6)	0.587 (8)	0.468 (3)	0.039 (13)*
O2	0.3808 (3)	0.8867 (4)	0.35486 (14)	0.0156 (5)
O3	0.9421 (3)	0.1722 (4)	0.44956 (14)	0.0133 (5)
O4	1.0688 (3)	0.2205 (4)	0.30548 (14)	0.0141 (5)
H4	1.173 (6)	0.144 (7)	0.332 (2)	0.026 (10)*
O5	0.7890 (3)	0.7805 (3)	0.30380 (14)	0.0123 (5)
O6	0.6993 (3)	0.4106 (4)	0.23156 (13)	0.0127 (4)
C1	0.4679 (4)	0.7060 (5)	0.38994 (19)	0.0108 (6)
C2	0.6954 (4)	0.6301 (5)	0.3722 (2)	0.0113 (6)
H2	0.782988	0.639980	0.433289	0.014*
C3	0.7155 (4)	0.3667 (5)	0.33022 (19)	0.0103 (6)
H3	0.591522	0.263933	0.348493	0.012*
C4	0.9202 (4)	0.2424 (5)	0.3672 (2)	0.0105 (6)
C5	0.7661 (4)	0.6609 (5)	0.2121 (2)	0.0124 (6)
C6	0.6025 (5)	0.7952 (6)	0.1454 (2)	0.0174 (7)
H6A	0.481549	0.683619	0.127887	0.021*
H6B	0.547171	0.945453	0.176471	0.021*
C7	0.7213 (5)	0.8670 (7)	0.0571 (2)	0.0276 (8)
H7A	0.704227	0.737514	0.007304	0.033*
H7B	0.669165	1.027909	0.030732	0.033*
C8	0.9535 (5)	0.8873 (7)	0.0939 (2)	0.0220 (7)
H8A	1.051505	0.869535	0.041494	0.026*
H8B	0.981059	1.048463	0.126290	0.026*
C9	0.9776 (4)	0.6711 (6)	0.1634 (2)	0.0161 (6)
H9A	1.097196	0.700938	0.210352	0.019*
H9B	1.003536	0.513540	0.129416	0.019*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0145 (11)	0.0154 (11)	0.0167 (13)	0.0014 (9)	0.0066 (9)	0.0018 (10)

O2	0.0148 (10)	0.0150 (10)	0.0172 (12)	0.0050 (9)	0.0011 (8)	0.0010 (10)
O3	0.0147 (10)	0.0140 (10)	0.0112 (11)	0.0015 (8)	0.0007 (8)	0.0017 (9)
O4	0.0120 (10)	0.0154 (11)	0.0153 (11)	0.0031 (8)	0.0034 (8)	0.0025 (9)
O5	0.0164 (10)	0.0109 (10)	0.0100 (11)	-0.0014 (8)	0.0030 (8)	-0.0012 (8)
O6	0.0178 (10)	0.0102 (9)	0.0099 (11)	-0.0003 (8)	-0.0003 (8)	-0.0005 (9)
C1	0.0146 (13)	0.0093 (12)	0.0085 (14)	-0.0004 (11)	-0.0002 (11)	-0.0040 (12)
C2	0.0136 (14)	0.0087 (13)	0.0117 (16)	0.0012 (10)	0.0015 (11)	-0.0005 (11)
C3	0.0127 (13)	0.0083 (12)	0.0103 (15)	-0.0005 (10)	0.0021 (11)	0.0001 (12)
C4	0.0100 (13)	0.0063 (13)	0.0151 (16)	-0.0005 (10)	0.0001 (11)	-0.0031 (12)
C5	0.0171 (14)	0.0110 (13)	0.0091 (15)	0.0011 (11)	0.0019 (11)	-0.0020 (12)
C6	0.0183 (15)	0.0182 (14)	0.0155 (17)	0.0050 (12)	-0.0003 (13)	-0.0006 (13)
C7	0.0310 (18)	0.035 (2)	0.0167 (18)	0.0068 (16)	0.0021 (14)	0.0092 (16)
C8	0.0258 (16)	0.0225 (16)	0.0185 (18)	0.0003 (14)	0.0089 (13)	0.0071 (15)
C9	0.0164 (14)	0.0163 (15)	0.0160 (17)	0.0014 (12)	0.0047 (12)	0.0012 (14)

Geometric parameters (Å, °)

O1—C1	1.325 (3)	C3—H3	1.0000
O1—H1	0.78 (4)	C5—C9	1.529 (4)
O2—C1	1.208 (3)	C5—C6	1.539 (4)
O3—C4	1.222 (3)	C6—C7	1.533 (4)
O4—C4	1.314 (3)	C6—H6A	0.9900
O4—H4	0.84 (4)	C6—H6B	0.9900
O5—C2	1.409 (3)	C7—C8	1.529 (4)
O5—C5	1.443 (3)	C7—H7A	0.9900
O6—C3	1.409 (3)	C7—H7B	0.9900
O6—C5	1.439 (3)	C8—C9	1.522 (4)
C1—C2	1.521 (4)	C8—H8A	0.9900
C2—C3	1.541 (4)	C8—H8B	0.9900
C2—H2	1.0000	C9—H9A	0.9900
C3—C4	1.519 (4)	C9—H9B	0.9900
C1—O1—H1	117 (3)	O5—C5—C6	111.9 (2)
C4—O4—H4	108 (2)	C9—C5—C6	106.2 (2)
C2—O5—C5	109.3 (2)	C7—C6—C5	106.0 (2)
C3—O6—C5	109.7 (2)	C7—C6—H6A	110.5
O2—C1—O1	125.4 (2)	C5—C6—H6A	110.5
O2—C1—C2	124.0 (2)	C7—C6—H6B	110.5
O1—C1—C2	110.5 (2)	C5—C6—H6B	110.5
O5—C2—C1	112.8 (2)	H6A—C6—H6B	108.7
O5—C2—C3	102.6 (2)	C8—C7—C6	103.9 (3)
C1—C2—C3	113.9 (2)	C8—C7—H7A	111.0
O5—C2—H2	109.1	C6—C7—H7A	111.0
C1—C2—H2	109.1	C8—C7—H7B	111.0
C3—C2—H2	109.1	C6—C7—H7B	111.0
O6—C3—C4	115.5 (2)	H7A—C7—H7B	109.0
O6—C3—C2	102.8 (2)	C9—C8—C7	103.1 (3)
C4—C3—C2	110.9 (2)	C9—C8—H8A	111.1

O6—C3—H3	109.1	C7—C8—H8A	111.1
C4—C3—H3	109.1	C9—C8—H8B	111.1
C2—C3—H3	109.1	C7—C8—H8B	111.1
O3—C4—O4	123.4 (2)	H8A—C8—H8B	109.1
O3—C4—C3	121.0 (2)	C8—C9—C5	104.8 (2)
O4—C4—C3	115.6 (2)	C8—C9—H9A	110.8
O6—C5—O5	105.2 (2)	C5—C9—H9A	110.8
O6—C5—C9	112.9 (2)	C8—C9—H9B	110.8
O5—C5—C9	109.6 (2)	C5—C9—H9B	110.8
O6—C5—C6	111.2 (2)	H9A—C9—H9B	108.9
C5—O5—C2—C1	-95.7 (2)	C3—O6—C5—O5	-9.5 (3)
C5—O5—C2—C3	27.4 (3)	C3—O6—C5—C9	110.0 (2)
O2—C1—C2—O5	-5.2 (4)	C3—O6—C5—C6	-130.8 (2)
O1—C1—C2—O5	177.0 (2)	C2—O5—C5—O6	-12.6 (3)
O2—C1—C2—C3	-121.7 (3)	C2—O5—C5—C9	-134.3 (2)
O1—C1—C2—C3	60.5 (3)	C2—O5—C5—C6	108.2 (2)
C5—O6—C3—C4	-95.4 (3)	O6—C5—C6—C7	-120.1 (3)
C5—O6—C3—C2	25.5 (3)	O5—C5—C6—C7	122.6 (3)
O5—C2—C3—O6	-32.0 (2)	C9—C5—C6—C7	3.0 (3)
C1—C2—C3—O6	90.3 (3)	C5—C6—C7—C8	-26.1 (3)
O5—C2—C3—C4	92.0 (3)	C6—C7—C8—C9	39.3 (3)
C1—C2—C3—C4	-145.7 (2)	C7—C8—C9—C5	-37.6 (3)
O6—C3—C4—O3	-172.3 (2)	O6—C5—C9—C8	143.4 (3)
C2—C3—C4—O3	71.3 (3)	O5—C5—C9—C8	-99.7 (3)
O6—C3—C4—O4	8.6 (3)	C6—C5—C9—C8	21.4 (3)
C2—C3—C4—O4	-107.8 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3 ⁱ	0.78 (4)	1.87 (4)	2.620 (3)	159 (4)
O4—H4...O2 ⁱⁱ	0.84 (4)	1.92 (4)	2.723 (3)	159 (3)
C2—H2...O3 ⁱⁱⁱ	1.00	2.34	3.315 (4)	166
C3—H3...O2 ^{iv}	1.00	2.43	3.358 (3)	155

Symmetry codes: (i) $-x+1, y+1/2, -z+1$; (ii) $x+1, y-1, z$; (iii) $-x+2, y+1/2, -z+1$; (iv) $x, y-1, z$.(2*R*,3*R*)-1,4-Dioxaspiro[4.5]decane-2,3-dicarboxylic acid (II)

Crystal data

C₁₀H₁₄O₆
M_r = 230.21
 Monoclinic, *P*2₁
a = 6.4272 (8) Å
b = 5.2976 (6) Å
c = 15.5678 (19) Å
 β = 94.469 (2)°
V = 528.45 (11) Å³
Z = 2
F(000) = 244

D_x = 1.447 Mg m⁻³
 Melting point: 413(1) K
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 361 reflections
 θ = 3–29°
 μ = 0.12 mm⁻¹
T = 100 K
 Needle, colourless
 0.39 × 0.15 × 0.05 mm

Data collection

Bruker SMART APEXII diffractometer	4329 measured reflections
Radiation source: fine-focus sealed tube	2612 independent reflections
Graphite monochromator	2503 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.015$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$\theta_{\text{max}} = 29.0^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.917$, $T_{\text{max}} = 0.995$	$h = -8 \rightarrow 8$
	$k = -7 \rightarrow 5$
	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2 + 0.0783P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2612 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
153 parameters	$\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$
1 restraint	$\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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.

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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.38484 (18)	0.5840 (2)	0.45476 (7)	0.0142 (2)
H1	0.275 (4)	0.638 (6)	0.4745 (17)	0.046 (8)*
O2	0.37180 (17)	0.9308 (2)	0.37124 (7)	0.0150 (2)
O3	0.92950 (17)	0.2135 (2)	0.45684 (7)	0.0124 (2)
O4	1.05961 (17)	0.2630 (2)	0.32878 (7)	0.0134 (2)
H4	1.158 (4)	0.171 (5)	0.3519 (15)	0.027 (6)*
O5	0.76550 (18)	0.8366 (2)	0.32166 (7)	0.0118 (2)
O6	0.70176 (17)	0.4547 (2)	0.25475 (7)	0.0116 (2)
C1	0.4607 (2)	0.7451 (3)	0.40041 (9)	0.0104 (3)
C2	0.6846 (2)	0.6758 (3)	0.38313 (9)	0.0099 (3)
H2	0.774689	0.688258	0.438295	0.012*
C3	0.7100 (2)	0.4108 (3)	0.34451 (9)	0.0099 (3)
H3	0.588324	0.303877	0.357764	0.012*
C4	0.9117 (2)	0.2852 (3)	0.38196 (10)	0.0103 (3)
C5	0.7505 (2)	0.7152 (3)	0.23867 (9)	0.0109 (3)
C6	0.9603 (2)	0.7413 (3)	0.20088 (9)	0.0145 (3)

H6A	1.069512	0.658928	0.239569	0.017*
H6B	0.996255	0.922393	0.196647	0.017*
C7	0.9553 (3)	0.6204 (4)	0.11126 (11)	0.0208 (4)
H7A	1.090749	0.648573	0.086579	0.025*
H7B	0.934204	0.435992	0.116324	0.025*
C8	0.7800 (3)	0.7324 (4)	0.05127 (10)	0.0233 (4)
H8A	0.775479	0.646187	-0.005267	0.028*
H8B	0.807902	0.913725	0.041928	0.028*
C9	0.5691 (3)	0.7025 (4)	0.08968 (10)	0.0191 (3)
H9A	0.535628	0.520808	0.094378	0.023*
H9B	0.458492	0.782178	0.050960	0.023*
C10	0.5734 (2)	0.8254 (3)	0.17929 (10)	0.0151 (3)
H10A	0.593000	1.009889	0.173941	0.018*
H10B	0.438602	0.795642	0.204323	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0135 (5)	0.0139 (6)	0.0160 (5)	0.0025 (5)	0.0065 (4)	0.0026 (5)
O2	0.0139 (5)	0.0142 (6)	0.0172 (5)	0.0044 (4)	0.0029 (4)	0.0027 (5)
O3	0.0127 (5)	0.0125 (6)	0.0122 (5)	0.0009 (4)	0.0014 (4)	0.0004 (4)
O4	0.0115 (5)	0.0133 (6)	0.0157 (5)	0.0032 (4)	0.0036 (4)	0.0017 (5)
O5	0.0156 (5)	0.0092 (5)	0.0111 (5)	-0.0026 (4)	0.0036 (4)	-0.0012 (4)
O6	0.0156 (5)	0.0087 (5)	0.0104 (5)	-0.0011 (4)	0.0005 (4)	0.0002 (4)
C1	0.0114 (6)	0.0102 (7)	0.0097 (6)	-0.0006 (5)	0.0010 (5)	-0.0031 (6)
C2	0.0101 (6)	0.0087 (7)	0.0110 (6)	0.0007 (5)	0.0020 (5)	0.0006 (5)
C3	0.0097 (6)	0.0090 (7)	0.0111 (6)	0.0015 (5)	0.0011 (5)	-0.0007 (5)
C4	0.0099 (6)	0.0066 (7)	0.0145 (7)	-0.0003 (5)	0.0008 (5)	-0.0011 (5)
C5	0.0125 (6)	0.0095 (7)	0.0108 (6)	0.0003 (5)	0.0020 (5)	-0.0007 (6)
C6	0.0141 (7)	0.0158 (8)	0.0142 (6)	-0.0018 (6)	0.0048 (5)	-0.0016 (6)
C7	0.0203 (8)	0.0265 (10)	0.0165 (7)	-0.0028 (7)	0.0079 (6)	-0.0053 (7)
C8	0.0288 (9)	0.0291 (10)	0.0126 (7)	-0.0068 (8)	0.0054 (6)	-0.0003 (7)
C9	0.0208 (8)	0.0239 (10)	0.0122 (7)	-0.0016 (7)	-0.0008 (6)	0.0028 (7)
C10	0.0149 (7)	0.0158 (8)	0.0145 (7)	0.0015 (6)	0.0000 (5)	0.0029 (6)

Geometric parameters (Å, °)

O1—C1	1.322 (2)	C5—C10	1.525 (2)
O1—H1	0.84 (3)	C6—C7	1.533 (2)
O2—C1	1.208 (2)	C6—H6A	0.9900
O3—C4	1.2229 (19)	C6—H6B	0.9900
O4—C4	1.3135 (18)	C7—C8	1.526 (3)
O4—H4	0.85 (3)	C7—H7A	0.9900
O5—C2	1.4107 (18)	C7—H7B	0.9900
O5—C5	1.4398 (18)	C8—C9	1.532 (2)
O6—C3	1.4135 (17)	C8—H8A	0.9900
O6—C5	1.441 (2)	C8—H8B	0.9900
C1—C2	1.529 (2)	C9—C10	1.538 (2)

C2—C3	1.541 (2)	C9—H9A	0.9900
C2—H2	1.0000	C9—H9B	0.9900
C3—C4	1.532 (2)	C10—H10A	0.9900
C3—H3	1.0000	C10—H10B	0.9900
C5—C6	1.519 (2)		
C1—O1—H1	112 (2)	C5—C6—H6A	109.4
C4—O4—H4	109.4 (15)	C7—C6—H6A	109.4
C2—O5—C5	109.65 (12)	C5—C6—H6B	109.4
C3—O6—C5	109.70 (12)	C7—C6—H6B	109.4
O2—C1—O1	125.41 (14)	H6A—C6—H6B	108.0
O2—C1—C2	123.59 (14)	C8—C7—C6	110.88 (15)
O1—C1—C2	110.89 (13)	C8—C7—H7A	109.5
O5—C2—C1	112.10 (12)	C6—C7—H7A	109.5
O5—C2—C3	103.28 (11)	C8—C7—H7B	109.5
C1—C2—C3	114.66 (12)	C6—C7—H7B	109.5
O5—C2—H2	108.9	H7A—C7—H7B	108.1
C1—C2—H2	108.9	C7—C8—C9	110.75 (14)
C3—C2—H2	108.9	C7—C8—H8A	109.5
O6—C3—C4	114.38 (12)	C9—C8—H8A	109.5
O6—C3—C2	103.84 (12)	C7—C8—H8B	109.5
C4—C3—C2	111.08 (12)	C9—C8—H8B	109.5
O6—C3—H3	109.1	H8A—C8—H8B	108.1
C4—C3—H3	109.1	C8—C9—C10	110.87 (14)
C2—C3—H3	109.1	C8—C9—H9A	109.5
O3—C4—O4	123.68 (14)	C10—C9—H9A	109.5
O3—C4—C3	120.74 (14)	C8—C9—H9B	109.5
O4—C4—C3	115.58 (13)	C10—C9—H9B	109.5
O5—C5—O6	105.80 (12)	H9A—C9—H9B	108.1
O5—C5—C6	107.89 (12)	C5—C10—C9	110.35 (14)
O6—C5—C6	111.46 (13)	C5—C10—H10A	109.6
O5—C5—C10	111.57 (13)	C9—C10—H10A	109.6
O6—C5—C10	108.05 (13)	C5—C10—H10B	109.6
C6—C5—C10	111.92 (13)	C9—C10—H10B	109.6
C5—C6—C7	110.97 (13)	H10A—C10—H10B	108.1
C5—O5—C2—C1	-99.25 (14)	C2—O5—C5—O6	-12.62 (15)
C5—O5—C2—C3	24.70 (14)	C2—O5—C5—C6	-132.02 (13)
O2—C1—C2—O5	-6.9 (2)	C2—O5—C5—C10	104.65 (14)
O1—C1—C2—O5	176.76 (12)	C3—O6—C5—O5	-6.39 (15)
O2—C1—C2—C3	-124.22 (16)	C3—O6—C5—C6	110.62 (13)
O1—C1—C2—C3	59.43 (16)	C3—O6—C5—C10	-126.00 (13)
C5—O6—C3—C4	-100.36 (14)	O5—C5—C6—C7	-178.91 (14)
C5—O6—C3—C2	20.87 (14)	O6—C5—C6—C7	65.34 (17)
O5—C2—C3—O6	-27.60 (14)	C10—C5—C6—C7	-55.80 (19)
C1—C2—C3—O6	94.65 (14)	C5—C6—C7—C8	55.80 (19)
O5—C2—C3—C4	95.81 (13)	C6—C7—C8—C9	-56.5 (2)
C1—C2—C3—C4	-141.94 (13)	C7—C8—C9—C10	56.9 (2)

O6—C3—C4—O3	-172.39 (14)	O5—C5—C10—C9	176.83 (13)
C2—C3—C4—O3	70.47 (18)	O6—C5—C10—C9	-67.27 (16)
O6—C3—C4—O4	7.99 (19)	C6—C5—C10—C9	55.82 (18)
C2—C3—C4—O4	-109.15 (15)	C8—C9—C10—C5	-56.08 (19)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3 ⁱ	0.84 (3)	1.80 (3)	2.6230 (16)	164 (3)
O4—H4...O2 ⁱⁱ	0.85 (3)	1.88 (3)	2.7116 (16)	164 (2)
C2—H2...O3 ⁱⁱⁱ	1.00	2.41	3.3818 (19)	164
C3—H3...O2 ^{iv}	1.00	2.44	3.392 (2)	160
C6—H6A...O4	0.99	2.52	3.255 (2)	131

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