



# Inversion dimers dominate the crystal packing in the structure of trimethyl citrate (trimethyl 2-hydroxypropane-1,2,3-tricarboxylate)

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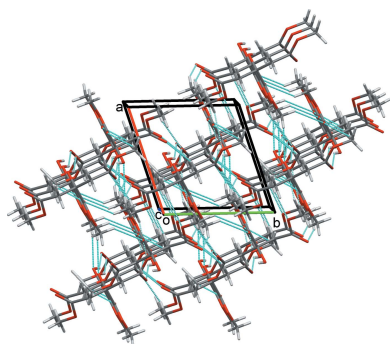
Trimethyl citrate, C<sub>9</sub>H<sub>14</sub>O<sub>7</sub> (systematic name: trimethyl 2-hydroxypropane-1,2,3-tricarboxylate), **2**, was prepared by the esterification of citric acid and methanol in the presence of thionyl chloride at 273 K. The bond lengths and angles in **2** compare closely with those observed in citric acid. The C—C bonds adjacent to the terminal carboxyl groups are significantly shorter than those around the central C atom. The central carboxylate group and the hydroxy group occur in the normal planar arrangement with an r.m.s. deviation of 0.0171 Å from the mean plane involving all six atoms in the central unit. The crystal structure is almost completely dominated by the formation of inversion dimers through an O—H···O hydrogen bond, together with an extensive array of weaker C—H···O contacts. These generate a three-dimensional network structure with molecules stacked along the *c*-axis direction.

## 1. Chemical context

Esters of citric acid have received significant attention because of their many applications. Their use as plasticizers has grown because of their low toxicity, compatibility with the host materials and low volatility (Labrecque *et al.*, 1997; Garg *et al.*, 2014). They were investigated for use in degradable thermoset polymers (Halpern *et al.*, 2014). In the biological field, trimethyl citrate is used to synthesize citrate-functionalized ciprofloxacin conjugates and their antimicrobial activities have been determined against a panel of clinically-relevant bacteria (Md-Saleh *et al.*, 2009). Several different methods and catalysts have been employed for the synthesis of trimethyl citrate from citric acid and methanol using, for example, thionyl chloride (Ilewska & Chimiak, 1994) and zirconium(IV) dichloride oxide hydrate (Sun *et al.*, 2006). We report here the esterification of citric acid to form trimethyl citrate, **2**, together with its molecular and crystal structure.

## 2. Structural commentary

The title compound, **2**, crystallizes in the triclinic space group *P* $\bar{1}$ , with one molecule in the asymmetric unit. The molecular structure of the compound, with the atom labelling, is shown in Fig. 1. The bond lengths and angles in **2** are comparable to those observed in citric acid, **1** (Glusker *et al.*, 1969; Roelofsen & Kanters, 1972; King *et al.*, 2011). The C2—C3 and C5—C6 bonds [1.506 (2) and 1.502 (2) Å, respectively] that bridge the outer terminal carboxyl groups are significantly shorter than those around the central C4 atom [C3—C4 = 1.5405 (19), C4—

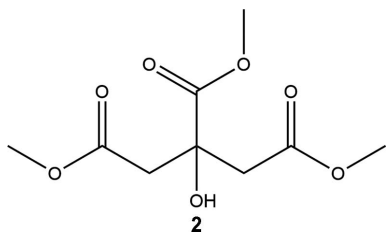


**Table 1**  
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1-H1B\cdots O4^i$	0.98	2.65	3.393 (2)	133
$C1-H1C\cdots O5^{ii}$	0.98	2.56	3.520 (2)	167
$C3-H3A\cdots O1^{iii}$	0.99	2.66	3.6388 (18)	170
$C5-H5A\cdots O2^{iv}$	0.99	2.51	3.4610 (18)	160
$C7-H7C\cdots O7^v$	0.98	2.53	3.3008 (19)	135
$C9-H9B\cdots O2^{iii}$	0.98	2.61	3.423 (2)	140
$C9-H9B\cdots O3^{vi}$	0.98	2.64	3.2576 (17)	121
$C9-H9C\cdots O7^{vii}$	0.98	2.61	3.4147 (19)	140
$O3-H3\cdots O5^v$	0.80 (2)	2.14 (2)	2.8428 (15)	147 (2)

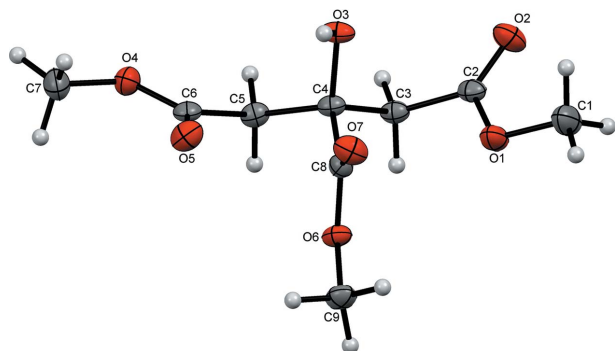
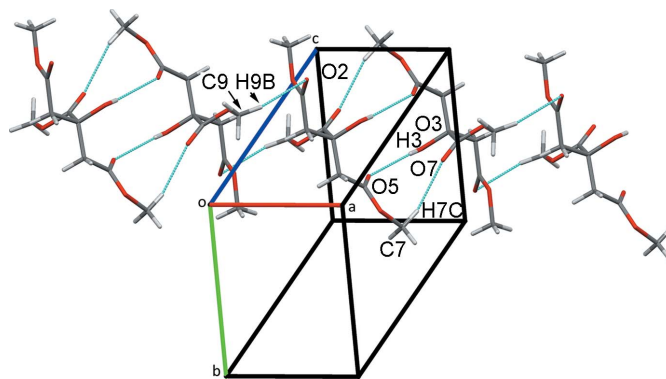
Symmetry codes: (i)  $x-1, y-1, z$ ; (ii)  $x, y-1, z$ ; (iii)  $-x, -y, -z+1$ ; (iv)  $-x+1, -y, -z+1$ ; (v)  $-x+1, -y+1, -z+2$ ; (vi)  $x-1, y, z$ ; (vii)  $-x, -y+1, -z+2$ .

$C5 = 1.5348$  (19) and  $C4-C8 = 1.5398$  (18) Å], an observation that mirrors what occurs in glycine itself. The carbonyl groups  $C2-O2$ ,  $C8-O7$  and  $C6-O5$  are clearly double bonds with similar bond lengths [1.2046 (18), 1.2036 (18) and 1.2082 (18) Å, respectively]. Furthermore, the marked discrepancy between the  $C(=O)-O$  and  $O-Me$  distances, with the latter significantly longer in all instances, reflects considerable delocalization in the  $C(=O)-O$  units. This is again consistent with what is seen in other similar structures. The central carboxylate group and the hydroxy group occur in the normal planar arrangement, with an  $O3-C4-C8-O6$  torsion angle of  $-178.95$  (11)° and an r.m.s. deviation of only 0.0171 Å from the best-fit mean plane through the  $O3, C4, C8, O7, O6$  and  $C9$  atoms.



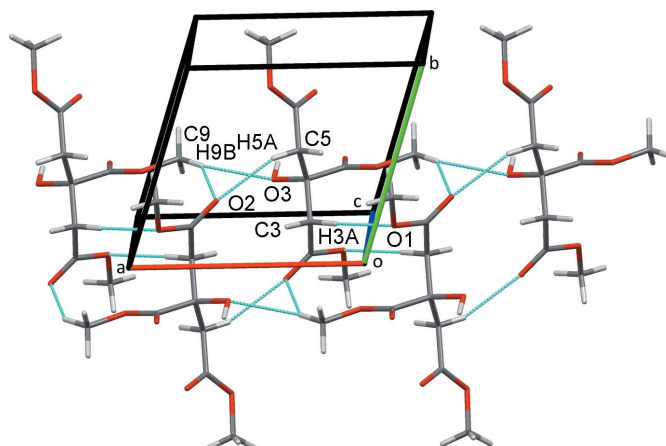
### 3. Supramolecular features

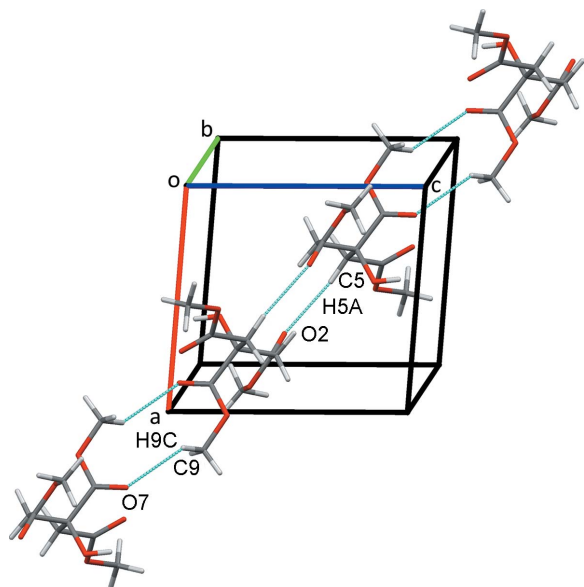
In the crystal, classical  $O3-H3\cdots O5$  hydrogen bonds form inversion dimers enclosing  $R_2^2(12)$  rings. These contacts are


**Figure 1**  
 The structure of **2**, showing the atom numbering, with ellipsoids drawn at the 50% probability level.

**Figure 2**  
 A view along  $c$  of chains of molecules of **2** formed along  $(10\bar{1})$  from pairs of inversion dimers.

supported by weaker inversion-related  $C7-H7C\cdots O7^v$  hydrogen bonds with  $R_2^2(16)$  ring motifs (Table 1). These dimers are linked into chains parallel to  $(10\bar{1})$  by inversion-related  $C9-H9B\cdots O2^{iii}$  contacts that also form  $R_2^2(16)$  rings (Fig. 2). H atoms from both of the methylene groups in the molecule are also involved in inversion-dimer formation. Pairs of  $C3-H3A\cdots O1^{iii}$  hydrogen bonds enclose  $R_2^2(8)$  rings that are linked by  $R_2^2(12)$  ring  $C5-H5A\cdots O2^{iv}$  interactions into chains along the  $a$ -axis direction. Weaker  $C9-H9B\cdots O3^{vi}$  hydrogen bonds further stabilize these chains (Fig. 3). The  $R_2^2(12)$  ring  $C5-H5A\cdots O2^{iv}$  interactions, mentioned previously, form more chains, this time linking another set of inversion dimers involving the  $R_2^2(10)$  ring  $C9-H9C\cdots O7^{vii}$  contacts. These contacts form chains of dimers that run along the  $ac$  diagonal (Fig. 4).

The only significant intermolecular contacts in the crystal structure not to result in inversion-dimer formation involve weak  $C-H\cdots O$  hydrogen bonds formed by the peripheral  $C1$  and central  $C9$  methyl groups.  $C1$  acts as a bifurcated donor forming  $C1-H1B\cdots O4^i$  and  $C1-H1C\cdots O5^{ii}$  contacts that combine with  $C9-H9B\cdots O3^{vi}$  hydrogen bonds to generate a sheet of molecules in the  $ab$  plane (Fig. 5). Overall, this extensive array of both classical and nonclassical inter-


**Figure 3**  
 Chains of molecules of **2** along the  $a$ -axis direction formed from pairs of inversion dimers.

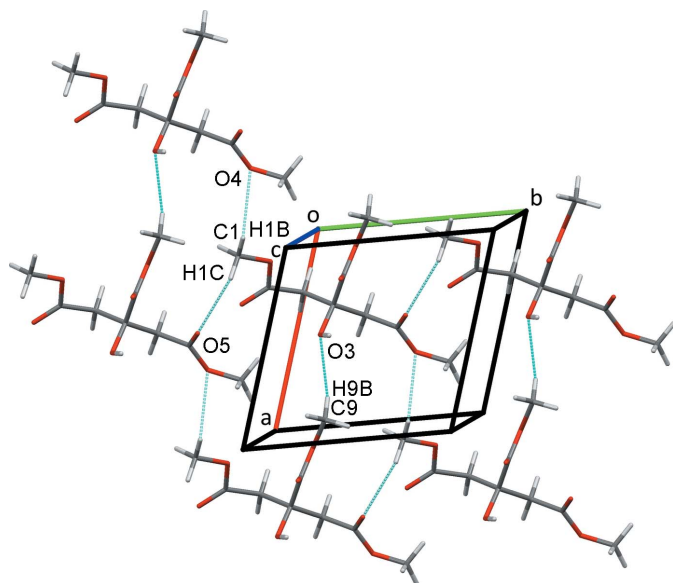


**Figure 4**  
Pairs of inversion dimers that link molecules of **2** into chains along the *ac* diagonal.

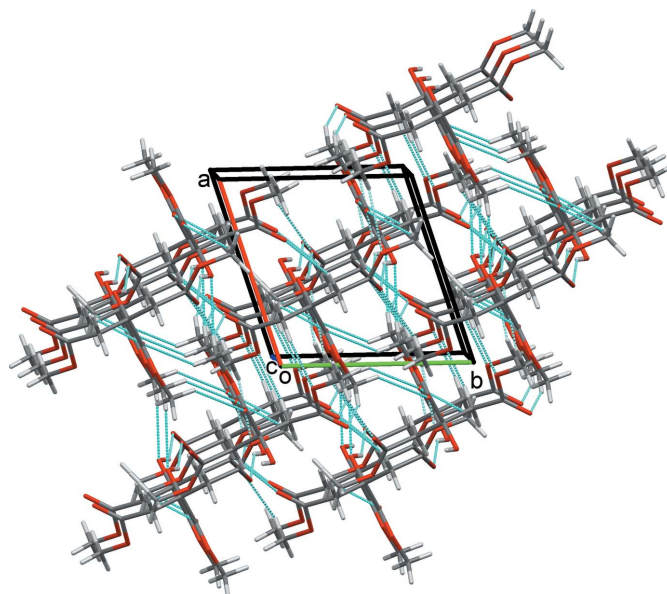
molecular contacts generates a three-dimensional network structure with molecules stacked along the *c*-axis direction (Fig. 6).

#### 4. Database survey

A search of the Cambridge Structural Database (Version 5.39, updated February 2018; Groom *et al.*, 2016) for the title compound gave no hits. In contrast, a search for the  $O_2CCH_2C(O)(CO_2)CH_2CO_2$  fragment incorporating both organic and metal organic structures gave an impressive 404

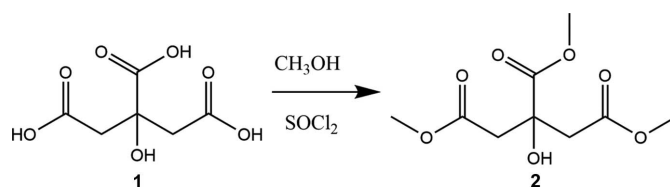


**Figure 5**  
A view along *c* of the sheet of molecules of **2** formed in the *ab* plane by weak C—H...O hydrogen bonds.



**Figure 6**  
The overall packing of **2** viewed along the *c*-axis direction.

hits. Limiting the search to organic structures, which eliminates the numerous metals salts of the citrate anions and the use of citrate as a ligand, reduced the hits to 124. In what follows, with few exceptions, only one or two recent examples of the plethora of different related systems are cited. The structure of citric acid itself has been reported several times, both in isolation (Glusker *et al.*, 1969) and as the monohydrate (Roelofsen & Kanters, 1972; King *et al.*, 2011). Eighteen examples of citric acid cocrystallized with various organic bases are also found (see, for example, Kerr *et al.*, 2016; Wang *et al.*, 2016). This search also revealed a lone neutral 1,5-dimethyl citrate (Li *et al.*, 2007*a*) and a single monoanionic dimethyl citrate derivative, (–)-brucinium (*R*)-1,2-dimethyl-citrate hydrate (Bergeron *et al.*, 1997), with no related dianions. No examples of 1-methyl citrate or any of its anions were found, but 6-methyl citrate with the carboxylate group on the central C atom has been reported (Li *et al.*, 2007*b*; Aliyu *et al.*, 2009). In contrast, structures of more than 80 citrate anions have been reported; these included 48 monoanions with the proton lost from both the central (Inukai *et al.*, 2017; Wang *et al.*, 2017) and peripheral carboxylate OH groups (Abraham *et al.*, 2016; Rammohan & Kaduk, 2016*a*). Sixteen examples of citrate dianions (Rammohan & Kaduk, 2016*b*, 2017*a*) and 17 citrate trianions (Rammohan & Kaduk, 2017*b,c*) were also found.



**Figure 7**  
The synthesis of the title compound (**2**).

## 5. Synthesis and crystallization

Citric acid (0.01 mol, 2.00 g) was dissolved in absolute methanol (50 mL) and the solution was cooled in an ice-bath under a nitrogen atmosphere. To this solution, thionyl chloride (0.08 mol, 6.0 mL) was added dropwise with efficient stirring at 273 K for 1 h and the solution was left stirring overnight at 298 K (Fig. 7). The solvent was removed *in vacuo* and the solid residue was dissolved in ethyl acetate (15 mL), dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure and the solid residue was purified by recrystallization from hexane/ethyl acetate (1:3 v/v) to yield 1.6 g (80%) of the title compound as white crystals.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Atom H3 of the OH group was located in a difference Fourier map and its coordinates refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The resulting O3–H3 distance of 0.80 (2) Å was acceptable. All H atoms bound to carbon were refined using a riding model, with C–H = 0.99 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for CH<sub>2</sub> H atoms, and C–H = 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for CH<sub>3</sub> H atoms.

## Acknowledgements

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Table 2

Experimental details.

Crystal data	
Chemical formula	C <sub>9</sub> H <sub>14</sub> O <sub>7</sub>
$M_r$	234.20
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
$a, b, c$ (Å)	7.8428 (3), 8.0256 (3), 9.3965 (3)
$\alpha, \beta, \gamma$ (°)	109.915 (1), 92.832 (1), 104.493 (1)
$V$ (Å <sup>3</sup> )	532.46 (3)
$Z$	2
Radiation type	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.11
Crystal size (mm)	0.24 × 0.16 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2001)
$T_{\text{min}}, T_{\text{max}}$	0.769, 0.897
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4914, 1989, 1873
$R_{\text{int}}$	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.110, 1.08
No. of reflections	1989
No. of parameters	151
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.30, -0.28

Computer programs: *APEX2* (Bruker, 2003), *SAINT* (Bruker, 2003), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2018* (Sheldrick, 2015), *PLATON* (Spek, 2009), *publCIF* (Westrip 2010) and *WinGX* (Farrugia 2012).

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## supporting information

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## Inversion dimers dominate the crystal packing in the structure of trimethyl citrate (trimethyl 2-hydroxypropane-1,2,3-tricarboxylate)

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### Computing details

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015), *PLATON* (Spek, 2009), *pubCIF* (Westrip 2010) and *WinGX* (Farrugia 2012).

### Trimethyl 2-hydroxypropane-1,2,3-tricarboxylate

#### Crystal data

$C_9H_{14}O_7$	$Z = 2$
$M_r = 234.20$	$F(000) = 248$
Triclinic, $P\bar{1}$	$D_x = 1.461 \text{ Mg m}^{-3}$
$a = 7.8428 (3) \text{ \AA}$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
$b = 8.0256 (3) \text{ \AA}$	Cell parameters from 3559 reflections
$c = 9.3965 (3) \text{ \AA}$	$\theta = 5.1\text{--}72.3^\circ$
$\alpha = 109.915 (1)^\circ$	$\mu = 1.11 \text{ mm}^{-1}$
$\beta = 92.832 (1)^\circ$	$T = 150 \text{ K}$
$\gamma = 104.493 (1)^\circ$	Block, colourless
$V = 532.46 (3) \text{ \AA}^3$	$0.24 \times 0.16 \times 0.10 \text{ mm}$

#### Data collection

Bruker APEXII CCD diffractometer	1989 independent reflections
Radiation source: X-ray, X-ray	1873 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.030$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{\text{max}} = 72.3^\circ$ , $\theta_{\text{min}} = 5.1^\circ$
$T_{\text{min}} = 0.769$ , $T_{\text{max}} = 0.897$	$h = -9 \rightarrow 9$
4914 measured reflections	$k = -9 \rightarrow 9$
	$l = -11 \rightarrow 11$

#### Refinement

Refinement on $F^2$	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.038$	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 0.2284P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1989 reflections	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
151 parameters	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
0 restraints	

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0409 (2)	−0.2623 (3)	0.7299 (2)	0.0381 (4)
H1A	−0.005169	−0.376371	0.639926	0.057*
H1B	−0.050722	−0.248183	0.796766	0.057*
H1C	0.146568	−0.268417	0.785887	0.057*
C2	0.22424 (19)	−0.0992 (2)	0.60115 (16)	0.0219 (3)
C3	0.26796 (18)	0.0716 (2)	0.56095 (16)	0.0207 (3)
H3A	0.160716	0.074354	0.502631	0.025*
H3B	0.361749	0.065717	0.494144	0.025*
C4	0.33242 (18)	0.25094 (19)	0.70328 (15)	0.0186 (3)
C5	0.40405 (19)	0.4110 (2)	0.64816 (16)	0.0212 (3)
H5A	0.503632	0.387793	0.590925	0.025*
H5B	0.308690	0.413571	0.576515	0.025*
C6	0.46821 (18)	0.5968 (2)	0.77536 (16)	0.0207 (3)
C7	0.6601 (2)	0.8984 (2)	0.8491 (2)	0.0328 (4)
H7A	0.565562	0.957176	0.844474	0.049*
H7B	0.768047	0.965634	0.821830	0.049*
H7C	0.685307	0.900853	0.953140	0.049*
C8	0.18196 (18)	0.28329 (18)	0.79919 (16)	0.0196 (3)
C9	−0.0983 (2)	0.3424 (2)	0.80083 (18)	0.0269 (3)
H9A	−0.130073	0.261138	0.858908	0.040*
H9B	−0.201720	0.322531	0.727756	0.040*
H9C	−0.061107	0.471599	0.871360	0.040*
O1	0.08823 (14)	−0.10558 (15)	0.68144 (14)	0.0288 (3)
O2	0.30055 (15)	−0.21698 (16)	0.56613 (13)	0.0314 (3)
O3	0.47114 (14)	0.22946 (16)	0.79070 (12)	0.0238 (3)
H3	0.472 (3)	0.284 (3)	0.880 (3)	0.036*
O4	0.60317 (14)	0.70848 (14)	0.74259 (12)	0.0262 (3)
O5	0.40234 (14)	0.64142 (15)	0.89107 (12)	0.0286 (3)
O6	0.04717 (13)	0.30097 (14)	0.71842 (11)	0.0220 (3)
O7	0.18789 (15)	0.29190 (16)	0.92982 (12)	0.0277 (3)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0306 (9)	0.0363 (9)	0.0600 (12)	0.0126 (7)	0.0154 (8)	0.0297 (9)
C2	0.0185 (7)	0.0249 (7)	0.0202 (7)	0.0083 (6)	−0.0007 (6)	0.0046 (6)
C3	0.0189 (7)	0.0253 (7)	0.0174 (7)	0.0085 (6)	0.0025 (5)	0.0056 (6)
C4	0.0160 (6)	0.0241 (7)	0.0160 (6)	0.0075 (5)	0.0018 (5)	0.0064 (5)
C5	0.0198 (7)	0.0260 (7)	0.0179 (7)	0.0071 (6)	0.0045 (5)	0.0076 (6)

C6	0.0164 (6)	0.0254 (7)	0.0209 (7)	0.0074 (5)	-0.0007 (5)	0.0088 (6)
C7	0.0347 (9)	0.0226 (8)	0.0398 (9)	0.0053 (6)	0.0003 (7)	0.0123 (7)
C8	0.0194 (7)	0.0188 (6)	0.0200 (7)	0.0062 (5)	0.0039 (6)	0.0055 (5)
C9	0.0188 (7)	0.0300 (8)	0.0304 (8)	0.0102 (6)	0.0073 (6)	0.0065 (6)
O1	0.0232 (5)	0.0287 (6)	0.0427 (7)	0.0120 (4)	0.0118 (5)	0.0189 (5)
O2	0.0350 (6)	0.0325 (6)	0.0339 (6)	0.0205 (5)	0.0107 (5)	0.0124 (5)
O3	0.0214 (5)	0.0358 (6)	0.0168 (5)	0.0152 (4)	0.0022 (4)	0.0078 (4)
O4	0.0247 (5)	0.0243 (5)	0.0306 (6)	0.0053 (4)	0.0054 (4)	0.0121 (4)
O5	0.0255 (6)	0.0327 (6)	0.0213 (5)	0.0058 (5)	0.0045 (4)	0.0037 (4)
O6	0.0166 (5)	0.0272 (5)	0.0212 (5)	0.0093 (4)	0.0026 (4)	0.0054 (4)
O7	0.0326 (6)	0.0366 (6)	0.0221 (5)	0.0174 (5)	0.0112 (4)	0.0145 (5)

*Geometric parameters (Å, °)*

C1—O1	1.4497 (19)	C5—H5B	0.9900
C1—H1A	0.9800	C6—O5	1.2083 (18)
C1—H1B	0.9800	C6—O4	1.3279 (18)
C1—H1C	0.9800	C7—O4	1.4494 (19)
C2—O2	1.2047 (18)	C7—H7A	0.9800
C2—O1	1.3372 (18)	C7—H7B	0.9800
C2—C3	1.506 (2)	C7—H7C	0.9800
C3—C4	1.5405 (19)	C8—O7	1.2036 (18)
C3—H3A	0.9900	C8—O6	1.3352 (17)
C3—H3B	0.9900	C9—O6	1.4537 (17)
C4—O3	1.4107 (16)	C9—H9A	0.9800
C4—C5	1.5348 (19)	C9—H9B	0.9800
C4—C8	1.5398 (18)	C9—H9C	0.9800
C5—C6	1.502 (2)	O3—H3	0.80 (2)
C5—H5A	0.9900		
O1—C1—H1A	109.5	C4—C5—H5B	108.8
O1—C1—H1B	109.5	H5A—C5—H5B	107.7
H1A—C1—H1B	109.5	O5—C6—O4	124.07 (14)
O1—C1—H1C	109.5	O5—C6—C5	124.44 (13)
H1A—C1—H1C	109.5	O4—C6—C5	111.46 (12)
H1B—C1—H1C	109.5	O4—C7—H7A	109.5
O2—C2—O1	123.32 (14)	O4—C7—H7B	109.5
O2—C2—C3	125.04 (13)	H7A—C7—H7B	109.5
O1—C2—C3	111.64 (12)	O4—C7—H7C	109.5
C2—C3—C4	112.59 (11)	H7A—C7—H7C	109.5
C2—C3—H3A	109.1	H7B—C7—H7C	109.5
C4—C3—H3A	109.1	O7—C8—O6	125.36 (13)
C2—C3—H3B	109.1	O7—C8—C4	123.63 (13)
C4—C3—H3B	109.1	O6—C8—C4	111.01 (11)
H3A—C3—H3B	107.8	O6—C9—H9A	109.5
O3—C4—C5	110.16 (11)	O6—C9—H9B	109.5
O3—C4—C8	109.64 (11)	H9A—C9—H9B	109.5
C5—C4—C8	111.26 (11)	O6—C9—H9C	109.5

O3—C4—C3	106.41 (11)	H9A—C9—H9C	109.5
C5—C4—C3	107.72 (11)	H9B—C9—H9C	109.5
C8—C4—C3	111.52 (11)	C2—O1—C1	115.46 (12)
C6—C5—C4	113.73 (11)	C4—O3—H3	109.9 (15)
C6—C5—H5A	108.8	C6—O4—C7	115.72 (12)
C4—C5—H5A	108.8	C8—O6—C9	115.65 (11)
C6—C5—H5B	108.8		
O2—C2—C3—C4	-116.42 (15)	C5—C4—C8—O7	-120.73 (15)
O1—C2—C3—C4	63.70 (15)	C3—C4—C8—O7	118.97 (15)
C2—C3—C4—O3	51.89 (14)	O3—C4—C8—O6	-178.93 (11)
C2—C3—C4—C5	170.01 (11)	C5—C4—C8—O6	58.96 (15)
C2—C3—C4—C8	-67.63 (15)	C3—C4—C8—O6	-61.34 (15)
O3—C4—C5—C6	-65.67 (14)	O2—C2—O1—C1	2.2 (2)
C8—C4—C5—C6	56.14 (15)	C3—C2—O1—C1	-177.89 (13)
C3—C4—C5—C6	178.65 (11)	O5—C6—O4—C7	-5.5 (2)
C4—C5—C6—O5	-34.35 (19)	C5—C6—O4—C7	172.48 (12)
C4—C5—C6—O4	147.68 (12)	O7—C8—O6—C9	3.0 (2)
O3—C4—C8—O7	1.38 (19)	C4—C8—O6—C9	-176.68 (11)

*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>
C1—H1B...O4 <sup>i</sup>	0.98	2.65	3.393 (2)	133
C1—H1C...O5 <sup>ii</sup>	0.98	2.56	3.520 (2)	167
C3—H3A...O1 <sup>iii</sup>	0.99	2.66	3.6388 (18)	170
C5—H5A...O2 <sup>iv</sup>	0.99	2.51	3.4610 (18)	160
C7—H7C...O7 <sup>v</sup>	0.98	2.53	3.3008 (19)	135
C9—H9B...O2 <sup>iii</sup>	0.98	2.61	3.423 (2)	140
C9—H9B...O3 <sup>vi</sup>	0.98	2.64	3.2576 (17)	121
C9—H9C...O7 <sup>vii</sup>	0.98	2.61	3.4147 (19)	140
O3—H3...O5 <sup>v</sup>	0.80 (2)	2.14 (2)	2.8428 (15)	147 (2)

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