

## Dodecahydroxycyclohexane dihydrate

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## Key indicators

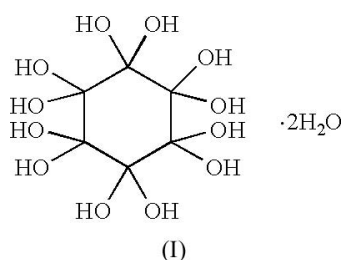
Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.033  
 $wR$  factor = 0.091  
Data-to-parameter ratio = 9.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

In the commercially available title compound,  $\text{C}_6\text{H}_{12}\text{O}_{12} \cdot 2\text{H}_2\text{O}$ , the dodecahydroxycyclohexane molecule has an inversion center. The crystal packing is characterized by a strong  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond involving the water molecules, and the dodecahydroxycyclohexane molecules are additionally linked by  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds of the hydroxyl groups, resulting in the formation of a three-dimensional network.

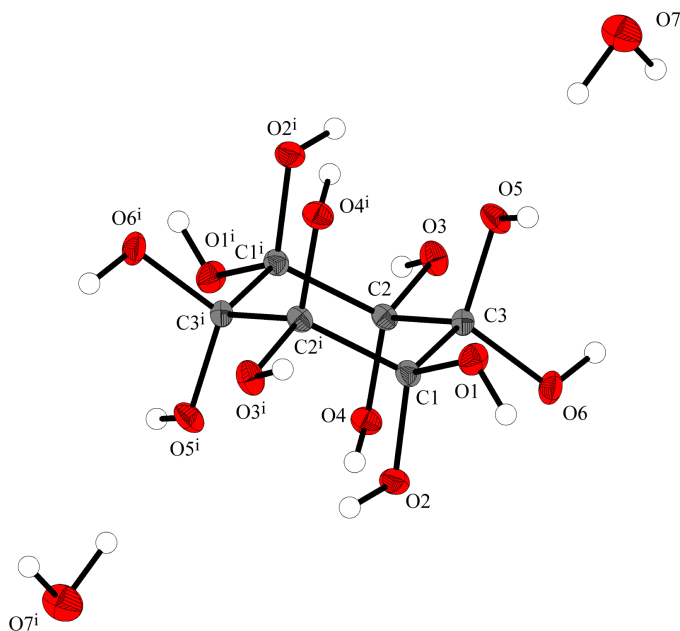
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Accepted 30 March 2005  
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## Comment

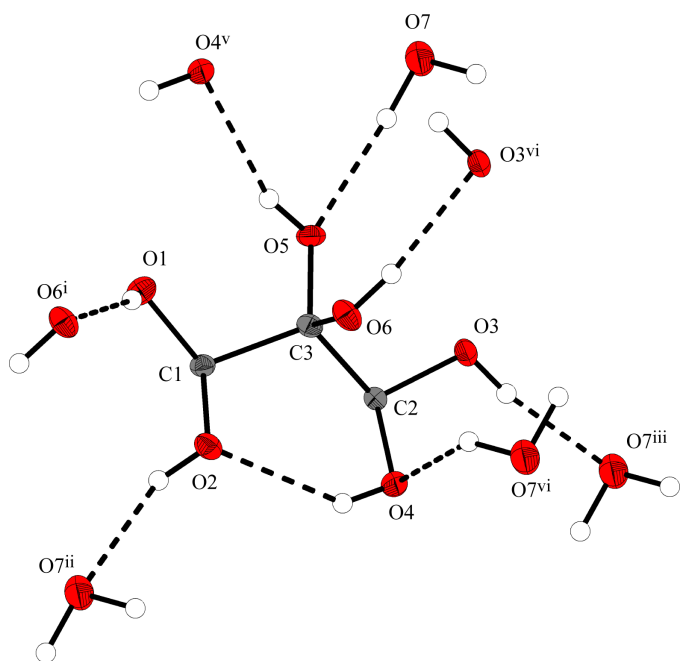
For a long time, the molecular structure of the commercially available 'hexaketocyclohexane octahydrate', the title compound, (I), has been the cause of controversial discussions and it is amazing that until now no X-ray structure determination has been carried out. Interestingly, the triquinoyl ring of this compound appears from the spectroscopic characterization to be dodecahydroxycyclohexane  $\text{C}_6(\text{OH})_{12}$  (West & Niu, 1970), but the products of amine condensation reactions, as well as an oxidation reaction with metallic copper, shows that the chemistry of (I) follows the path of hexaketocyclohexane  $\text{C}_6\text{O}_6$  (Catalano *et al.*, 1994; Speier *et al.*, 1997). In order to unearth the truth, the structure of (I) has been determined.



The molecular structure of (I) is shown in Fig. 1. The cyclohexane ring lies about an inversion center and exhibits an undistorted chair conformation with 12 OH groups, six in axial and six in equatorial positions. All C—C bonds and bond angles (Table 1) fall in the expected ranges derived from other cyclohexanols. The C—O bonds are about 0.025 Å shorter than the typical value for such bonds in a similar environment (Linden, 1995). There are seven intermolecular and one intramolecular hydrogen bond (Table 2), with  $\text{O} \cdots \text{O}$  in the range 2.704 (2)–2.916 (2) Å. All the hydroxyl groups except O1 act as hydrogen-bond donors and acceptors, either with other hydroxyl groups or with the water molecules, forming a three-dimensional network (Fig. 2). The hydrogen bond between O4 and O2 is intramolecular and a closer inspection of the intermolecular bond patterns reveals that O1, accepting

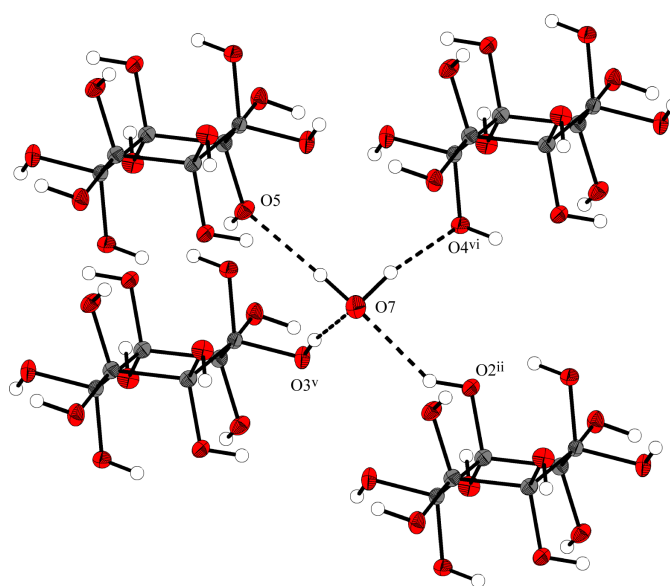

**Figure 1**

A view of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]


**Figure 2**

The hydrogen-bonding scheme in (I), showing the asymmetric unit of the organic molecule with its surroundings. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry codes: (i)  $x, y - 1, z$ ; (ii)  $2 - x, -y, 2 - z$ ; (iii)  $x - 1, y, z$ ; (iv)  $1 - x, 1 - y, 1 - z$ ; (v)  $1 + x, y, z$ ; (vi)  $1 - x, 1 - y, 2 - z$ .]

A hydrogen bond from O6, does not serve as an intermolecular hydrogen-bond donor. The water accepts and donates two hydrogen bonds. Its fourfold coordination shell (Fig. 3), formed by atoms O2, O3, O4 and O5, can be approximated by a very distorted tetrahedron.


**Figure 3**

Distorted tetrahedral coordination shell of the water molecule in (I). [Symmetry codes: (ii)  $2 - x, -y, 2 - z$ ; (v)  $1 + x, y, z$ ; (vi)  $1 - x, 1 - y, 2 - z$ .]

## Experimental

In a typical reaction, powdered sodium tetrahydroxyquinone (16.2 g, 50 mmol; Fatiadi & Sager, 1983) was added in portions over a period of 10 min to a stirred solution of 25%  $\text{HNO}_3$  (38 ml). The temperature of the vigorous reaction was controlled at  $318 \pm 5$  K using an ice bath. Compound (I) crystallized from the resulting yellow solution as colorless plates suitable for an X-ray structure determination [yield 17.55 g, 80%; m.p. 367–369 K (decomposition)].

### Crystal data

$\text{C}_6\text{H}_{12}\text{O}_{12} \cdot 2\text{H}_2\text{O}$   
 $M_r = 312.19$   
 Triclinic,  $P\bar{1}$   
 $a = 6.1829$  (8) Å  
 $b = 7.0696$  (8) Å  
 $c = 7.3023$  (6) Å  
 $\alpha = 70.443$  (8)°  
 $\beta = 80.153$  (8)°  
 $\gamma = 63.973$  (10)°  
 $V = 270.16$  (5) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.919$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 22 reflections  
 $\theta = 9\text{--}18^\circ$   
 $\mu = 0.20$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Plate, colourless  
 $0.47 \times 0.43 \times 0.10$  mm

### Data collection

Nonius MACH3 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
 $T_{\min} = 0.945$ ,  $T_{\max} = 0.976$   
 1046 measured reflections  
 948 independent reflections  
 893 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 7$   
 $k = -7 \rightarrow 8$   
 $l = -8 \rightarrow 8$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 1.9%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.091$   
 $S = 1.10$   
 948 reflections  
 98 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2382P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.155 (19)

**Table 1**  
Selected geometric parameters (Å, °).

O1—C1	1.402 (2)	O6—C3	1.408 (2)
O2—C1	1.397 (2)	C1—C3 <sup>i</sup>	1.553 (2)
O3—C2	1.393 (2)	C1—C2	1.562 (2)
O4—C2	1.416 (2)	C2—C3	1.554 (2)
O5—C3	1.390 (2)		
O2—C1—O1	111.93 (13)	O3—C2—C1	108.62 (13)
O2—C1—C3 <sup>i</sup>	106.13 (13)	O4—C2—C1	109.99 (13)
O1—C1—C3 <sup>i</sup>	109.27 (13)	C3—C2—C1	113.08 (13)
O2—C1—C2	111.45 (13)	O5—C3—O6	111.14 (13)
O1—C1—C2	105.63 (13)	O5—C3—C1 <sup>i</sup>	111.13 (14)
C3 <sup>i</sup> —C1—C2	112.52 (13)	O6—C3—C1 <sup>i</sup>	106.69 (13)
O3—C2—O4	107.37 (13)	O5—C3—C2	107.33 (13)
O3—C2—C3	107.66 (13)	O6—C3—C2	109.66 (13)
O4—C2—C3	109.92 (13)	C1 <sup>i</sup> —C3—C2	110.93 (13)

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

**Table 2**  
Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...O6 <sup>vii</sup>	0.82	2.00	2.791 (2)	161
O2—H2...O7 <sup>ii</sup>	0.82	2.06	2.761 (2)	143
O3—H3...O7 <sup>viii</sup>	0.82	1.89	2.704 (2)	171
O4—H4...O2 <sup>i</sup>	0.82	2.09	2.768 (2)	140
O5—H5...O4 <sup>v</sup>	0.82	2.11	2.897 (2)	161
O6—H6...O3 <sup>vi</sup>	0.82	1.97	2.769 (2)	163
O7—H7A...O4 <sup>vi</sup>	0.96	2.05	2.877 (2)	143
O7—H7B...O5	0.95	1.96	2.916 (2)	175

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

The water H atoms were located in difference density maps, while the H atoms of the hydroxyl groups were positioned geometrically. Restraints were applied to the bond lengths and to the distance between the H atoms of the hydroxyl groups to stabilize the structure

during initial refinement. All non-H atoms were refined with anisotropic displacement parameters, employing a rigid-bond restraint to  $U_{ij}$  of pairs of bonded atoms (Rollett, 1970). The H atoms were allowed to ride on the coordinates of their parent atoms during the final refinement, with hydroxyl O—H = 0.82 Å and water O—H fixed at the values obtained in free refinement. The  $U_{iso}(H)$  values were taken as  $1.2U_{eq}(O)$ . The hydroxyl groups were allowed to rotate around the C—O bonds.

Data collection: *CAD-4 Software* (Nonius, 1994); cell refinement: *CAD-4 Software*; data reduction: *OpenMoleN* (Nonius, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXL97*.

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## supporting information

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*Crystal data*

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 $M_r = 312.19$   
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 Hall symbol:  $-P1$   
 $a = 6.1829$  (8) Å  
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 $\beta = 80.153$  (8)°  
 $\gamma = 63.973$  (10)°  
 $V = 270.16$  (5) Å<sup>3</sup>

$Z = 1$   
 $F(000) = 164$   
 $D_x = 1.919$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 22 reflections  
 $\theta = 9$ – $18^\circ$   
 $\mu = 0.20$  mm<sup>-1</sup>  
 $T = 295$  K  
 Plate, colourless  
 $0.47 \times 0.43 \times 0.10$  mm

*Data collection*

Nonius MACH3  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (North et al., 1968)  
 $T_{\min} = 0.945$ ,  $T_{\max} = 0.976$   
 1046 measured reflections

948 independent reflections  
 893 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.010$   
 $\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 3.0^\circ$   
 $h = 0 \rightarrow 7$   
 $k = -7 \rightarrow 8$   
 $l = -8 \rightarrow 8$   
 3 standard reflections every 7200 min  
 intensity decay: 1.9%

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.091$   
 $S = 1.10$   
 948 reflections  
 98 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.2382P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.43$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97,  
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.155 (19)

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.2756 (2)	0.2131 (2)	0.61259 (18)	0.0196 (3)
H1	0.3392	0.0804	0.6258	0.023*
O2	0.6829 (2)	0.12722 (19)	0.61615 (17)	0.0182 (3)
H2	0.7012	0.0875	0.7337	0.022*
O3	0.4065 (2)	0.3354 (2)	0.89185 (17)	0.0192 (3)
H3	0.3008	0.2894	0.9268	0.023*
O4	0.1347 (2)	0.6042 (2)	0.67023 (18)	0.0179 (3)
H4	0.1205	0.7020	0.5673	0.021*
O5	0.7677 (2)	0.4402 (2)	0.71644 (18)	0.0193 (3)
H5	0.8615	0.4998	0.6763	0.023*
O6	0.4379 (2)	0.7556 (2)	0.74223 (17)	0.0202 (4)
H6	0.4816	0.7043	0.8550	0.024*
O7	1.0816 (3)	0.1603 (2)	1.04555 (19)	0.0289 (4)
H7A	0.9602	0.2124	1.1401	0.035*
H7B	0.9742	0.2469	0.9401	0.035*
C1	0.4533 (3)	0.2953 (3)	0.5717 (2)	0.0143 (4)
C2	0.3803 (3)	0.4570 (3)	0.6963 (2)	0.0142 (4)
C3	0.5388 (3)	0.5886 (3)	0.6498 (2)	0.0145 (4)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0200 (7)	0.0178 (6)	0.0249 (7)	-0.0116 (5)	0.0006 (5)	-0.0064 (5)
O2	0.0183 (7)	0.0165 (6)	0.0160 (6)	-0.0038 (5)	-0.0035 (5)	-0.0033 (5)
O3	0.0237 (7)	0.0247 (7)	0.0120 (6)	-0.0144 (6)	-0.0009 (5)	-0.0024 (5)
O4	0.0143 (6)	0.0195 (7)	0.0180 (6)	-0.0059 (5)	-0.0004 (5)	-0.0046 (5)
O5	0.0158 (6)	0.0220 (7)	0.0206 (7)	-0.0096 (5)	-0.0056 (5)	-0.0021 (5)
O6	0.0296 (8)	0.0189 (7)	0.0153 (6)	-0.0101 (6)	-0.0028 (5)	-0.0078 (5)
O7	0.0272 (8)	0.0337 (8)	0.0207 (7)	-0.0107 (6)	0.0012 (6)	-0.0051 (6)
C1	0.0137 (8)	0.0147 (8)	0.0156 (8)	-0.0068 (7)	-0.0019 (6)	-0.0038 (7)
C2	0.0140 (8)	0.0161 (8)	0.0120 (8)	-0.0061 (7)	-0.0012 (6)	-0.0031 (7)
C3	0.0161 (9)	0.0144 (8)	0.0148 (9)	-0.0065 (7)	-0.0024 (6)	-0.0053 (7)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C1	1.402 (2)	O5—H5	0.8200
O1—H1	0.8200	O6—C3	1.408 (2)
O2—C1	1.397 (2)	O6—H6	0.8200
O2—H2	0.8200	O7—H7A	0.9621
O3—C2	1.393 (2)	O7—H7B	0.9548
O3—H3	0.8200	C1—C3 <sup>i</sup>	1.553 (2)
O4—C2	1.416 (2)	C1—C2	1.562 (2)
O4—H4	0.8200	C2—C3	1.554 (2)
O5—C3	1.390 (2)	C3—C1 <sup>i</sup>	1.553 (2)
C1—O1—H1	109.5	O3—C2—O4	107.37 (13)
C1—O2—H2	109.5	O3—C2—C3	107.66 (13)
C2—O3—H3	109.5	O4—C2—C3	109.92 (13)
C2—O4—H4	109.5	O3—C2—C1	108.62 (13)
C3—O5—H5	109.5	O4—C2—C1	109.99 (13)
C3—O6—H6	109.5	C3—C2—C1	113.08 (13)
H7A—O7—H7B	93.1	O5—C3—O6	111.14 (13)
O2—C1—O1	111.93 (13)	O5—C3—C1 <sup>i</sup>	111.13 (14)
O2—C1—C3 <sup>i</sup>	106.13 (13)	O6—C3—C1 <sup>i</sup>	106.69 (13)
O1—C1—C3 <sup>i</sup>	109.27 (13)	O5—C3—C2	107.33 (13)
O2—C1—C2	111.45 (13)	O6—C3—C2	109.66 (13)
O1—C1—C2	105.63 (13)	C1 <sup>i</sup> —C3—C2	110.93 (13)
C3 <sup>i</sup> —C1—C2	112.52 (13)		
O2—C1—C2—O3	-53.70 (17)	O3—C2—C3—O5	50.92 (17)
O1—C1—C2—O3	68.08 (16)	O4—C2—C3—O5	167.58 (12)
C3 <sup>i</sup> —C1—C2—O3	-172.78 (13)	C1—C2—C3—O5	-69.07 (17)
O2—C1—C2—O4	-170.94 (12)	O3—C2—C3—O6	-69.91 (16)
O1—C1—C2—O4	-49.17 (17)	O4—C2—C3—O6	46.74 (17)
C3 <sup>i</sup> —C1—C2—O4	69.97 (17)	C1—C2—C3—O6	170.09 (13)
O2—C1—C2—C3	65.75 (18)	O3—C2—C3—C1 <sup>i</sup>	172.49 (13)
O1—C1—C2—C3	-172.48 (13)	O4—C2—C3—C1 <sup>i</sup>	-70.85 (17)
C3 <sup>i</sup> —C1—C2—C3	-53.3 (2)	C1—C2—C3—C1 <sup>i</sup>	52.50 (19)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O6 <sup>ii</sup>	0.82	2.00	2.791 (2)	161
O2—H2 $\cdots$ O3	0.8	2.36	2.782 (2)	113
O2—H2 $\cdots$ O7 <sup>iii</sup>	0.82	2.06	2.761 (2)	143
O3—H3 $\cdots$ O7 <sup>iv</sup>	0.82	1.89	2.704 (2)	171
O4—H4 $\cdots$ O2 <sup>i</sup>	0.82	2.09	2.768 (2)	140
O4—H4 $\cdots$ O5 <sup>i</sup>	0.82	2.46	2.877 (2)	112
O5—H5 $\cdots$ O1 <sup>v</sup>	0.82	2.56	2.931 (2)	109
O5—H5 $\cdots$ O4 <sup>v</sup>	0.82	2.11	2.897 (2)	161

---

O5—H5···O1 <sup>i</sup>	0.82	2.35	2.748 (2)	110
O6—H6···O3 <sup>vi</sup>	0.82	1.97	2.769 (2)	163
O7—H7A···O4 <sup>vi</sup>	0.96	2.05	2.877 (2)	143
O7—H7A···O6 <sup>vi</sup>	0.96	2.40	3.211 (2)	142
O7—H7B···O5	0.95	1.96	2.916 (2)	175

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