



Crystal structure of β -D,L-fructose

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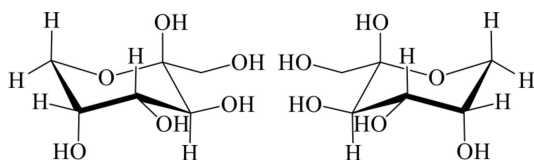
The title compound, $C_6H_{12}O_6$, was crystallized from an aqueous solution of equimolar mixture of D- and L-fructose (1,3,4,5,6-pentahydroxyhexan-2-one, *arabino*-hexulose or levulose), and it was confirmed that D-fructose (or L-fructose) formed β -pyranose with a 2C_5 (or 5C_2) conformation. In the crystal, two O—H...O hydrogen bonds between the hydroxy groups at the C-1 and C-3 positions, and at the C-4 and C-5 positions connect homochiral molecules into a column along the *a* axis. The columns are linked by other O—H...O hydrogen bonds between D- and L-fructose molecules, forming a three-dimensional network.

Keywords: crystal structure; hydrogen bonding; racemic compound; rare sugar.

CCDC reference: 1422317

1. Related literature

For crystal structures of chiral β -D-fructose, racemic β -D,L-allose and racemic β -D,L-psicose, see: Kanters *et al.* (1977); Ishii, Senoo *et al.* (2015); Ishii, Sakane *et al.* (2015), respectively. For the synthesis of chiral L-fructose, see: Itoh & Izumori (1996).



2. Experimental

2.1. Crystal data

$C_6H_{12}O_6$
 $M_r = 180.16$
Triclinic, $P\bar{1}$
 $a = 5.43124$ (19) Å
 $b = 7.2727$ (3) Å
 $c = 10.1342$ (4) Å
 $\alpha = 69.120$ (2)°
 $\beta = 83.907$ (2)°
 $\gamma = 78.381$ (2)°
 $V = 366.09$ (2) Å³
 $Z = 2$
Cu $K\alpha$ radiation
 $\mu = 1.30$ mm⁻¹
 $T = 296$ K
 $0.10 \times 0.10 \times 0.10$ mm

2.2. Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (ABSCOR; Rigaku, 1995)
 $T_{\min} = 0.729$, $T_{\max} = 0.878$
6710 measured reflections
1329 independent reflections
1211 reflections with $F^2 > 2.0\sigma(F^2)$
 $R_{\text{int}} = 0.079$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.08$
1329 reflections
115 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.32$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

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

| D—H...A | D—H | H...A | D...A | D—H...A |
|----------------------------|------|-------|-------------|---------|
| O1—H1A...O3 ⁱ | 0.82 | 2.28 | 2.9202 (14) | 135 |
| O2—H2A...O1 ⁱⁱ | 0.82 | 1.93 | 2.7224 (13) | 161 |
| O3—H3A...O4 ⁱⁱⁱ | 0.82 | 1.96 | 2.7831 (18) | 177 |
| O4—H4A...O5 ^{iv} | 0.82 | 2.01 | 2.7893 (13) | 158 |
| O5—H5A...O4 ^v | 0.82 | 2.05 | 2.8431 (12) | 163 |

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

Data collection: *RAPID-AUTO* (Rigaku, 2009); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR2011* (Burla *et al.*, 2012); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *CrystalStructure* (Rigaku, 2014); software used to prepare material for publication: *CrystalStructure*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5416).

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supporting information

Acta Cryst. (2015). E71, o719–o720 [doi:10.1107/S2056989015016503]

Crystal structure of β -D,L-fructose

Tomohiko Ishii, Tatsuya Senoo, Akihide Yoshihara, Kazuhiro Fukada and Genta Sakane

S1. Comment

Fructose, especially in *D*-fructose, is one of the most famous, fundamental and important monosaccharides in sugar family, and has been under intense investigation. On the other hand, *L*-fructose is classified into a rare sugar, and hardly exists in nature. In this study we investigate to create a novel racemic single-crystal including these *D*- and *L*-fructoses together with the ratio of 1: 1. The space group is triclinic $P\bar{1}$ ($Z = 2$), which is significantly different from our previous reports of the racemic β -*D,L*-allose (monoclinic $P2_1/c$, $Z = 4$; Ishii, Senoo *et al.*, 2015) and psicose (orthorhombic $Pna2_1$, $Z = 4$; Ishii, Sakane *et al.*, 2015). In the unit cell, the *D*- and *L*-molecules are located with the heterochiral hydrogen bonding networks (O3—H3A \cdots O4). As shown in Fig. 2, two homochiral hydrogen bonding networks (O1—H1A \cdots O3 and O4—H4A \cdots O5) have also been observed along to the *a*-axis. Additional two heterochiral hydrogen bonds (O2—H2A \cdots O1 and O5—H5A \cdots O4) are also confirmed (Fig. 3).

S2. Experimental

D-Fructose was purchased from Wako Pure Chemical Industries. *L*-Fructose was prepared from *L*-psicose by enzymatic epimerization using *D*-tagatose 3-epimerase (Itoh & Izumori, 1996). *D*-Fructose and *L*-fructose were mixed in equal amount and dissolved in hot water to give a 70 wt% solution. And these samples were kept at room temperature. After one day, small single crystals were obtained in a hermetically sealed test tube.

S3. Refinement

H atoms bounded to methine-type C (H3B, H4B, H5B) and methylene-type C (H1B, H1C, H6A, H6B) were positioned geometrically with C—H = 0.98 and 0.97 Å, respectively, and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms bounded to O (H1A, H2A, H3A, H4A, H5A) were positioned geometrically (O—H = 0.82 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$, allowing for free rotation of the OH groups.

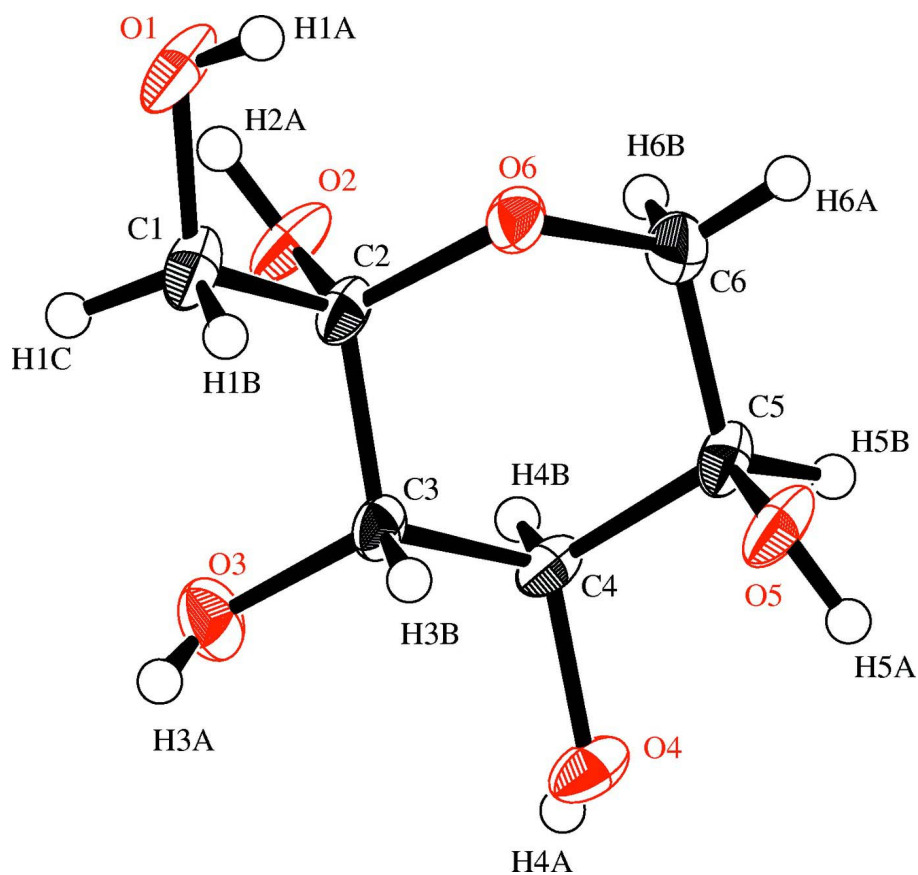


Figure 1

ORTEP view of the title compound with the atom-labeling scheme. The thermal ellipsoids of all non-hydrogen atoms are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

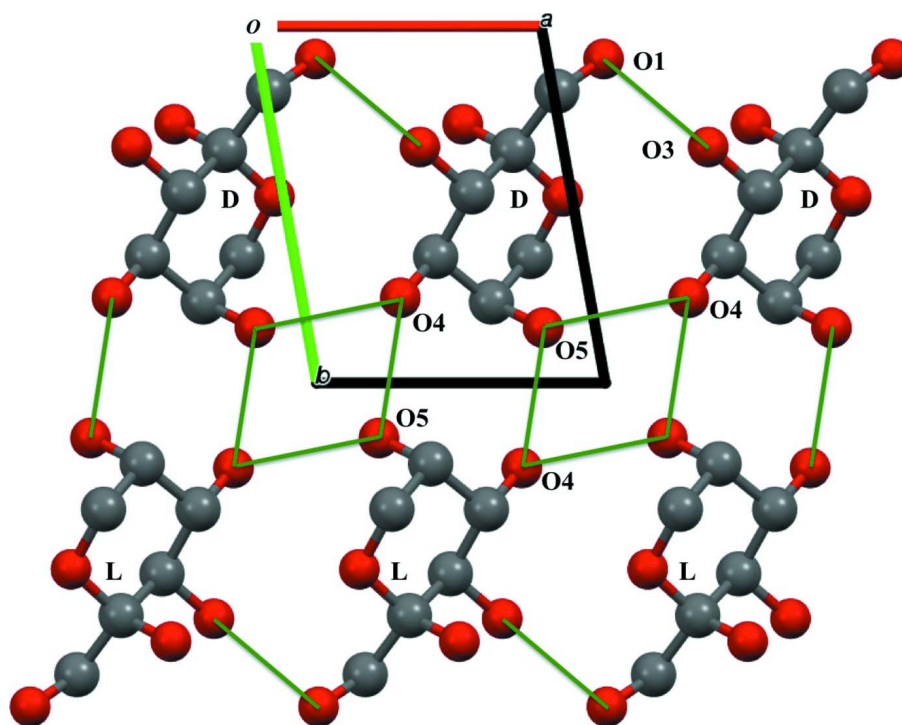
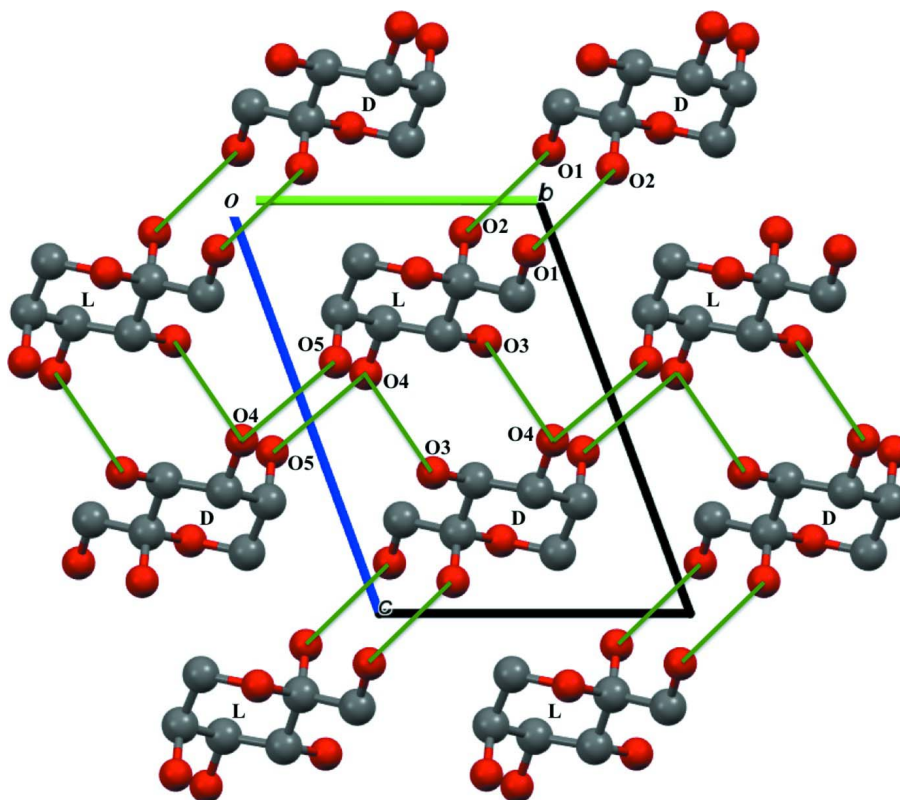


Figure 2

Part of the packing diagram of the title compound viewed down the *c*-axis, showing the hydrogen-bonding network (green solid lines).

**Figure 3**

Part of the packing diagram of the title compound viewed down the *a*-axis, showing the hydrogen-bonding network (green solid lines).

1,3,4,5,6-Pentahydroxyhexan-2-one

Crystal data

$C_6H_{12}O_6$

$M_r = 180.16$

Triclinic, $P\bar{1}$

$a = 5.43124 (19) \text{ \AA}$

$b = 7.2727 (3) \text{ \AA}$

$c = 10.1342 (4) \text{ \AA}$

$\alpha = 69.120 (2)^\circ$

$\beta = 83.907 (2)^\circ$

$\gamma = 78.381 (2)^\circ$

$V = 366.09 (2) \text{ \AA}^3$

$Z = 2$

$F(000) = 192.00$

$D_x = 1.634 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54187 \text{ \AA}$

Cell parameters from 4534 reflections

$\theta = 4.7\text{--}68.4^\circ$

$\mu = 1.30 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colorless

$0.10 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Rigaku R-AXIS RAPID
diffractometer

Detector resolution: $10.000 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*ABSCOR*; Rigaku, 1995)

$T_{\min} = 0.729$, $T_{\max} = 0.878$

6710 measured reflections

1329 independent reflections

1211 reflections with $F^2 > 2.0\sigma(F^2)$

$R_{\text{int}} = 0.079$

$\theta_{\max} = 68.2^\circ$, $\theta_{\min} = 4.7^\circ$

$h = -6 \rightarrow 6$

$k = -8 \rightarrow 8$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.095$
 $S = 1.08$
 1329 reflections
 115 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
 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.1404P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL2013* (Sheldrick,
 2015)
 Extinction coefficient: 0.125 (6)

Special details

Refinement. Refinement was performed using all reflections. The weighted R -factor (wR) and goodness of fit (S) are based on F^2 . R -factor (gt) are based on F . The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R -factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| O1 | 1.19555 (19) | 0.09152 (15) | 0.87814 (12) | 0.0325 (3) |
| O2 | 0.66671 (18) | 0.27440 (15) | 0.92243 (11) | 0.0287 (3) |
| O3 | 0.50386 (19) | 0.33842 (16) | 0.65941 (12) | 0.0294 (3) |
| O4 | 0.34223 (18) | 0.76120 (15) | 0.58108 (11) | 0.0264 (3) |
| O5 | 0.81908 (18) | 0.84537 (14) | 0.60893 (12) | 0.0290 (3) |
| O6 | 0.96847 (17) | 0.47716 (14) | 0.82413 (11) | 0.0223 (3) |
| C1 | 1.0136 (3) | 0.1818 (2) | 0.77318 (17) | 0.0265 (4) |
| C2 | 0.8236 (2) | 0.34747 (19) | 0.80373 (15) | 0.0195 (3) |
| C3 | 0.6557 (2) | 0.46432 (19) | 0.67791 (15) | 0.0190 (3) |
| C4 | 0.4906 (3) | 0.6455 (2) | 0.70256 (15) | 0.0200 (3) |
| C5 | 0.6558 (3) | 0.77295 (19) | 0.72899 (16) | 0.0223 (3) |
| C6 | 0.8182 (3) | 0.6457 (2) | 0.85210 (16) | 0.0254 (4) |
| H1A | 1.30779 | 0.15812 | 0.86062 | 0.0390* |
| H1C | 0.92594 | 0.08085 | 0.76811 | 0.0318* |
| H1B | 1.0976 | 0.23653 | 0.68208 | 0.0318* |
| H2A | 0.74136 | 0.16995 | 0.97716 | 0.0345* |
| H3A | 0.55367 | 0.31042 | 0.58847 | 0.0353* |
| H3B | 0.76216 | 0.5097 | 0.59244 | 0.0227* |
| H4A | 0.19353 | 0.75392 | 0.60178 | 0.0317* |
| H4B | 0.37832 | 0.60041 | 0.78545 | 0.0240* |
| H5A | 0.74552 | 0.94902 | 0.55285 | 0.0348* |
| H5B | 0.55062 | 0.8858 | 0.75058 | 0.0268* |
| H6A | 0.92669 | 0.72507 | 0.86923 | 0.0305* |
| H6B | 0.71231 | 0.59981 | 0.93633 | 0.0305* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|------------|
| O1 | 0.0202 (6) | 0.0153 (5) | 0.0465 (8) | -0.0003 (4) | -0.0014 (5) | 0.0066 (5) |

| | | | | | | |
|----|------------|------------|------------|-------------|-------------|-------------|
| O2 | 0.0251 (6) | 0.0190 (5) | 0.0265 (6) | 0.0006 (4) | 0.0037 (5) | 0.0074 (4) |
| O3 | 0.0292 (6) | 0.0280 (6) | 0.0361 (7) | -0.0153 (5) | -0.0002 (5) | -0.0118 (5) |
| O4 | 0.0160 (5) | 0.0236 (6) | 0.0298 (6) | -0.0001 (4) | -0.0051 (4) | 0.0019 (5) |
| O5 | 0.0208 (5) | 0.0154 (5) | 0.0385 (7) | -0.0035 (4) | -0.0014 (5) | 0.0060 (5) |
| O6 | 0.0186 (5) | 0.0164 (5) | 0.0309 (6) | -0.0004 (4) | -0.0061 (4) | -0.0071 (4) |
| C1 | 0.0223 (7) | 0.0144 (7) | 0.0389 (9) | -0.0022 (6) | -0.0001 (6) | -0.0054 (6) |
| C2 | 0.0176 (7) | 0.0123 (6) | 0.0242 (8) | -0.0039 (5) | 0.0003 (6) | -0.0007 (5) |
| C3 | 0.0177 (7) | 0.0140 (7) | 0.0233 (8) | -0.0070 (5) | -0.0006 (6) | -0.0020 (6) |
| C4 | 0.0158 (7) | 0.0163 (7) | 0.0213 (8) | -0.0018 (5) | -0.0019 (6) | 0.0013 (6) |
| C5 | 0.0198 (7) | 0.0131 (7) | 0.0315 (9) | -0.0005 (5) | -0.0002 (6) | -0.0060 (6) |
| C6 | 0.0272 (8) | 0.0199 (7) | 0.0304 (8) | -0.0015 (6) | -0.0044 (6) | -0.0107 (6) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|------------|---------|
| O1—C1 | 1.4153 (19) | O1—H1A | 0.820 |
| O2—C2 | 1.4017 (16) | O2—H2A | 0.820 |
| O3—C3 | 1.419 (2) | O3—H3A | 0.820 |
| O4—C4 | 1.4395 (16) | O4—H4A | 0.820 |
| O5—C5 | 1.4305 (17) | O5—H5A | 0.820 |
| O6—C2 | 1.423 (2) | C1—H1C | 0.970 |
| O6—C6 | 1.4298 (19) | C1—H1B | 0.970 |
| C1—C2 | 1.520 (2) | C3—H3B | 0.980 |
| C2—C3 | 1.5304 (19) | C4—H4B | 0.980 |
| C3—C4 | 1.521 (2) | C5—H5B | 0.980 |
| C4—C5 | 1.517 (2) | C6—H6A | 0.970 |
| C5—C6 | 1.5075 (19) | C6—H6B | 0.970 |
| C2—O6—C6 | 113.25 (10) | C4—O4—H4A | 109.467 |
| O1—C1—C2 | 111.97 (14) | C5—O5—H5A | 109.473 |
| O2—C2—O6 | 111.23 (13) | O1—C1—H1C | 109.215 |
| O2—C2—C1 | 112.44 (10) | O1—C1—H1B | 109.220 |
| O2—C2—C3 | 107.69 (10) | C2—C1—H1C | 109.218 |
| O6—C2—C1 | 105.55 (11) | C2—C1—H1B | 109.221 |
| O6—C2—C3 | 109.06 (10) | H1C—C1—H1B | 107.907 |
| C1—C2—C3 | 110.86 (13) | O3—C3—H3B | 109.026 |
| O3—C3—C2 | 109.62 (10) | C2—C3—H3B | 109.028 |
| O3—C3—C4 | 110.08 (11) | C4—C3—H3B | 109.024 |
| C2—C3—C4 | 110.04 (13) | O4—C4—H4B | 109.255 |
| O4—C4—C3 | 110.05 (13) | C3—C4—H4B | 109.253 |
| O4—C4—C5 | 109.74 (10) | C5—C4—H4B | 109.254 |
| C3—C4—C5 | 109.27 (11) | O5—C5—H5B | 109.808 |
| O5—C5—C4 | 110.97 (14) | C4—C5—H5B | 109.810 |
| O5—C5—C6 | 107.71 (11) | C6—C5—H5B | 109.807 |
| C4—C5—C6 | 108.69 (11) | O6—C6—H6A | 109.512 |
| O6—C6—C5 | 110.67 (14) | O6—C6—H6B | 109.511 |
| C1—O1—H1A | 109.469 | C5—C6—H6A | 109.511 |
| C2—O2—H2A | 109.478 | C5—C6—H6B | 109.513 |
| C3—O3—H3A | 109.476 | H6A—C6—H6B | 108.082 |

| | | | |
|-------------|--------------|-------------|--------------|
| C2—O6—C6—C5 | -61.73 (13) | C1—C2—C3—C4 | -172.62 (10) |
| C6—O6—C2—O2 | -58.74 (12) | O3—C3—C4—O4 | -62.10 (13) |
| C6—O6—C2—C1 | 179.03 (9) | O3—C3—C4—C5 | 177.33 (9) |
| C6—O6—C2—C3 | 59.88 (13) | C2—C3—C4—O4 | 176.97 (10) |
| O1—C1—C2—O2 | -68.49 (15) | C2—C3—C4—C5 | 56.41 (12) |
| O1—C1—C2—O6 | 52.95 (13) | O4—C4—C5—O5 | -58.98 (13) |
| O1—C1—C2—C3 | 170.90 (9) | O4—C4—C5—C6 | -177.25 (10) |
| O2—C2—C3—O3 | -57.21 (15) | C3—C4—C5—O5 | 61.77 (12) |
| O2—C2—C3—C4 | 63.99 (14) | C3—C4—C5—C6 | -56.50 (14) |
| O6—C2—C3—O3 | -178.02 (10) | O5—C5—C6—O6 | -61.97 (15) |
| O6—C2—C3—C4 | -56.82 (13) | C4—C5—C6—O6 | 58.34 (14) |
| C1—C2—C3—O3 | 66.18 (13) | | |

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 <i>A</i> ...O3 ⁱ | 0.82 | 2.28 | 2.9202 (14) | 135 |
| O2—H2 <i>A</i> ...O1 | 0.82 | 2.60 | 2.9721 (14) | 110 |
| O2—H2 <i>A</i> ...O1 ⁱⁱ | 0.82 | 1.93 | 2.7224 (13) | 161 |
| O3—H3 <i>A</i> ...O4 ⁱⁱⁱ | 0.82 | 1.96 | 2.7831 (18) | 177 |
| O4—H4 <i>A</i> ...O5 ^{iv} | 0.82 | 2.01 | 2.7893 (13) | 158 |
| O5—H5 <i>A</i> ...O4 ^v | 0.82 | 2.05 | 2.8431 (12) | 163 |

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