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Biphenyl-3,3',4,4'-tetracarboxylic acid dihydrate

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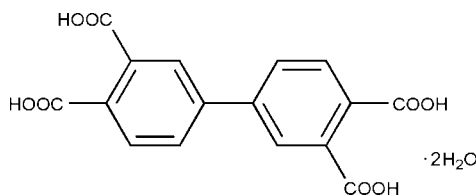
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.033; wR factor = 0.090; data-to-parameter ratio = 11.4.

The asymmetric unit of the title compound, $\text{C}_{16}\text{H}_{10}\text{O}_8 \cdot 2\text{H}_2\text{O}$, contains one-half of the centrosymmetric organic molecule and one water molecule. The dihedral angles between the carboxylate groups and the adjacent phenyl ring are 71.31 (3) and 16.67 (3)°, while the carboxylate groups are oriented at a dihedral angle of 72.01 (3)°. In the crystal structure, intermolecular $\text{O}-\text{H} \cdots \text{O}$ and bifurcated $\text{O}-\text{H} \cdots (\text{O}, \text{O})$ hydrogen bonds link the molecules to form a three-dimensional supramolecular network.

Related literature

For general background, see: Du *et al.* (2006, 2007); Desiraju (2003); Yaghi *et al.* (2003); Li *et al.* (2008). For a related structure, see: Coles *et al.* (2002). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{10}\text{O}_8 \cdot 2\text{H}_2\text{O}$ $M_r = 366.27$ Triclinic, $P\bar{1}$ $a = 5.5858$ (16) Å $b = 6.6618$ (19) Å $c = 11.086$ (3) Å $\alpha = 93.126$ (5)° $\beta = 91.404$ (4)° $\gamma = 109.110$ (4)° $V = 388.81$ (19) Å³ $Z = 1$
Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹ $T = 296$ (2) K
 $0.28 \times 0.24 \times 0.22$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2001)

 $T_{\min} = 0.943$, $T_{\max} = 0.973$ 1992 measured reflections
1362 independent reflections
1222 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.033$ $wR(F^2) = 0.090$ $S = 1.08$

1362 reflections

120 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.16$ e Å⁻³
 $\Delta\rho_{\min} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H} \cdots A$ | $D-\text{H}$ | $\text{H} \cdots A$ | $D \cdots A$ | $D-\text{H} \cdots A$ |
|--|--------------|---------------------|--------------|-----------------------|
| $\text{O1}-\text{H1} \cdots \text{O3}^{\text{i}}$ | 0.82 | 1.88 | 2.683 (3) | 168 |
| $\text{O4}-\text{H4} \cdots \text{O5}^{\text{ii}}$ | 0.82 | 1.79 | 2.599 (3) | 169 |
| $\text{O5}-\text{H5A} \cdots \text{O3}^{\text{iii}}$ | 0.85 | 2.45 | 3.129 (3) | 137 |
| $\text{O5}-\text{H5A} \cdots \text{O2}^{\text{iv}}$ | 0.85 | 2.22 | 2.892 (3) | 136 |
| $\text{O5}-\text{H5B} \cdots \text{O2}$ | 0.85 | 1.95 | 2.801 (3) | 175 |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

We acknowledge Tianjin Normal University for their active cooperation in this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2568).

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supporting information

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Biphenyl-3,3',4,4'-tetracarboxylic acid dihydrate

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S1. Comment

Non-covalent intermolecular interactions, mainly hydrogen bonding and aromatic stacking, play the key role to perfectly project and regulate the detailed crystal packing of supramolecular materials (Du *et al.*, 2006; Desiraju, 2003). Aromatic carboxylates have also been proved to be effective building blocks in constructing various architectures (Yaghi *et al.*, 2003; Li *et al.*, 2008; Du *et al.*, 2007). However, the crystal structures of these polycarboxyl acids themselves are rarely reported (Coles *et al.*, 2002). We synthesized the title compound under hydrothermal condition, and report herein its crystal structure.

The asymmetric unit of the title compound (Fig. 1) contains one-half of the centrosymmetric molecule and one water molecule. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The intramolecular O—H \cdots O hydrogen bonding (Table 1) of the carboxylate O2 atom to the water molecule may cause to a small difference in the C1=O2 [1.2031 (18) Å] and C8=O3 [1.2156 (17) Å] double bonds of the carboxylate groups. The dihedral angles between the planar carboxylate groups (O1/C1/O2) and (O3/C8/O4) and the adjacent phenyl ring A (C2–C7) are 71.31 (3)° and 16.67 (3)°, respectively, while the carboxylate groups are oriented at a dihedral angle of 72.01 (3)°.

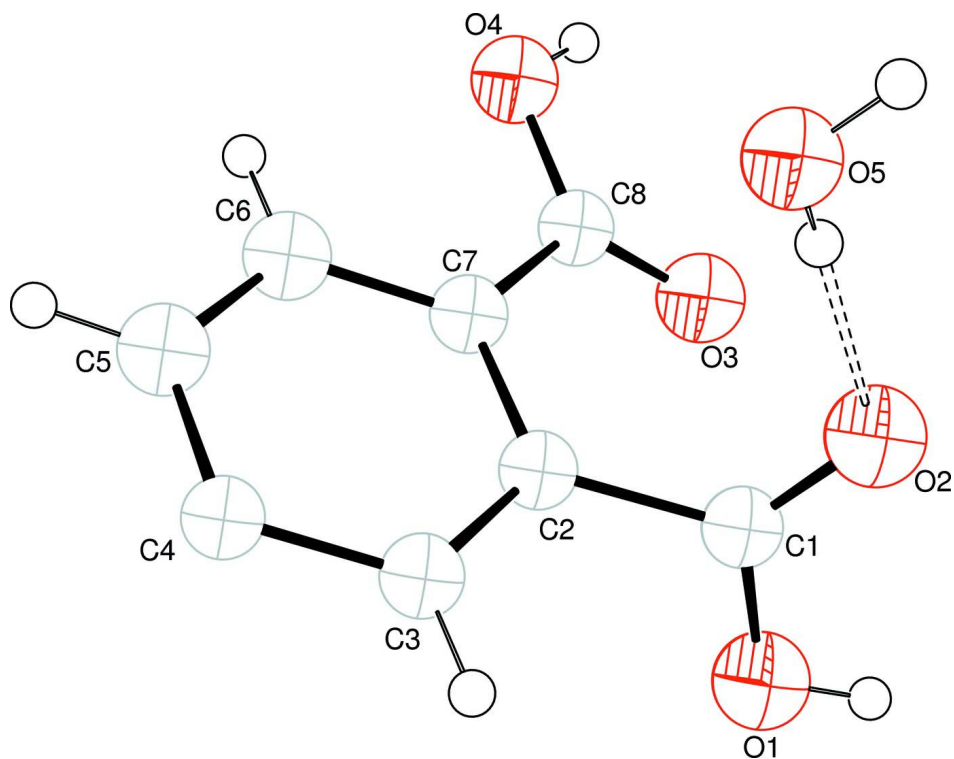
In the crystal structure, intra- and intermolecular O—H \cdots O hydrogen bonds (Table 1) link the molecules to form a 3-D supramolecular network. Firstly, the O1—H1 \cdots O3 hydrogen bonds between the carboxyl units connect them into a 1-D zigzag chain (Fig. 2). Then, water molecules play the acceptor and donor roles, respectively, to participate in the formation of O4—H4 \cdots O5 and O5—H5B \cdots O2 hydrogen bonds, giving rise to a 2-D supramolecular layer (Fig. 3). Finally, water molecules further act as donors to interconnect the supramolecular layers into 3-D networks with O5—H5A \cdots O3 and O5—H5A \cdots O2 hydrogen bonds (Fig. 4).

S2. Experimental

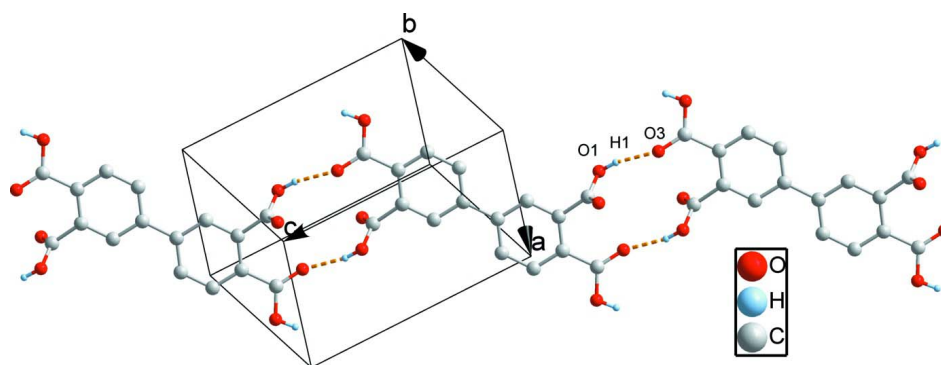
The title compound was recrystallized from the mixture of H₂O (15 ml) and HNO₃ (0.5 ml) under the hydrothermal conditions on cooling from 393 K. Colorless block shaped crystals were obtained at room temperature.

S3. Refinement

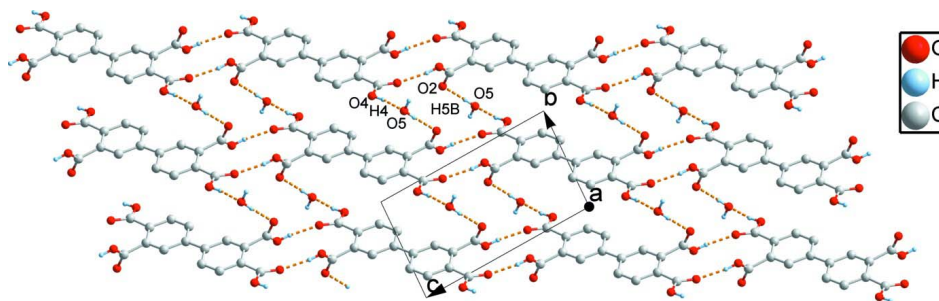
H atoms were positioned geometrically, with O—H = 0.82 Å (for OH), 0.85 Å (for OH₂) and C—H = 0.93 Å for aromatic H, respectively, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$, where $x = 1.2$ for aromatic H and $x = 1.5$ for all other H atoms.

**Figure 1**

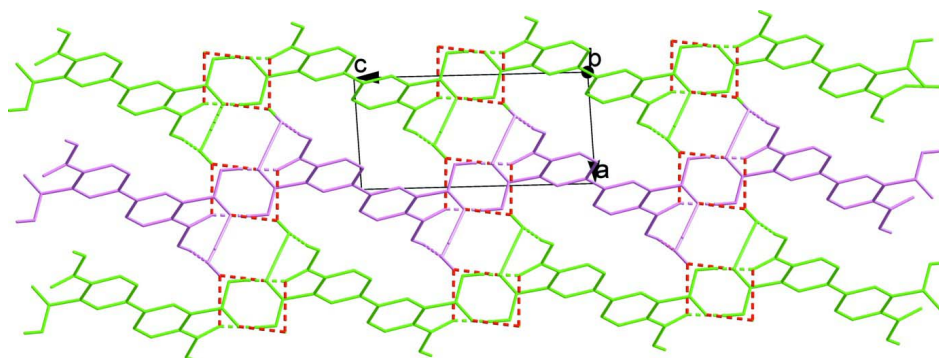
The asymmetric unit of the title molecule with the atom-numbering scheme. Hydrogen bond is shown as dashed line.

**Figure 2**

The one dimensional hydrogen bonded chain showing hydrogen bonds between the carboxyl units. Other H atoms have been omitted for clarity.


Figure 3

The two dimensional hydrogen-bonding layered structure along [011] direction.


Figure 4

The three dimensional hydrogen-bonded supramolecular network. The adjacent layers are shown in green and rose colors, and interlayer hydrogen bonds are shown as red dashed lines.

Biphenyl-3,3',4,4'-tetracarboxylic acid dihydrate

Crystal data

$C_{16}H_{10}O_8 \cdot 2H_2O$

$M_r = 366.27$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 5.5858 (16) \text{ \AA}$

$b = 6.6618 (19) \text{ \AA}$

$c = 11.086 (3) \text{ \AA}$

$\alpha = 93.126 (5)^\circ$

$\beta = 91.404 (4)^\circ$

$\gamma = 109.110 (4)^\circ$

$V = 388.81 (19) \text{ \AA}^3$

$Z = 1$

$F(000) = 190$

$D_x = 1.564 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1245 reflections

$\theta = 3.2\text{--}27.8^\circ$

$\mu = 0.13 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Block, colourless

$0.28 \times 0.24 \times 0.22 \text{ mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2001)

$T_{\min} = 0.943$, $T_{\max} = 0.973$

1992 measured reflections

1362 independent reflections

1222 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.008$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -6 \rightarrow 6$

$k = -7 \rightarrow 7$

$l = -9 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.090$
 $S = 1.08$
 1362 reflections
 120 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
 $w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.0831P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|---------------|----------------------------------|
| O1 | 1.2031 (2) | 0.8456 (2) | 0.40618 (9) | 0.0535 (3) |
| H1 | 1.2130 | 0.8530 | 0.4803 | 0.080* |
| O2 | 0.7989 (2) | 0.6702 (2) | 0.43405 (9) | 0.0528 (3) |
| O3 | 0.8059 (2) | 1.09274 (19) | 0.35300 (9) | 0.0501 (3) |
| O4 | 0.5352 (2) | 1.08299 (18) | 0.20056 (9) | 0.0473 (3) |
| H4 | 0.4952 | 1.1658 | 0.2468 | 0.071* |
| O5 | 0.3760 (2) | 0.35552 (17) | 0.32212 (8) | 0.0433 (3) |
| H5A | 0.2608 | 0.2949 | 0.3695 | 0.065* |
| H5B | 0.4996 | 0.4558 | 0.3561 | 0.065* |
| C1 | 0.9670 (3) | 0.7526 (2) | 0.36863 (12) | 0.0355 (3) |
| C2 | 0.9236 (2) | 0.7450 (2) | 0.23342 (11) | 0.0327 (3) |
| C3 | 1.0093 (3) | 0.6076 (2) | 0.16299 (12) | 0.0352 (3) |
| H3 | 1.1062 | 0.5354 | 0.1992 | 0.042* |
| C4 | 0.9533 (3) | 0.5744 (2) | 0.03778 (11) | 0.0329 (3) |
| C5 | 0.8074 (3) | 0.6846 (3) | -0.01240 (12) | 0.0426 (4) |
| H5 | 0.7650 | 0.6639 | -0.0949 | 0.051* |
| C6 | 0.7238 (3) | 0.8241 (3) | 0.05735 (12) | 0.0423 (4) |
| H6 | 0.6272 | 0.8963 | 0.0210 | 0.051* |
| C7 | 0.7815 (3) | 0.8586 (2) | 0.18104 (11) | 0.0341 (3) |
| C8 | 0.7072 (3) | 1.0210 (2) | 0.25400 (12) | 0.0349 (3) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|------------|-------------|-------------|
| O1 | 0.0436 (6) | 0.0853 (9) | 0.0246 (5) | 0.0135 (6) | -0.0053 (4) | -0.0055 (5) |

| | | | | | | |
|----|-------------|------------|------------|------------|-------------|-------------|
| O2 | 0.0502 (7) | 0.0738 (8) | 0.0232 (5) | 0.0062 (6) | 0.0020 (5) | -0.0023 (5) |
| O3 | 0.0567 (7) | 0.0651 (7) | 0.0316 (6) | 0.0290 (6) | -0.0118 (5) | -0.0202 (5) |
| O4 | 0.0621 (7) | 0.0599 (7) | 0.0298 (5) | 0.0363 (6) | -0.0068 (5) | -0.0100 (5) |
| O5 | 0.0480 (6) | 0.0484 (6) | 0.0323 (5) | 0.0154 (5) | 0.0033 (4) | -0.0044 (4) |
| C1 | 0.0423 (8) | 0.0418 (8) | 0.0231 (7) | 0.0164 (6) | -0.0016 (6) | -0.0054 (6) |
| C2 | 0.0342 (7) | 0.0396 (7) | 0.0216 (6) | 0.0095 (6) | -0.0006 (5) | -0.0030 (5) |
| C3 | 0.0408 (8) | 0.0430 (8) | 0.0240 (7) | 0.0175 (6) | -0.0019 (5) | -0.0016 (5) |
| C4 | 0.0375 (7) | 0.0372 (7) | 0.0226 (6) | 0.0114 (6) | -0.0003 (5) | -0.0032 (5) |
| C5 | 0.0589 (10) | 0.0540 (9) | 0.0202 (7) | 0.0276 (8) | -0.0063 (6) | -0.0065 (6) |
| C6 | 0.0559 (9) | 0.0521 (9) | 0.0265 (7) | 0.0297 (8) | -0.0055 (6) | -0.0043 (6) |
| C7 | 0.0373 (7) | 0.0390 (7) | 0.0244 (7) | 0.0113 (6) | -0.0004 (5) | -0.0036 (6) |
| C8 | 0.0381 (7) | 0.0403 (8) | 0.0250 (7) | 0.0120 (6) | 0.0007 (6) | -0.0025 (6) |

Geometric parameters (Å, °)

| | | | |
|-----------------------|--------------|-----------------------|--------------|
| O1—C1 | 1.3065 (18) | C2—C7 | 1.399 (2) |
| O1—H1 | 0.8200 | C3—C4 | 1.4047 (19) |
| O2—C1 | 1.2031 (18) | C3—H3 | 0.9300 |
| O3—C8 | 1.2156 (17) | C4—C5 | 1.388 (2) |
| O4—C8 | 1.3052 (17) | C4—C4 ⁱ | 1.492 (3) |
| O4—H4 | 0.8200 | C5—C6 | 1.380 (2) |
| O5—H5A | 0.8500 | C5—H5 | 0.9300 |
| O5—H5B | 0.8502 | C6—C7 | 1.3901 (19) |
| C1—C2 | 1.5080 (18) | C6—H6 | 0.9300 |
| C2—C3 | 1.380 (2) | C7—C8 | 1.4874 (19) |
| C1—O1—H1 | 109.5 | C3—C4—C4 ⁱ | 121.05 (15) |
| C8—O4—H4 | 109.5 | C6—C5—C4 | 121.45 (13) |
| H5A—O5—H5B | 114.3 | C6—C5—H5 | 119.3 |
| O2—C1—O1 | 123.81 (12) | C4—C5—H5 | 119.3 |
| O2—C1—C2 | 122.09 (13) | C5—C6—C7 | 121.10 (14) |
| O1—C1—C2 | 114.00 (12) | C5—C6—H6 | 119.5 |
| C3—C2—C7 | 120.53 (12) | C7—C6—H6 | 119.5 |
| C3—C2—C1 | 117.84 (12) | C6—C7—C2 | 118.11 (13) |
| C7—C2—C1 | 121.39 (12) | C6—C7—C8 | 120.75 (13) |
| C2—C3—C4 | 121.34 (13) | C2—C7—C8 | 121.04 (12) |
| C2—C3—H3 | 119.3 | O3—C8—O4 | 123.78 (13) |
| C4—C3—H3 | 119.3 | O3—C8—C7 | 122.06 (13) |
| C5—C4—C3 | 117.43 (13) | O4—C8—C7 | 114.11 (11) |
| C5—C4—C4 ⁱ | 121.52 (14) | | |
| O2—C1—C2—C3 | -104.45 (17) | C5—C6—C7—C2 | -1.1 (2) |
| O1—C1—C2—C3 | 72.09 (17) | C5—C6—C7—C8 | 175.44 (14) |
| O2—C1—C2—C7 | 70.0 (2) | C3—C2—C7—C6 | 1.8 (2) |
| O1—C1—C2—C7 | -113.51 (16) | C1—C2—C7—C6 | -172.41 (13) |
| C7—C2—C3—C4 | -1.2 (2) | C3—C2—C7—C8 | -174.64 (12) |
| C1—C2—C3—C4 | 173.25 (13) | C1—C2—C7—C8 | 11.1 (2) |
| C2—C3—C4—C5 | -0.3 (2) | C6—C7—C8—O3 | -161.23 (14) |

| | | | |
|---------------------------|--------------|-------------|--------------|
| C2—C3—C4—C4 ⁱ | -179.98 (15) | C2—C7—C8—O3 | 15.2 (2) |
| C3—C4—C5—C6 | 1.1 (2) | C6—C7—C8—O4 | 16.55 (19) |
| C4 ⁱ —C4—C5—C6 | -179.21 (16) | C2—C7—C8—O4 | -167.06 (13) |
| C4—C5—C6—C7 | -0.4 (3) | | |

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

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---------------------------|------------|--------------|--------------|----------------|
| O1—H1...O3 ⁱⁱ | 0.82 | 1.88 | 2.683 (3) | 168 |
| O4—H4...O5 ⁱⁱⁱ | 0.82 | 1.79 | 2.599 (3) | 169 |
| O5—H5A...O3 ^{iv} | 0.85 | 2.45 | 3.129 (3) | 137 |
| O5—H5A...O2 ^v | 0.85 | 2.22 | 2.892 (3) | 136 |
| O5—H5B...O2 | 0.85 | 1.95 | 2.801 (3) | 175 |

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