Crystal structure and Hirshfeld surface analysis of 4,4′-dimethoxybiphenyl-3,3′,5,5′-tetracarboxylic acid dihydrate

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In the crystal of the title compound, $C_{18}H_{14}O_{10} \cdot 2H_2O$, the arene rings of the biphenyl moiety are tilted at an angle of 24.3 (1)°, while the planes passing through the carboxyl groups are rotated at angles of 8.6 (1) and 7.7 (1)° out of the plane of the benzene ring to which they are attached. The crystal structure is essentially stabilized by O—H⋯O bonds. Here, the carboxyl groups of neighbouring host molecules are connected by cyclic $R_2^2(8)$ synthons, leading to the formation of a three-dimensional network. The water molecules in turn form helical supramolecular strands running in the direction of the crystallographic c-axis (chain-like water clusters). The second H atom of each water molecule provides a link to a methoxy O atom of the host molecule. A Hirshfeld surface analysis was performed to quantify the contributions of the different intermolecular interactions, indicating that the most important contributions to the crystal packing are from H⋯O/O⋯H (37.0%), H⋯H (26.3%), H⋯C/C⋯H (18.5%) and C⋯O/O⋯C (9.5%) interactions.

1. Chemical context

Our studies on the molecular recognition of mono- and oligosaccharides with artificial receptors led to the development of various acyclic (Mazik, 2009, 2012) and macrocyclic (Lippe & Mazik, 2013, 2015; Amrhein et al., 2016; Amrhein & Mazik, 2021; Leibiger et al., 2022) receptor architectures. Among the acyclic compounds, those with a central aromatic core carrying three or more functionalized side arms as recognition groups have proven to be effective carbohydrate receptors. Their binding properties can be fine-tuned by varying the structural subunits of these compounds. In this context, benzene (Stapf et al., 2020; Köhler et al., 2020, 2021; Kaiser et al., 2019), fluorene (Seidel & Mazik, 2020, 2023), diphenylmethane (Mazik & König, 2007; Mazik & Buthe, 2009; Koch et al., 2014) or biphenyl units (Mazik & König, 2006) were used as the central aromatic platform of the receptor structures. Representatives of the last mentioned receptors can be prepared, for example, on the basis of biphenyl-3,3′,5,5′-tetracarboxylic acid (Mazik & König, 2006). In this article we describe the crystal structure of the hydrate of 4,4′-dimethoxy-biphenyl-3,3′,5,5′-tetracarboxylic acid, which is also a valuable precursor for the synthesis of receptors with a biphenyl-based scaffold.
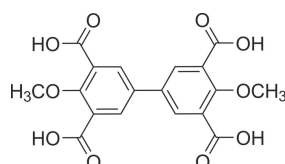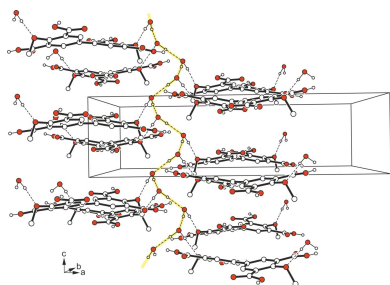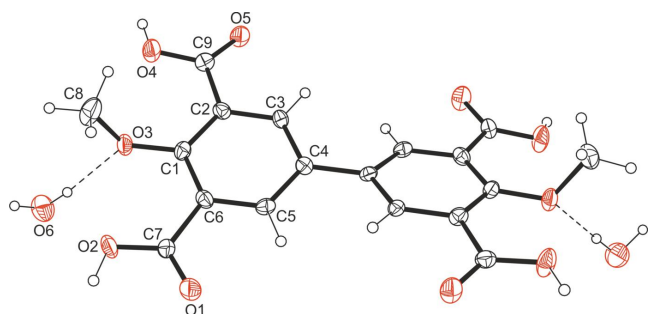
Figure 1
Perspective view (*ORTEP* diagram) including atom labeling of the 1:2 host–guest complex of the title molecule with water. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

2. Structural commentary

The title compound, $C_{18}H_{14}O_{10} \cdot 2H_2O$, crystallizes in the tetragonal space group $I4_1cd$ with one half [the second half is generated by the symmetry operation $1 - x$, $1 - y$, z] of the biphenyl-4,4′-dimethoxy-3,3′,5,5′-tetracarboxylic acid (host) molecule and one water molecule (guest) in the asymmetric unit of the cell. A perspective view of the 1:2 host–guest unit is shown in Fig. 1. The two benzene rings of the biphenyl moiety are twisted at an angle of 24.3 (1)°. The mean planes passing the carboxy groups are inclined at angles of 8.6 (1) and 7.7 (1)° with respect to the planes of the respective benzene rings. The bond lengths within the host molecule resemble those found in the crystal structure of biphenyl-3,3′,5,5′-tetracarboxylic acid (Coles *et al.*, 2002).

3. Supramolecular features and Hirshfeld surface analysis

The crystal structure is mainly stabilized by O—H···O bonds (Table 1). On the one hand, these hydrogen bonds contribute to t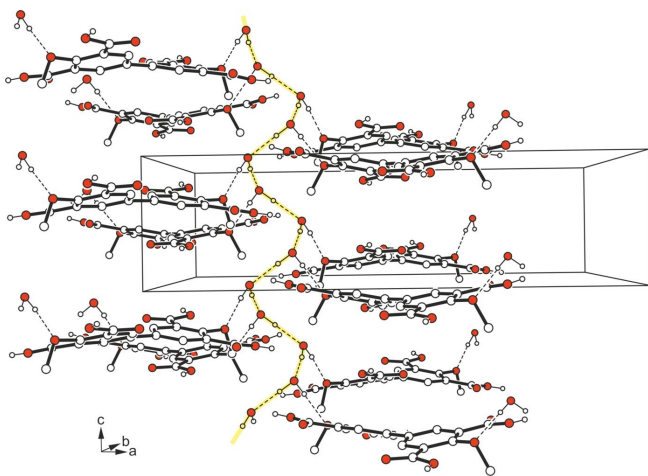he connection of the host molecules *via* cyclic synthons of the structure $R_2^2(8)$ (Etter *et al.*, 1990; Etter, 1991; Bernstein *et al.*, 1995), thus creating a three-dimensional cross-linking of these molecules. On the other hand, the water molecules in turn form infinite helical strands running in the *c*-axis direction (Fig. 2). The arrangement of the water molecules in this helical structure corresponds to the fourfold symmetry element (4_1 axis) of the crystal structure. The second H atom of the water molecule serves as a binding site for a hydrogen bond to the O atom of the methoxy group (Fig. 3). Taking the interactions between the water molecules into account, their arrangement could also be described as water clusters, which belong to the class of infinite chains (for nomenclature of water clusters, see: Infantes & Motherwell, 2002; Mascal *et al.*, 2006; for examples of other water clusters reported by our group, see: Rosin *et al.*, 2017). Furthermore, the H···*Cg* distances of 2.96 and 2.99 Å involving the hydrogen atoms H3 and H5 (symmetry operations: x, $1 - y$, $\frac{1}{2} + z$; $1 - x$, y, $-\frac{1}{2} + z$) indicate the presence of weak C—H···π interactions. A packing diagram of the title compound viewed along the *c*-axis direction is presented in Fig. 4.

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O2—H1$O2\cdots$O5[i]	0.88 (6)	1.80 (6)	2.663 (4)	166 (7)
O4—H1$O4\cdots$O1[ii]	0.88 (3)	1.74 (3)	2.611 (4)	174 (7)
O6—H1$O6\cdots$O6[iii]	0.91 (3)	1.86 (3)	2.768 (4)	173 (5)
O6—H2$O6\cdots$O3	0.90 (3)	2.04 (3)	2.941 (5)	174 (7)

Symmetry codes: (i) $-y + 1$, $-x + \frac{1}{2}$, $z - \frac{1}{4}$; (ii) $-y + \frac{1}{2}$, $-x + 1$, $z + \frac{1}{4}$; (iii) y, $-x + \frac{1}{2}$, $z + \frac{1}{4}$.

Figure 2
Part of the crystal structure of the title compound showing the helical strands of O—H···O-bonded water molecules running along the *c*-axis direction. Dashed lines represent hydrogen-bond interactions.
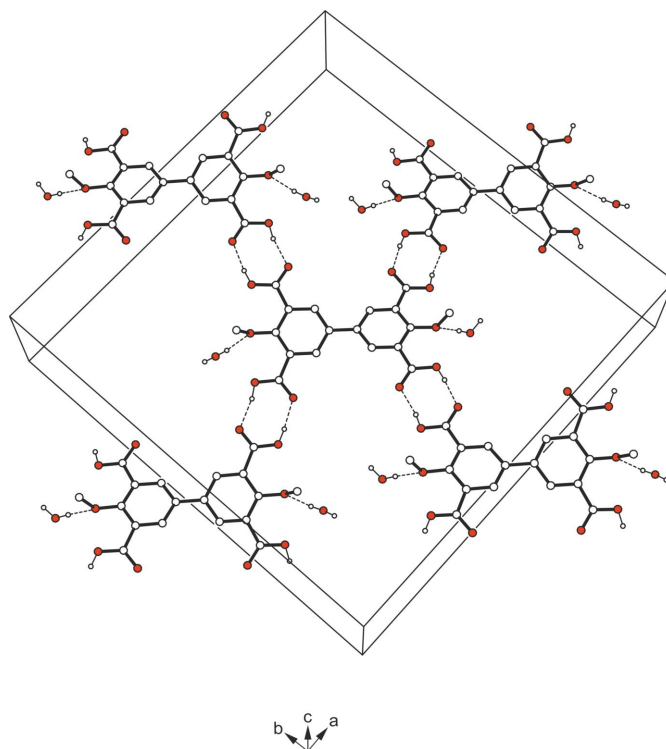

Figure 3
Part of the crystal structure of the title compound showing the mode of hydrogen bonding.
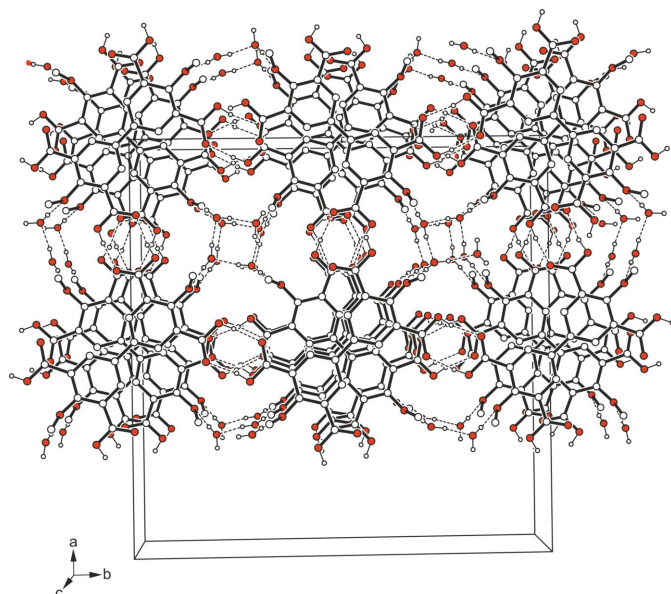
Figure 4
Packing diagram of the title compound viewed down the crystallographic *c*-axis. Dashed lines represent hydrogen-bond interactions.

In order to visualize and quantify intermolecular interactions a Hirshfeld surface analysis (Spackman & Byrom, 1997; McKinnon *et al.*, 1998) was performed using *Crystal-Explorer* (Version 21.5, Spackman *et al.*, 2021). The Hirshfeld surface mapped over d_{norm} using a standard surface resolution with a fixed colour scale of −0.7603 to 1.5689 a.u. is shown in Fig. 5. The red spots on the d_{norm} surface represent O—H⋯O hydrogen bonds. The full two-dimensional fingerprint plots
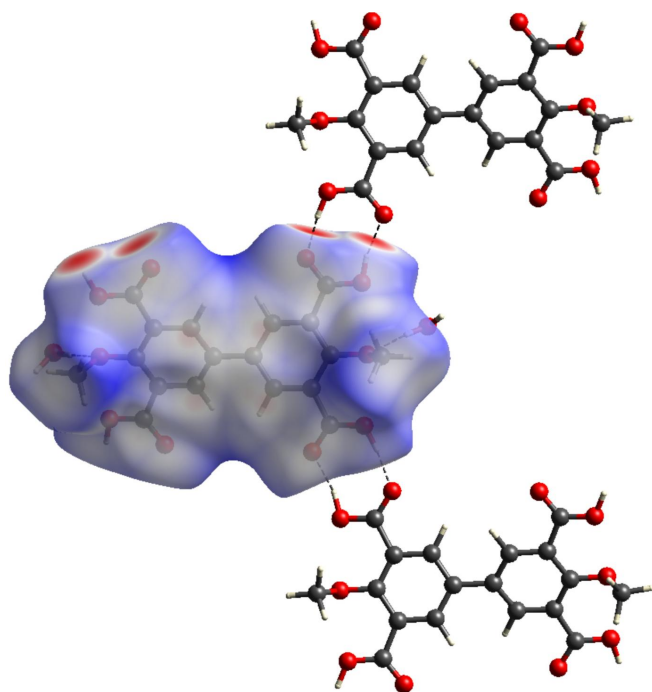

Figure 5
View of the three-dimensional Hirshfeld surface of the title compound, plotted over d_{norm} in the range −0.7606 to 1.5689 a.u., generated with *CrystalExplorer* (Spackman *et al.*, 2021)
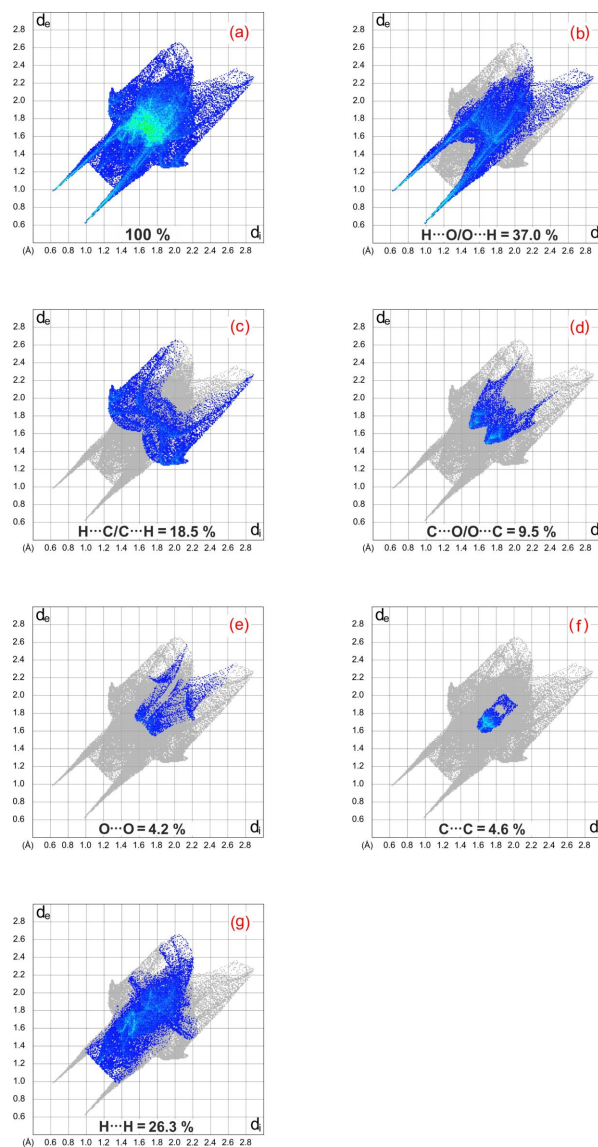
Figure 6
Two-dimensional fingerprint plots of the title compound, showing (*a*) all interactions, and delineated into (*b*) H⋯O/O⋯H, (*c*) H⋯C/C⋯H, (*d*) C⋯O/O⋯C, (*e*) O⋯O, (*f*) C⋯C and (*g*) H⋯H interactions. The d_i and d_e values represent the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

and those delineated into different types of interactions (McKinnon, 2007) are illustrated in Fig. 6. They reveal that H⋯O/O⋯H contacts (Fig. 6*b*), *i.e.* strong hydrogen bonds, contribute 37.0% of the Hirshfeld surface. The two weakly pronounced wings in the fingerprint plot prove the presence of intermolecular interactions of the C—H⋯π type. H⋯H contacts represent 26.3% of the fingerprint plot, while H⋯C/C⋯H and C⋯O/O⋯C contacts cover 18.5% and 9.5% of the Hirshfeld surface, respectively.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.44, update April 2023; Groom *et al.*, 2016) for 4,4′-disub-

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{14}O_{10}\cdot 2H_2O$
M_r	426.32
Crystal system, space group	Tetragonal, $I4_1cd$
Temperature (K)	123
a, c (Å)	24.069 (3), 6.4468 (8)
V (Å^3)	3734.6 (9)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	$0.40 \times 0.03 \times 0.03$
Data collection	
Diffractometer	Stoe IPDS 2T
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14573, 1914, 1502
R_{int}	0.055
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.093, 1.08
No. of reflections	1914
No. of parameters	153
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.20
Absolute structure	Flack x determined using 575 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons et al., 2013)
Absolute structure parameter	−2.2 (10)

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2002), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008), *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *ShelXle* (Hübschle et al., 2011).

stituted derivatives of biphenyl-3,3′,5,5′-tetracarboxylic acid gave no hits; however, the crystal structure of biphenyl-3,3′,5,5′-tetracarboxylic acid is known (refcode: PUYTEI; Coles et al., 2002). A comparison between the structure of the title compound and the unsolvated structure of biphenyl-3,3′,5,5′-tetracarboxylic acid (PUYTEI) provides a hint about the influence of the water molecules on the packing of the crystal structure. The difference in the space-group symmetries ($I4_1cd$ vs $P2_1/c$) suggests structural differences. In the structure of PUYTEI, a supramolecular arrangement of three interpenetrating corrugated layers forms structure domains that extend parallel to the crystallographic *ac* plane. Within a given corrugated layer, adjacent molecules are also linked *via* their carboxyl groups through eight-membered ring synthons. Furthermore, the molecules within the structure domains are arranged such that offset π–π-stacking interactions [$d(Cg\cdots Cg)$ = 3.636 Å] are effective between their aromatic units.

5. Synthesis and crystallization

To a mixture of 760 mg (1.51 mmol) of 4,4′-dimethoxy-3,3′,5,5′-biphenyltetracarboxylic acid tetraethyl ester and 60 mL of water, 1.01 g (17.9 mmol) of potassium hydroxide were added. After heating to boiling point for up to 18 h, the solution was cooled and acidified with semi-concentrated sulfuric acid. The white solid was filtered and dried under reduced pressure. Yield 96% (578 mg, 1.48 mmol); m.p. 528 K. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 3.85 (*s*, 6H), 8.08 (*s*, 4H), 13.31 (*br. s*, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 63.0, 128.4, 131.0, 133.1, 157.1, 166.7. Single crystals suitable for X-ray analysis were obtained by recrystallizing the resulting solid from water.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The non-hydrogen atoms were refined anisotropically. The carboxyl H atoms and the hydrogen atoms of the water molecules were identified in difference-Fourier maps and their U_{iso} parameters refined freely. All other H atoms were placed in calculated positions and refined using a riding model with C—H = 0.95–0.98 Å and $U_{iso}(H)$ = 1.2 or 1.5 $U_{eq}(C)$.

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Crystal structure and Hirshfeld surface analysis of 4,4′-dimethoxy-biphenyl-3,3′,5,5′-tetracarboxylic acid dihydrate

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Computing details

4,4′-Dimethoxybiphenyl-3,3′,5,5′-tetracarboxylic acid dihydrate

Crystal data

$C_{18}H_{14}O_{10} \cdot 2H_2O$	$D_x = 1.516$ Mg m^{-3}
$M_r = 426.32$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $I4_1cd$	Cell parameters from 1164 reflections
$a = 24.069$ (3) Å	$\theta = 3.7–23.3°$
$c = 6.4468$ (8) Å	$\mu = 0.13$ mm^{-1}
$V = 3734.6$ (9) Å^3	$T = 123$ K
$Z = 8$	Needle, colorless
$F(000) = 1776$	$0.40 \times 0.03 \times 0.03$ mm

Data collection

Stoe IPDS 2T diffractometer	1914 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	1502 reflections with $I > 2\sigma(I)$
Plane graphite monochromator	$R_{int} = 0.055$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 26.5°$, $\theta_{min} = 2.7°$
rotation method scans	$h = -30 \rightarrow 30$
14573 measured reflections	$k = -30 \rightarrow 30$
	$l = -7 \rightarrow 8$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 2.9912P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.039$	
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
1914 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}
153 parameters	Absolute structure: Flack x determined using 575 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
4 restraints	
Hydrogen site location: mixed	Absolute structure parameter: -2.2 (10)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.51833 (11)	0.31455 (13)	0.2339 (6)	0.0237 (8)
O2	0.42995 (12)	0.28601 (12)	0.2186 (6)	0.0239 (8)
H1O2	0.449 (3)	0.256 (3)	0.185 (12)	0.05 (2)*
O3	0.35137 (11)	0.35799 (11)	0.3165 (6)	0.0179 (5)
O4	0.28338 (12)	0.43760 (11)	0.4265 (6)	0.0248 (8)
H1O4	0.2495 (15)	0.450 (3)	0.443 (13)	0.07 (2)*
O5	0.31378 (12)	0.52496 (11)	0.4093 (6)	0.0222 (7)
C1	0.39269 (17)	0.39659 (18)	0.3264 (9)	0.0140 (6)
C2	0.37996 (17)	0.45289 (16)	0.3673 (7)	0.0140 (9)
C3	0.42244 (16)	0.49250 (17)	0.3661 (6)	0.0127 (9)
H3	0.413302	0.530267	0.392110	0.015*
C4	0.47773 (17)	0.47854 (17)	0.3282 (9)	0.0124 (5)
C5	0.48953 (17)	0.42264 (17)	0.2878 (7)	0.0137 (9)
H5	0.526771	0.412055	0.259073	0.016*
C6	0.44816 (17)	0.38202 (16)	0.2884 (7)	0.0142 (9)
C7	0.46785 (15)	0.32382 (17)	0.2435 (7)	0.0156 (9)
C8	0.33949 (17)	0.32976 (16)	0.5113 (7)	0.0271 (9)
H8A	0.308463	0.303926	0.491492	0.041*
H8B	0.329565	0.357244	0.617154	0.041*
H8C	0.372435	0.309100	0.556346	0.041*
C9	0.32219 (16)	0.47463 (15)	0.4027 (8)	0.0155 (9)
O6	0.30431 (14)	0.28767 (14)	−0.0127 (6)	0.0401 (8)
H1O6	0.302 (2)	0.2570 (16)	0.070 (7)	0.042 (15)*
H2O6	0.321 (3)	0.309 (3)	0.084 (9)	0.09 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0149 (13)	0.0148 (15)	0.041 (2)	0.0036 (10)	0.0022 (14)	−0.0036 (15)
O2	0.0179 (13)	0.0110 (15)	0.043 (2)	−0.0020 (11)	0.0022 (14)	−0.0074 (15)
O3	0.0136 (13)	0.0131 (13)	0.0270 (12)	−0.0032 (9)	0.0003 (12)	−0.0021 (12)
O4	0.0101 (14)	0.0168 (14)	0.047 (2)	0.0004 (10)	0.0038 (15)	−0.0043 (14)
O5	0.0126 (13)	0.0170 (13)	0.037 (2)	0.0036 (10)	0.0038 (15)	−0.0010 (14)
C1	0.0113 (19)	0.0159 (19)	0.0146 (14)	−0.0022 (11)	−0.0012 (17)	0.0004 (17)
C2	0.0126 (19)	0.0133 (18)	0.016 (2)	0.0019 (15)	−0.0009 (17)	−0.0020 (17)
C3	0.0131 (17)	0.0119 (18)	0.013 (2)	−0.0007 (14)	−0.0030 (18)	−0.0004 (17)
C4	0.0117 (19)	0.0137 (19)	0.0118 (14)	0.0007 (10)	−0.0030 (16)	−0.0001 (17)
C5	0.0093 (17)	0.0163 (19)	0.016 (2)	0.0034 (14)	−0.0002 (17)	−0.0001 (19)
C6	0.019 (2)	0.0106 (19)	0.014 (2)	−0.0002 (15)	0.0004 (18)	−0.0002 (17)

C7	0.0157 (17)	0.0125 (19)	0.019 (2)	−0.0012 (15)	0.0031 (19)	0.0006 (17)
C8	0.022 (2)	0.024 (2)	0.035 (2)	−0.0026 (16)	0.0039 (18)	0.0104 (18)
C9	0.0138 (19)	0.0166 (18)	0.016 (2)	0.0024 (15)	−0.0012 (18)	0.0016 (17)
O6	0.045 (2)	0.0366 (18)	0.039 (2)	−0.0051 (15)	−0.0063 (16)	−0.0029 (16)

Geometric parameters (Å, º)

O1—C7	1.237 (4)	C3—C4	1.394 (6)
O2—C7	1.298 (5)	C3—H3	0.9500
O2—H1O2	0.88 (6)	C4—C5	1.400 (6)
O3—C1	1.363 (4)	C4—C4^i	1.489 (6)
O3—C8	1.456 (5)	C5—C6	1.396 (6)
O4—C9	1.300 (5)	C5—H5	0.9500
O4—H1O4	0.88 (3)	C6—C7	1.507 (6)
O5—C9	1.229 (4)	C8—H8A	0.9800
C1—C6	1.402 (6)	C8—H8B	0.9800
C1—C2	1.414 (6)	C8—H8C	0.9800
C2—C3	1.398 (6)	O6—H1O6	0.91 (3)
C2—C9	1.503 (6)	O6—H2O6	0.90 (3)
C7—O2—H1O2	105 (4)	C4—C5—H5	119.1
C1—O3—C8	114.9 (4)	C5—C6—C1	120.3 (4)
C9—O4—H1O4	117 (5)	C5—C6—C7	115.2 (4)
O3—C1—C6	121.1 (4)	C1—C6—C7	124.5 (3)
O3—C1—C2	120.3 (4)	O1—C7—O2	123.9 (4)
C6—C1—C2	118.6 (2)	O1—C7—C6	119.1 (4)
C3—C2—C1	119.6 (4)	O2—C7—C6	117.0 (3)
C3—C2—C9	116.1 (3)	O3—C8—H8A	109.5
C1—C2—C9	124.2 (3)	O3—C8—H8B	109.5
C4—C3—C2	122.3 (4)	H8A—C8—H8B	109.5
C4—C3—H3	118.8	O3—C8—H8C	109.5
C2—C3—H3	118.8	H8A—C8—H8C	109.5
C3—C4—C5	117.3 (2)	H8B—C8—H8C	109.5
C3—C4—C4^i	121.3 (5)	O5—C9—O4	123.6 (4)
C5—C4—C4^i	121.4 (5)	O5—C9—C2	120.1 (4)
C6—C5—C4	121.9 (4)	O4—C9—C2	116.4 (3)
C6—C5—H5	119.1	H1O6—O6—H2O6	95 (6)
C8—O3—C1—C6	90.3 (6)	C4—C5—C6—C7	−179.6 (5)
C8—O3—C1—C2	−92.3 (6)	O3—C1—C6—C5	176.4 (4)
O3—C1—C2—C3	−176.6 (5)	C2—C1—C6—C5	−1.1 (9)
C6—C1—C2—C3	0.9 (9)	O3—C1—C6—C7	−2.7 (8)
O3—C1—C2—C9	0.1 (8)	C2—C1—C6—C7	179.8 (4)
C6—C1—C2—C9	177.6 (4)	C5—C6—C7—O1	8.4 (7)
C1—C2—C3—C4	−0.8 (8)	C1—C6—C7—O1	−172.4 (5)
C9—C2—C3—C4	−177.8 (4)	C5—C6—C7—O2	−172.1 (4)
C2—C3—C4—C5	0.9 (8)	C1—C6—C7—O2	7.1 (7)
C2—C3—C4—C4^i	−179.9 (3)	C3—C2—C9—O5	6.7 (7)

C3—C4—C5—C6	−1.1 (8)	C1—C2—C9—O5	−170.1 (5)
C4[i]—C4—C5—C6	179.7 (3)	C3—C2—C9—O4	−172.8 (4)
C4—C5—C6—C1	1.2 (8)	C1—C2—C9—O4	10.4 (7)

Symmetry code: (i) −x+1, −y+1, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1O2···O5[ii]	0.88 (6)	1.80 (6)	2.663 (4)	166 (7)
O4—H1O4···O1[iii]	0.88 (3)	1.74 (3)	2.611 (4)	174 (7)
O6—H1O6···O6[iv]	0.91 (3)	1.86 (3)	2.768 (4)	173 (5)
O6—H2O6···O3	0.90 (3)	2.04 (3)	2.941 (5)	174 (7)

Symmetry codes: (ii) −y+1, −x+1/2, z−1/4; (iii) −y+1/2, −x+1, z+1/4; (iv) y, −x+1/2, z+1/4.