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1,1′-Biphenyl-2,2′,5,5′-tetracarboxylic acid

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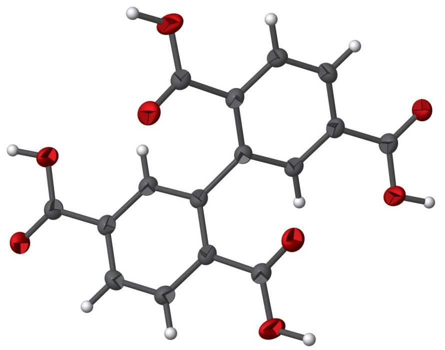
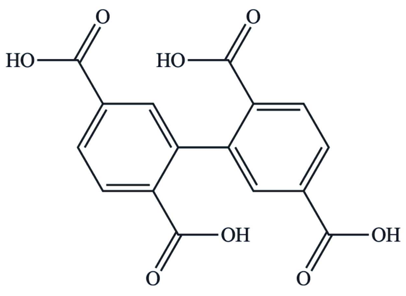
In the title compound, $C_{16}H_{10}O_8$ or H_4bptc, the dihedral angle between the planes of the phenyl rings is 51.90 (4)°. The asymmetric unit contains one half-molecule; complete molecules are generated by a twofold rotation axis. In the crystal, O—H⋯O and C—H⋯O hydrogen-bonding generate a two-dimensional supramolecular network. In addition, weak π–π interactions are also observed.

3D view



Chemical scheme



Structure description

Polycarboxylate ligands, as good candidates for the construction of coordination polymers (CPs), have attracted the interest of many researchers (Su *et al.*, 2014; Tian *et al.*, 2011). For example, the anion of 1,1′-biphenyl-2,2′,5,5′-tetracarboxylic acid (H_4bptc) can bridge multiple metal centres *via* a variety of bonding modes, providing an abundance of structural motifs (Sun *et al.*, 2010; Jia *et al.*, 2010). As part of a study to design and attempt the assembly of coordination polymers employing H_4bptc as an *exo*-multidentate ligand we reacted H_4bptc with $MnCl_2$ and half an equivalent of base under hydrothermal conditions. However, no complex of Mn^{II} was formed, but instead crystals of H_4bptc were obtained.

The molecular structure is illustrated in Fig. 1. The title compound crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit consists of half a molecule, complete molecules are generated by a twofold rotation axis. The phenyl ring has a maximum deviation of 0.0144 (12) Å for atom C5. The C7 and C8 atoms deviate from the mean plane of the ring to which they are attached by 0.1191 (7) and 0.0987 (8) Å, respectively. The carboxyl O atoms (O1, O2, O3 and O4) deviate by 0.6257 (9), −0.3566 (1), −0.0388 (1) and 0.3591 (2) Å, respectively, from the best plane of the phenyl ring. The dihedral angle between the planes of the phenyl rings is 51.90 (4)°, showing the molecule to have a twisted conformation. In the compounds 1,1′-biphenyl-2,2′,4,4′-tetracarboxylic

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acid (Bu *et al.*, 2010), 1,1′-biphenyl-2,2′,3,3′-tetracarboxylic acid (Holý *et al.*, 2004), and 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid (Holý *et al.*, 1999), which are similar to the title compound but substituted at the two 2-positions of the benzene rings, the rings are twisted by 71.63 (5), 88.68 (5) and 86.26 (6)°, respectively. In the isomers substituted at the 3-positions such as 1,1′-biphenyl-3,3′,4,4′-tetracarboxylic acid (Li *et al.*, 2009) and 1,1′-biphenyl-3,3′,5,5′-tetracarboxylic acid (Coles *et al.*, 2002), the dihedral angles of the biphenyl unit are 0 and 40.71 (8)°, respectively. This indicates that substitution at the 2-position impacts the planarity of the biphenyl unit. The steric hindering effect of a 2-substituent obviously plays a key factor in biphenyl planarity in the isomers of 1,1′-biphenyl-tetracarboxylic acids.

In the crystal, the molecules are connected through O—H⋯O and C—H⋯O hydrogen bonds (Table 1) as well as π–π interactions, leading to the formation of a supramolecular network. All O atoms participate in the hydrogen-bonded network. Individual molecules are linked by strong O—H⋯O double hydrogen bonds into carboxylic acid dimers [$R_2^2(8)$ hydrogen-bond motif, Fig. 2] which, if considered as tectons, suggest that the self-assembling properties of interactions

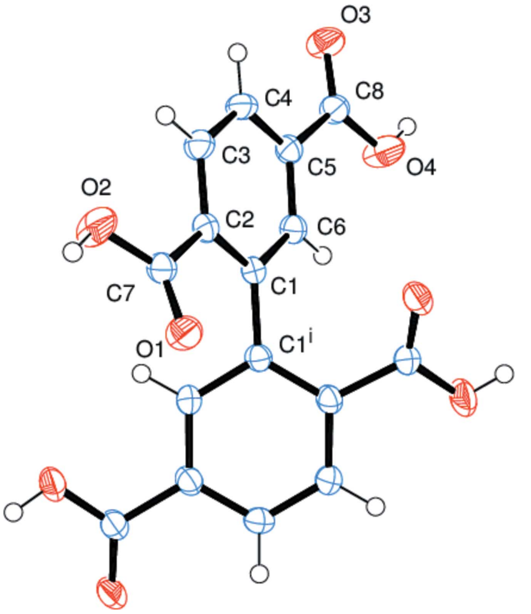

Figure 1
View of the title molecule with 30% probability displacement ellipsoids. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

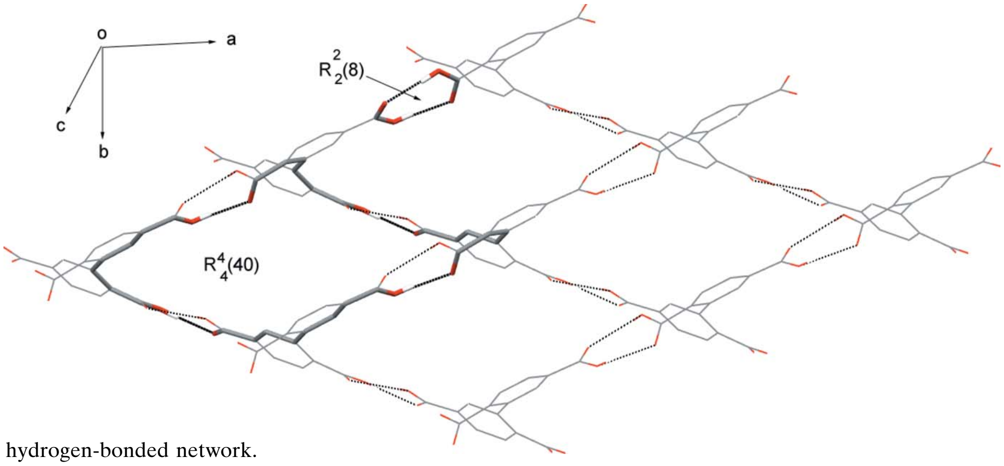

Figure 2
The two-dimensional hydrogen-bonded network.

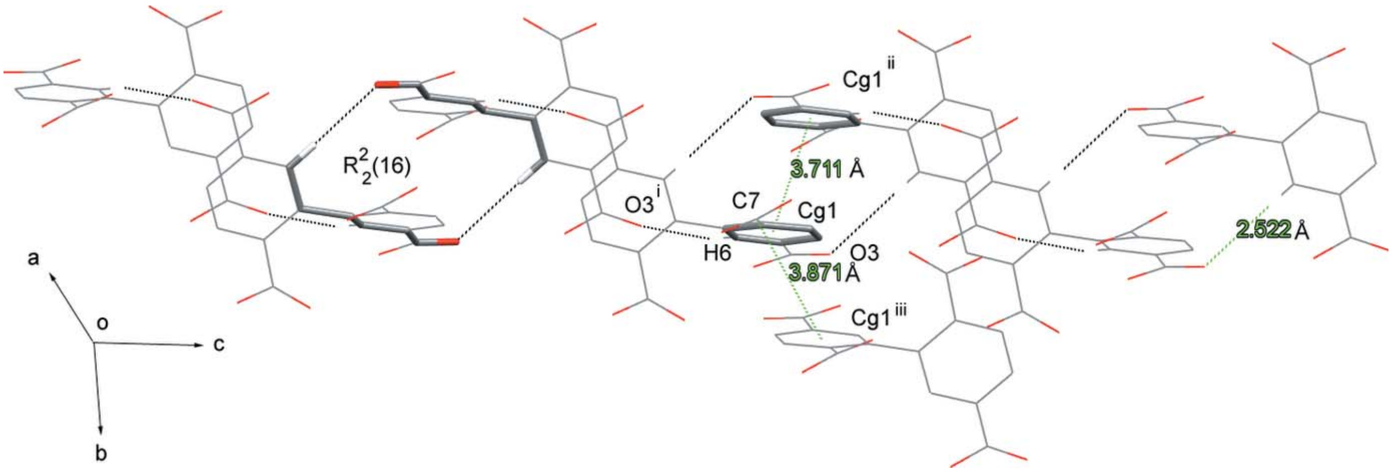

Figure 3
View down the *c* axis of the interpenetrating corrugated sheets that comprise the crystal structure. [Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $-x, -y, -z$; (iii) $-x, 1 - y, -z$.]

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$O3$^{\rm i}$	0.93	2.52	3.438 (2)	168
O2—H2$\cdots$O3$^{\rm ii}$	0.99	1.67	2.6615 (17)	176
O4—H4$A\cdots$O1$^{\rm iii}$	0.96	1.70	2.6535 (16)	174

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

result in a unilayered sheet with a supramolecular $R^4_4(40)$ rhombus motif. From a topological point of view, the two-dimensional structure is a (4,4) network when the fused biphenyls are considered as nodes (Fig. 2). The overall supramolecular assembly also includes C—H$\cdots$O hydrogen bonds (carboxylic acids in the position 5,5′-substituent at the biphenyl) and other weak interactions (Table 1). A supramolecular chain with $R^2_2(16)$ rings is formed in the c-axis direction *via* the C6—H6$\cdots$O3(x, $-y$, $\frac{1}{2}+z$) hydrogen-bond (Fig. 3). π–$\pi^{\rm ii}$ [symmetry code (ii) $-x$, $-y$, $-z$; centroid-to-centroid distance = 3.711 (1) Å] interactions between the C1–C6 rings strengthen the chains proceeding in this direction. On the other side of the phenyl ring, there is a COOH$\cdots\pi(-x,1-y,-z)$ stacking interaction (carboxylic acids in the 2,2′-position at the biphenyl) with a C$\cdots$centroid distance of 3.871 (1) Å (Fig. 3).

Synthesis and crystallization

A mixture containing $MnCl_2 \cdot 4H_2O$ (0.2 mmol, 39.4 mg), H_4bptc (0.2 mmol, 66.0 mg), KOH (0.2 mmol, 11.2 mg) and H_2O (6 ml) was stirred for 30 min at room temperature. The reaction mixture was sealed in a Teflon-lined stainless steel vessel and then heated to 393 K for three days. The resulting solution was allowed to gradually cool to room temperature. Colorless block-shaped crystals were collected by filtration and washed with water.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{10}O_8$
M_r	330.24
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	298
a, b, c (Å)	17.5105 (15), 7.7068 (7), 10.6885 (13)
β (°)	107.553 (1)
V (Å^3)	1375.3 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.13
Crystal size (mm)	0.22 × 0.19 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2000)
$T_{\rm min}$, $T_{\rm max}$	0.679, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3734, 1227, 979
$R_{\rm int}$	0.023
(sin $\theta/\lambda)_{\rm max}$ (Å^{-1})	0.596
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.099, 1.04
No. of reflections	1227
No. of parameters	113
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.18, −0.18

Computer programs: *APEX2* and *SAINT* (Bruker, 2000), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

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full crystallographic data

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1,1′-Biphenyl-2,2′,5,5′-tetracarboxylic acid

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1,1′-Biphenyl-2,2′,5,5′-tetracarboxylic acid

Crystal data

$C_{16}H_{10}O_8$	$F(000) = 680$
$M_r = 330.24$	$D_x = 1.595$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 17.5105$ (15) Å	Cell parameters from 4946 reflections
$b = 7.7068$ (7) Å	$\theta = 2.0$–28.7°
$c = 10.6885$ (13) Å	$\mu = 0.13$ mm^{-1}
$\beta = 107.553$ (1)°	$T = 298$ K
$V = 1375.3$ (2) Å^3	Block, colorless
$Z = 4$	0.22 × 0.19 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer	1227 independent reflections
Radiation source: fine-focus sealed tube	979 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.023$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$\theta_{\text{max}} = 25.0°$, $\theta_{\text{min}} = 2.4°$
$T_{\text{min}} = 0.679$, $T_{\text{max}} = 0.746$	$h = -20\rightarrow20$
3734 measured reflections	$k = -9\rightarrow6$
	$l = -12\rightarrow12$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.7133P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR(F^2) = 0.099$	$\Delta\rho_{\text{max}} = 0.18$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{\text{min}} = -0.18$ e Å^{-3}
1227 reflections	
113 parameters	
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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.00860 (9)	0.2360 (2)	0.18570 (15)	0.0226 (4)

C2	−0.04525 (9)	0.2980 (2)	0.06844 (15)	0.0246 (4)
C3	−0.02754 (9)	0.2807 (2)	−0.04963 (16)	0.0291 (4)
H3	−0.0642	0.3189	−0.1271	0.035*
C4	0.04383 (10)	0.2077 (2)	−0.05290 (16)	0.0289 (4)
H4	0.0553	0.1973	−0.1320	0.035*
C5	0.09824 (9)	0.1500 (2)	0.06265 (16)	0.0264 (4)
C6	0.07976 (9)	0.1613 (2)	0.17983 (16)	0.0255 (4)
H6	0.1158	0.1180	0.2562	0.031*
C7	−0.12042 (9)	0.3912 (2)	0.06627 (16)	0.0279 (4)
C8	0.17699 (10)	0.0806 (2)	0.06039 (16)	0.0300 (4)
O1	−0.12872 (7)	0.46968 (17)	0.16061 (12)	0.0367 (4)
O2	−0.17566 (7)	0.3840 (2)	−0.04713 (12)	0.0498 (4)
H2	−0.2235 (13)	0.448 (3)	−0.0423 (7)	0.075*
O3	0.19187 (7)	0.04896 (19)	−0.04157 (12)	0.0443 (4)
O4	0.22832 (7)	0.0609 (2)	0.17623 (12)	0.0534 (5)
H4A	0.2783 (14)	0.021 (3)	0.1674 (3)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0187 (8)	0.0260 (8)	0.0230 (8)	−0.0030 (6)	0.0059 (6)	−0.0011 (6)
C2	0.0186 (8)	0.0289 (9)	0.0258 (8)	−0.0002 (7)	0.0058 (7)	−0.0010 (7)
C3	0.0226 (8)	0.0394 (10)	0.0236 (9)	0.0040 (7)	0.0043 (7)	0.0007 (7)
C4	0.0285 (8)	0.0373 (10)	0.0231 (8)	0.0018 (8)	0.0109 (7)	−0.0014 (7)
C5	0.0207 (8)	0.0316 (10)	0.0270 (9)	0.0005 (7)	0.0075 (7)	−0.0028 (7)
C6	0.0194 (8)	0.0304 (9)	0.0251 (9)	0.0021 (7)	0.0044 (6)	0.0017 (7)
C7	0.0212 (8)	0.0362 (10)	0.0254 (9)	0.0027 (7)	0.0057 (7)	0.0024 (7)
C8	0.0238 (9)	0.0386 (10)	0.0280 (9)	0.0041 (7)	0.0084 (8)	−0.0030 (8)
O1	0.0270 (6)	0.0499 (8)	0.0329 (7)	0.0103 (6)	0.0085 (6)	−0.0054 (6)
O2	0.0270 (7)	0.0843 (11)	0.0315 (8)	0.0225 (7)	−0.0014 (6)	−0.0091 (7)
O3	0.0282 (7)	0.0753 (10)	0.0306 (7)	0.0160 (7)	0.0106 (6)	−0.0064 (7)
O4	0.0265 (7)	0.1027 (13)	0.0284 (7)	0.0241 (7)	0.0044 (6)	−0.0048 (7)

Geometric parameters (Å, º)

C1—C6	1.391 (2)	C5—C6	1.388 (2)
C1—C2	1.405 (2)	C5—C8	1.486 (2)
C1—C1^{i}	1.493 (3)	C6—H6	0.9300
C2—C3	1.394 (2)	C7—O1	1.221 (2)
C2—C7	1.494 (2)	C7—O2	1.3040 (19)
C3—C4	1.381 (2)	C8—O3	1.219 (2)
C3—H3	0.9300	C8—O4	1.301 (2)
C4—C5	1.386 (2)	O2—H2	0.99 (3)
C4—H4	0.9300	O4—H4A	0.96 (3)
C6—C1—C2	118.01 (14)	C4—C5—C8	119.52 (15)
C6—C1—C1^{i}	118.27 (16)	C6—C5—C8	120.50 (15)
C2—C1—C1^{i}	123.60 (15)	C5—C6—C1	121.52 (15)

C3—C2—C1	120.16 (14)	C5—C6—H6	119.2
C3—C2—C7	117.87 (14)	C1—C6—H6	119.2
C1—C2—C7	121.91 (14)	O1—C7—O2	123.28 (15)
C4—C3—C2	120.80 (15)	O1—C7—C2	123.30 (15)
C4—C3—H3	119.6	O2—C7—C2	113.40 (14)
C2—C3—H3	119.6	O3—C8—O4	123.70 (15)
C3—C4—C5	119.49 (15)	O3—C8—C5	122.41 (16)
C3—C4—H4	120.3	O4—C8—C5	113.87 (14)
C5—C4—H4	120.3	C7—O2—H2	109.5
C4—C5—C6	119.96 (14)	C8—O4—H4A	109.5
C6—C1—C2—C3	1.3 (2)	C2—C1—C6—C5	0.9 (2)
C1^{i}—C1—C2—C3	−174.80 (12)	C1^{i}—C1—C6—C5	177.23 (13)
C6—C1—C2—C7	−175.63 (15)	C3—C2—C7—O1	−151.99 (17)
C1^{i}—C1—C2—C7	8.3 (2)	C1—C2—C7—O1	25.0 (3)
C1—C2—C3—C4	−1.9 (3)	C3—C2—C7—O2	26.5 (2)
C7—C2—C3—C4	175.08 (16)	C1—C2—C7—O2	−156.53 (16)
C2—C3—C4—C5	0.4 (3)	C4—C5—C8—O3	−10.7 (3)
C3—C4—C5—C6	1.8 (3)	C6—C5—C8—O3	170.92 (17)
C3—C4—C5—C8	−176.53 (16)	C4—C5—C8—O4	167.89 (16)
C4—C5—C6—C1	−2.5 (2)	C6—C5—C8—O4	−10.5 (2)
C8—C5—C6—C1	175.82 (15)		

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···O3^{ii}	0.93	2.52	3.438 (2)	168
O2—H2···O3^{iii}	0.99	1.67	2.6615 (17)	176
O4—H4*A*···O1^{iv}	0.96	1.70	2.6535 (16)	174

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