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Biphenyl-3,3′,5,5′-tetracarboxylic acid

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.005 Å
R factor = 0.067
wR factor = 0.203
Data-to-parameter ratio = 13.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of biphenyl-3,3′,5,5′-tetracarboxylic acid, $C_{16}H_{10}O_8$, forms a supramolecular assembly of three interpenetrating corrugated sheets.

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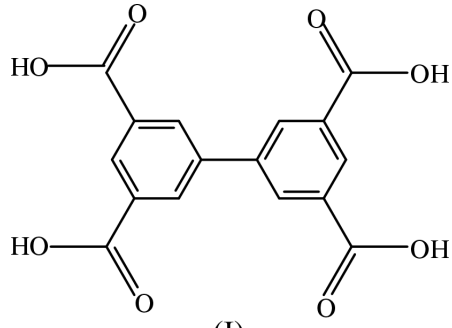
Comment

The title compound, (I), is composed of two essentially planar benzene-3,5-dicarboxylic acid groups that are orientated at a dihedral angle of 40.66 (7)° with respect to each other (Fig. 1). The bond lengths and angles in the molecule are in accordance with standard values (Orpen *et al.*, 1992) derived from the Cambridge Structural Database (CSD; Allen & Kennard, 1993).



(I)

All four of the carboxylic acid groups in (I) form the classic cyclic $R_2^2(8)$ hydrogen-bond motif (Etter *et al.*, 1990) with the acid groups of neighbouring molecules (Table 1). These interactions result in a two-dimensional sheet with a 4^4 network topology (Fig. 2). While the carboxylic acid groups are essentially coplanar with their respective phenyl rings, the

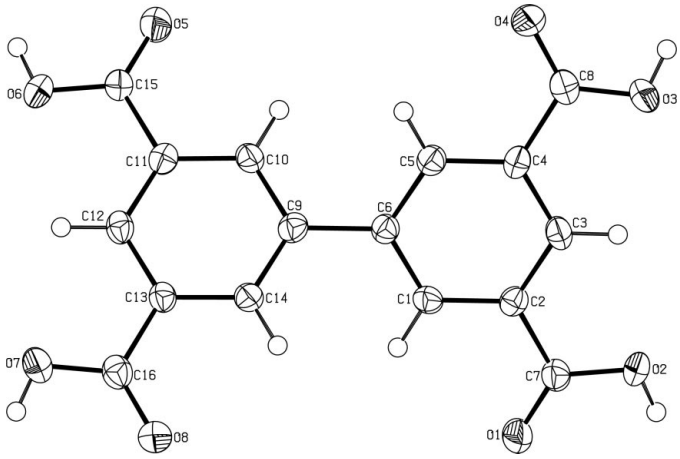


Figure 1
View of (I) (50% probability displacement ellipsoids).

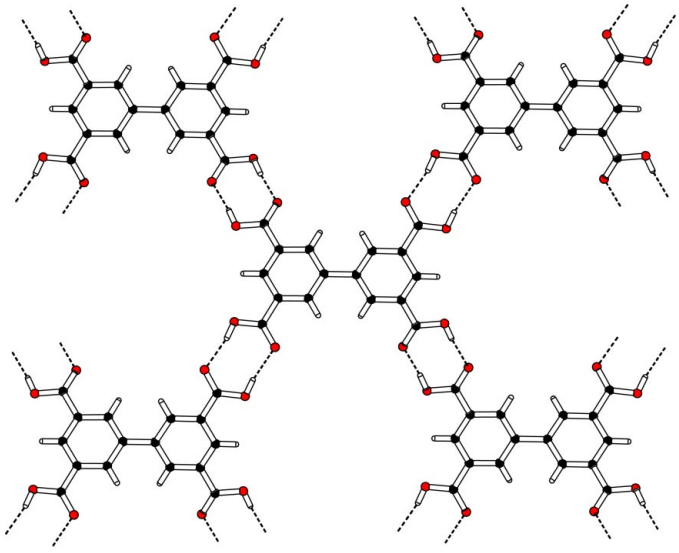


Figure 2
View down the *b* axis, showing the two-dimensional hydrogen-bonded network of (I).

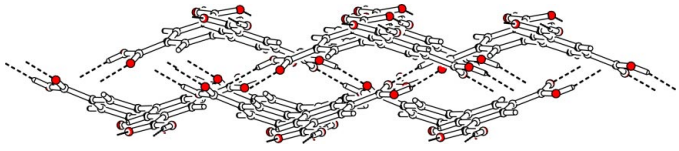


Figure 3
View down the *c* axis of the interpenetrating corrugated sheets that comprise the crystal structure of (I).

twist in the central C—C bond results in a corrugated structure. Thus, the supramolecular structure of this material comprises three, mutually interwoven, corrugated sheets (Fig. 3).

The structure of (I) compares well with other highly symmetric benzene polycarboxylic acids. In these molecules, where strong and predictable hydrogen bonding determines the network topology, there is a clear relationship between the molecular symmetry (the number of acid groups) and the two-dimensional network formed by the tesselation of these flat molecules. For example, the benzenedicarboxylic acids all form one-dimensional hydrogen-bonded ribbons (CSD refcode PHTHAC: Nowacki & Jaggi, 1957; BENZDC01: Alcala & Martínez-Carrera, 1972; TEPHTH: Bailey & Brown, 1967). 1,3,5-Benzenetricarboxylic acid (BTCOAC; Duchamp & Marsh, 1969) forms a 6^3 two-dimensional network, whilst 1,2,3,4,5,6-benzenehexacarboxylic acid (MELLIT; Darlow, 1961) forms a 3^6 two-dimensional net. The 1,3,5-benzenetricarboxylic acid shows further similarity with (I), in that the two-dimensional network contains very large hexagonal cavities, through which nine separate sheets interpenetrate in a supramolecular fashion, to yield a three-dimensional interwoven structure.

Experimental

Biphenyl-3,3′,5,5′-tetracarboxylic acid, (I) (Burton & Kenner, 1923), was, in this case, synthesized by a two-step procedure. 5-Iodo-*m*-xylene (6.00 g, 25 mmol) and copper powder (2.46 g, 38 mmol) were heated to 503 K under autogenious pressure for 50 h. The solid copper residues were removed by filtration and the coupled product, 3,3′,5,5′-tetramethylbiphenyl, was purified by column chromatography (hexane/silica) (0.98 g, 37%). A suspension of 3,3′,5,5′-tetramethylbiphenyl (0.6 g, 2.9 mmol) in water (125 ml) was treated with $KMnO_4$ (3.6 g, 22.8 mmol) and heated under reflux for 100 h. Filtration, followed by acidification with aqueous HCl, afforded the tetracarboxylic acid (0.28 g, 30%), which was recrystallized under hydrothermal conditions on cooling from 503 K.

Crystal data

$C_{16}H_{10}O_8$
M_r = 330.24
Monoclinic, $P2_1/c$
a = 8.1662 (7) Å
b = 14.3524 (14) Å
c = 12.093 (1) Å
β = 109.590 (4)°
V = 1335.3 (2) Å^3
Z = 4
D_x = 1.643 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 752 reflections
θ = 1–27.5°
μ = 0.14 mm^{-1}
T = 120 (2) K
Block, colourless
0.16 × 0.14 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.979, T_{max} = 0.993
16 495 measured reflections
2965 independent reflections
1309 reflections with $I > 2\sigma(I)$
R_{int} = 0.122
θ_{max} = 27.4°
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.203
S = 0.98
2965 reflections
221 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0991P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O5^{i}	0.84	1.80	2.631 (3)	173
O3—H3A···O8^{ii}	0.84	1.84	2.656 (3)	165
O6—H6···O1^{iii}	0.84	1.81	2.637 (3)	168
O7—H7···O4^{iv}	0.84	1.82	2.650 (3)	170

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

H atoms were constrained to idealized positions, with their displacement parameters riding on the values of their parent atoms.

Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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