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Tetrakis(4-carboxyphenyl)methane–dimethyl sulfoxide–toluene (1/4/1)

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Key indicators

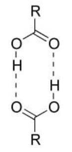
Single-crystal X-ray study
T = 225 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.066
wR factor = 0.190
Data-to-parameter ratio = 14.9

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

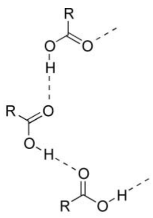
The title compound [systematic name: 4,4′,4″,4‴-methanetetrayltetracarboxylic acid–dimethyl sulfoxide–toluene (1/4/1)], $C_{29}H_{20}O_8$, crystallizes from dimethyl sulfoxide (DMSO)/toluene to yield a structure in which the four carboxylic acid groups of each molecule donate a single hydrogen bond to the O atom of four molecules of DMSO. Packing of the resulting aggregates, which have crystallographic twofold symmetry, leaves space for the inclusion of partially disordered molecules of toluene, leading to the formation of crystals of overall composition tetrakis(4-carboxyphenyl)methane–dimethyl sulfoxide–toluene (1/4/1).

Comment

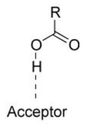
A productive strategy in crystal engineering exploits molecules in which cores with well defined structures are attached to multiple functional groups that participate in strong directional interactions according to reliable motifs (Dunitz, 2003). Such compounds tend to crystallize in ways that place molecules in predetermined positions with respect to their neighbors. Molecules of this type, which have been called tectons, from the Greek word for builder (Simard *et al.*, 1991), constitute the basic elements of a rational nanoscale construction set. Hydrogen bonds have proven to be particularly effective in directing tectonic association. Among the hydrogen-bonding groups that have been used most extensively are carboxyl groups, which are known to participate in various motifs, including cyclic dimer, *viz*. type I, catemer, type II, and adduct, type III, with basic acceptors (Desiraju, 1989; Leiserowitz, 1976).



(I)



(II)



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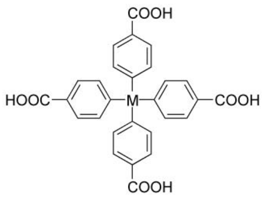

(IV) (M = C)
(V) (M = Si)

doi:10.1107/S1600536805002485

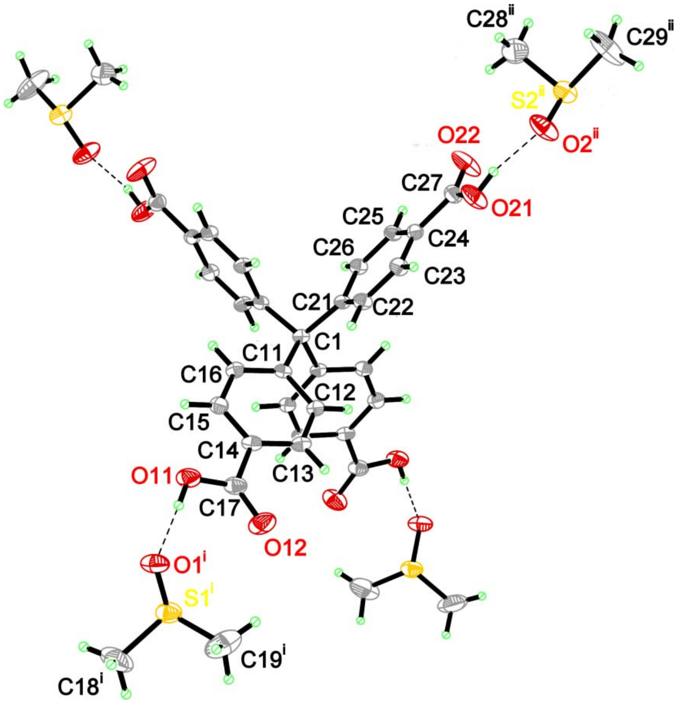

Figure 1
View of the structure of $(IV)\cdot 4DMSO\cdot C_7H_8$, with the atom-numbering scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level, and H atoms are represented by spheres of arbitrary radii. Hydrogen bonds appear as broken lines, and toluene has been omitted for clarity. The unlabeled part of the molecule is related by the symmetry operation $(-x, y, -z + \frac{1}{2})$. [Symmetry code: (i) $x, 1 + y, z$; (ii): $x, y - 1, z$.]

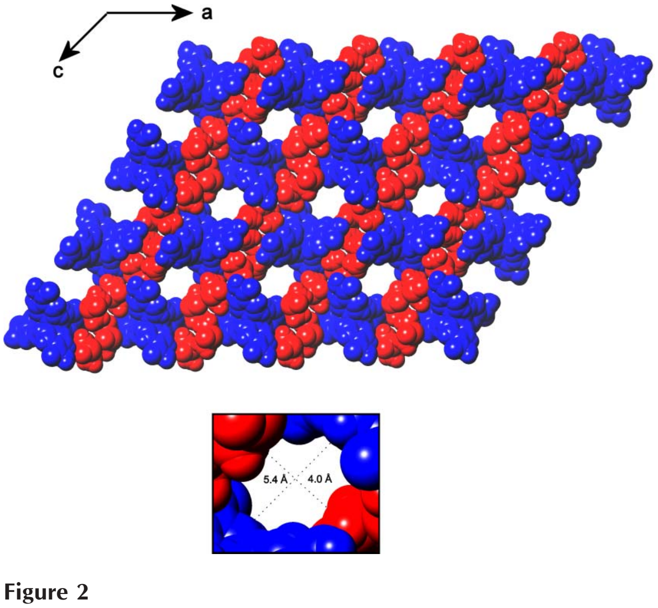

Figure 2
View along the *b* axis of the structure of $(IV)\cdot 4DMSO\cdot C_7H_8$, showing a 2 × 3 × 2 array of unit cells. Toluene has been omitted for clarity, and atoms are shown as spheres of van der Waals radii in order to reveal the cross-sections of the channels. Molecules of the title compound appear in blue and molecules of DMSO are shown in red. The enlarged view of the channels shows that the cross-sections measure 5.4 × 4.0 Å^2.

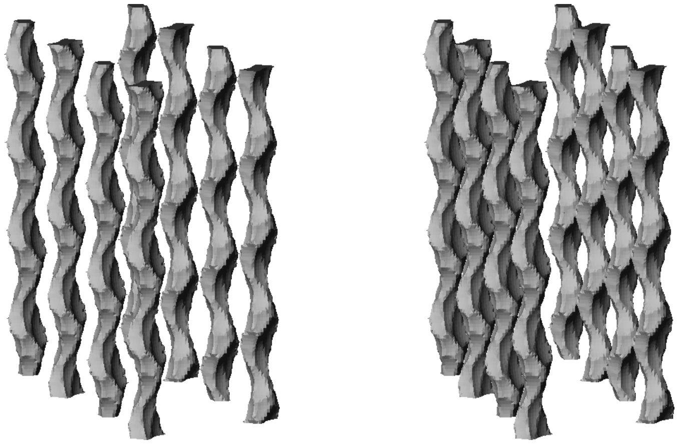

Figure 3
Stereoscopic representation of the parallel helical channels defined by the structure of (IV). The image shows a 2 × 4 × 1 array of unit cells viewed with the *b* axis vertical. The outsides of the channels appear in light gray, and dark gray is used to show where the channels are cut by the boundaries of the array. The surface of the channels is defined by the possible locus of the center of a sphere of diameter 3.0 Å as it rolls over the surface of the ordered structure built from hydrogen-bonded subunits of composition $(IV)\cdot 4DMSO$ (Laliberté *et al.*, 2004*a*).

Of special promise in crystal engineering are compounds such as tetrakis(4-carboxyphenyl)methane, (IV), in which multiple carboxy groups are attached to a rigid core. The structure of the analogous silane, (V), has been reported (Lambert *et al.*, 1997), and the tetracarboxylate salt of compound (IV) has been used as a ligand to construct networks held together by coordination to metals (Chun *et al.*, 2004; Kim *et al.*, 2001). However, tetraacid (IV) itself has not yet been exploited in supramolecular chemistry, and its crystal structure has not been previously reported. We show here that crystallization of compound (IV) from dimethyl sulfoxide (DMSO)/toluene yields an inclusion complex built from subunits of composition tetrakis(4-carboxyphenyl)methane–dimethyl sulfoxide, held together by four hydrogen bonds of type III.

The hydrogen-bonded units found in the crystal structure of compound $(IV)\cdot 4DMSO\cdot C_7H_8$ are shown in Fig. 1. Each carboxy group serves as a donor of a single $O-H\cdots O$ hydrogen bond to the basic O atom of a molecule of DMSO. The observed hydrogen-bonding motif III and the associated geometric parameters (Table 1) are similar to those found in other adducts of benzoic acids with DMSO (Dale & Elsegood, 2003; Jin *et al.*, 2003). Each carboxy group lies close to the mean plane of the aromatic ring to which it is bonded. No direct interactions between molecules of tetraacid (IV) are observed, and the distance between the central C atoms of the closest neighbors is 7.269 (5) Å. In contrast, cohesion in crystals of tetraphenylmethane itself results primarily from multiple phenyl embraces (Scudder & Dance, 2002). Each molecule of tetraacid (IV) has C_2 symmetry, and the $C-C-C$ angles at the core range from 104.7 (3) to 111.7 (1)°. Crystallization of the analogous silane (V) from acetic acid results in a completely different structure in which three of the four carboxy groups per molecule associate directly, by forming motif I with the corresponding groups of three neighbors, leading to formation of a three-connected puckered sheet (Lambert *et al.*, 1997). The remaining carboxy group forms hydrogen bonds with a molecule of acetic acid according to motif I, thereby capping the sheets and forming a close-packed structure of composition (V)·CH_3COOH.

The aggregates (IV)·4DMSO pack as shown in Fig. 2 to create space for the inclusion of toluene. The guests are partially disordered and occupy helical channels that run parallel to the *b* axis (Fig. 3). The cross-sections of the channels are approximately 5.4×4.0 Å^2, and 27% of the volume of the crystals is accessible to guests, as measured by standard methods (Laliberté *et al.*, 2004*a*). It is interesting to note that tetraphenylmethane itself, and simple derivatives with substituents that do not engage in hydrogen bonding, typically crystallize as close-packed structures with essentially no space available for the inclusion of guests (Laliberté *et al.*, 2004*b*; Jetti & Nangia, 2000).

Experimental

Tetrakis(4-carboxyphenyl)methane was prepared by the reported method (Grimm *et al.*, 1986). Crystals were grown by allowing toluene to diffuse slowly into a solution of tetrakis(4-carboxyphenyl)methane in DMSO.

Crystal data

$C_{29}H_{20}O_8 \cdot C_7H_8 \cdot 4C_2H_6OS$
$M_r = 901.10$
Monoclinic, $C2/c$
$a = 28.723\ (15)$ Å
$b = 7.269\ (5)$ Å
$c = 26.824\ (9)$ Å
$\beta = 123.61\ (3)^\circ$
$V = 4664\ (5)$ Å^3
$Z = 4$

$D_x = 1.283$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20.0\text{–}21.0^\circ$
$\mu = 2.36$ mm^{-1}
$T = 225\ (2)$ K
Plate, colorless
$0.50 \times 0.14 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian from crystal shape
$T_{min} = 0.38$, $T_{max} = 0.87$
32 349 measured reflections
4410 independent reflections
3266 reflections with $I > 2\sigma(I)$

$R_{int} = 0.067$
$\theta_{max} = 69.9^\circ$
$h = -34 \rightarrow 34$
$k = -8 \rightarrow 8$
$l = -32 \rightarrow 32$
6 standard reflections frequency: 60 min intensity decay: 3.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.190$
$S = 1.01$
4410 reflections
295 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.136P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00030 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O1^{i}	0.83	1.78	2.608 (3)	174
O21—H21···O2^{ii}	0.83	1.76	2.574 (3)	168

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H bond lengths of 0.94 (aromatic CH), 0.97 (CH_3) and O—H 0.83 Å (OH), and isotropic displacement parameters equal to 1.2 (CH) or 1.5 (CH_3 and OH) times U_{eq} of the parent atom. The toluene molecule is disordered over an inversion center and was refined using an idealized benzene ring and by applying restraints on atomic displacement parameters.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997) and *ATOMS* (Shape Software, 2002); software used to prepare material for publication: *SHELXTL*.

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