Tetramethyl biphenyl-3,5,3',5'-tetracarboxylate benzene sesquisolvate

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Key indicators

Single-crystal X-ray study
$T = 150$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.148
Data-to-parameter ratio = 8.2

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

The title structure, $C_{20}H_{18}O_8 \cdot 1.5C_6H_6$, is a tetrasubstituted biphenyl which has a pseudo-inversion centre between the two halves. The benzene solvent molecules lie in special positions, one with twofold rotation symmetry and two with inversion symmetry. The tetramethyl ester molecule is twisted and forms a supramolecular assembly of stacked sheets.

Comment

The title structure, (I), is composed of a biphenyl skeleton symmetrically substituted in the 3- and 5-positions by methyl ester moieties. Each molecule in the asymmetric unit is solvated by 1.5 benzene molecules. The bond lengths and angles in the molecule are in accordance with standard values (Orpen *et al.*, 1992) derived from the Cambridge Structural Database (Allen & Kennard, 1993).

(I)
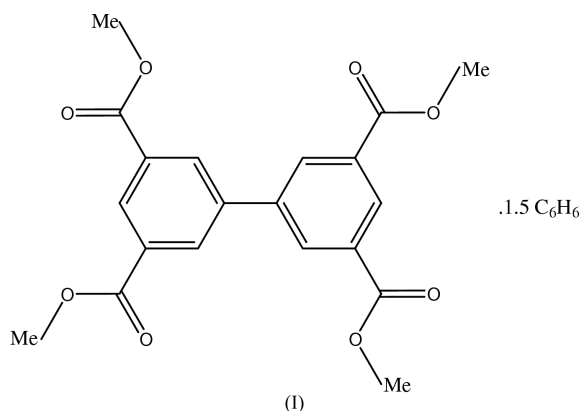
The two phenyl groups in the centre of the dimer are oriented at a dihedral angle of 30.73 (13)° with respect to each other. This value is in the same range as those reported for similar 3,5-disubstituted biphenyls (Coles *et al.*, 2002, and references therein), where the barrier to rotation about the phenyl–phenyl bond is presumably restricted by H···H interactions in the 2- and 6-positions on the phenyl groups. Aside from the methyl H atoms, the ester groups lie in the plane of the phenyl moiety to which they are attached.

The supramolecular assembly of the crystal structure is that of a corrugated sheet, formed by hydrogen bonds to three of the carbonyl O atoms, where C1—H1B···O3^{i} = 2.782 (5) Å, C19—H19B···O5^{ii} = 2.620 (4) Å and C15—H15B···O7^{iii} = 2.580 (5) Å [symmetry codes: (i) x, $-y+2$, $z-1/2$; (ii) $-x$, $-y+1/2$, $-z$; (iii) x, $-y+2$, $z+1/2$]. These sheets stack on top of each other, which results in π–π interactions between neighbours; for a sheet above, $Cg1$···$Cg2^{iv}$ = 3.879 (8) Å and, for a sheet below, $Cg1$···$Cg2^{v}$ = 3.747 (8) Å, [symmetry codes: (iv) $1/2-x$, $-1/2+y$, $1/2-z$; (v) $1/2-x$, $1/2+y$, $1/2-z$; $Cg1$ and $Cg2$ are the centroids of rings C3/C4/C5/C8/C9/C10 and C11/C12/C13/C16/C17/C20 respectively].
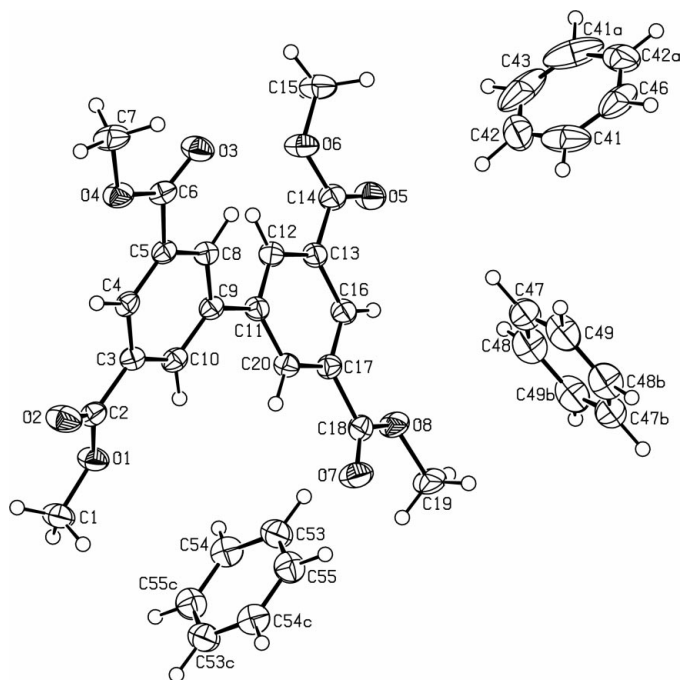
Figure 1
View of the asymmetric unit of (I) together with the symmetry-generated second half of each benzene molecule (50% probability displacement ellipsoids).

Experimental

The title compound was synthesized according to literature methods (Burton & Kenner, 1923; Grahl, 1895; Delzenne & Laridon, 1969) with the following modifications. Dimethyl 5-iodoisophthalate (2 g, 0.0062 mol) was ground together with copper powder (2 g, 0.031 mol) in a mortar and placed in an autoclave at 503 K for 20 h. A hard pellet was formed which dissolved in dichloromethane. After filtration removed the copper residue, the solvent was removed *in vacuo*. Recrystallization was achieved from benzene. Compound (I) (0.35 g) was collected in 29% yield. δ_H (300 MHz, CDCl$_2$-d_2, Me$_4$Si, p.p.m.): 3.97 (12H, *s*, CH$_3$), 8.52 (4H, *s*, ArH), 8.68 (2H, *s*, ArH). δ_C (75.48 MHz, CDCl$_2$-d_2, Me$_4$Si, p.p.m.): 53.48, 129.37, 131.03, 132.73, 141.01, 166.87. One of the ^{1}H NMR resonances is due to benzene, as confirmed in the crystal structure. CIMS: 387.2 (M+H$^+$), 404.2 (M+NH$_4^+$).

Crystal data

C$_{20}$H$_{18}$O$_8$·1.5C$_6$H$_6$	$D_x = 1.362$ Mg m^{-3}
$M_r = 503.51$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 16139
$a = 37.557$ (7) Å	reflections
$b = 7.0816$ (14) Å	$\theta = 5.1$–$23.2°$
$c = 22.498$ (4) Å	$\mu = 0.10$ mm^{-1}
$\beta = 124.86$ (3)°	$T = 150$ (2) K
$V = 4909.9$ (16) Å^3	Needle, colourless
$Z = 8$	$0.48 \times 0.07 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	3642 independent reflections
φ and ω scans	2251 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.167$
(*SORTAV*; Blessing, 1997)	$\theta_{max} = 23.6°$
$T_{min} = 0.954$, $T_{max} = 0.999$	$h = -42 \rightarrow 42$
18113 measured reflections	$k = -7 \rightarrow 7$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
3642 reflections	$\Delta\rho_{min} = -0.26$ e Å^{-3}
442 parameters	Extinction correction: *SHELXL*97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0019 (3)

H atoms, located in a difference map, were refined isotropically (apart from H43, which could not be located in a difference map and was included in a calculated position with its displacement parameter tied to that of its parent atom). Refinement was performed with the data truncated to $\theta = 23.6°$. At higher angles, significant numbers of reflections were not observed, due to the small size and needle habit of the crystal, despite the intensities being measured from a rotating anode source with a CCD detector. This produces a poor internal agreement statistic for the data set.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; 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); software used to prepare material for publication: *SHELXL*97.

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