organic papers

2,3,2′,3′-Tetramethylbiphenyl

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The title compound, $C_{16}H_{18}$, was synthesized by a palladium-catalyzed boronic acid cross-coupling reaction. A crystallographic twofold axis passes through the mid-point of the C—C bond connecting the two rings. In the crystal structure, two fairly close C—H···π(arene) contacts appear to be the only significant intermolecular interactions.

Comment

The title compound, (I), was synthesized using the *tert*-butyl group as a positional protective group (Tashiro & Yamato, 1979). We obtained (I) in excellent yield using a Suzuki cross-coupling reaction (Miyaura, 2002). The crystal structure of the related 2,3,3′,4′-tetramethylbiphenyl, (II), has already been reported (Robertson & Price, 2005).

(I)
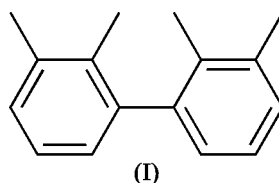
The molecular structure of (I) is shown in Fig. 1. A crystallographic twofold axis passes through the mid-point of the C6—C6A bond. All bond distances and angles are as expected. The dihedral angle between the planes of the two benzene rings is 69.9 (3)°, compared with the value of 54.10 (7)° in (II). The larger angle in (I) may be related to the greater steric hindrance from the two 2,2′-methyl groups in (I) compared with the two 2,3′-methyl groups in (II). The molecule adopts a *cis* configuration, with all the methyl groups on the same side of the biphenyl unit.
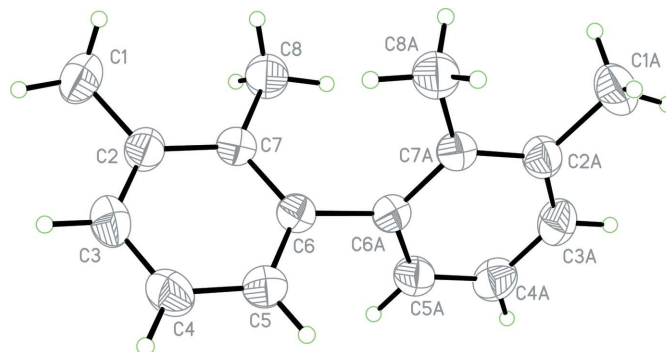
Figure 1
The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres. Atoms labelled with the suffix A are related by the symmetry operator ($1 - x$, y, $\frac{3}{2} - z$).

There are no significant π–π stacking interactions, but two intermolecular weak C—H$\cdots\pi$(arene) interactions may be effective in stabilizing the crystal structure (Table 1 and Fig. 2).

Experimental

The title compound was synthesized according to the procedure described by Robertson & Price (2005), using the same quantities but substituting 2,3-dimethylbromobenzene for 3,4-dimethylbromo-benzene. Crystals were obtained by dissolving (I) (1.0 g) in petroleum ether (20 ml) and evaporating the solvent slowly at room temperature for about 25 d.

Crystal data

$C_{16}H_{18}$	$Z = 4$
$M_r = 210$	$D_x = 1.120$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.536$ (3) Å	$\mu = 0.06$ mm^{-1}
$b = 6.5150$ (13) Å	$T = 293$ (2) K
$c = 14.754$ (3) Å	Block, colourless
$\beta = 106.49$ (3)°	$0.40 \times 0.30 \times 0.20$ mm
$V = 1247.6$ (4) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	1221 independent reflections
$\omega/2\theta$ scans	1007 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.034$
$T_{min} = 0.975$, $T_{max} = 0.988$	$\theta_{max} = 26.0°$
2438 measured reflections	3 standard reflections
	every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 0.4P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.135$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.16$ e Å^{-3}
1221 reflections	$\Delta\rho_{min} = -0.14$ e Å^{-3}
74 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.087 (8)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$B$$\cdots$Cg1^i	0.96	2.85	3.729 (2)	152
C4—H4$A$$\cdots$Cg1^{ii}	0.93	2.90	3.7429 (18)	150

Symmetry codes: (i) $x + \frac{3}{2}, y + \frac{1}{2}, z + 1$; (ii) $x + 1, -y, z + \frac{1}{2}$.

H atoms were placed in calculated postions, with C—H = 0.93 or 0.96 Å, and were included in the refinement in the riding-model
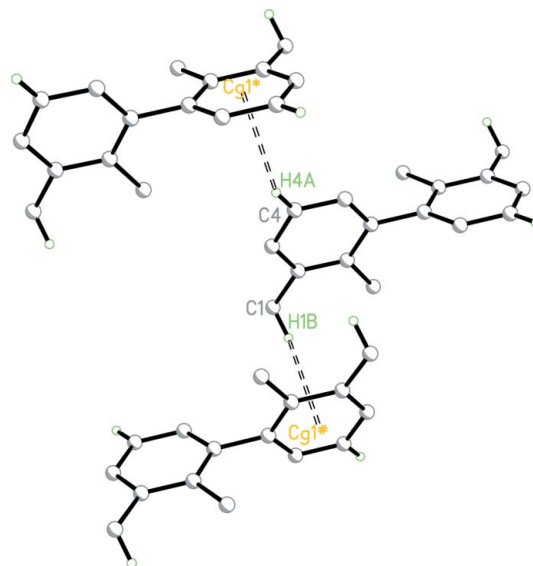

Figure 2
Part of the crystal structure of (I), with dashed lines indicating intermolecular C—H$\cdots\pi$(arene) interactions. Only H atoms involved in the interactions are shown. [Symmetry codes: (#) $\frac{3}{2} + x, \frac{1}{2} + y, 1 + z$; (*) $1 + x, -y, \frac{1}{2} + z$.]

approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl H.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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supporting information

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$M_r = 210$	$D_x = 1.120$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
$a = 13.536$ (3) Å	$\theta = 10$–14°
$b = 6.5150$ (13) Å	$\mu = 0.06$ mm^{-1}
$c = 14.754$ (3) Å	$T = 293$ K
$\beta = 106.49$ (3)°	Block, colourless
$V = 1247.6$ (4) Å^3	$0.40 \times 0.30 \times 0.20$ mm
$Z = 4$	

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Radiation source: fine-focus sealed tube	1007 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.034$
$\omega/2\theta$ scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.9°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -16 \rightarrow 16$
	$k = 0 \rightarrow 8$
$T_{min} = 0.975$, $T_{max} = 0.988$	$l = -18 \rightarrow 18$
2438 measured reflections	3 standard reflections every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + 0.4P]$
$wR(F^2) = 0.135$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
1221 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
0 restraints	Extinction correction: SHELXL97 (Sheldrick, 1997), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.087 (8)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	0.60823 (13)	−0.2539 (3)	0.52560 (11)	0.0588 (5)
H1A	0.6625	−0.2237	0.4976	0.088*
H1B	0.5432	−0.2512	0.4777	0.088*
H1C	0.6191	−0.3876	0.5541	0.088*
C2	0.60805 (10)	−0.0951 (2)	0.60029 (9)	0.0418 (4)
C3	0.68030 (10)	0.0615 (2)	0.61880 (10)	0.0481 (4)
H3A	0.7282	0.0681	0.5845	0.058*
C4	0.68268 (11)	0.2081 (2)	0.68705 (11)	0.0504 (4)
H4A	0.7315	0.3126	0.6983	0.061*
C5	0.61188 (10)	0.1977 (2)	0.73835 (10)	0.0450 (4)
H5A	0.6133	0.2959	0.7845	0.054*
C6	0.53833 (9)	0.0422 (2)	0.72183 (8)	0.0369 (4)
C7	0.53573 (10)	−0.1056 (2)	0.65187 (9)	0.0379 (4)
C8	0.45546 (12)	−0.2723 (2)	0.63029 (11)	0.0532 (5)
H8A	0.4119	−0.2581	0.6711	0.080*
H8B	0.4887	−0.4039	0.6404	0.080*
H8C	0.4146	−0.2612	0.5656	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0661 (10)	0.0609 (10)	0.0570 (9)	0.0039 (8)	0.0296 (7)	−0.0114 (8)
C2	0.0432 (7)	0.0436 (8)	0.0407 (7)	0.0038 (6)	0.0151 (5)	0.0006 (6)
C3	0.0434 (8)	0.0570 (9)	0.0493 (8)	−0.0015 (6)	0.0217 (6)	0.0048 (7)
C4	0.0480 (8)	0.0477 (9)	0.0580 (9)	−0.0138 (6)	0.0188 (6)	−0.0007 (7)
C5	0.0507 (8)	0.0394 (8)	0.0470 (8)	−0.0060 (6)	0.0174 (6)	−0.0057 (6)
C6	0.0396 (7)	0.0343 (7)	0.0385 (7)	0.0009 (5)	0.0135 (5)	0.0022 (5)
C7	0.0399 (7)	0.0346 (7)	0.0399 (7)	−0.0005 (5)	0.0127 (5)	0.0003 (5)
C8	0.0601 (9)	0.0492 (9)	0.0546 (8)	−0.0153 (7)	0.0233 (7)	−0.0110 (7)

Geometric parameters (Å, º)

C1—C2	1.5120 (19)	C4—H4A	0.9300
C1—H1A	0.9600	C5—C6	1.3928 (19)
C1—H1B	0.9600	C5—H5A	0.9300
C1—H1C	0.9600	C6—C7	1.4046 (18)

C2—C3	1.386 (2)	C6—C6ⁱ	1.502 (2)
C2—C7	1.4016 (18)	C7—C8	1.5049 (19)
C3—C4	1.381 (2)	C8—H8A	0.9600
C3—H3A	0.9300	C8—H8B	0.9600
C4—C5	1.381 (2)	C8—H8C	0.9600
C2—C1—H1A	109.5	C4—C5—C6	120.81 (13)
C2—C1—H1B	109.5	C4—C5—H5A	119.6
H1A—C1—H1B	109.5	C6—C5—H5A	119.6
C2—C1—H1C	109.5	C5—C6—C7	119.66 (12)
H1A—C1—H1C	109.5	C5—C6—C6ⁱ	118.34 (10)
H1B—C1—H1C	109.5	C7—C6—C6ⁱ	121.97 (10)
C3—C2—C7	119.42 (12)	C2—C7—C6	119.34 (12)
C3—C2—C1	120.02 (13)	C2—C7—C8	119.58 (12)
C7—C2—C1	120.56 (13)	C6—C7—C8	121.06 (12)
C4—C3—C2	121.45 (13)	C7—C8—H8A	109.5
C4—C3—H3A	119.3	C7—C8—H8B	109.5
C2—C3—H3A	119.3	H8A—C8—H8B	109.5
C5—C4—C3	119.32 (13)	C7—C8—H8C	109.5
C5—C4—H4A	120.3	H8A—C8—H8C	109.5
C3—C4—H4A	120.3	H8B—C8—H8C	109.5
C7—C2—C3—C4	0.0 (2)	C1—C2—C7—C6	179.05 (12)
C1—C2—C3—C4	−179.52 (13)	C3—C2—C7—C8	178.45 (13)
C2—C3—C4—C5	0.3 (2)	C1—C2—C7—C8	−2.1 (2)
C3—C4—C5—C6	−0.2 (2)	C5—C6—C7—C2	0.59 (19)
C4—C5—C6—C7	−0.3 (2)	C6ⁱ—C6—C7—C2	178.71 (12)
C4—C5—C6—C6ⁱ	−178.47 (13)	C5—C6—C7—C8	−178.28 (13)
C3—C2—C7—C6	−0.44 (19)	C6ⁱ—C6—C7—C8	−0.2 (2)

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···*Cg*1ⁱⁱ	0.96	2.85	3.729 (2)	152
C4—H4*A*···*Cg*1ⁱⁱⁱ	0.93	2.90	3.7429 (18)	150

Symmetry codes: (ii) *x*+3/2, *y*+1/2, *z*+1; (iii) *x*+1, −*y*, *z*+1/2.