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2,3,3′,4′-Tetramethylbiphenyl

Andrew J. Robertson and Daniel J. Price*

WestCHEM, Department of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ, Scotland

Correspondence e-mail: d.price@chem.gla.ac.uk

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Key indicators

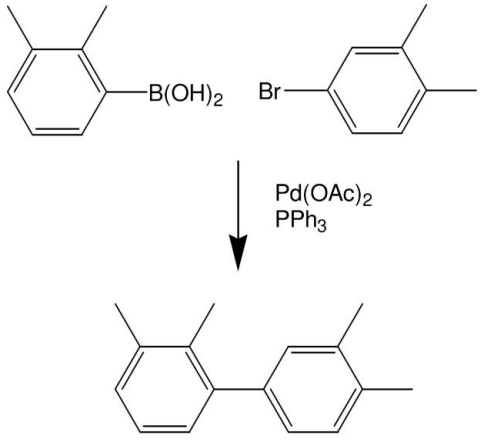
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.049
wR factor = 0.127
Data-to-parameter ratio = 18.0

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

2,3,3′,4′-Tetramethylbiphenyl, $C_{16}H_{18}$, was synthesized in a palladium-catalysed boronic acid cross-coupling reaction. In the solid state, these weakly interacting unsymmetrical molecules show an apparent dimerization of the *ortho*-dimethylphenyl groups, a packing motif that is seen in a significant number of other *ortho*-dimethylphenyl-containing compounds.

Comment

2,3,3′,4′-Tetramethylbiphenyl, (I), has been reported previously as a minor product in an oxidative coupling reaction (Norman *et al.*, 1973). We obtained (I) in excellent yield using a Suzuki cross-coupling reaction (Miyaura, 2002). The unsymmetrical molecules of this compound crystallize in the space group $P\overline{1}$ with an asymmetric unit consisting of a single molecule (Fig. 1). All bond distances and angles in the molecule are normal. The two benzene rings are twisted by 54.10 (7)° from coplanarity. The molecule adopts a *cis* conformation in the solid, with all the methyl groups to one side of the biphenyl rings.



(I)

Overall, the packing of these unsymmetrical molecules is complex and not easily visualized. However, one intermolecular motif does stand out; the *ortho*-dimethylphenyl groups appear to show a certain self-complementarity. Examination of all the intermolecular contacts reveals that the shortest intermolecular C···C (~3.7 Å) and C—H···aryl π interactions are associated with this motif (Fig. 2). Both *ortho*-dimethylphenyl rings show this interaction, and both have an inversion centre between the interacting molecules. The orientation of each methyl group is such that one of the H atoms is directed to the midpoint of an aryl C···C bond. This looks like a weak hydrogen-bonding interaction. An exam-

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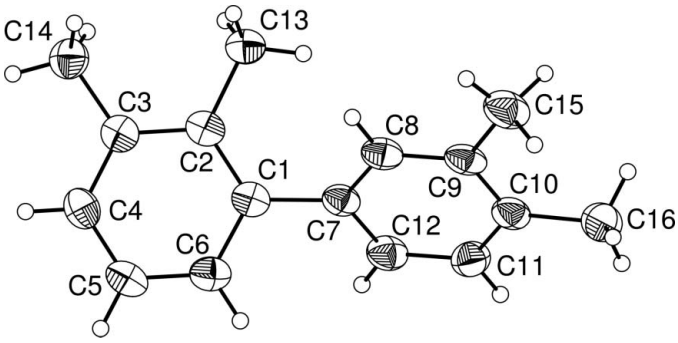

Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 70% probability level.

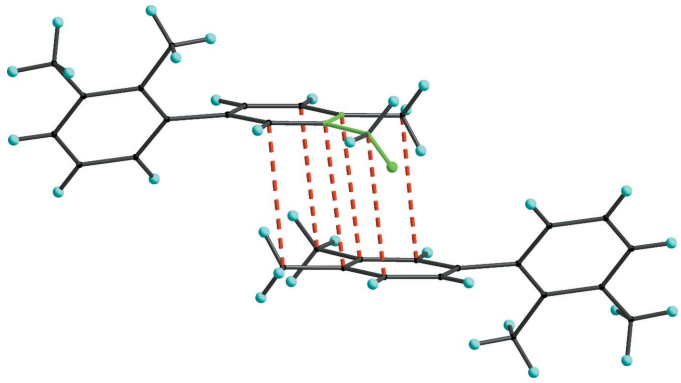

Figure 2
The motif showing the shortest intermolecular interactions in (I). The key C···C distances are shown in red, and one of the four C—C—C—H torsion angles is shown in green.

ination of the Cambridge Structural Database (Version 5.26; Allen, 2002) was performed to estimate the significance of this motif. We find that 19% of *ortho*-dimethylaryl-containing compounds appear to show this motif, having the six C···C intermolecular interactions shown in Fig. 2 shorter than 4 Å. Analysis of the distribution of torsion angles that correspond to C2—C3—C14—H14*A* and C3—C2—C13—H13*B* in (I) was performed on 198 structures showing this interaction (group 1), and for the remaining 848 structures that do not (group 2). Although the location of H atoms in X-ray crystallography is often problematic, it is common practice to refine this angle even when all else is constrained. Thus, we believe this analysis to be meaningful. Both groups of compounds show peaks in the histograms at 0, 30 and 60°, with an anomalous spike superimposed on a more normal distribution of the peak at 60°, and no statistically significant difference is seen in the distribution of methyl group orientations between these two groups (Fig. 3).

These results suggest that the interaction is not greatly affected by the $-CH_3$ orientation. They do not exclude the idea that a very weak hydrogen-bonding interaction may exist here. It must also be realised that, in the group 2 stuctures, other interaction motifs and geometries may give rise to the extra stability of the ~60° methyl group torsion angle.

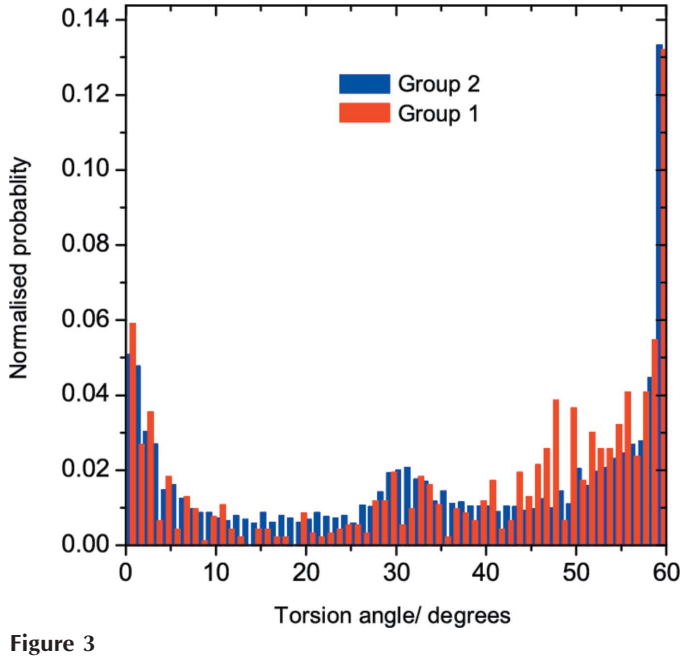

Figure 3
A plot of the distribution of C—C—C—H torsion angles for *ortho*-dimethylphenyl-containing compounds which appear to show this type of interaction (group 1: red) and for the group of *ortho*-dimethylphenyl that do not (group 2: blue). Data taken from 1046 structures in the Cambridge Structural Database.

Experimental

A mixture of 3,4-dimethylbromobenzene (4.400 g, 23.75 mmol), 2,3-dimethylphenylboronic acid (4.279 g, 28.55 mmol), palladium(II) acetate (0.1334 g, 0.595 mmol), triphenylphosphine (0.3889 g, 1.486 mmol), sodium(I) carbonate (5.083 g, 47.55 mmol), acetonitrile (30 ml) and water (30 ml) was heated to reflux for 24 h under an inert nitrogen atmosphere. The mixture was acidified with dilute HCl to remove the carbonate ions. The reaction mixture was then filtered, and the solvent removed on a rotary evaporator. Distilled water (30 ml) was then added, and the organic product extracted into dichloromethane (3 × 30 ml). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude product was recrystallized from ethanol (3.856 g, 77.1%). $C_{16}H_{18}$ requires C 91.37, H 8.63%; found C 91.23, H 8.62%. ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.25 (C1), 140.10 (C7), 137.09 (C3 or C9), 136.09 (C9 or C3), 134.84 (C10), 134.03 (C2), 130.66 (C11), 129.21 (C4), 128.58 (C8), 127.71 (C5), 126.80 (C6 or C12), 125.15 (C12 or C6), 20.73 (CH_3), 19.86 (CH_3), 19.48 (CH_3), 17.02 (CH_3); *m*/*z* 210.11 [*M*] (ESMS+); *m*/*z* 210.1408 [$^{12}C_{16}{}^{1}H_{18}$] (high resolution ESMS+); IR ν/cm^{-1} (KBr): 3160, 3038, 3018, 2995, 2985, 2943, 2920, 2882, 2860, 1502, 1463, 1455, 1380, 1308, 1278, 1243, 1221, 1197, 1180, 1163, 1136, 1110, 1083, 1061, 1045, 1020, 985, 965, 921, 898, 891, 820, 780, 758, 746, 720, 642, 600.

Crystal data

$C_{16}H_{18}$
M_r = 210.30
Triclinic, $P\overline{1}$
a = 7.6018 (5) Å
b = 7.7685 (5) Å
c = 11.6547 (7) Å
α = 77.106 (3)°
β = 81.047 (3)°
γ = 64.506 (3)°
V = 604.19 (7) Å^3
Z = 2
D_x = 1.156 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4912 reflections
θ = 0.1–27.5°
μ = 0.07 mm^{-1}
T = 293 (2) K
Prism, colourless
0.45 × 0.16 × 0.14 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.830, T_{max} = 0.991
9018 measured reflections
2731 independent reflections
1819 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 27.4°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
S = 1.04
2731 reflections
152 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.0932P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.038 (9)

Aryl H atoms were placed in ideal positions (C—H = 0.93 Å) and treated as riding, with a common refined U_{iso} = 0.0259 (17) Å^2. Methyl H atoms were constrained in rigid groups with free rotation about the C—C bond (C—H = 0.96 Å) and a common refined U_{iso} = 0.0388 (14) Å^2.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

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α = 77.106 (3)°
β = 81.047 (3)°
γ = 64.506 (3)°
V = 604.19 (7) Å^3
Z = 2
F(000) = 228
D_x = 1.156 Mg m^{-3}
Melting point: 41 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4912 reflections
θ = 0.1–27.5°
μ = 0.07 mm^{-1}
T = 293 K
Prism, colourless
0.45 × 0.16 × 0.14 mm

Data collection

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θ_{max} = 27.4°, θ_{min} = 1.8°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.127
S = 1.04
2731 reflections
152 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.0932P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.038 (9)

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	0.0416 (2)	0.76311 (19)	0.79774 (12)	0.0212 (3)
C6	−0.1272 (2)	0.7959 (2)	0.74562 (13)	0.0249 (4)
H6	−0.1222	0.8023	0.6646	0.0259 (17)*
C7	0.2222 (2)	0.7366 (2)	0.71854 (12)	0.0216 (3)
C2	0.0334 (2)	0.75530 (19)	0.92023 (13)	0.0216 (3)
C9	0.5602 (2)	0.5383 (2)	0.65895 (13)	0.0243 (4)
C3	−0.1433 (2)	0.77877 (19)	0.98797 (13)	0.0223 (4)
C10	0.5521 (2)	0.6757 (2)	0.55642 (13)	0.0249 (4)
C8	0.3968 (2)	0.5716 (2)	0.73800 (13)	0.0240 (4)
H8	0.4039	0.4807	0.8063	0.0259 (17)*
C12	0.2170 (2)	0.8719 (2)	0.61679 (13)	0.0261 (4)
H12	0.1035	0.9837	0.6016	0.0259 (17)*
C11	0.3798 (2)	0.8414 (2)	0.53772 (13)	0.0270 (4)
H11	0.3735	0.9342	0.4705	0.0259 (17)*
C4	−0.3070 (2)	0.8096 (2)	0.93287 (13)	0.0256 (4)
H4	−0.4232	0.8243	0.9779	0.0259 (17)*
C5	−0.2998 (2)	0.8189 (2)	0.81191 (14)	0.0263 (4)
H5	−0.4104	0.8404	0.7761	0.0259 (17)*
C15	0.7436 (2)	0.3550 (2)	0.68240 (14)	0.0333 (4)
H15A	0.7214	0.2740	0.7532	0.0388 (14)*
H15B	0.8485	0.3873	0.6917	0.0388 (14)*
H15C	0.7774	0.2871	0.6172	0.0388 (14)*
C13	0.2088 (2)	0.7251 (2)	0.98124 (13)	0.0251 (4)
H13A	0.2554	0.5995	1.0303	0.0388 (14)*
H13B	0.1720	0.8229	1.0290	0.0388 (14)*
H13C	0.3104	0.7339	0.9231	0.0388 (14)*
C16	0.7252 (2)	0.6461 (2)	0.46789 (14)	0.0323 (4)
H16A	0.6907	0.7514	0.4022	0.0388 (14)*
H16B	0.7628	0.5264	0.4407	0.0388 (14)*
H16C	0.8323	0.6416	0.5044	0.0388 (14)*
C14	−0.1574 (2)	0.7706 (2)	1.11946 (13)	0.0282 (4)
H14A	−0.2898	0.7989	1.1501	0.0388 (14)*
H14B	−0.1180	0.8644	1.1356	0.0388 (14)*
H14C	−0.0734	0.6435	1.1564	0.0388 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0228 (8)	0.0144 (7)	0.0258 (8)	−0.0059 (6)	−0.0044 (6)	−0.0038 (6)
C6	0.0264 (8)	0.0215 (8)	0.0256 (8)	−0.0063 (7)	−0.0059 (6)	−0.0063 (6)
C7	0.0217 (8)	0.0212 (7)	0.0236 (8)	−0.0075 (6)	−0.0046 (6)	−0.0080 (6)
C2	0.0237 (8)	0.0143 (7)	0.0273 (8)	−0.0074 (6)	−0.0053 (6)	−0.0031 (6)
C9	0.0229 (8)	0.0237 (8)	0.0276 (8)	−0.0055 (6)	−0.0081 (6)	−0.0112 (6)
C3	0.0252 (8)	0.0151 (7)	0.0266 (8)	−0.0086 (6)	−0.0034 (6)	−0.0020 (6)
C10	0.0218 (8)	0.0301 (8)	0.0251 (8)	−0.0081 (7)	−0.0039 (6)	−0.0129 (6)
C8	0.0258 (8)	0.0211 (7)	0.0262 (8)	−0.0080 (6)	−0.0077 (6)	−0.0061 (6)
C12	0.0230 (8)	0.0224 (8)	0.0277 (8)	−0.0022 (6)	−0.0063 (6)	−0.0057 (6)
C11	0.0272 (9)	0.0280 (8)	0.0229 (8)	−0.0085 (7)	−0.0036 (7)	−0.0033 (6)
C4	0.0224 (8)	0.0220 (8)	0.0330 (9)	−0.0098 (6)	−0.0008 (6)	−0.0055 (6)
C5	0.0229 (8)	0.0236 (8)	0.0338 (9)	−0.0083 (6)	−0.0082 (7)	−0.0058 (6)
C15	0.0254 (9)	0.0322 (9)	0.0374 (10)	−0.0023 (7)	−0.0081 (7)	−0.0119 (7)
C13	0.0276 (8)	0.0243 (8)	0.0245 (8)	−0.0108 (7)	−0.0049 (6)	−0.0038 (6)
C16	0.0260 (9)	0.0390 (9)	0.0313 (9)	−0.0088 (7)	−0.0016 (7)	−0.0146 (7)
C14	0.0307 (9)	0.0269 (8)	0.0283 (8)	−0.0143 (7)	−0.0017 (7)	−0.0022 (6)

Geometric parameters (Å, º)

C1—C6	1.404 (2)	C9—C10	1.403 (2)
C1—C2	1.408 (2)	C9—C15	1.5111 (19)
C1—C7	1.492 (2)	C3—C4	1.394 (2)
C6—C5	1.377 (2)	C3—C14	1.508 (2)
C7—C12	1.391 (2)	C10—C11	1.390 (2)
C7—C8	1.3983 (19)	C10—C16	1.507 (2)
C2—C3	1.408 (2)	C12—C11	1.388 (2)
C2—C13	1.5138 (19)	C4—C5	1.389 (2)
C9—C8	1.390 (2)		
C6—C1—C2	119.24 (14)	C10—C9—C15	120.36 (14)
C6—C1—C7	117.23 (13)	C4—C3—C2	119.58 (13)
C2—C1—C7	123.52 (13)	C4—C3—C14	119.58 (13)
C5—C6—C1	121.39 (14)	C2—C3—C14	120.83 (13)
C12—C7—C8	117.57 (14)	C11—C10—C9	118.47 (14)
C12—C7—C1	120.03 (13)	C11—C10—C16	120.25 (14)
C8—C7—C1	122.25 (13)	C9—C10—C16	121.28 (13)
C1—C2—C3	119.34 (13)	C9—C8—C7	122.40 (14)
C1—C2—C13	121.78 (13)	C11—C12—C7	120.60 (13)
C3—C2—C13	118.87 (13)	C12—C11—C10	121.66 (14)
C8—C9—C10	119.29 (13)	C5—C4—C3	121.24 (14)
C8—C9—C15	120.35 (14)	C6—C5—C4	119.21 (14)