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2,3,3′,4′-Tetramethylbiphenyl

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Key indicators

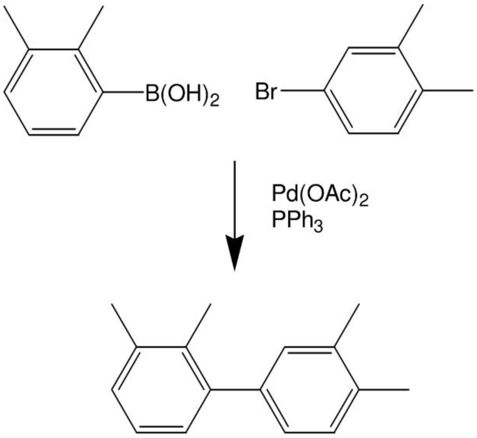
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.049
wR factor = 0.127
Data-to-parameter ratio = 18.0

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$\cdots$C (~3.7 Å) and C—H$\cdots$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$\overset{\cdots}{-}$C bond. This looks like a weak hydrogen-bonding interaction. An exam-

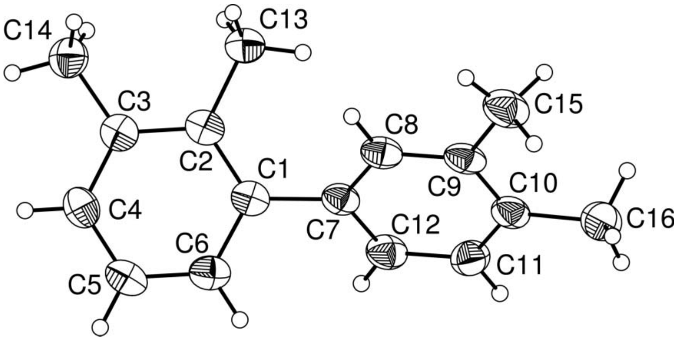


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 70% probability level.

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$\cdots$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.

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.

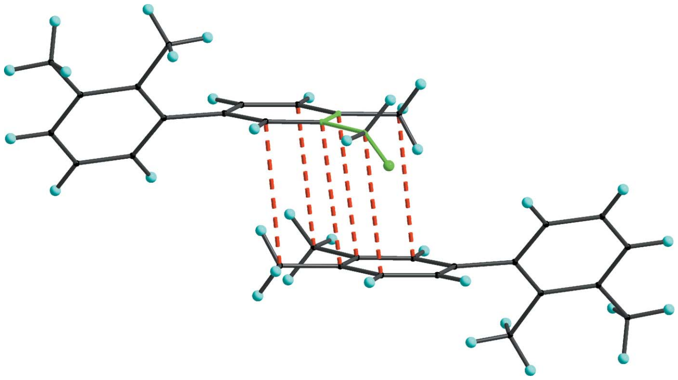


Figure 2
The motif showing the shortest intermolecular interactions in (I). The key C$\cdots$C distances are shown in red, and one of the four C—C—C—H torsion angles is shown in green.

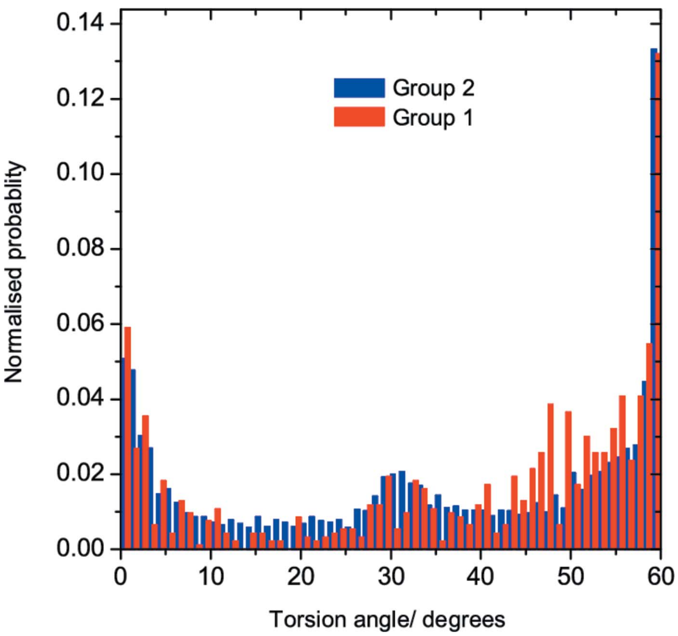


Figure 3
A plot of the distribution of C—C—C—H torsion angles for *ortho*-dimethylphenyl-containing compounds which appear to show this type of interaction (group 1: red) and for the group of *ortho*-dimethylphenyl that do not (group 2: blue). Data taken from 1046 structures in the Cambridge Structural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

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*α 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 $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\max} = 27.4^\circ$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 15$

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 $U_{\rm iso}$ = 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 $U_{\rm iso}$ = 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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