

Secondary interactions in two related terphenyl derivatives: 2',5'-dimethyl-*p*-terphenyl and 2',5'-bis(bromomethyl)-*p*-terphenyl

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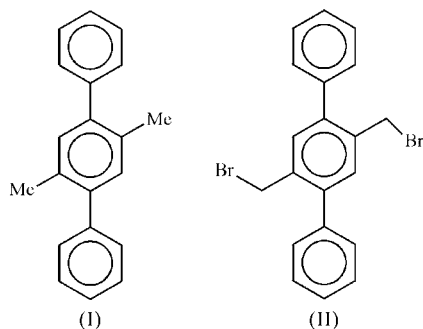
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In 2',5'-dimethyl-*p*-terphenyl, C₂₀H₁₈, which displays pseudo-symmetry (the true space group is *Pna*2₁, but less satisfactory refinement can also be achieved in *Pbcn*), the molecules are linked into chains by two short C—H··· π interactions to the centroid of the central ring. In 2',5'-bis(bromomethyl)-*p*-terphenyl, C₂₀H₁₆Br₂, the polar CH₂Br groups cause molecules to aggregate *via* C—H···Br and Br···Br interactions, forming a layer structure, in which the phenyl rings project outwards from the central, more polar, region.

Comment

We are interested in the packing geometry of terphenyl derivatives and have recently published the structures of 2,5,2'',5''-tetramethyl-*p*-terphenyl (Jones *et al.*, 2005) and 2,2''-bis(bromomethyl)-*p*-terphenyl (Jones & Kuś, 2005). The packing of the former is determined by C—H··· π interactions from one aromatic H atom and one methyl H atom to the



centroid of an outer ring, and the packing of the latter, which displays crystallographic inversion symmetry, by two C_{Ar}—H···Br interactions (but no Br···Br contacts shorter than 4.1 Å). We present here the structures of 2',5'-dimethyl-*p*-terphenyl, (I), and 2',5'-bis(bromomethyl)-*p*-terphenyl, (II), which are both used in stages of the synthesis of

diphenyl[2.2]paracyclophane (Czuchajowski & Zemanek, 1990).

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Neither molecule displays imposed crystallographic symmetry. Bond lengths and angles, *e.g.* the single bond lengths between the rings [1.501 (6) and 1.489 (6) Å for (I), and 1.488 (4) and 1.494 (4) Å for (II)], are normal. The two angles at unsubstituted atoms of the central rings are slightly widened from the ideal value of 120° in both structures (Tables 1 and 3). A search of the Cambridge Structural Database (Version 5.27; Allen, 2002) for aromatic C₆ rings with a 1,2,4,5 substitution pattern of C—C single bonds (excluding 1,2,4,5-tetracyanobenzene derivatives) gave 106 hits, with 242 individual C—C—C angles at the unsubstituted C atoms. Values ranged from 118.5 to 129.9° (mean value 122.8°); only three values lie below 120°.

In (I), the interplanar angles from the central benzene ring to phenyl rings 1 (*i.e.* C11—C16) and 3 (C31—C36) are 61.2 (2) and 61.5 (2)°, respectively, in the same direction, so that the outer phenyl rings are approximately parallel. In (II), the angles are 58.5 (1) and 75.2 (1)° in opposite senses. The angle subtended by the ring centroids is 179.7° in (I) and 176.3° in (II). The Br atoms in (II) are both directed away from the central ring to the same side.

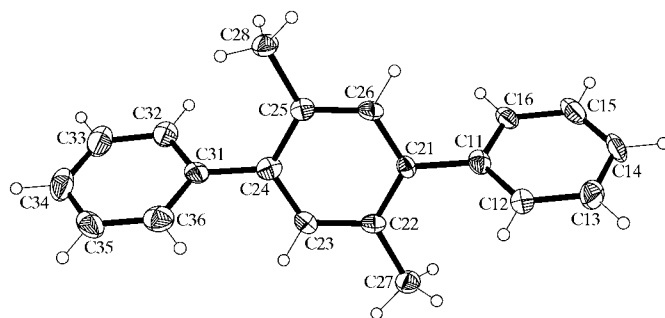


Figure 1
The molecule of (I). Displacement ellipsoids represent 50% probability levels.

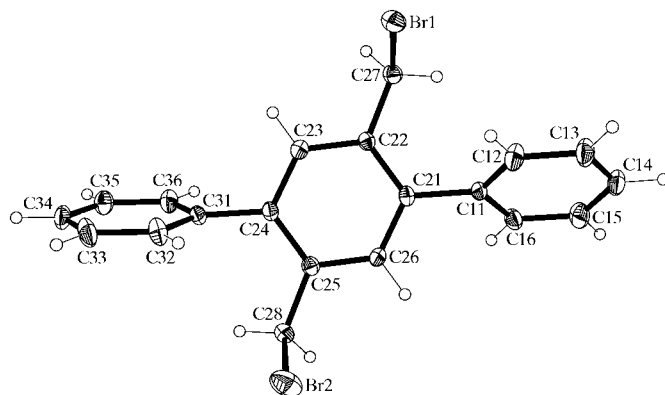


Figure 2
The molecule of (II). Displacement ellipsoids represent 50% probability levels.

The packing of (I) is characterized by five C—H $\cdots\pi$ contacts (Table 2; C_{gn} is the centre of gravity of ring n), of which the first two, from H atoms of the outer rings to the inner ring centroid C_{g2} , are much shorter and more linear than the others and may reasonably be described as ‘weak’ hydrogen bonds (Desiraju & Steiner, 1999). They connect neighbouring molecules related by the a -glide plane to form chains of molecules parallel to the a axis (Fig. 3). Each molecule accepts one and donates one hydrogen bond to each of its neighbours in the chain.

The bromomethyl groups in (II) would be expected to form weak hydrogen bonds because of the slight polarization, *viz.* Br δ^- /H δ^+ , and also to be involved in Br \cdots Br contacts (Pedirreddi *et al.*, 1994). This is indeed the case, in contrast to 2,2'-bis(bromomethyl)-*p*-terphenyl (see above); the molecules of (II) aggregate so as to form a polar layer parallel to the ab plane (Table 4 and Fig. 4), with the outer rings projecting outwards from the plane and interdigitating with the next layer. The two contacts Br1 \cdots Br1($1-x, 2-y, 1-z$) and Br1 \cdots Br2($-x, 1-y, 1-z$) [Br \cdots Br = 3.7776 (8) and 3.8886 (7) Å; C—Br \cdots Br = 75.7 (1) $^\circ$ ($\times 2$), and 93.82 (1) and 138.26 (1) $^\circ$] combine to form an approximately linear inversion-symmetric Br $_4$ unit with a Br \cdots Br \cdots Br angle of 143.46 (2) $^\circ$. The first contact is ‘type I’ according to the classification of Pedirreddi *et al.* (1994), with both C—C \cdots Br angles equal; the second is intermediate between types I and II (the latter type, with one angle *ca* 90 $^\circ$ and one *ca* 180 $^\circ$, is thought to indicate an attractive interaction between the Br atoms). Within the layer, two interactions of the form C—H $\cdots\pi$ (Table 4) are supported, although these are not drawn explicitly in Fig. 4. The hydrogen bond C14—H14 \cdots Br2ⁱⁱⁱ (for symmetry code, see Table 4) connects neighbouring layers.

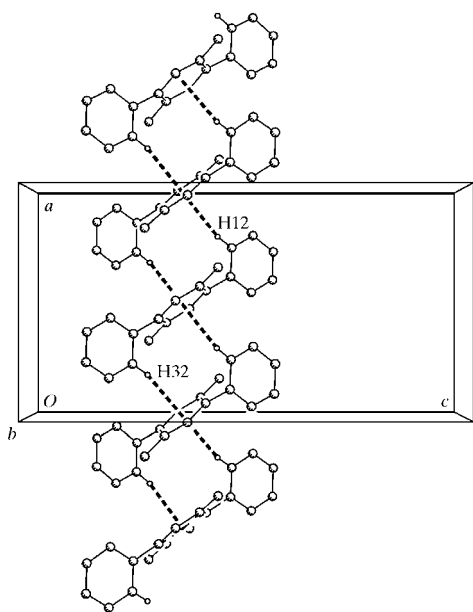


Figure 3

The packing of (I), showing a chain of molecules, viewed parallel to the b axis. Dashed lines indicate C—H $\cdots\pi$ interactions.

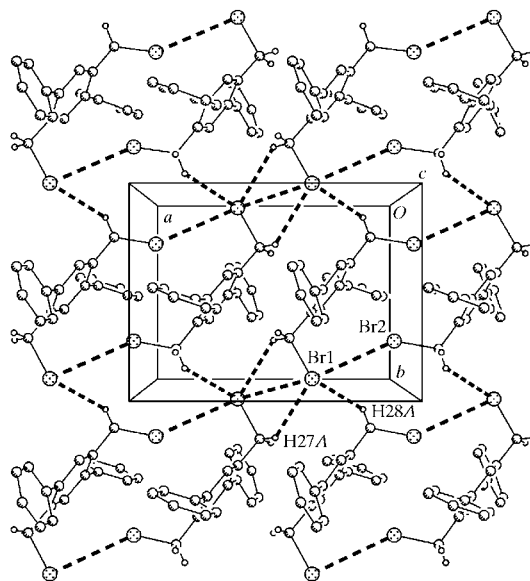


Figure 4

The packing of (II), showing the layer structure, viewed parallel to the c axis. Dashed lines indicate C—H \cdots Br and Br \cdots Br interactions. The following labelled atoms involve symmetry operations: Br2 at ($-x, -y+1, -z+1$); H27A at ($-x+1, -y+2, -z+1$); H28A at ($x, y+1, z$).

Experimental

Compound (I) was synthesized from *p*-xylene and cyclohexene according to the methods described by Deuschel (1951) and Ebel & Deuschel (1956). Compound (II) was obtained from (I) according to the method of Czuchajowski & Zemanek (1990). The analytical and spectroscopic data are consistent with the literature. Single crystals of (I) and (II) were grown by slow evaporation of an ethanol solution or a hexane/chloroform mixture, respectively. NMR data for (I): ^1H (CDCl_3 , 400 MHz): δ 7.48–7.36 (*m*, 10H), 7.19 (*s*, 2H), 2.31 (*s*, 6H); ^{13}C (100 MHz): δ 141.73, 140.85, 132.59, 131.85, 129.25, 128.09, 126.77, 19.93. NMR data for (II): ^1H NMR (CDCl_3 , 400 MHz): δ 7.56–7.37 (*m*, 12H), 4.49 (*s*, 4H); ^{13}C NMR (100 MHz): δ 141.67, 139.28, 135.51, 132.96, 128.98, 128.44, 127.76, 31.38.

Compound (I)

Crystal data

$\text{C}_{20}\text{H}_{18}$	$Z = 4$
$M_r = 258.34$	$D_x = 1.185 \text{ Mg m}^{-3}$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 10.5331$ (10) Å	$\mu = 0.07 \text{ mm}^{-1}$
$b = 6.8752$ (6) Å	$T = 133$ (2) K
$c = 20.0035$ (18) Å	Tablet, colourless
$V = 1448.6$ (2) Å 3	$0.35 \times 0.30 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	1755 independent reflections
ω scan	1546 reflections with $I > 2\sigma(I)$
12571 measured reflections	$R_{\text{int}} = 0.102$
	$\theta_{\text{max}} = 28.3^\circ$

Table 1

Selected geometric parameters (Å, $^\circ$) for (I).

C11—C21	1.501 (6)	C24—C31	1.489 (6)
C24—C23—C22	123.7 (4)	C25—C26—C21	123.2 (4)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.147$
 $S = 1.12$
 1755 reflections
 183 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.2909P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$Cg1$, $Cg2$ and $Cg3$ are the centroids of rings C11–C16, C21–C26 and C31–C36, respectively

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C12–H12 \cdots Cg2 ⁱ	0.95	2.76	3.692 (5)	167
C32–H32 \cdots Cg2 ⁱⁱ	0.95	2.72	3.653 (5)	166
C14–H14 \cdots Cg3 ⁱⁱⁱ	0.95	2.95	3.672 (6)	134
C34–H34 \cdots Cg1 ^{iv}	0.95	3.14	3.776 (6)	126
C27–H27B \cdots Cg1 ^v	0.98	3.02	3.616 (5)	121
C28–H28A \cdots Cg3 ^{vi}	0.98	2.87	3.607 (5)	132

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

Compound (II)

Crystal data

$C_{20}H_{16}Br_2$
 $M_r = 416.15$
 Monoclinic, $P2_1/n$
 $a = 11.1019$ (12) \AA
 $b = 8.2736$ (11) \AA
 $c = 17.726$ (2) \AA
 $\beta = 90.248$ (4) $^\circ$
 $V = 1628.2$ (3) \AA^3

$Z = 4$
 $D_x = 1.698 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 4.97 \text{ mm}^{-1}$
 $T = 133$ (2) K
 Tablet, colourless
 $0.30 \times 0.30 \times 0.13 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.394$, $T_{\max} = 0.564$
 (expected range = 0.366–0.524)

30410 measured reflections
 4955 independent reflections
 3628 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 30.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.132$
 $S = 1.04$
 4955 reflections
 199 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2 + 4.9114P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.53 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.66 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

Br1–C27	1.981 (3)	C11–C21	1.488 (4)
Br2–C28	1.958 (4)	C24–C31	1.494 (4)
C21–C22–C27	122.6 (3)	C21–C26–C25	122.6 (3)
C23–C22–C27–Br1	81.6 (3)	C26–C25–C28–Br2	77.6 (4)

Table 4

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$Cg1$ and $Cg2$ are the centroids of rings C11–C16 and C21–C26, respectively.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C27–H27A \cdots Br1 ⁱ	0.99	3.11	3.807 (4)	128
C28–H28A \cdots Br1 ⁱⁱ	0.99	3.00	3.876 (4)	148
C14–H14 \cdots Br2 ⁱⁱⁱ	0.95	3.13	3.833 (4)	132
C36–H36 \cdots Cg1 ^{iv}	0.95	3.01	3.779 (5)	139
C27–H27A \cdots Cg2 ^{iv}	0.95	3.02	3.540 (4)	114

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

Structure (I) is pseudosymmetric; it can be solved and refined in the centrosymmetric space group $Pbcn$ (with the a and c axes exchanged from the current setting) with half a molecule in the asymmetric unit, but (i) the R values are significantly worse ($R1 = 10\%$ and $wR2 = 29\%$), (ii) the U values are more anisotropic (corresponding to a forced superposition of both molecule halves), (iii) the scaling factor $\text{mean}(F_o^2)/\text{mean}(F_c^2)$ for the weakest reflections is 19 in $Pbcn$ compared with 2 in $Pna2_1$, and all the badly fitting reflections are weak and have $F_o > F_c$, and (iv) the absences for the third glide plane are not exactly obeyed (mean $I/\sigma = 5$). In the absence of significant anomalous scattering, Friedel pairs were merged and the Flack (1983) parameter is thus meaningless. To improve refinement stability, the common components of displacement factors of neighbouring atoms were restrained to be equal using the command DELU (SHELXL97; Sheldrick, 1997).

There are some problems with residual electron density in (II). The largest feature of $2.5 \text{ e } \text{\AA}^{-3}$ (not exceptionally large for a polybrominated organic substance) lies 0.95 \AA from Br2 and might well be explained as a residual absorption error or possibly a poor representation of the actual displacement of Br2 in terms of an ellipsoid. Two further features lie close to H28A and might represent alternative positions for Br2. A refinement of the site-occupation factor of Br2 with no other changes gave the value 0.916 (2). Possible causes might be a disorder as mentioned above or contamination by a non-brominated compound. The initially isolated sample of (II) did indeed show a trace of the non-brominated material in its NMR spectrum, but was recrystallized several times to provide the crystal for analysis. Contamination by Cl is unlikely but just possible (the solvents CCl_4 , $CHCl_3$ and CH_2Cl_2 were used at various stages); we have not noticed such contamination in any of a wide variety of other brominated hydrocarbons prepared by similar methods. Attempts to refine disorder models were not entirely convincing. The crystal quality was not very good (irregular reflection profiles), which may of course be a result of some undefined contamination. We believe that the structure as presented is unlikely to be severely in error, and therefore simply draw attention to these negative features whilst admitting that we have no totally satisfactory remedy.

Methyl H atoms were clearly identified in difference syntheses, idealized and refined as rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model. C–H bond lengths were fixed at 0.99 (methylene), 0.98 (methyl) or 0.95 \AA (aromatic), and methyl H–C–H angles at 109.5° . $U_{\text{iso}}(\text{H})$ values were fixed at 1.2 times $U_{\text{eq}}(\text{C})$ of the parent atom.

For both compounds, data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3053). Services for accessing these data are described at the back of the journal.

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