Synthesis and structures of 8-benzyl[2.2]metaparacyclophanes

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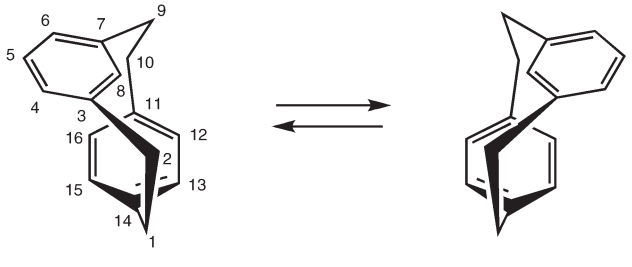
A convenient preparation of 8-benzyl[2.2]metaparacyclophanes using $TiCl_4$ catalysed Friedel–Crafts benzylation of arenes with 8-bromomethyl[2.2]metaparacyclophane is described. The structures of these novel 8-benzyl[2.2]metaparacyclophanes in solution are also discussed.

Keywords: cyclophanes, Friedel–Crafts benzylation, chemical shifts, ring current effect, conformation

[2.2]MPCP ([2.2]metaparacyclophane) was first prepared[1] via acid-catalysed rearrangement of [2.2]paracyclophane. Since then, [2.2] of MPCP has been prepared by other synthetic methods.[2–9] A versatile procedure, appropriate for the synthesis of substituted derivatives, makes use of 2,11-dithia[3.3]MPCP as a precursor.[3] The *meta*-bridged benzene ring of [2.2]MPCP has been shown to undergo conformational flipping[2,3,6,8,10–12] with a substantial energy barrier (*ca* 80 kJ mol^{-1}), so that elevated temperatures (about 400 K) were required for the interconversion to be revealed on NMR time scale. A large part of this energy barrier is believed to arise from steric destabilisation of the transition state in which the 8-hydrogen atom of the *meta*-bridged ring impinges into the π-electron cloud of the *para*-bridged one.

According to X-ray crystallographic studies of [2.2]MPCP,[13] the deformations of benzene rings in [2.2]MPCP are similar to those of the corresponding rings in [2.2]*para*- and [2.2]*meta*-cyclophane, with *para*- and *met*a-bridged rings bent in a boat- and a chair-like form, respectively. The angle between the two aromatic planes defined by the carbon atoms, 3, 4, 6, and 7, on one hand, and 12, 13, 15, and 16, on the other, is about 13°. Note that the angle between the 11, 12, 16-plane and 10, 11-bond vector (or between 13, 14, 15-plane and 1, 14-bond vector) is even larger than the analogous angle in [2.2]paracyclophane. The para-briged moiety of [2.2]MPCP is thus more strongly tilted than those of the isomeric compound. The rotation of the methyl group (which is fixed above the *para*-benzene ring) of 8-methyl[2.2]MPCP appears to be hindered, if not blocked. However, proton resonance measurements down to –20 °C show no rotation barrier for the molecule in solution.[14]

Thus introduction of methyl substituted benzyl groups to the 8-position of [2.2] of MPCP might increase the rotation barrier around the [2.2]MPCP-CH_2–Ar for the molecule in solution. It is surprising that there have been no reports on the preparation of 8-(methyl substituted benzyl)[2.2]MCPs despite the fact that the chemical shift of the 2, 3, and 4-methyl substituent provides a convenient probe for ^{1}H NMR studies of any possible conformational changes. There has been substantial interest in investigating the structures of 8-(methyl substituted benzyl)[2.2]MPCPs. We report here the convenient preparation of 8-(methyl substituted benzyl)[2.2]MPCPs using $TiCl_4$ catalysed Friedel-Crafts benzylation of arenes with 8-bromomethyl[2.2]MPCP **2**.



Scheme 1

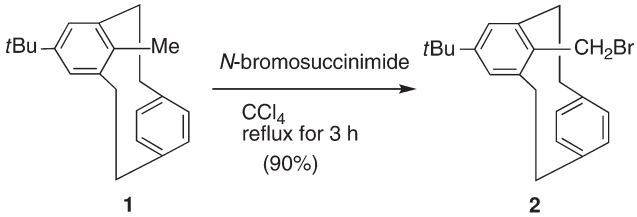
Results and discussion

The preparative route of 8-bromomethyl[2.2]MPCP **2** is shown in Scheme 2 following our previous reported procedure.[15,16] Thus bromination of **1**[14,17–21] with *N*-bromosucccinimide (NBS) in the presence of benzoyl peroxide under CCl_4 reflux for 3 h afforded the desired 8-bromomethy[2.2]MPCP **2** in 90% yield.

The $TiCl_4$-catalysed benzylation of various arenes with 8-bromomethyl-5-*tert*-butyl[2.2]MPCP **2** was carried out under various conditions and the results are compiled in Table 1. The $TiCl_4$-catalysed benzylation of benzene with compound **2** at 20 °C for 5 min led to benzylation reaction affording the desired 8-benzyl[2.2]MCP **3a** in 21% yield along with the recovery of the starting compound **2** in 79% yield. The prolonged reaction time to 2 h under the same reaction conditions above led to increase the yield of 8-benzyl[2.2]MPCP **3a** to 81%.

The $TiCl_4$-catalysed benzylation of methylarenes with compound **2** at 20 °C led to a benzylation reaction within 5 min affording the desired 8-(methyl substituted benzyl) [2.2] MPCPs **3b–g** in good yields. Methyl functions increased the yield of the benzylation product because of its high electron-donating ability which is similar to normal aromatic benzylation.[22] Thus, the yields of **3** are comparable for toluene, *o*-xylene, *m*-xylene, *p*-xylene, and mesitylene, and somewhat lower for benzene which is the same as $TiCl_4$-catalysed benzylation. The reaction is generally applicable for arenes that normally undergo Friedel–Crafts benzylation. As shown in Table 1, the present method provides excellent yields of diphenylmethanes **3**, and no concomitant *trans-tert*-butylation was observed under the reaction conditions.

The amount of the catalyst used relative to 8-bromomethyl [2.2]MPCP **2** was between 0.5 and 1.5 by molar ratio. Optimum yields were obtained with 1.5 mole of catalyst, whereas a 0.5 molar ratio gave only slightly lower yields and the prolonged reaction time to complete the present benzylation reaction. It is difficult, however, to assess properly the selectivity of the reactions and the exact nature of the reaction. The substrate and positional selectivity of the present benzylation reaction under the $TiCl_4$ catalyst was found to be almost the same as that obtained by the reaction with benzyl halides under the $TiCl_4$ catalyst.[23]



1 **2**

Scheme 2

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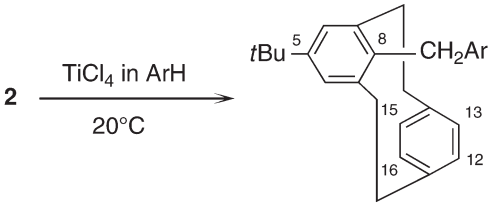


3 a; Ar= C_6H_5
b; Ar= 2-Me-C_6H_4
c; Ar= 4-Me-C_6H_4
d; Ar= 3,4-$(Me)_2$-C_6H_3
e; Ar= 2,4-$(Me)_2$-C_6H_3
f ; Ar= 2,5-$(Me)_2$-C_6H_3
g; Ar= 2,4,6-$(Me)_3$-C_6H_2

Scheme 3

The structures of **3a**–**g** were determined on the basis of their elemental analyses and spectral data. The ^{1}H NMR spectrum of **3a** in $CDCl_3$ shows a singlet at δ 3.57 ppm for methylene protons of benzyl group at 8-position which is in a strongly shielding region of opposite *para*-bridged benzene.[24–30] It was also found that the ^{1}H NMR spectrum of **3a** shows a doublet (J = 1.0 Hz) at δ 5.80 ppm for internal aromatic C-15 and C-16 protons which are in a strongly shielding region of opposite *meta*-bridged benzene ring and δ 7.05 ppm for external aromatic C-12 and C-13 protons, respectively. The mass spectral data for **3a** (M^+ = 354) strongly support 8-benzyl[2.2]MPCP structure. Similar findings were observed in compounds **3b**–**g**.

The benzyl protons of the above-prepared 8-(methyl substituted benzyl)[2.2] of MPCPs **3b**–**g** are also observed as a singlet in ^{1}H NMR spectra at 25 °C. The conformation of 8-(methyl substituted benzyl)[2.2]MPCPs **3b**–**g** has been evaluated by dynamic ^{1}H NMR spectroscopy. However, for instance, the methylene protons of 8-(2-tolylmethyl)[2.2]MPCP **3b** appear each as a singlet even below –60 °C ($CDCl_3/CS_2$ 1/3), and the rate of the rotation around the [2.2]MCP-CH_2–Ar of **3b** is faster than the NMR time scale above this temperature. Similar findings were obtained in other 8-(2-methyl substituted benzyl)[2.2]MPCPs **3e**–**g**. These results indicate that the rotation barrier around the [2.2]MPCP-CH_2–Ar **3e–g** are still quite low in spite of the introduction of methyl group at the 2-position of the 8-benzyl group.

To study the structures of 8-(methyl substituted benzyl)[2.2]MPCPs **3b**–**3g** in more detail by using chemical shifts, we have attemped to prepare the corresponding reference compound **5**. In fact, the similar $TiCl_4$-catalysed benzylation of benzene and methylarenes with 2-bromomethyl-5-*tert*-butyl-1,3-dimethylbenzene **4** at 20 °C for 4 h led to a benzylation reaction within 4 h affording the desired benzylated product **5a**–**g** in good yields.

Table 1 $TiCl_4$ catalysed benzylation of arenes with **2**[a]

Run	ArH	Reaction time/min	Yield/%[b,c]	Recovery of **2**
1	benzene	120	**3a** (81) [75]	19
2	toluene	5	**3b** (0.4), **3c** (92) [87]	7.6
3	*o*-xylene	5	**3d** (93) [90]	7
4	*m*-xylene	5	**3e** (95) [91]	5
5	*p*-xylene	5	**3f** (98) [92]	2
6	mesitylene	5	**3g** (99) [93]	1

[a] [Ar-H]:[**2**] = 30 : 1 [mol/mol]; [$TiCl_4$]:[**2**] = 1.5 : 1 [mol/mol].
[b] The yields were determined by GLC. analysis.
[c] Isolated yields are shown in square brackets.

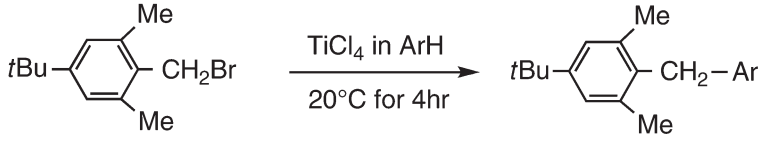
Table 2 Chemical shifts of the methylene protons and aromatic protons of 8-benzyl[2.2]MPCPs **3a** and 8-(methyl substituted benzyl)[2.2]MPCPs **3b–g**[a]

Substrate		δ_{CH2}	$\delta_{C\text{-}4,6}$	$\delta_{C\text{-}12,13}$	$\delta_{C\text{-}15,16}$
3a	H	3.57	6.77	7.05	5.80
3b	2-Me	3.47	6.79	7.11	5.82
3c	4-Me	3.44	6.74	7.06	5.78
3d	3,4-$(Me)_2$	3.49	6.75	7.07	5.79
3e	2,4-$(Me)_2$	3.34	6.70	7.01	5.73
3f	2,5-$(Me)_2$	3.43	6.68	7.00	5.72
3g	2,4,6-$(Me)_3$	3.55	6.79	7.16	5.79

[a] Determined in $CDCl_3$ using $SiMe_4$ as a reference.

The values of the chemical shifts of the methylene protons and aromatic protons of 8-benzyl[2.2]MPCPs **3a** and 8-(methyl substituted benzyl)[2.2]MPCPs **3b**–**g** are summarised in Table 2. The chemical shifts of the methylene protons in 8-(methyl substituted benzyl)[2.2]MPCPs **3b**–**3g** (δ = 3.34–4.55 ppm) are in an upper field than those (δ = 3.82–4.00 ppm) in the reference compounds **5a**–**5g** ($\Delta\delta$ = 0.40–0.53 ppm). It was also found that the chemical shifts of internal aromatic C-15 and C-16 protons (δ = 5.72–5.82 ppm) are also in the upper field than that of *p*-xylene (δ = 7.04 ppm) due to being in a strongly shielding region of opposite meta-bridged benzene ring ($\Delta\delta$ = 1.22–1.32 ppm). On the other hand, the chemical shifts of external aromatic C-12 and C-13 protons (δ = 7.00–7.16 ppm) are almost same as that of *p*-xylene.

The values of the chemical shifts differences of the methyl protons and aromatic protons of the 8-(methyl substituted benzyl) group between [2.2]MPCPs **3** and the reference compounds **5** are also summarised in Table 3. The upper field chemical shifts are observed for the 2-methyl protons on the 8-(methyl substituted benzyl) group in **3e**–**3g** ($\Delta\delta$ = 0.26–0.38 ppm) but smaller upper field shift was observed in **3b** ($\Delta\delta$ = 0.07 ppm). Interestingly, the aromatic proton at the 6-position of 8-(methyl substituted benzyl) group in **3b**, **3e** and **3f** was shifted upper field at δ 5.74–5.96 ppm ($\Delta\delta$ = 0.56–0.65 ppm)



4

5 a; Ar = C_6H_5 (76%)
b; Ar = 2-Me-C_6H_4 (3%)
c; Ar = 4-Me-C_6H_4 (82%)
d; Ar = 3,4-$(Me)_2$-C_6H_3 (85%)
e; Ar = 2,4-$(Me)_2$-C_6H_3 (87%)
f ; Ar = 2,5-$(Me)_2$-C_6H_3 (86%)
g; Ar = 2,4,6-$(Me)_3$-C_6H_2 (90%)

Scheme 4

Table 3 Chemical shifts of the methyl protons and aromatic protons of 8-(methyl substituted benzyl) group in [2.2]MPCPs **3a** and **3b–g**[a]

Substrate		$\delta_{2\text{-Me}}(\Delta\delta)$[c]	$\delta_{6\text{-H}}(\Delta\delta)$[c]	$\delta_{3\text{-H}}(\Delta\delta)$[c]
3a	H	–	6.68 (0.25)	7.05 (0.09)
3b	2-Me	2.35 (0.07)	5.96 (0.56)	6.93 (0.25)[b]
3c	4-Me	–	6.56 (0.41)	6.86 (0.18)
3d	3,4-$(Me)_2$	–	6.36 (0.45)	6.81 (0.12)
3e	2,4-$(Me)_2$	2.07 (0.30)	5.79 (0.65)	6.54 (0.25)
3f	2,5-$(Me)_2$	1.99 (0.38)	5.74 (0.59)	6.80 (0.27)
3g	2,4,6-$(Me)_3$	1.82 (0.26)	–	6.61 (0.17)

[a] Determined in $CDCl_3$ using $SiMe_4$ as a reference.
[b] The midpoint value of multiplets.
[c] $(\Delta\delta) = \delta_{reference} - \delta_{MPCP}$

than those in the unsubstituted **3c** and **3d** (δ 6.56 and 6.36 ppm) ($\Delta\delta$ = 0.41 and 0.45 ppm). The much larger upfield shifts are observed in the 8-(2-tolylmethyl)[2.2]MPCPs **3b**, **3e** and **3f**. Thus, the chemical shifts of the aromatic proton at the 6-position of 8-(2-tolylmethyl) [2.2]MPCPs **3b**, **3e** and **3f** should be strongly affected by the methyl group at the 2-position of 2-tolylmethyl group. The interaction between the methyl group at the 2-position and opposite *para*-benzene ring might be much more unfavourable for 8-(2-methylbenzyl)[2.2]MPCPs **3b**, **3e** and **3f**. Thus, the steric repulsion of 2-methyl group for the opposite *para*-benzene ring and the methylene groups at the both bridged ethylene chains could shorten the distance between the aromatic proton at the 6-position and the opposite *para*-benzene ring as well as the distance between the methyl group at the 2-position of 8-(2-methylbenzyl) group and *meta*-benzene ring.

From these findings, it is concluded that 8-(2-methylbenzyl)[2.2]MPCP **3b** has the conformers **A** and **B** and that 8-(2-methylbenzyl)[2.2]MPCP **3b** might exist preferentially in conformer **A** because of steric repulsion between the 2-methyl group and the bridged ethylene bonds. Accordingly, the 2-methyl protons and aromatic proton at the 6-position of 2-methylbenzyl group in **3b** are located in the region affected by the ring current of the aromatic rings on both the same side and the opposite aromatic rings. Although it is difficult to conclude from the available results that the structure of di- and trimethylsubstituterd analogues **3e–g**, which showed the slightly different chemical shifts from that of **3b**, one might suppose the increased π-density of the tolylmethyl group by introduction of electron-donating methyl groups might lead to adopting the different conformation arising from the interaction between the aromatic ring of tolylmethyl group and the *para*-benzene ring.

Conclusions

We have demonstrated $TiCl_4$ catalysed Friedel–Crafts benzylation of arenes with 8-bromomethyl[2.2]MPCP **2** to afford the corresponding 8-benzyl[2.2]MPCPs **3**. The rotation barrier around the 8-(methyl substituted benzyl)[2.2]MPCP **3b** and **3e–g** are still quite low in spite of the introduction of methyl group at the *ortho* position of the 8-benzyl group. Interestingly, the 2-methyl protons and aromatic proton at the 6-position of the 8-(methyl substituted benzyl) group in **3b** and **3e–g** are affected by the ring current of both the aromatic ring on the same side and that of the opposite *para*-benzene ring. Further studies on the chemical properties of the 8-(methyl substituted benzyl) of [2.2]MPCPs **3** are in progress.

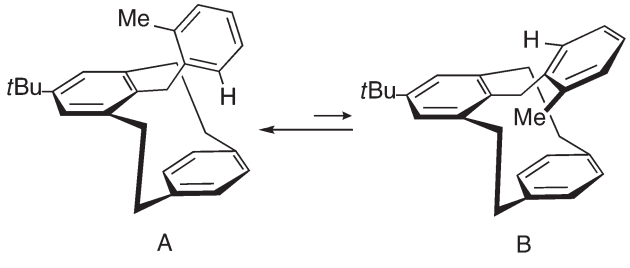


Fig. 1 Structure of 8-(2-methylbenzyl)[2.2]MPCP 3b.

Experiment

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5. G.L.C. analyses were performed by Shimadzu gas chromatograph, GC-14A; Silicone OV-1, 2 m; programmed temperature rise, 12 °C/min; carrier gas nitrogen, 25 mL min^{-1}.

The preparation of 5-*tert*-butyl-8-methyl[2.2]MPCP **1**[15] and 4-*tert*-butyl-2,6-dimethylbromomethylbenzene **4**[16,31] have been previously described.

Bromination of 5-tert-*butyl-8-methyl[2.2]metaparacyclophane* (**1**) *with N-bromo of succinimide:* After a mixture of 5-*tert*-butyl-8-methyl [2.2]metaparacyclophane **1** (3.03 g, 10.88 mmol), *N*-bromosuccinimide (2.32 g, 13.06 mmol), and benzoyl peroxide (100 mg) in carbon tetrachloride (150 mL) had been refluxed for 7 h, the precipitates formed were filtered off. The filtrate was washed with 10% sodium hydroxide and water. The organic layer was dried over sodium sulfate and evaporated *in vacuo* to leave a colourless solid which was recrystallised from hexane to give 8-bromomethy*l*-5-*tert*-butyl[2.2] metaparacyclophane **2** (3.50 g, 90%) as colourless prisms; m.p. 163–164 °C; δ_H ($CDCl_3$) 1.32 (9H, s, *t*Bu), 2.65–2.82 (6H, m, CH_2), 3.16–3.20 (2H, m, CH_2), 4.23 (2H, s, CH_2), 5.77 (2H, d, *J* = 1.2 Hz, Ar*H*), 6.81 (2H, s, Ar*H*) and 6.96 (2H, d, *J* = 1.2 Hz, Ar*H*); *m*/*z* 356 and 358 (M^+) (Found: C, 70.60; H, 7.11. $C_{21}H_{25}Br$ (357.34) requires C, 70.59; H, 7.05%).

Benzylation of benzene with 8-bromomethyl-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**2**): $TiCl_4$ (0.16 mL butyl[2.2]metaparacyclophane **2** (358 mg, 1.0 mmol) in benzene (2.67 mL, 30 mmol) at 0 °C. After the reaction mixture had been stirred at room temperature for 2 h, it was poured into ice-water and extracted with benzene. The extract was dried over anhydrous sodium sulfate and concentrated. The residue was subjected to silica-gel (Wako, C-300; 100 g) column chromatography using as eluent hexane–benzene (1:1) to give 8-benzyl-5-di-*tert*-butyl[2.2]metaparacyclophane **3a** (266 mg, 75%) as colourless prisms (from EtOH), m.p.136–138 °C; δ_H ($CDCl_3$) 1.32 (9H, s, *t*Bu), 2.52–2.67 (4H, m, CH_2), 2.80–2.87 (2H, m, CH_2), 3.15–3.23 (2H, m, CH_2), 3.57 (2H, s, Ar-CH_2), 5.80 (2H, d, *J* = 1.0 Hz, $H_{15,16}$), 6.68 (2H, d, *J* = 7.4 Hz, Ar*H*), 6.77 (2H, s, $H_{4,6}$) and 6.99–7.09 (5H, m, $H_{12,13}$, Ar*H*); *m*/*z* 354 (M^+) (Found: C, 91.21; H, 8.62. $C_{27}H_{30}$ (354.54) requires C, 91.47; H, 8.53%).

Benzylation of arenes with **2** was carried out using the same procedure as described above and product yields are compiled in Table 1.

8-(2-Methylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3b**): Colourless prisms (from EtOH), m.p.147–149 °C; δ_H ($CDCl_3$) 1.35 (9H, s, *t*Bu), 2.35 (3H, s, *Me*), 2.47–2.71 (4H, m, CH_2), 3.11–3.22 (4H, m, CH_2), 3.47 (2H, s, Ar-CH_2), 5.82 (2H, d, *J* = 1.0 Hz, $H_{15,16}$), 5.96 (1H, d, *J* = 7.5 Hz, Ar*H*), 6.79 (2H, s, $H_{4,6}$), 6.81(1H, dd, *J* = 7.5, 6.6 Hz, Ar*H*), 6.92 (1H, dd, *J* = 7.5, 6.6 Hz, Ar*H*), 7.03 (1H, d, *J* = 7.5 Hz, Ar*H*) and 7.11 (2H, d, *J* = 1.0 Hz, $H_{12,13}$); *m*/*z* 368 (M^+) (Found: C, 91.11; H, 8.62. $C_{28}H_{32}$ (368.56) requires C, 91.25; H, 8.75%).

8-(4-Methylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3c**): Colourless prisms (from EtOH), m.p.140–141 °C; δ_H ($CDCl_3$) 1.18 (9H, s, *t*Bu), 2.17 (3H, s, *Me*), 2.40–3.30 (8H, m, CH_2), 3.44 (2H, s, Ar-CH_2), 5.78 (2H, d, *J* = 1.0 Hz, $H_{15,16}$), 6.56 (2H, d, *J* = 8.0 Hz, Ar*H*), 6.74 (2H, s, $H_{4,6}$), 6.86 (2H, d, *J* = 8.0 Hz, Ar*H*) and 7.06 (2H, d, *J* = 1.0 Hz, $H_{12,13}$); *m*/*z* 368 (M^+) (Found: C, 91.20; H, 8.84. $C_{28}H_{32}$ (368.56) requires C, 91.25; H, 8.75%).

8-(3,4-Dimethylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3d**): Colourless prisms (from EtOH), m.p.158–160 °C; δ_H ($CDCl_3$) 1.31

(9H, s, *t*Bu), 2.08 (6H, s, *Me*), 2.55–2.66 (4H, m, CH_2), 2.81–2.88 (2H, m, CH_2), 3.12–3.21 (2H, m, CH_2), 3.49 (2H, s, Ar-CH_2), 5.79 (2H, d, J = 1.0 Hz, $H_{15,16}$), 6.36 (1H, d, J = 7.8 Hz, Ar*H*), 6.50 (1H, s, Ar*H*), 6.75 (2H, s, $H_{4,6}$), 6.81 (1H, d, J = 7.8 Hz, Ar*H*) and 7.07 (2H, d, J = 1.0 Hz, $H_{12,13}$); *m/z* 382 (M^+) (Found: C, 90.88; H, 9.05. $C_{29}H_{34}$ (382.59) requires C, 91.04; H, 8.96%).

8-(2,4-Dimethylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3e**): Colourless prisms (from EtOH), m.p.134–135 °C; δ_H ($CDCl_3$) 1.26 (9H, s, *t*Bu), 2.07 (3H, s, *Me*), 2.22 (3H, s, *Me*), 2.40–2.60 (8H, m, CH_2), 3.34 (2H, s, Ar-CH_2), 5.73 (2H, d, J = 1.0 Hz, $H_{15,16}$), 5.79 (1H, d, J = 7.8 Hz, Ar*H*), 6.54 (1H, d, J = 7.8 Hz, Ar*H*), 6.70 (2H, s, $H_{4,6}$), 6.77 (1H, s, Ar*H*) and 7.01 (2H, d, J = 1.0 Hz, $H_{12,13}$); *m/z* 382 (M^+) (Found: C, 90.83; H, 9.04. $C_{29}H_{34}$ (382.59) requires C, 91.04; H, 8.96%).

8-(2,5-Dimethylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3f**): Colourless prisms (from EtOH), m.p.109–111 °C; δ_H ($CDCl_3$) 1.35 (9H, s, *t*Bu), 1.99 (3H, s, *Me*), 2.28 (3H, s, *Me*), 2.50–2.70 (6H, m, CH_2), 3.12–3.16 (2H, m, CH_2), 3.43 (2H, s, Ar-CH_2), 5.72 (2H, d, J = 1.0 Hz, $H_{15,16}$), 5.74 (1H, s, Ar*H*), 6.50 (1H, d, J = 7.5 Hz, Ar*H*), 6.68 (2H, s, $H_{4,6}$), 6.80 (1H, d, J = 7.5 Hz, Ar*H*), and 7.00 (2H, d, J = 1.0 Hz, $H_{12,13}$); *m/z* 382 (M^+) (Found: C, 90.89; H, 8.93. $C_{29}H_{34}$ (382.59) requires C, 91.04; H, 8.96%).

8-(2,4,6-Trimethylbenzyl)-5-tert-*butyl*[*2.2*]*metaparacyclophane* (**3g**): Colourless prisms (from EtOH), m.p.151–153 °C; δ_H ($CDCl_3$) 1.29 (9H, s, *t*Bu), 1.82 (6H, s, *Me*), 2.14 (3H, s, *Me*), 2.41–2.57 (6H, m, CH_2), 3.13–3.55 (2H, m, CH_2), 3.55 (2H, s, Ar-CH_2), 5.79 (2H, d, J = 1.0 Hz, $H_{15,16}$), 6.61 (2H, s, Ar*H*), 6.79 (2H, s, $H_{4,6}$) and 7.16 (2H, s, Ar*H*); *m/z* 396 (M^+) (Found: C, 90.91; H, 9.05. $C_{30}H_{36}$ (396.62) requires C, 90.85; H, 9.15%).

Benzylation of arenes with 2-bromomethyl-5-tert-*butyl-1,3-dimethylbenzene* (**4**): $TiCl_4$ (0.16 mL, 1.5 mmol) was added to a solution of **4** (255 mg, 1.0 mmol) in benzene (2.67 mL, 30 mmol) at 0 °C. After the reaction mixture had been stirred at room temperature for 2 h, it was poured into ice-water and extracted with benzene. The extract was dried over anhydrous sodium sulfate and concentrated. The residue was subjected to silica-gel (Wako, C-300; 100 g) column chromatography using as eluent hexane–benzene (1:1) to give 4-*tert*-butyl-2,6-dimethyldiphenylmethane **5a** (192 mg, 76%) as colourless needles (from EtOH), m.p. 43–45 °C; δ_H ($CDCl_3$) 1.24 (9H, s, *t*Bu), 2.15 (6H, s, *Me*), 3.94 (2H, s, ArCH_2), 6.93 (2H, d, J = 8.3 Hz, Ar*H*), 6.99 (2H, s, Ar*H*), 7.07 (1H, d, J = 8.3 Hz, Ar*H*) and 7.14 (2H, t, J = 7.8 Hz, Ar*H*); *m/z* 252 (M^+) (Found: C, 90.34; H 9.53. $C_{19}H_{24}$ (252.40) requires C, 90.42; H, 9.58%).

Benzylation of **4** with arenes was carried out using the same procedure as described above and product yields are compiled in Scheme 4.

(*4*-tert-*Butyl-2,6-dimethylphenyl)(2-methylphenyl)methane* (**5b**): Colourless needles (from EtOH), m.p. 76–77 °C; δ_H ($CDCl_3$) 1.34 (9H, s, *t*Bu), 2.18 (6H, s, *Me*), 2.42 (3H, s, *Me*), 3.87 (2H, s, ArCH_2), 6.52 (1H, d, J = 7.3 Hz, Ar*H*), 7.00 (1H, t , J = 7.8 Hz, Ar*H*), 7.10 (1H, d, J = 8.8 Hz, Ar*H*), 7.09 (2H, s, Ar*H*) and 7.18 (1H, t, J = 7.3 Hz, Ar*H*); *m/z* 266 (M^+) (Found: C, 90.34; H 9.53. $C_{20}H_{26}$ (266.43) requires C, 90.16; H, 9.84%).

(*4*-tert-*Butyl-2,6-dimethylphenyl)(4-methylphenyl)methane* (**5c**): Colourless needles (from EtOH), m.p. 56–57 °C; δ_H ($CDCl_3$) 1.31 (9H, s, *t*Bu), 2.23 (6H, s, *Me*), 2.29 (3H, s, *Me*), 3.97 (2H, s, ArCH_2), 6.97 (2H, d, J = 8.1 Hz, Ar*H*), 7.04 (2H, d, J = 8.1 Hz, Ar*H*) and 7.06 (2H, s, Ar*H*); *m/z* 266 (M^+) (Found: C, 90.39; H, 9.68. $C_{20}H_{26}$ (266.43) requires C, 90.16; H, 9.84%).

(*4*-tert-*Butyl-2,6-dimethylphenyl)(3,4-dimethylphenyl)methane* (**5d**): Colourless needles (from EtOH), 143 °C/ 2 torr, m.p. 38–40 °C; δ_H ($CDCl_3$) 1.31 (9H, s, *t*Bu), 2.16 (6H, s, *Me*), 2.23 (6H, s, *Me*), 3.93 (2H, s, ArCH_2), 6.69 (1H, d, J = 6.8 Hz, Ar*H*), 6.81 (1H, s, Ar*H*), 6.93 (1H, d, J = 6.8 Hz, Ar*H*) and 7.05 (2H, s, Ar*H*); *m/z* 280 (M^+) (Found: C, 89.79; H, 10.08. $C_{21}H_{28}$ (280.46) requires C, 89.94; H, 10.06%).

(*4*-tert-*Butyl-2,6-dimethylphenyl)(2,4-dimethylphenyl)methane* (**5e**): Colourless needles (from EtOH), m.p.81–82 °C; δ_H ($CDCl_3$) 1.33 (9H, s, *t*Bu), 2.17 (6H, s, *Me*), 2.26 (3H, s, *Me*), 2.37 (3H, s, *Me*), 3.82 (2H, s, ArCH_2), 6.44 (1H, d, J = 7.8 Hz, Ar*H*), 6.79 (1H, d, J = 7.8 Hz, Ar*H*), 7.00 (1H, s , Ar*H*) and 7.08 (2H, s, Ar*H*); *m/z* 280 (M^+) (Found: C, 90.10; H, 9.93. $C_{21}H_{28}$ (280.46) requires C, 89.94; H, 10.06%).

(*4*-tert-*Butyl-2,6-dimethylphenyl)(2,5-dimethylphenyl)methane* (**5f**): Colourless needles (from EtOH), m.p. 120–122 °C; δ_H ($CDCl_3$) 1.34 (9H, s, *t*Bu), 2.14 (3H, s, *Me*), 2.18 (6H, s, *Me*), 2.37 (3H, s, *Me*), 3.83 (2H, s, ArCH_2), 6.33 (1H, s, Ar*H*), 6.89 (1H, d, J = 7.3 Hz, Ar*H*), 7.07 (1H, d , J = 7.3 Hz, Ar*H*) and 7.08 (2H, s, Ar*H*); *m/z* 280 (M^+) (Found: C, 90.07; H, 10.13. $C_{21}H_{28}$ (280.49) requires C, 89.94; H, 10.06%).

(*4*-tert-*Butyl-2,6-dimethylphenyl)(2,4,6-trimethylphenyl)methane* (**5g**): Colourless needles (from EtOH), m.p. 75–77 °C; δ_H ($CDCl_3$) 1.28 (9H, s, *t*Bu), 2.08 (6H, s, *Me*), 2.11 (6H, s, *Me*), 2.24 (3H, s, *Me*), 4.00 (2H, s, ArCH_2), 6.78 (2H, s, Ar*H*) and 6.95 (2H, s, Ar*H*); *m/z* 294 (M^+) (Found: C, 89.91; H,10.45. $C_{22}H_{30}$ (294.46) requires C, 89.73; H, 10.27%).

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