

Synthesis of 'crushed fullerene' C₆₀H₃₀

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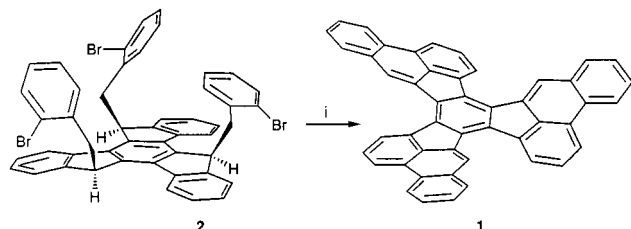
The synthesis of benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]tribenzo[*l*:*l'*:*l''*]-triacephenanthrylene (C₆₀H₃₀) has been accomplished by a triple palladium-catalysed arylation of a *syn*-trialkylated truxene.

Part of the recent outburst in the chemistry of bowl-shaped polycyclic aromatic hydrocarbons (polyarenes)^{1,2} concerns their potential use as starting materials for the development of syntheses of fullerenes as alternatives to those based on the vaporisation of graphite.²⁻⁴ Indeed, fullerenes have been formed pyrolytically in low yield from aromatic hydrocarbons such as naphthalene and corannulene.² Additionally, the development of practical syntheses of functionalised bowl-shaped polyarenes should allow for the construction of fullerene-like molecular cages with polycyclic aromatic substructures. Progress towards the synthesis of giant polyarenes is also of interest in the area of materials science.⁵

We have recently completed a synthesis of polyarene **1**, benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]triacephenanthrylene,⁶ using the palladium-catalysed intramolecular arylation reaction that we previously applied for the preparation of benzo[*e*]acephenanthrylenes and related polycyclic aromatic hydrocarbons.⁷ The synthesis of **1** was carried out by the intramolecular arylation of *syn*-trialkylated truxene⁸ **2** by using Pd(OAc)₂ as the catalyst at 130 °C in DMF (Scheme 1), while cyclisation of the *anti*-isomer of **2** had to be performed at 150 °C under otherwise identical conditions.⁶

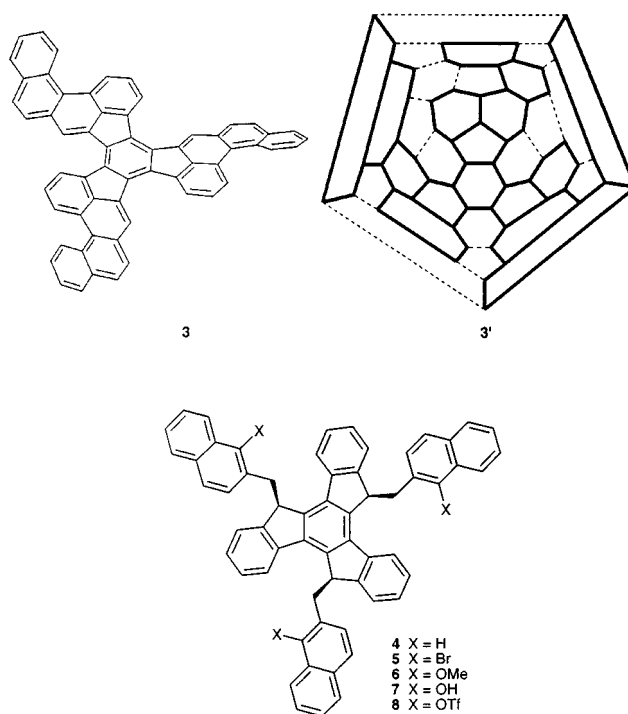
We decided to apply this approach for the synthesis of the higher analogue **3**, benzo[1,2-*e*:3,4-*e'*:5,6-*e''*]tribenzo[*l*:*l'*:*l''*]-triacephenanthrylene. Polyarene **3** contains a decacyclene core (highlighted in boldface in **3'**) fused with three naphthyl units and possesses half of the rings of C₆₀ as shown in the Schlegel diagram **3'**.

The alkylation of the lithium trianion of truxene with 2-bromomethylnaphthalene gave selectively the *anti*-isomer of **4**. Initial isomerisation to the more stable *syn*-isomer **5** failed under the standard conditions (heating with KOBu^t in Bu^tOH)⁶ due to the insolubility of the *anti*-isomer. However, simple addition of a small amount of CH₂Cl₂ as co-solvent allowed for the almost quantitative conversion of the *anti*-isomer into **4** (75% overall yield). The preparation of the required starting material for the palladium-catalysed arylation was carried out by the alkylation of the lithium trianion of truxene with



Scheme 1 Reagents and conditions: i, Pd(OAc)₂, BnMe₃NBr, K₂CO₃, DMF, 130 °C, 71%.

† The EI mass spectrum of **1** is available as supplementary data, see <http://www.rsc.org/suppdata/cc/1999/2431/>



1-bromo-2-bromomethylnaphthalene⁹ to give the *anti*-stereoisomer of **5** as the major compound, which was isomerised with KOBu^t in Bu^tOH under refluxing conditions to give *syn*-5,10,15-tris(1-bromo-2-naphthylmethyl)truxene **5** (62%). Similarly, **6** was obtained by using 2-bromomethyl-1-methoxynaphthalene¹⁰ as the electrophile in the alkylation reaction, followed by base-catalysed isomerization (85% overall yield). Demethylation of **6** with BBr₃ in CH₂Cl₂ at -78 °C afforded trisnaphthol **7** (83%), which was treated with Tf₂O and 2,6-lutidine in CH₂Cl₂ (-30 to 0 °C) to give tris(triflate) **8** (52%).¹¹

Treatment of **5** with Pd(OAc)₂ (10–20 mol%) in the presence of BnMe₃NBr and K₂CO₃ or NaOAc in DMF or DMA at 110–160 °C gave complex reaction mixtures of insoluble materials. However, use of higher amounts of Pd(OAc)₂ (100 mol%, 0.3 equiv.) led to cleaner reaction mixtures from which **3** could be isolated in 42% yield.^{12†} Treatment of tris(triflate) **8** in the presence of Pd(PPh₃)₂Cl₂ (150 mol%) and excess NaOPiv in DMA (120 °C, 26 h) also led to **3**, albeit in lower yield (11%).¹³

Polyarene **3** is a highly insoluble substance and its ¹H NMR could only be determined in 1,1,2,2-tetrachloroethane-*d*₂ at 130 °C. The EI-MS of **3** was very revealing since it showed the molecular ion at *m/z* 750 as the base peak along with characteristic M²⁺ and M³⁺ peaks at 375 and 248, respectively (Fig. 1). Additionally, peaks corresponding to loss of two (*m/z* 748, 6%), four (*m/z* 746, 4%), and six hydrogens (*m/z* 744, 2%) were clearly observed in the EI-MS. No C₆₀⁺ (*m/z* 720) was observed in the mass spectrum. Polyarene **1** showed a similar EI mass spectrum to that of **3** under identical conditions, with

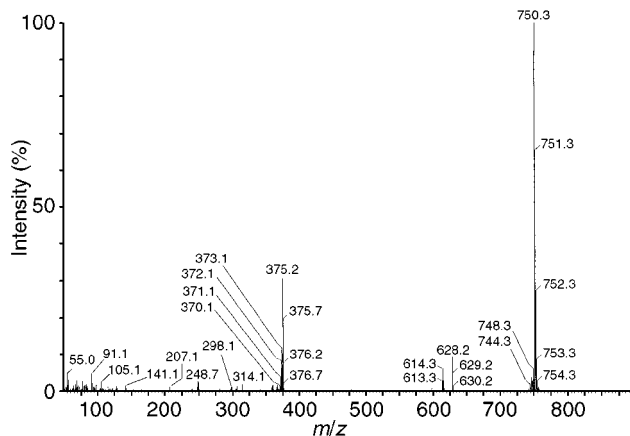
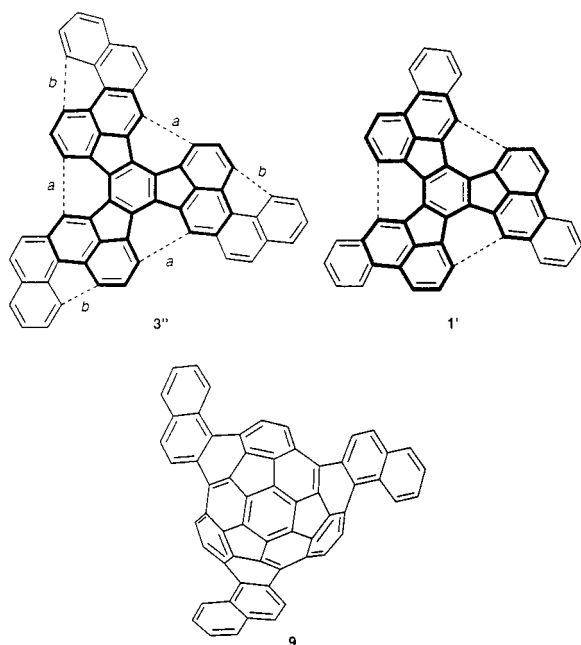


Fig. 1 EI-MS (probe temperature: 600 °C, ion source: 300 °C, 90 eV) of **3**.



dehydrogenations presumably corresponding to that shown in **1'**.¹⁴ This result suggests that under the conditions of the EI spectrum, **3** suffers the cyclodehydrogenations labelled *a* (**3''**).

The synthesis of **3** from **5** highlights the synthetic utility of the intramolecular C–H activation through aryl–palladium complexes.¹⁵ Now readily available polyarene **3** could serve as the starting material for the preparation of **9** (C₆₀H₂₄) by a triple cyclodehydrogenation analogous to that recently carried out on decacyclene by Scott to form the fullerene fragment C₃₆H₁₂.¹⁶ Additionally, bowl-shaped open fullerene **9** could be a direct precursor of C₆₀ by a cascade of cyclodehydrogenation reactions.³ Efforts along these lines are in progress.

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Notes and references

‡ *Synthesis of 3*: A mixture of **5** (150 mg, 0.15 mmol), Pd(OAc)₂ (34 mg, 0.15 mmol), BnMe₃NBr (69 mg, 0.3 mmol) and K₂CO₃ (207 mg, 1.5 mmol) in DMA (8 ml) was stirred at 140 °C for 36 h. The mixture was cooled to 23 °C and the solid was filtered off and washed with CH₂Cl₂ and acetone. The solid was suspended in aqueous NaCN and stirred for 1 h. The solid was filtered off and washed with water and acetone to give **3** as a clear brown powder (47 mg, 42%): mp > 300 °C; δ_H(1,1,2,2-tetrachloroethane-*d*₂, 130 °C, 300 MHz) 9.26–9.01 (m, 12 H), 8.13–8.02 (m, 12 H), 7.80–7.69 (m, 6 H); *m/z* (EI) (probe temperature: 600 °C, ion source: 300 °C, 90 eV) *m/z* 750 (M⁺, 100%), 748 (M⁺–2, 6), 746 (M⁺–4, 4%), 744 (M⁺–6, 2%), 375 (M²⁺, 30%), 248 (M³⁺, 2%).

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