1 PERKIN COMMUNICATION

Towards a synthesis of C_3-tribenzohemifullerene, a $C_{42}H_{18}$ fragment of [60]fullerene

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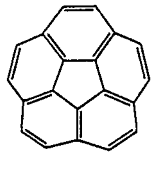
A short, simple synthesis of C_3-trinaphthotriphenylene 6, $C_{42}H_{24}$, from readily available precursors involving threefold Wittig reactions and threefold oxidative photocyclizations is reported; flash vacuum pyrolysis of 6 in the quest for C_3-tribenzohemifullerene 5, $C_{42}H_{18}$, has so far led only to the formation of monobridged product 12, $C_{42}H_{22}$.

One of the exciting spin-offs of the fullerene era is the emerging interest in the synthesis and chemistry of 'bowl-shaped' polycyclic aromatic hydrocarbons, particularly those representing a dominant motif on the fullerene surface.[1] These new molecular entities (bucky bowls),[1b] with two distinct reactive surfaces, are expected to exhibit physico-chemical characteristics different from their planar analogues on account of enhanced strain and the presence of curvature.[1] However, 'bucky-bowls' unlike 'bucky-balls' are not encountered during graphite vaporization regimes and, therefore, need to be accessed through classical synthetic design. Several research groups around the world have joined this quest and the recent successful syntheses of several 'bowl-shaped' polycyclic aromatic hydrocarbons *e.g.* C_{20}-corannulene **1**,[2] C_3-hemifullerene **2**,[3] C_5-hemifullerene **3** (5,5-circulene)[3b,4] and C_{36}-triacenaphthotriphenylene **4**,[5] bear testimony to these creative endeavors. As a part of our continuing interest[2f,6] in the synthesis of fullerene fragments, we became interested in the bowl-shaped hydrocarbons **5** ($C_{42}H_{18}$), a tribenzo-annulated derivative of **2**, possessing C_3-symmetry and representing 70% of the carbon content of a [60]fullerene cage. Herein, we disclose an exceptionally short and simple synthetic strategy towards **5**.



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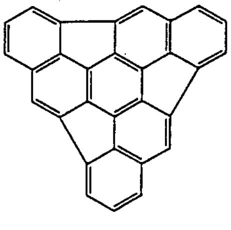

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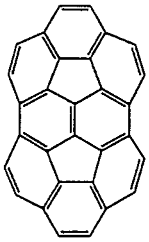

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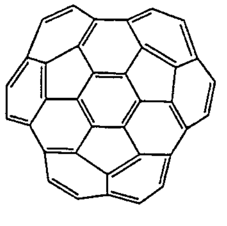

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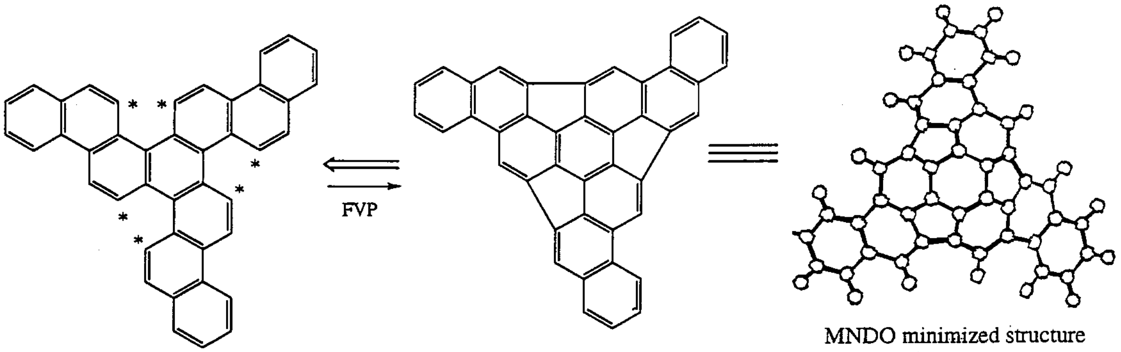
Retrosynthetically, we identified a C_3-symmetrical trinaphthotriphenylene **6**[7] as a logical precursor in which key connectivities could be established at the starred positions through threefold transannular cyclodehydrogenation under flash vacuum pyrolysis (FVP) conditions. MNDO calculations[8] revealed that sequential C–C connections in **6** ($C_{42}H_{24}$) leading to the monobridged $C_{42}H_{22}$, dibridged $C_{42}H_{20}$ and finally to the targeted $C_{42}H_{18}$ **5** showed an increase in ΔH_f of 11.5, 37.3 and 52.0 kcal mol^{-1}, respectively. The average interatomic distance between the starred positions in **6** was 3.05 Å, well within the acceptable range for the contemplated transannular bridging. The corresponding distances in the monobridged $C_{42}H_{22}$ were somewhat larger (3.23 Å) and in the dibridged $C_{42}H_{20}$, even larger (3.59 Å). Overall, these calculated parameters appeared encouraging enough to motivate us to embark on a synthesis of **6** and study its response to FVP protocols. As yet unknown, the C_3-trinaphthotriphenylene **6** is not only a promising precursor of **5** but is quite interesting in its own right as its three intersecting, extended phenanthrene-like (branched 5-phenacenes) structural motifs, define ribbon-like patterns on the graphite sheet (Fig. 1, see bold outline). Indeed, linear [*n*]phenacenes have drawn attention very recently as potential new materials.[9]

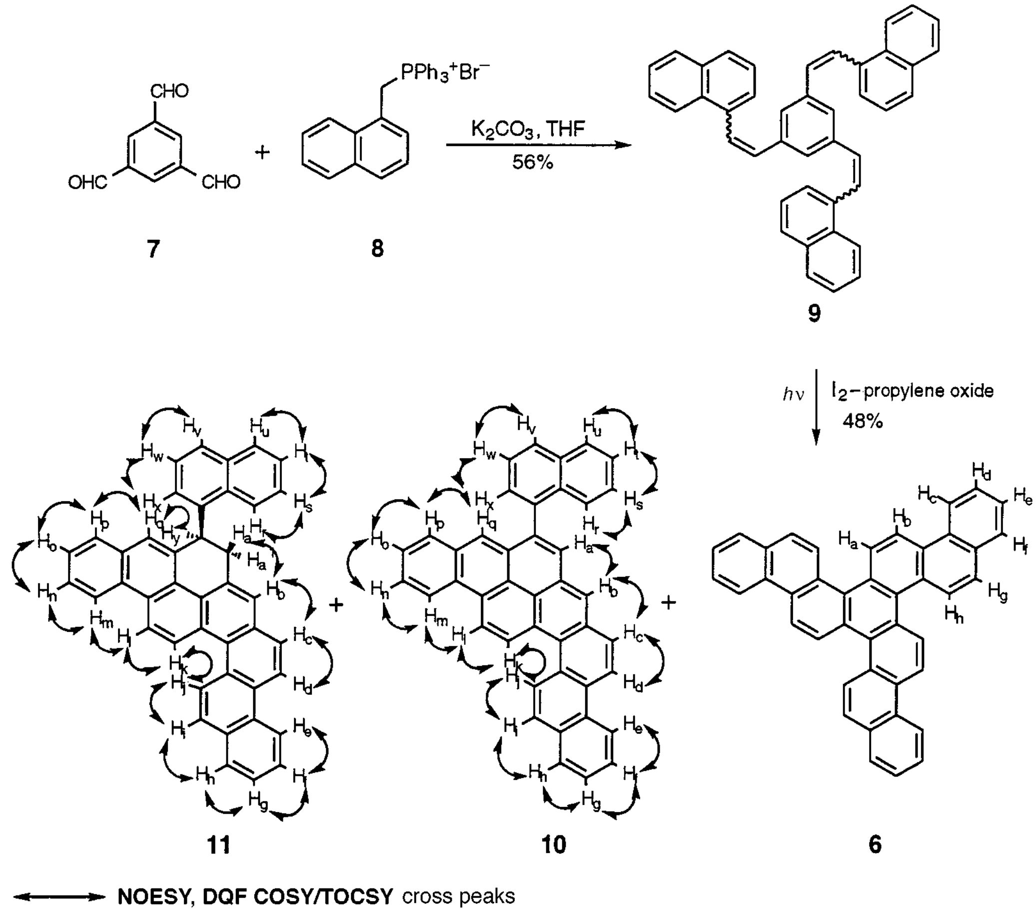
Our approach to **6** emanated from two readily available building-blocks, 1,3,5-triformylbenzene **7** and 1-methylnaphthalene. A threefold Wittig reaction between **7** and the ylide derived from 1-naphthylmethyl(triphenyl)phosphonium bromide **8** furnished **9** as a mixture of *E*- and *Z*-isomers. The stereo-



MNDO minimized structure

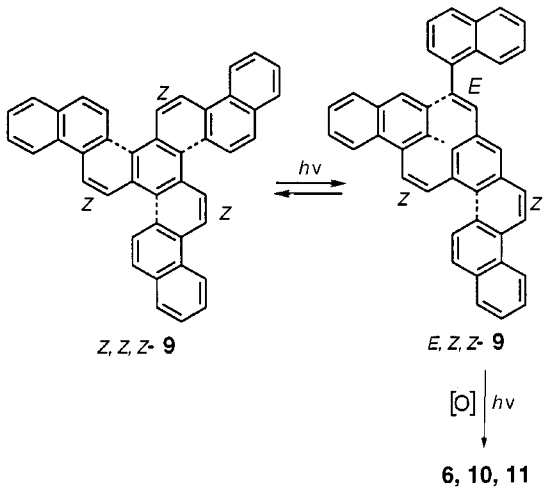
6

5



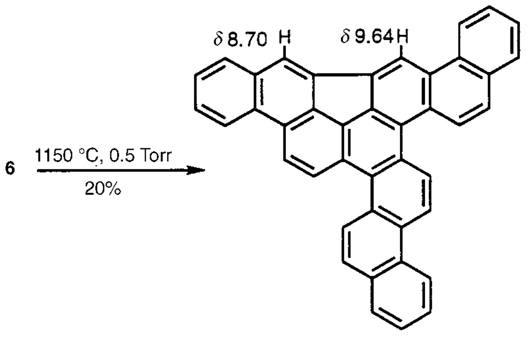
Scheme 1

isomeric mixture **9** was subjected to threefold oxidative photocyclization by irradiation with a 450 W Hg lamp in the presence of catalytic I_2 to furnish a complex mixture from which the desired C_3-symmetric compound **6** (9%) and two other large polycyclic aromatic sheets **10** (32%)[7] and **11** (7%)[7] were isolated through extensive chromatography, Scheme 1. The structure of **6** (*m/z* 528 M^+) was secured through its simple ^{1}H NMR spectrum (*twelve* characteristic deshielded protons of the fjord region between δ 8.90–9.10) and 14-line ^{13}C NMR spectrum (C_3-symmetry). Structures of the unsymmetrical cyclization products **10** and **11** were deduced through incisive analyses of the high-field ^{1}H NMR (TOCSY, DQF COSY and NOESY) spectral data and important correlations and NOEs are indicated on their structures. Formation of **6**, **10** and **11** is shown in Scheme 2. While **6** originates through photocyclization–oxidation of the *Z*,*Z*,*Z*-form of **9**, **10** and **11** are most likely derived from the *E*,*Z*,*Z*-**9**. It is reasonable to assume that both *Z*,*Z*,*Z*- and *E*,*Z*,*Z*-forms of **9** are either present in the Wittig product or are accessible through photochemical *E*,*Z*-isomerizations. Thus, our C_3-symmetry precursor **6**, embodying ten aromatic rings, could be acquired in just two steps with the formation of six C–C bonds, albeit in low yield, due to deviation to **10** and **11** during the photochemical step.



Scheme 2

When **6** was subjected to FVP at 1150 °C (0.5 Torr) through a quartz tube, only a single product **12** (20%)[7] could be isolated from the pyrolysate by column chromatography. The structure of **12** followed from its mass spectrum (*m/z* 526 M^+) and the appearance of two diagnostic singlets at δ 9.64 and 8.7 in the ^{1}H NMR spectrum. In addition, a series of doublets due to the deshielded protons of the fjord region between δ 9.00–9.40 further corroborated the assigned structure. While the formation of **12** during the FVP of **6** was in consonance with our projected approach towards **5**, it appears that the activation required for the C–H bond cleavage at the starred positions



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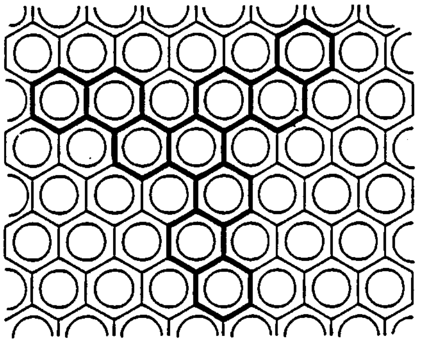

Fig. 1

to establish all the contemplated transannular bridges is not attainable even at 1150 °C. Similar observations have been made recently for other related systems.[1,6d,10] We are, therefore, taking recourse to suitably substituted (halogen) derivatives of **6**, which will promote transannular bridging. Nevertheless, the present study has laid firm ground for such future endeavors.

Experimental

C_3-Trinaphthotriphenylene 6

To a suspension of the Wittig salt **8** (21 g, 43.34 mmol), prepared from 1-bromomethylnaphthalene and triphenylphosphine, in dry THF (25 ml) at room temperature was added solid K_2CO_3 (6 g, 43.41 mmol) and 18-crown-6 (catalytic amount) and the mixture was stirred for about 1 h. 1,3,5-Triformylbenzene (1 g, 6.17 mmol) in THF (10 ml) was introduced and the stirring was continued for 10 h at room temperature (30 °C). The reaction mixture was diluted with diethyl ether, washed with brine, dried (Na_2SO_4) and concentrated. The residue was charged on a silica gel column and elution with hexane gave the Wittig product **9** (1.9 g, 56%) as a mixture of *E*,*Z*-isomers as revealed by ^1H NMR spectroscopy. A solution of **9** (300 mg, 0.56 mmol) in dry benzene (900 ml) was purged with N_2, and I_2 (570 mg, 2.24 mmol) and propylene oxide (20 ml, 285 mmol) were added to it.[11] This solution was irradiated with a 450 W Hanovia medium pressure Hg lamp in a quartz vessel through a Pyrex filter for 2 h. The reaction mixture was concentrated and chromatographed over a silica gel column. Elution with 2% hexane–dichloromethane furnished **6** (29 mg, 9%), **10** (98 mg, 32%) and **11** (23 mg, 7%). Spectral data for these compounds is as follows. **6**: δ_H(200 MHz, $CDCl_3$, *J*/Hz) 9.10 (d, 3H, *J* 9, H_a), 9.0 (d, 3H, *J* 9, H_h), 8.92 (d, 3H, *J* 9, H_b), 8.90 (d, 3H, *J* 9, H_c), 8.06 (d, 3H, *J* 8, H_g), 8.0 (d, 3H, *J* 8, H_f), 7.8 (dd, 3H, *J* 9 and 7, H_d), 7.73 (dd, 3H, *J* 9 and 7, H_e); δ_C(50 MHz, $CDCl_3$) 131.7, 130.3, 130.2, 129.1, 128.2 (2C), 127.1, 126.9, 126.8 (2C), 126.1, 125.7, 123.4, 120.9; *m/z* (FAB) 528 (M^+). **10**: δ_H(400 MHz, $CDCl_3$, *J*/Hz) 9.6 (d, *J* 9.4, H_k), 9.28 (d, *J* 9, H_j), 9.26 (d, *J* 9.4, H_l), 9.0 (d, *J* 8.4, H_m), 8.9 (d, *J* 9, H_d), 8.8 (d, *J* 8, H_e), 8.4 (s, H_b), 8.3 (d, *J* 9, H_e), 8.09 (d, *J* 9, H_i), 8.08 (br d, *J* 8, H_h, H_v), 8.03 (d, *J* 8.4, H_u), 7.96 (s, H_a, H_z), 7.9 (d, *J* 8, H_p), 7.8 (dd, *J* 8.4, 7.5, H_n), 7.78–7.69 (m, H_r, H_f, H_w, H_x, H_g), 7.6 (dd, *J* 8, 7.5, H_o), 7.5 (dd, *J* 8.4, 7, H_t), 7.28 (dd, *J* 8.4, 7, H_s); δ_C(50 MHz, $CDCl_3$) 138.6, 138.2, 133.8, 133.0, 131.8, 131.3, 130.9, 130.5, 130.1, 129.7, 129.5, 129.2, 128.2, 127.8, 127.5, 127.2, 126.6, 126.0, 125.7, 125.2, 124.8, 123.4, 122.9, 122.1, 121.7, 120.8; *m/z* 528 (M^+). **11**: δ_H(400 MHz, $CDCl_3$, *J*/Hz) 9.3 (d, *J* 9.4, H_k), 9.1 (d, *J* 9.1, H_j), 8.9 (d, *J* 9.4, H_l), 8.88 (d, *J* 8.2, H_m), 8.85 (d, *J* 8.2, H_e), 8.84 (d, *J* 8.7, H_d), 8.29 (m, H_r), 8.06 (d, *J* 7.8, H_h), 8.04 (d, *J* 9.1, H_i), 8.03 (d, *J* 8.7, H_c), 7.96 (m, H_v), 7.78 (s, H_b), 7.78 (d, *J* 7.5, H_u), 7.75–7.69 (m, H_f, H_p, H_n, H_g), 7.58 (t, *J* 7.5, H_o), 7.54 (m, H_s, H_t), 7.49 (s, H_q), 7.3 (t, *J* 7.5, H_w), 7.17 (d, *J* 7.5, H_x), 5.6 (dd, *J* 9, 5.6, H_y), 4.07 (dd, *J* 14.9, 9.0, H_a), 3.9 (dd, *J* 14.9, 5.6, $H_{a'}$); δ_C(100 MHz, $CDCl_3$) 139.4, 136.6, 133.7, 132.2, 131.8, 131.5, 130.6, 129.1, 128.4, 128.2, 127.5, 126.7, 126.5, 126.2, 126.6, 125.7, 125.5, 123.3, 122.6, 120.8, 36.6, 30.0; *m/z* 530 (M^+).

Flash vacuum pyrolysis of 6

The trinaphthotriphenylene **6** (15 mg, 0.02 mmol) was subjected to flash vacuum pyrolysis in a quartz vessel at 1150 °C (0.5 Torr) in a slow stream of N_2. The material collected on the cold finger (~9 mg) was carefully chromatographed on a silica gel column (3% dichloromethane–hexane eluent) to furnish recovered starting material **6** (~5 mg) and monobridged compound **12** (2 mg). δ_H(400 MHz, $CDCl_3$, *J*/Hz) 9.64 (s, 1H), 9.31 (d, *J* 8.4, 1H), 9.0 (d, *J* 8, 1H), 9.09 (d, *J* 9.2, 1H), 9.07 (d, *J* 8, 1H), 9.0 (d, *J* 8, 1H), 8.87 (d, *J* 8.5, 1H), 8.82 (d, *J* 9, 1H), 8.70 (s, 1H), 8.37 (d, *J* 8, 1H), 8.13 (d, *J* 8, 1H), 8.12–7.4 (series of m, 11H); *m/z* 526 (M^+).

Acknowledgements

We thank CSIR for supporting this research project and a research fellowship to G. P. G. M. thanks the Indian National Science Academy for the award of a Ramanujan Research Professorship. S. R. S. was a guest researcher from the MS University and wishes to thank the University of Hyderabad for their hospitality.

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7 Systematic IUPAC names: **6**: naphtho[2,1-*a*]phenanthro[1,2-*f*]picene; **10**: 9-(1-naphthyl)benzo[*rst*]naphtho[2,1-*a*]pentaphene **11**: (9*R*)-9-(1-naphthyl)-8,9-dihydrobenzo[*rst*]naphtho[2,1-*a*]pentaphene **12**: acephenanthryleno[5,4,3-*def*]naphtho[2,1-*a*]picene.

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Paper 7/02911J
Received 29*th April* 1997
Accepted 18*th June* 1997