

Towards the Design of Tricyclopenta[*def,jkl,pqr*]triphenylene ('Sumanene'): a 'Bowl-shaped' Hydrocarbon featuring a Structural Motif Present in C₆₀ (Buckminsterfullerene)

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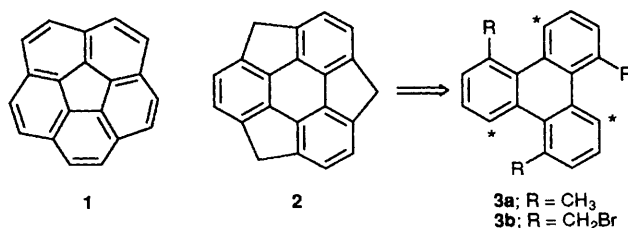
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A short synthesis of C₃ symmetry 1,5,9-trimethyltriphenylene **3a** and its further elaboration to methyl dicyclopenta[*def,jkl*]triphenylene is reported.

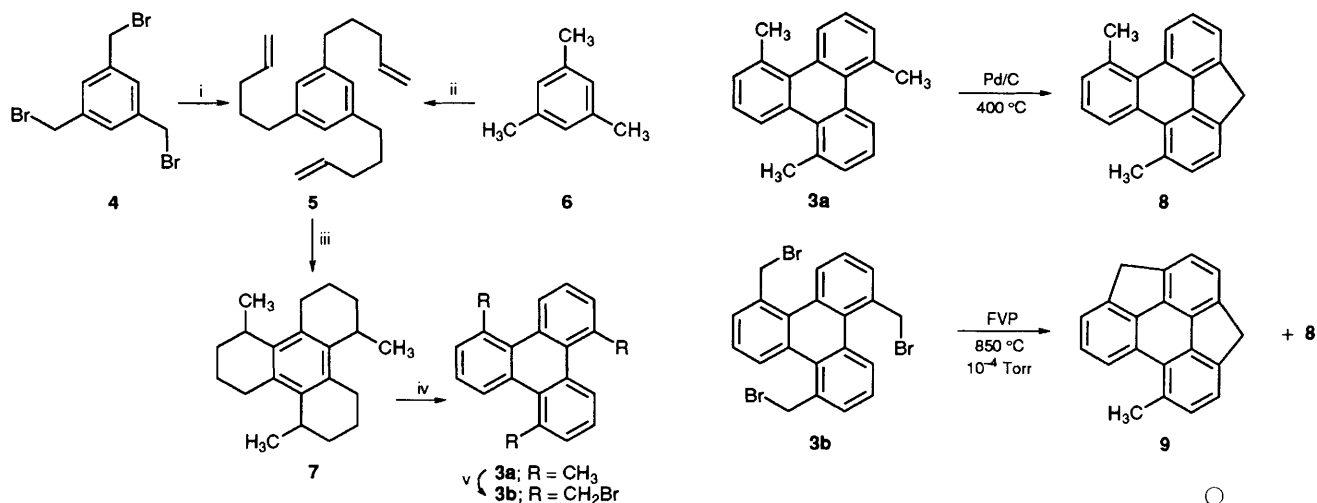
Despite commercial availability and improved preparative access, the *de novo* design of C₆₀ and its siblings is a challenging and formidable synthetic proposition. The primary task in the synthetic endeavour towards C₆₀ is the identification and assembly of smaller, readily recognizable, structural fragments that can be further built upon. Two structural features that readily identify themselves in C₆₀ can be represented, in equivalent hydrocarbon forms, as the 'bowl-shaped' C₂₀-corannulene **1**¹ and C₂₁-sumanene **2**.[†] While the former has been synthesized and continues to receive attention,^{1,b,c} the latter, to our knowledge, remains unknown and little progress, if any, has been reported towards

its synthesis. In this communication, we disclose our synthetic strategy aimed at **2** and the progress achieved so far.

Our approach to **2** delineated retrosynthetically (**2** → **3**) hinged on the pivotal role of a trisubstituted triphenylene like **3** of C₃ symmetry in which the substituent could be exploited to establish the three methylene bridges across the starred positions. Molecular mechanics calculations (MMX) indicated



[†] The shape of **2**, with the ring edges on the rim resembling petals, is reminiscent of a flower ('Suman' in Hindi and Sanskrit) and we propose the trivial name 'Sumanene' for this C₂₁-hydrocarbon.



Scheme 1 Reagents and yield: i, CH₂=CH-CH₂CH₂MgBr, Li₂CuCl₄, tetrahydrofuran (THF), -10 → 25 °C, 3 h, 45%; ii, a, BuⁿLi, tetramethylethylenediamine (TMEDA), C₆H₆, 90 °C, 5 h, then b, CH₂=CH-[CH₂]₂Br, 5 °C, 25%; iii, BF₃(g), C₆H₆, 25 °C, 2 h, 55%; iv, DDQ, C₆H₆, 95 °C, 2 h, 46% v, *N*-bromosuccinimide, azoisobutyronitrile, CCl₄, 95 °C, 2 h, 60%

that sequential placement of each methylene bridge in **3a** led to strain energy (ΔE_s) build-up of 4.4, 19.9 and 49.4 kcal mol⁻¹ (1 cal = 4.184 J), respectively, on the way to **2** and the distances between the methyl group carbon and the bridging carbons were 3.03 Å in **3a**, 3.07 and 3.15 Å in the mono-bridged and 3.35 Å in the di-bridged compound. These features were considered promising enough in the context of the **3a** → **2** transformation and we first ventured to develop a short synthesis of 1,5,9-trimethyltriphenylene **3a**.

Dilithium tetrachlorocuprate catalysed cross-coupling reaction between 1,3,5-tris(bromomethyl)benzene **4** and the Grignard reagent derived from 4-bromobut-1-ene furnished the 1,3,5-tripentenylated benzene **5** in one step. Alternatively, the trianion generated from mesitylene **6** on quenching with 4-bromobut-1-ene also furnished **5** in a one-pot operation but in lower yield. The trialkene **5** on exposure to gaseous BF₃ smoothly cyclized to give the tetracycle **7**. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dehydrogenation of **7** furnished the 1,5,9-trimethyltriphenylene (Scheme 1). In accordance with its symmetry, **3a**[†] exhibited only one methyl singlet and seven lines in the ¹H and ¹³C NMR spectra, respectively.

For further elaboration of **3a** towards **2**, we first tried direct cyclodehydrogenation. Pd/C mediated dehydrogenation of **3a** furnished the mono-bridged compound **8**[‡] (*m/z* 268, M⁺) in up to 70% yield, with some minor uncharacterized products (*ca.* 15%). Subjecting **8** to further dehydrogenation or **3a** to flash-vacuum pyrolysis (FVP) at higher temperatures was not successful. Taking a cue from the recent success in coran-

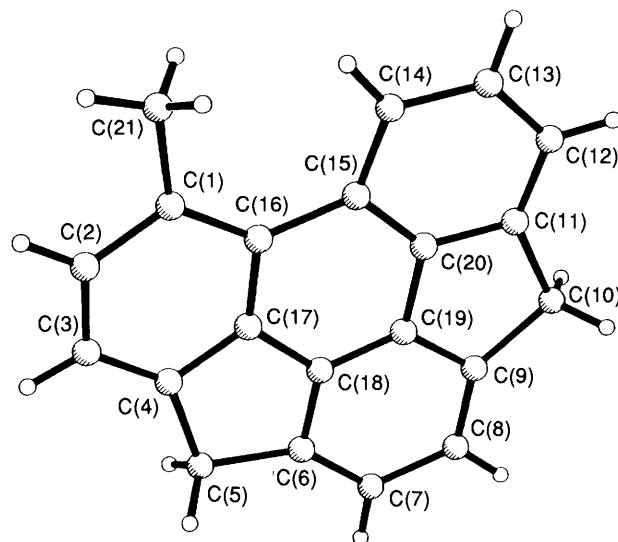


Fig. 1 PLUTO diagram of **9**

nulene **1** synthesis,^{1b,c} we transformed **3a** to 1,5,9-tribromomethyltriphenylene **3b** (Scheme 1). When **3b** was subjected to FVP³ at 850 °C, a 20% yield of di-bridged **9**[†] and mono-bridged **8** (87:13) could be realized.[§] The structure of **9**[‡] (*m/z* 266, M⁺) followed from its ¹H NMR data, particularly the presence of two methylene singlets at δ 4.44 and 4.40 and a methyl singlet at δ 3.09 along with the aromatic resonances. This was further corroborated by the ¹³C NMR resonances due to two methylene carbons at δ 40.26 and 39.81 and a methyl group at δ 23.04. A confirmatory X-ray crystal structure determination was carried out and a perspective is shown in Fig. 1.[¶]

[§] Reductive replacement of bromine atom by hydrogen during FVP conditions has been observed before.^{1b}

[‡] All new compounds were characterized on the basis of their ¹H and ¹³C NMR and mass spectroscopic-analytical data. *Selected spectral data*: **3a**: m.p. 123 °C; ¹H NMR (100 MHz, CDCl₃): δ 2.92 (9H, s), 7.26–7.46 (6H, m) and 8.20 (3H, t); ¹³C NMR (25.0 MHz, CDCl₃): δ 26.06, 124.83, 125.71, 131.07, 132.01, 132.30 and 134.30. **8**: m.p. 192 °C; ¹H NMR (200 MHz, CDCl₃): δ 3.13 (3H, s), 3.20 (3H, s), 4.24 (2H, s), 4.46–7.71 (6H, m), 8.62 (1H, d, *J* 8.0 Hz) and 8.87 (1H, d, *J* 7.8 Hz); ¹³C NMR (50 MHz, CDCl₃): δ 25.95, 27.63, 36.60, 122.01, 122.15, 124.76, 125.55, 126.50, 126.55, 130.84, 131.74, 137.43, 139.40 and 142.00. **9**: m.p. 247.5 °C; ¹H NMR (200 MHz, CDCl₃): δ 3.09 (3H, s), 4.40 (2H, s), 4.44 (2H, s), 7.44 (1H, d, *J* 7.3 Hz), 7.58 (1H, d, *J* 7.8 Hz), 7.66 (1H, dd, *J*₁ = *J*₂ = 8.0 Hz), 7.64 (1H, d, *J* 7.3 Hz), 7.66 (2H, s) and 8.47 (1H, d, *J* 7.8 Hz); ¹³C NMR (50 MHz, CDCl₃): δ 23.04, 39.81, 40.26, 122.59, 122.99, 125.12, 127.36, 129.96, 135.20, 137.12, 137.71, 139.18, 142.45 and 144.74. In **8** and **9** several overlapping carbon signals are observed.

[¶] *Crystal data*: for C₂₁H₁₄, *M* = 266.3, monoclinic, space group *P*2₁/*c*, *a* = 9.419(2), *b* = 11.386(2), *c* = 13.409(3) Å, β = 107.47(2)°, *V* = 1372(5) Å³, *Z* = 4, *D*_c = 1.207 Mg m⁻³, *F*(000) = 560, μ = (Mo-K α) = 0.073 mm⁻¹, 294 K. No. of data measured 2046, no. of unique reflections 1798, no. of observed reflections with *F* \geq 3 σ (*F*), 1060, no. of parameters 190. Diffraction data were collected on a Siemens R3m/v diffractometer with graphite monochromated Mo-K α radiation, (λ = 0.71073 Å, ω -scan) at room temp. between 3 \leq θ \leq 45°. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SHELXTL-PLUS⁵) and refined by full-matrix least-squares methods. The final *R* value was 0.064 (*R*_w = 0.068). Maximum shift/error = 0.001, maximum and minimum peaks in the final Fourier difference synthesis +0.28, -0.21 e Å⁻³. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Acquisition of **9** from **3b** augurs well for further evolution towards **2**, although so far we have been unable to confirm its presence in the pyrolysate from **3b**. Efforts aimed at obtaining **2** via derivatives of **3a** are in progress and will be reported in due course.

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References

- 1 (a) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, 1966, **88**, 380; (b) L. T. Scott, M. M. Hashemi and M. S. Bratcher, *J. Am. Chem. Soc.*, 1992, **114**, 1920; (c) A. Borchardt, A. Fuchicello, K. V. Kilway, K. K. Baldrige and J. S. Siegel, *J. Am. Chem. Soc.*, 1992, **114**, 1921.
- 2 P. Canonne and A. Regnault, *Tetrahedron Lett.*, 1969, 243.
- 3 Flash vacuum pyrolyses were carried out on a home-built system similar to that described by H. A. Staab and M. Haenel, *Chem. Ber.*, 1973, **106**, 2190.
- 4 To our knowledge, attempts to prepare dicyclopentatriphenylenes of the type **9** have not been successful so far. However, a di-thia analogue has been reported: see L. H. Klemm, E. Hall, L. Cousins and C. E. Klopfenstein, *J. Heterocycl. Chem.*, 1989, **26**, 345.
- 5 G. M. Sheldrick, SHELXTL-PLUS Version 4.2, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1990.