

Rapid Communication

A synthetic approach towards Pinakene, a C₂₈H₁₄ fragment of [70]- fullerene

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During a projected synthesis of 4,7,11,14- tetramethyldibenzo [*fg,op*] naphthacene **3** en route to Pinakene **2**, a [70]-fullerene fragment, an unprecedented photochemical reaction leads to dimethylnaphthacene derivative **7**. Flash vacuum pyrolysis on **7** leads to **8** via a transannular bridging.

While the 'gold-rush' towards the exploration of the chemistry of fullerenes continues unabated¹, there are spinoffs in the form of emerging synthetic interest² in accessing curved, non-planar aromatic fragments and siblings of these new carbon allotropes, which might possess novel physico-chemistry characteristics. Noteworthy progress towards the synthesis of several C₆₀ fragments has already been achieved during the past few years.² However, synthetic efforts towards the fragments of [C₇₀]- fullerene **1** have yet to mark much headway.³ Recently, we have recognized 'Pinakene' **2**, a C₂₈H₁₄ bowl-shaped hydrocarbon as a dominant sub-unit of **1**, and delineated its molecular structure based on MNDO

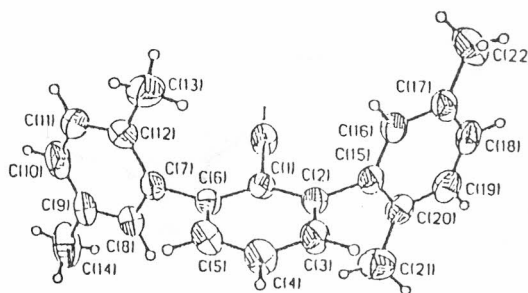
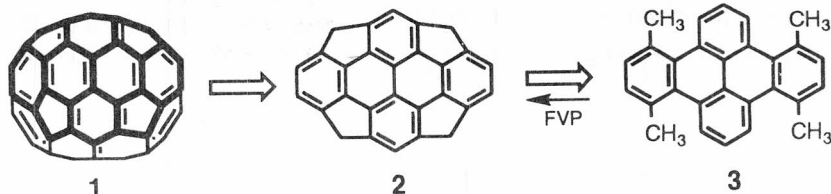


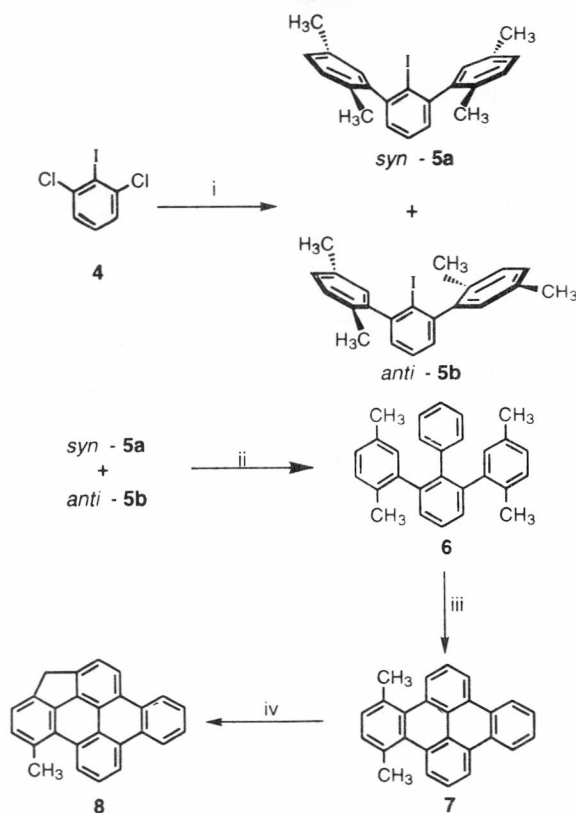
Figure 1

and MM2 calculations⁴. In this effort, a possible synthetic approach to **2** was also considered and 4,7,11,14- tetramethyldibenzo [*fg,op*] naphthacene **3** was identified as a key precursor, in which thermally induced four-fold transannular bridging could be induced under flash vacuum pyrolysis conditions. A literature search revealed that synthetic routes to the dibenzonaphthacene system were relatively few and neither the strained **3** (*E_s* 83.1 kcal/mol) nor any derivative bearing an alkyl substituent in *peri*-position were known. Thus, devising a synthesis of **3** and evaluating the feasibility of the contemplated bridging process (**3**→**2**) became our initial concern and some interesting observations in this quest form the subject matter of this communication.

Hart reaction⁵ of 2,5-dimethylphenylmagnesium bromide with 2,6- dichloriodobenzene **4** and quenching the reaction with iodine furnished a mixture of configurationally stable iodoterphenyl derivatives, *syn*-**5a** and *anti*-**5b**, from which the latter readily- crystallized and was identified through X-ray crystal structure determination (Figure 1)⁶.

Palladium catalyzed Suzuki cross-coupling reaction between **5a,b** and cyclicphenylboronate ester furnished a highly crowded *m*- terphenyl derivative **6** (Scheme I) as a mixture of rotamers. Irradiation of **6** under conditions of oxidative photoelectrocyclization, to our surprise, furnished 4,7- dimethyl-





Reagents & yields: (i) 2,5-Dimethylphenylmagnesiumbromide, THF, Δ , I_2 , 80%; (ii) Phenyl boronate ester, Et_3N , PPh_3 , $Pd(OAc)_2$, DMF, $140^\circ C$, 40% (iii) 450W Hg Lamp, Vycor, C_6H_6 : Acetone, (80:20), Cat. I_2 , -20%; (iv) FVP, $950^\circ C$, 0.1 torr (quant. based on recovery of 7)

dibenzo[*fg,op*]naphthacene 7, instead of the expected 3. The structure of 7⁷ was secured through its spectral characteristics, particularly through 2D NMR (1H - 1H COSY) experiments. Formation of 7 could involve an unprecedented photodearylation-rearylation process in which the *p*-xylene moiety in 6 is exchanged with a phenyl moiety from the solvent benzene prior to photocyclization. The driving force for the photodearylation of 6 is the mitigation of steric strain and is probably manifested through the cleavage of one of the ArC—CAr (CH_3)₂ bonds and rearylation through solvent capture. We are not aware of any example of such photodearylation process in the literature. Alternately, it is possible that 3 is indeed formed during the photo-irradiation, but suffers unprecedented loss of methyl groups to fur-

nish 7. However, we have been unable to detect 3 in photolystate from 6.

The feasibility of the proposed transannular bridging was explored by subjecting 4,7-dimethyldibenzonaphthacene 7 to flash vacuum pyrolysis. The only product isolated in this reaction was the mono-bridged compound 8⁷ (~15% conversion), whose structure was revealed through the spectral data. Further efforts towards incorporating additional bridges on to dibenzonaphthacene framework, via the appropriately placed halogen substituents are in progress.

Acknowledgement

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References

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- Data was collected on a Siemens R3m/V diffractometer and refined using Shelxtl Plus. Crystal data for the compound $C_{22}H_{21}$: Transparent plate crystals, Triclinic, Space group P-1, $a = 6.979(1)$, $b = 10.175(1)$ and $c = 13.711(1)$ Å, $\alpha = 92.0(1)$, $\beta = 97.2(1)$, $\gamma = 98.2(1)^\circ$, $V = 954.69$ Å³, $Z = 2$, $T = 293K$, $D_c = 1.434$ mg-m⁻³, crystal dimensions $0.15 \times 0.17 \times 0.13$ mm³, 2762 reflections measured, $2\theta_{max} = 45^\circ$, $0 \leq h \leq 7$, $-10 \leq k \leq 10$, $-14 \leq l \leq 14$, 2516 unique reflections ($R_{int} = 0.021$ averaging double measured) and 2304 observed with $I \geq 3\sigma(I)$, $\mu = 1.68$ mm⁻¹. Final $R = 0.032$ and $R_w = 0.046$ {208 parameters and $w = 1/\sigma^2 \{(Fo) + 0.000878Fo^2\}$ maximum shift/error = 0.001, $\Delta\rho_{max} = 0.56e$ Å⁻³, $\Delta\rho_{min} = -0.92e$ Å⁻³.
- Selected spectral data — 7: 1H NMR (200 MHz, $CDCl_3$): δ 8.92 (d, 2H, $J = 10$ Hz), 8.87 (d, 2H, $J = 10$ Hz), 8.72 (d, 2H, $J = 9$ Hz), 8.63 (s, 2H), 8.01-8.09 (m, 2H), 7.57 (d, 2H, $J = 8$ Hz), 2.68 (s, 6H); MS: 330 [M^+]. 8: 1H NMR (400 MHz, $CDCl_3$): δ 0.84 (d, 1H, $J = 8$ Hz), 8.82 (d, 1H, $J = 8$ Hz), 8.80 (d, 1H, $J = 8$ Hz), 8.70 (d, 1H, $J = 8$ Hz), 8.66 (d, 1H, $J = 8$ Hz), 8.42 (d, 1H, $J = 8$ Hz), 8.10 (d, 1H, $J = 8$ Hz), 8.04 (d, 1H, $J = 8$ Hz), 7.70 (m, 2H), 7.51 (d, 1H, $J = 8$ Hz), 4.53 (s, 2H), 2.68 (s, 3H); MS: 328 [M^+].