



Polycyclic Hydrocarbons

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A Short and Efficient Synthesis of the [3]Triangulene Ring System

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Abstract: Triangulenes are of current interest for potential applications in molecular electronics. We describe here a three step synthesis of the 4,8,12-trihydro[3]triangulenium cation by cascade cyclization of a tetra-benzyl alcohol precursor in triflic acid solution. This stable carbocation is easily observed by NMR and optical spectroscopy and is highly fluorescent. Quenching of the cation into basic solutions or by hydride transfer from triethylsilane provides access to stable dihydro and tetrahydro[3]triangulenes. These neutral species interconvert with cations in a complex series of proton and hydride transfers. This route provides several important [3]triangulene precursors. Preliminary experiments designed to generate [3]triangulene in the solution phase provide evidence for its formation and rapid oligomerization.

Triangular-shaped aromatic hydrocarbons (Figure 1) comprise a homologous series of open shell structures, beginning with the well-studied phenalenyl radical (1).^[1-3] Higher homologs **2**, **3** and **4** are expected to exist as di-, tri- and tetraradicals, respectively; all have been predicted to possess high spin ground states.^[4-9] Synthetic attempts to make [3]triangulene (**2**) were first described by Clar in 1953^[10-12] although the first example of a triangulene ring system had been reported much earlier by Weiss.^[13,14]



Figure 1. The [n]triangulene series (n = rings on a side).

Among milestones in triangulene chemistry, the aromatic [3]triangulene dianion has been prepared from the Clar route.^[15] Synthesis and ESR spectroscopy of 2,6,10-tri-*tert*-butyl triangulene confirmed the existence of a kinetically unstable ground state triplet.^[16] 4,8,12-Trioxotriangulenes are well known, including the stable radical.^[17,18] There is a growing literature predicting the chemistry of **2**^[19–22] and a variety of heterocyclic versions are known.^[23–30] In spite of much

effort in this field, the parent substance **2**, commonly known as triangulene or Clar's hydrocarbon, was only recently prepared and observed as single molecules by scanning probe microscopy.^[31] Similar experiments describing the molecular-scale preparation of higher homologues **3** and **4** by surface-assisted dehydrogenation of suitable precursors have been reported very recently.^[32, 33]

Further development in the evolving triangulene field requires efficient syntheses. Earlier synthetic routes to the allcarbon ring system of **2** are relatively lengthy;^[31] improvements in the Clar route to triangulene precursors have been reported as this work was under review.^[34] We report here a very short and efficient synthesis of the [3]triangulene ring system by cascade cyclization that provides multiple precursors to **2** and potential derivatives. Preliminary efforts to generate **2** in the solution phase are also described.

Scheme 1 summarizes our route to the [3]triangulene ring system. Taking advantage of the 3-fold symmetry of this structure, condensation of three equivalents of protected benzyl alcohol **5** with diethyl carbonate afforded **6** in a single synthetic step and high yield. Palladium catalyzed deprotection yielded tetraol **7**. Sequential ring closing strategies have been reported earlier but we envisioned a cascade cyclization of benzyl cations. It is noteworthy that the 4,8,12-trioxytriangulenium cation was prepared in 1964 by Martin and Smith through a structurally similar cascade cyclization forming new aryl ether linkages.^[23]



Scheme 1. Synthesis of the 4,8,12-trihydro[3]triangulenium ion.

Attempts at cyclization of 7 with catalysts and acidic media known to promote benzyl cation chemistry afforded incomplete cyclization or mixtures of the desired products and oligomers, often with poor mass balances. As one example, exposure of 7 to polyphosphoric acid/water at 100 °C gave nearly quantitative conversion to 8. This result supports initial ionization at the central hydroxyl group and capture of the cation by one of the proximate benzyl alcohols.

An NMR experiment provided the key to complete cyclization. When tetraol 7 was added to an NMR tube

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containing 1M TfOD in DCE- d_4 at ambient temperature, the dark green solution immediately exhibited very simple ¹H and ¹³C NMR spectra, displaying three unique hydrogens and six carbon signals for the major species in solution. These data support formation of the symmetrical 4,8,12-trihydro-[3]triangulenium ion (9). DFT computations on 9 predict a D_{3h} symmetrical structure, with calculated NMR chemical shifts in good agreement with experiment. NMR samples of cation 9 were stable for > 24 h. As expected, exposure of the partially cyclized structure 8 to the same acidic reaction conditions led cleanly to 9.

Optical spectroscopy of **9** also supports this structure. The absorption spectrum in TfOH/DCE ($\lambda_{max} = 404.5$ and 463.5 nm), is similar but shifted to longer wavelength relative to the triphenylmethyl cation ($\lambda_{max} = 411.5$ and 433.5 nm), consistent with improved conjugation in the planar structure. TDDFT calculations correctly predict intensities for the two longest wavelength absorption bands but computed transition energies are too high, as previously seen for cations.^[35] These two absorption bands arise due to electronic excitation to the LUMO from pairs of degenerate bonding orbitals. Cation **9** showed strong fluorescence, with a lifetime of ca. 5 ns, as measured by single photon counting. By comparison, the more flexible triphenylmethyl cation showed much weaker fluorescence, as judged by photon intensity and a higher signal/noise ratio.

We next turned to larger scale reactions (Scheme 2, Table 1), with the goal of preparing stable dihydro and tetrahydro[3]triangulenes. After preparation of cation **9** by the method described above, neutralization by hydride transfer during slow addition to triethylsilane in DCM produced a mixture composed primarily of hydrocarbons **10–12** in 96% isolated yield. The three components were separable by flash chromatography, providing pure samples of each hydrocarbon. Dihydrotriangulene **12** has been described previously as a precursor to $2^{[31]}$ and its dianion^[15] but has only been prepared according to the longer synthetic route of Clar.^[11,12] Our spectral data match those reported earlier. 1,2,3,8-Tetrahydrotriangulene **(11)** is a new derivative of olympicene,^[36] possessing one additional saturated ring. Isomeric tetrahydrotriangulene **10** is also a new substance, confidently



Scheme 2. Cation conversion to dihydro- and tetrahydrotriangulenes.

Table 1: Synthesis of dihydro- and tetrahydro[3]triangulenes from the 4,8,12-trihydrotriangulenium cation (9).

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Reduction conditions	10	11	12	Total yield	
Et₃SiH/DCM	38%	9%	49%	96%	
Sat. NaHCO ₃	-	27%	53%	80%	
Et_3N/DCM	-	-	66%	66%	

characterized by its very simple ¹H and ¹³C NMR spectra. The central methine hydrogen in **10** appears as a quartet (J = 5.5 Hz) in the NMR spectrum because of long range coupling to the three pseudoaxial methylene hydrogens. ⁵J Homoallylic coupling has been described previously in 1,4-cyclohexadienes.^[37] The predicted structure of **10** from DFT computations is modestly bowl-shaped. Neutralization of **9** by addition to saturated aqueous NaHCO₃ afforded a mixture of **11** and **12**, while slow addition to Et₃N gave a 66% isolated yield of pure **12**.

Olympicene is known to undergo air oxidation at the methylene carbon^[36] and thus **11** is a logical precursor to ketone **13**, a substance isolated by Clar in his initial synthetic study.^[12] Consistent with this expectation, exposure of solutions of **11** to air over 24 h (Scheme 3) led to partial conversion to ketone **13**. Air oxidation of **12** has been reported previously^[31] but the product was not identified. We find that diketone **14** is the major product. This oxidation is more efficiently carried out by reaction of **12** at ambient temperature with excess TEMPO, giving **14** in 44 % yield after chromatography.



Scheme 3. Benzylic oxidation.

The products in Table 1 suggest a complex series of proton and hydride transfers, which pass through triangulenium ion **9** and other cations. Scheme 4 summarizes likely connections, along with relative energies of isomeric neutral and cationic species, as estimated by DFT computations.

To further understand these interconversions, we exposed pure samples of 10, 11 and 12 to TfOD in DCE- d_4 , monitoring reactions by NMR spectroscopy and using DFT computations to predict the NMR spectra of likely cationic intermediates. Results of initial reaction were dependent on TfOD concentration. Exposure of 10 to TfOD/DCE- d_4 led to cation 9, the presumed result of central hydride abstraction. A similar experiment with 12 gave a mixture of 9 (88%) and two other cations believed to be 16 (9%) and 18 (3%). Cation 16 is the likely product of hydride abstraction from phenylanthracene 15, a substance not observed here although it was described earlier by Clar.^[10-12] Structure 15 is the expected product of initial deprotonation of 9, an easily reversible process. We have shown earlier that anthracene is fully protonated in 1M TfOH solution^[38] and **15** should be more basic than anthracene. Cation 16 is C4 protonated triangulene 2. Upon standing for 72 h, the solution led to a mixture of 9 (92%)



Scheme 4. Interconnections of neutral and cationic species, with relative free energies (IEFPCM(DCE)/B3LYP/6-31+G(d,p) for isomers.

and **18** (8%). This same aromatic olympicenium ion^[39] (**18**) is formed cleanly by reaction of **11** with TfOD.

Observed chemical shifts for the cations are in good agreement with computation. According to the DFT free energies, aromatic cation **18** is the most stable $C_{22}H_{15}^+$ isomer in this series. Consistent with this prediction, an NMR sample of this cation is stable for over 2 months. During the same period, an NMR sample of higher energy isomer **9** has converted ca. 66% to **18**. Among neutral structures, **12** is predicted to be the most stable dihydrotriangulene; this may explain its selective formation from reaction of **9** with triethylamine, likely by the sequence $9 \rightarrow 15 \rightarrow 16 \rightarrow 12$. Full characterization of these fascinating interconversions will require more detailed study.

As a preliminary exploration of the solution-phase chemistry of **2**, the reaction of dihydrotriangulene **12** with *p*chloranil (2 equivalents) was monitored by ¹H NMR and optical spectroscopy. The UV-VIS spectrum showed a new λ_{max} at 628 nm, which decayed over 24 h. This is unlikely to be **2** which is predicted by TDDFT calculations (SI) to have a longest wavelength triplet-triplet absorption between 400– 500 nm. NMR analysis showed only oxidation product **19** remaining in solution. LDI-TOF analysis of the solid reaction product revealed a complex spectrum (SI Figure 2) with masses stretching up to ca.1400 Da. We believe this result supports the formation of higher oligomers of **2**.

The history of the [3]triangulene ring system now spans nearly a century, with the first example reported in 1925.^[14]



Scheme 5. Attempt to generate [3]triangulene in solution.

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Diverse heterocyclic analogues are known but the absence of an efficient synthesis for the parent hydrocarbon has limited exploration and applications of [3]triangulenes. Clar's initial quest for the parent hydrocarbon $2^{[12]}$ was only fulfilled on a molecular scale by Pavlicek and co-workers in 2017.^[31] The first molecular-scale preparations of higher homologues [4]and [5]triangulene have very recently been reported as further milestones^[32,33] in this rapidly evolving field. Di- and tetrahydro[3]triangulenes are now more available through this work and a parallel study reported recently by Juríček and co-workers.^[34] Our preliminary efforts to generate [3]triangulene in the solution phase provide evidence for rapid oligomerization, as might be expected for this highly reactive substance. We believe it should be possible to tame the solution phase reactivity of 2 through appropriate chemical traps.

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Conflict of interest

The authors declare no conflict of interest.

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