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Synthesis and Characterization of Multiply Fused Dehydrobenzoannulenoannulene Topologies

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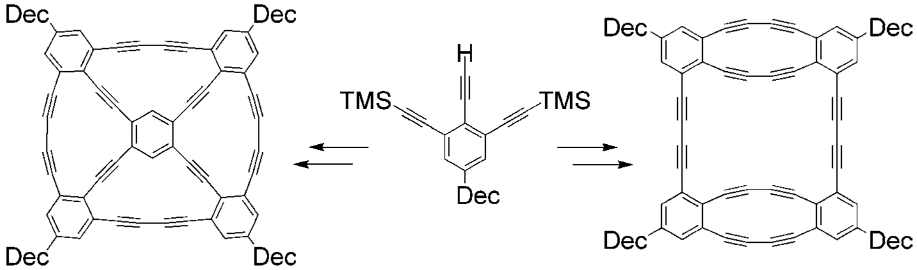
ABSTRACT



From a common precursor, two unusual dehydrobenzoannulene topologies have been synthesized utilizing either Pd-catalyzed or Cu-mediated oxidative homocoupling as the ring-closure step.

Carbon-rich materials comprise a fascinating branch of organic chemistry that has received a great amount of attention in recent years as a result of their unique chemical and physical properties.[1] Specifically, advances in the field of dehydroannulene chemistry have allowed the synthesis and study of a wide array of cyclic topologies including annulenes of various sizes, symmetries, shapes, and substitutions.[2] These macrocycles are often optically and nonlinear optically active,[3] may polymerize topochemically to furnish polydiacetylenic tubes or "bucky" materials,[4] and have frequently been used as sensitive probes for studies of aromaticity.[5] Advances in the field of Pd-mediated alkyne cross-coupling reactions have brought about construction of increasingly larger and more complex dehydrobenzoannulene (DBA) systems.[2a] Recently, we reported an oxidative Pd-catalyzed alkyne homocoupling procedure for the assembly of diacetylenic annulenes.[6] We now disclose the successful extension of this chemistry to the synthesis of DBA **1** (Figure 1), comprising fused 14- and 15-membered rings and

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belonging to a previously unattainable class of π-extended fenestrane-type[7] systems. We also herein describe the synthesis of a second unique DBA topology (**2**) from a shared precursor.

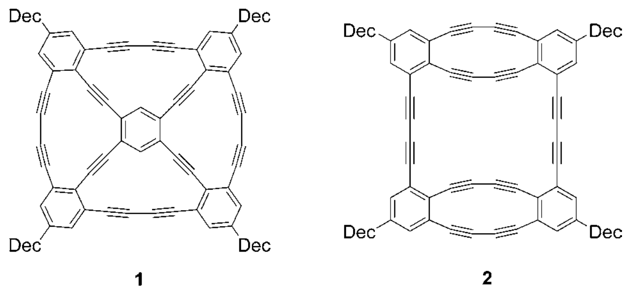


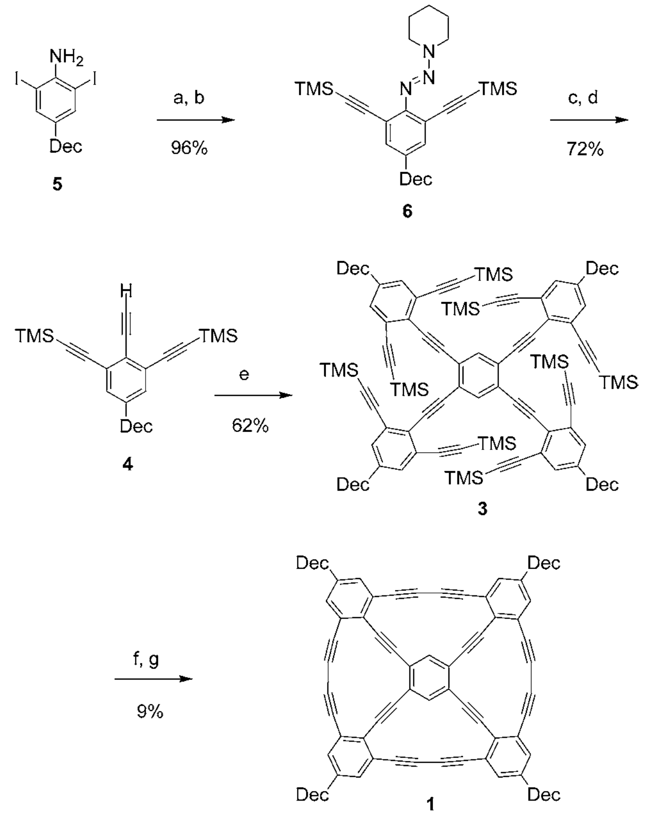
Figure 1. Target macrocycles **1** and **2**.

There existed two main difficulties in the synthesis of macrocycle **1** that had to be overcome for its successful construction. The first obstacle was designing a system to minimize the large amount of steric bulk crowding the central ring of the precyclized material **3** (Scheme 1). The second difficulty to surmount was the closure of all four rings around the periphery of the DBA.

Our annulene syntheses typically take advantage of the difference in reactivity of trimethylsilyl (TMS) vs triisopropylsilyl (TIPS) groups for protection of the alkynes to be used for cross-coupling vs homocoupling. However, the steric bulk from installing the necessary eight TIPS groups around the central ring would be impossible to achieve in this new system. The preparation of **3** instead relied upon the use of the smaller TMS groups. Triyne **4** seemed to be the ideal precursor for this synthesis, relying on only one alkyne protecting group and a terminal alkyne that was easily attached via the Stille reaction.

The synthesis proceeded by an initial triazene formation from diiodoaniline **5**[8] followed by cross-coupling of TMSA to the iodo positions, giving **6** in 96% yield (Scheme 1). Decomposition of the triazene and iodide substitution was accomplished by heating in MeI at 140 °C. A Stille cross-coupling of ethynyltributylstannane gave triyne **4** in 72% yield. Sonogashira cross-coupling of **4** with 1,2,4,5-tetraiodobenzene required heating at reflux for 60 h to give the precyclized polyyne **3** in 62%, which is a respectable 89% per cross-coupling transformation. The TMS groups were next removed with tetrabutylammonium fluoride (TBAF), and the material was immediately subjected to cyclization.

Scheme 1[a]



[a] Reagents and conditions: (a) (i) HCl, $NaNO_2$, THF, MeCN, H_2O; (ii) piperidine, K_2CO_3, MeCN, H_2O; (b) TMSA, $Pd(PPh_3)_2Cl_2$, CuI, *i*Pr_2NH, THF; (c) MeI, 140 °C; (d) $Bu_3SnC{\equiv}CH$, $Pd(PPh_3)_4$, THF, reflux; (e) 1,2,4,5-tetraiodobenzene, $Pd(PPh_3)_4$, CuI, *i*Pr_2NH, THF, reflux; (f) TBAF, THF; (g) Pd(dppe)Cl_2, $Pd(PPh_3)_2Cl_2$, CuI, I_2, *i*Pr_2NH, THF, 55 °C.

No detectable annulene products were found from the Cu-mediated Glaser coupling of **3**, which gave only oligomeric byproducts. To induce ring closure we turned to oxidative Pd-catalyzed homocoupling.[6,9] A distinct advantage of this route is the ability to tailor the reactivity of the catalyst by judicious choice of ligand. We have previously found that the *cis*-bidentate ligand 1,2-diphenylphosphinoethane (dppe) favorably forms 14-membered annulenes with the geometry present in **1**.[6] We also determined $Pd(PPh_3)_2Cl_2$ will satisfactorily provide 15-membered DBAs, which are also present in macrocycle **1**. Initial closure of one ring should further facilitate cyclization by optimizing the geometry of terminal alkyne groups for subsequent ring closures. By using a

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mixture of the two aforementioned Pd-catalysts and 0.5 equiv of I_2 as an oxidant, synthesis of the first full wheel-type DBA **1** was achieved in 9% yield (55% per cyclization). To further minimize oligomer formation, polyyne **3** was slowly injected over a period of 60 h into the catalyst solution. However, with the lengthy reaction time, we observed noticeable degradation of the Pd catalyst under the moderate temperature and oxidative conditions of the reaction. Therefore, addition of fresh catalyst at 24 h increments was required to complete the formation of the product. Material consisting of only three cyclized rings and two terminal alkynes was isolated in significant amounts if fresh Pd was not added.

According to molecular modeling calculations,[10] fenestrane **1** should adopt a slight bowl shape, which would help explain its remarkable solubility and stability. The ^1H NMR data were in agreement with known bis[15]- and bis[14]annulene systems (**7** and **8**, Figure 2) reported by Haley.[6] The intraannular proton confirmed a large anisotropic deshielding effect ($\delta = 8.41$ ppm) due to close proximity to the central alkyne bonds. The opposite effect was observed for the protons of the outer phenyls ($\delta = 7.06$, 7.03 ppm) because these alkynes are bent away. As a result of the excellent solubility of the DBA, a ^{13}C NMR spectrum was also acquired and agreed with the structural assignment. DSC data of **1** showed a broad exotherm starting ~250 °C indicative of random polymerization/decomposition.

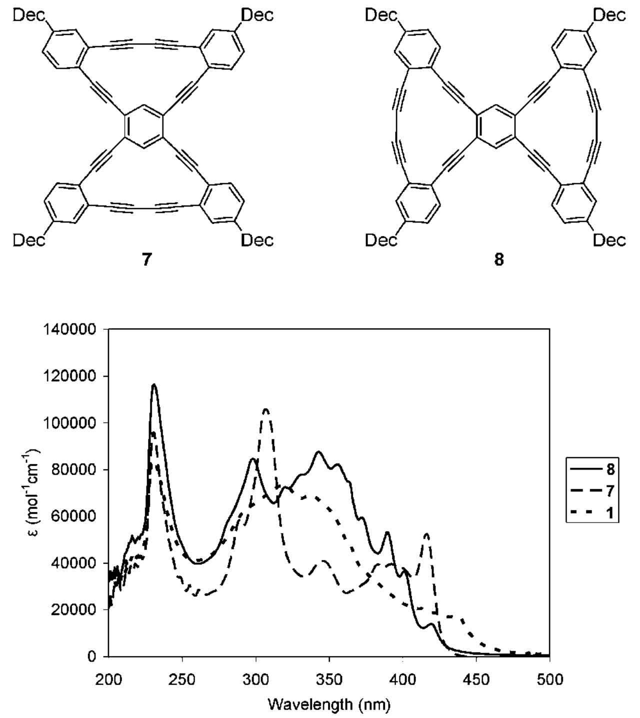
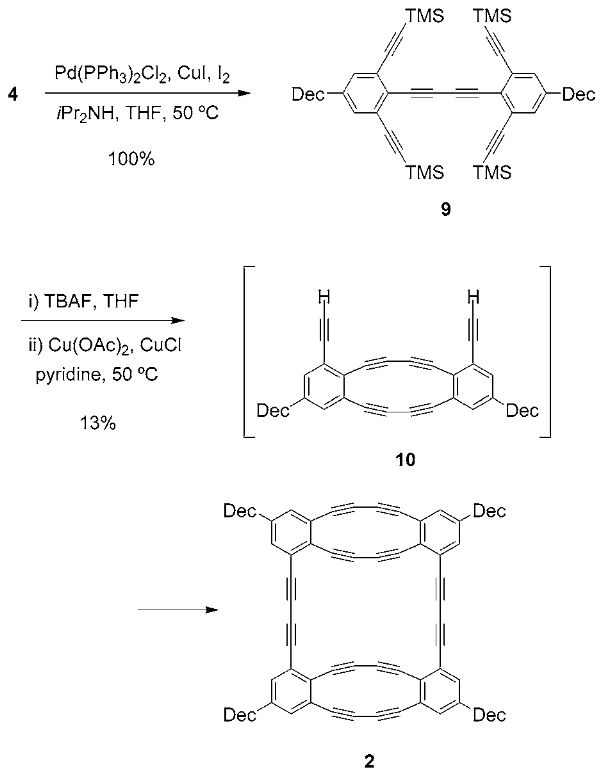


Figure 2. Electronic absorption spectra of fenestrane **1** and bisannulenes **7** and **8**.

The electronic absorption spectrum of **1** (Figure 2) displays similarities to those of the bis[15]- and bis[14]annulenes **7** and **8**. A red-shift of the absorption cutoff and broadening of the absorption bands due to increased overall conjugation and the more complex conjugated circuits is present in the spectrum of fenestrane **1**.

Through a series of intermolecular dimerizations of triyne **4**, the synthesis of another annulene of unique aesthetic appeal was possible. DBA **2** consists of two strained dehydrobenzo[12]annulenes fused to a central [24]annulene core. Triyne **4** was dimerized in quantitative yield to give **9** (Scheme 2). After removal of the TMS groups with TBAF, the polyyne was subjected to Cu-mediated homocoupling. [12]Annulenes such as **10** are known to form via this Cu/pyridine procedure.[2b,4c,11] Again in this ring system, an initial intramolecular homocoupling optimizes the geometry for subsequent cyclizations. The terminal alkynes of intermediate **10** are aligned parallel to each other and allow facile dimerization and cyclization providing the novel annulene **2** as a bright yellow solid in 13% yield.

Scheme 2



DBA **2** exhibited very low solubility in common organic solvents due to the large size and planarity of the macrocycle.[10] The solubility in $CDCl_3$ was enough to acquire ^1H NMR data, although inadequate for ^{13}C NMR characteriza-

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(10) PM3(*tm*) calculations performed on an SGI Octane workstation using Spartan SGI version 5.1.3 by Wave function Inc., 1998. See Supporting Information for minimized structures.

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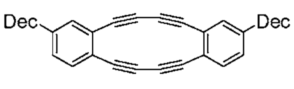

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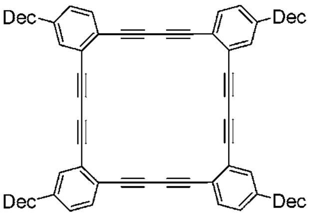

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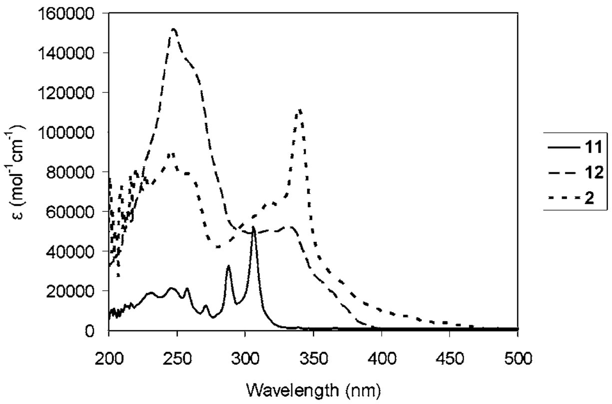

Figure 3. Electronic absorption spectra of annulenoannulene **2** and model annulenes **11** and **12**.

tion. Compared to **1**, the arene protons on **2** exhibit a much more significant upfield shift (δ 6.95, 6.74) due to the higher degree of bending in the diynes as well as the presence of an anti-aromatic ring current in the two fused [12]annulenes. The DSC data of **2** displayed a broad exotherm peak similar to that of fenestrane **1**, although at a lower temperature of ~110 °C as a result of increased instability.

For comparison, the [12]- and [24]annulene substructures **11** and **12** were constructed.[12] The electronic absorption spectra of **2** display similarities with both annulene subunits. [24]Annulene **12** contains two major absorption bands also present in **2**, although the cutoff of the fused planar DBA is ~75 nm lower in energy (Figure 3). Also present in **2** are the sharp absorption peaks of **11**, although because of the increased conjugation of the larger annulene these peaks display an increase in absorption and a bathochromic shift of 35 nm.

In conclusion, we have developed a straightforward synthesis of two complex dehydrobenzoannulene topologies utilizing our successful developments with oxidative Pd homocoupling chemistry. We have also demonstrated the effect of ring fusion on the electronic absorption properties of these annulenes. In the future we will continue our ongoing efforts toward the synthesis of larger and more complex DBA systems.

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Supporting Information Available: Detailed experimental procedures and spectral data for compounds **1**−**4**, **6**, **9**, **11**, and **12** and their intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] See Supporting Information for details.