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Dehydrobenzoannulene–Dimethyldihydropyrene Hybrids: Model Systems for the Synthesis of Molecular Aromatic Probes

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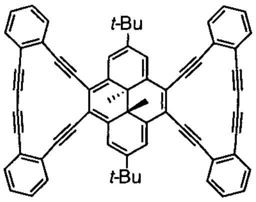
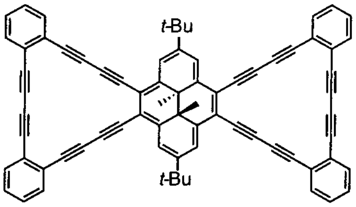
ABSTRACT



1



2

Synthesis of two novel dehydrobenzoannulene–dimethyldihydropyrene (DBA–DDP) hybrids has been achieved using a Pd/Cu cross-coupling strategy.

The resurgence of dehydrobenzoannulene (DBA) chemistry over the past decade has seen the assembly of a tremendous variety of new macrocycles.[1] The main impetus for the renewed interest has been predictions that DBAs and related highly conjugated, carbon-rich compounds[2] will exhibit interesting materials behavior such as nonlinear optical activity[3] and liquid crystallinity.[4] Nevertheless, several questions persist regarding this class of annulenes, especially with respect to their electronic character. There has been considerable debate as to whether planar, conjugated DBAs can sustain induced ring currents.[5] Experimental[6] and theoretical evidence[6b] support claims of aromatic and antiaromatic behavior in DBAs; however, the only protons available for NMR aromaticity studies are the arene protons. The induced ring current effects on these protons, attributable to the large macrocycles, will be weak because of the localized aromaticity of the benzene rings, the inclusion of triple bonds, and the size of the macrocycles.[5]

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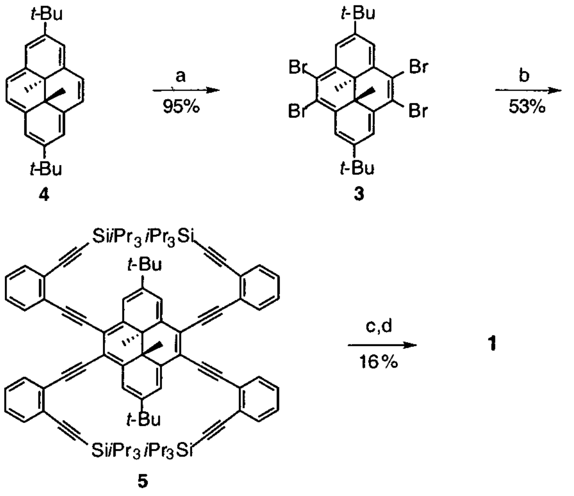
Studies have shown that dimethyldihydropyrene (DDP) can be used as a molecular probe for measuring aromaticity.[7] The DDP core provides a convenient handle on the ring current of fused aromatic systems, as it has two easily observable monitors: the chemical shift of the aromatic protons ($\delta \sim 9$ ppm) and the internal methyl protons ($\delta \sim -4.06$ ppm for **4**). Any change in the ring current of the DDP core induced by a fused arene will alter the shielding/deshielding of these two resonances. This effect can be quantified by comparison with a reference structure such as benzene.[8]

To date, no DDP systems have been constructed which incorporate weakly diatropic molecules such as DBAs. This is mostly due to the difficulty in synthesizing larger annulene-fused DDP macrocycles. DBA−DDP hybrids **1** and **2** represent our efforts to develop synthetic strategies for the construction of DBA-fused DDPs and to determine the viability of using DDP to probe the aromatic character of DBAs. In addition, it has been shown that the aromaticity of the annulenes fused on opposing faces of a DDP can facilitate photoinduced isomerization to form the corresponding [2.2]metacyclophanedienes.[9] If the hybrids could fine-tune this isomerization, it may be possible to use these systems as molecular photoswitches.[10]

The synthetic route to hybrids **1** and **2** is based on tetrabromo DDP **3**[11] (Scheme 1). Although aryl bromides are usually less reactive than their aryl iodide analogues, tetraiodination of DDP **4** proved to be problematic with standard methods. Tetrabromo DDP **3** exhibited sluggish cross coupling below 120 °C, consistent with other bromoarenes, as well as instability above this temperature. A literature example where acetylenes were successfully coupled to less reactive phenanthrolines[12] gave satisfactory results upon inclusion of DMF as cosolvent. Using these conditions, excess 1-ethynyl-2-(triisopropylsilylethynyl)benzene[6c] was reacted with tetrabromide **3** to produce α,ω-polyyne **5**. Desilylation using Bu_4NF, followed by cyclization with CuCl under pseudo-high-dilution conditions, provided bis[14]-DBA−DDP hybrid **1** as a reddish-brown solid in 8% overall yield.

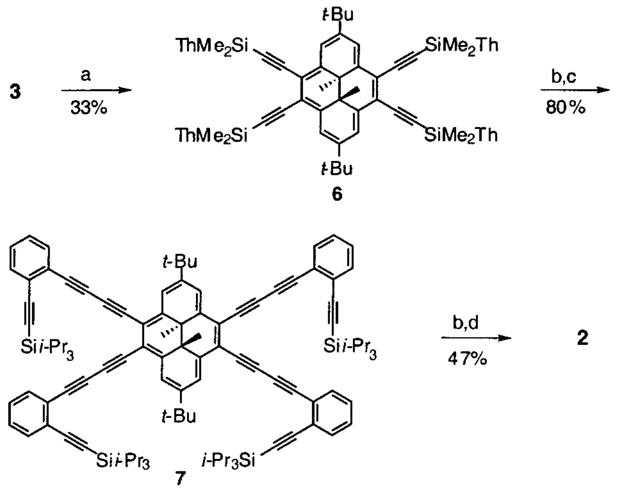
Scheme 1[a]



[a] Reagents: (a) Br_2, CCl_4; (b) 1-ethynyl-2-(triisopropylsilylethynyl)benzene, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, CuI, Et_3N, DMF; (c) Bu_4NF, THF, MeOH; (d) CuCl, MeOH, pyridine.

The preparation of bis[18]DBA−DDP **2** required a different synthetic route (Scheme 2). Since phenylbutadiynes are much less stable than the corresponding phenylacetylenes, a phenylbutadiyne moiety could not be used with the elevated temperature necessary to produce **5**. Instead, the diacetylenic linkage in the α,ω-polyyne was established through acetylene−acetylene cross coupling. Four equivalents of (dimethylthexylsilyl)acetylene were coupled to **3** to give DDP **6** in 33% yield.

Scheme 2[a]



[a] Reagents: (a) $ThMe_2SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, CuI, Et_3N, DMF; (b) Bu_4NF, THF, MeOH; (c) 1-(bromoethynyl)-2-(triisopropylsilylethynyl)benzene, $Pd(dba)_2$, CuI, LiCl, DMSO; (d) $Cu(OAc)_2$, MeOH, pyridine.

Treatment of 1-ethynyl-2-(triisopropylsilylethynyl)benzene with BuLi followed by elemental bromine furnished the corresponding bromoacetylene in good yield. This material was in turn coupled to desilylated **6** using a procedure recently developed by Cai and Vasella[13] to give polyyne **7** in 80% yield. Although the cyclization of polyyne **5** could,

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after desilylation with Bu_4NF, be accomplished with CuCl, polyyne **7** required the use of $Cu(OAc)_2$ under pseudo-high-dilution conditions to give bis-[18]DBA−DDP **2** as a green-black solid in 12% overall yield.

The UV−vis spectra of hybrids **1** and **2** are shown in Figure 1. Not surprisingly, **2** exhibits greater absorption due to increased π-conjugation density compared to **1**. It is noteworthy that both compounds display a moderately strong absorption in the 750−780 nm region, which reflects the extensive conjugation throughout these macrocycles.

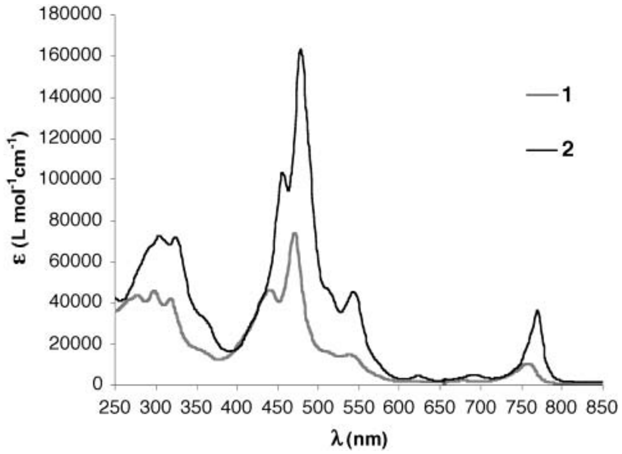

Figure 1. Electronic absorption spectra of hybrids **1** and **2**.

Although competitive resonance structures in these bis-fused systems preclude using the DDP protons for estimations of the aromaticity of DBAs, we observe a chemical shift difference between the α,ω-polyynes and the cyclized hybrids that is consistent with previously studied DBAs.[6] Once cyclized, the protons on the benzene rings shift downfield compared to the corresponding polyynes ($\delta\Delta = 0.15-0.35$ ppm).[14] Although this is opposite of what would be expected from a significant ring current in the annulene core, since this would lower the ring current in the benzene rings in the same fashion as previously demonstrated for arene-fused DDP systems, it is consistent with through-space deshielding caused by the interior annulene ring current. This would explain why the protons proximal to the annulene core, i.e., ortho to the acetylenes, are shifted more than the distal protons. We also observe that the change in chemical shifts is greater for the DBA−DDP hybrids than for the analogous tribenzo-DBA systems ($\delta\Delta = 0.04-0.08$ ppm). This would be expected if the ring current of the annulene core is affected less by a DDP than by a benzene ring. Indeed, studies have shown that the DDP is less aromatic than benzene and hence less able to bond fix a fused arene.[7]

The procedures developed herein should allow mono-fused DBA−DDP hybrids to be constructed. The corresponding mono systems should provide quantitative evidence of the ring current of DBAs. Tuning of the isomerization of the DDP core through fusion of different DBAs may also be possible. When strongly aromatic rings such as benzene are used, the cyclophanediene dominates and the pyrene can only be seen for a short time at low temperature.[9b] With more weakly aromatic systems, as we believe ours to be, the pyrene isomer prevails. Arene-fused DDP hybrids have already shown potential as photoswitches,[10] and experiments are in progress to determine whether our DBA−DDP hybrids can be used in this manner.

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Note Added after ASAP: This Letter was released ASAP on 4/27/01 with extraneous text in Figure 1. The print and final Web version (5/24/01) are correct.

Supporting Information Available: Selected spectroscopic data for compounds **1**, **2**, and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Steric interactions with the pyrene protons and the *tert*-butyl groups prevent accurate comparisons of the bay protons on **1** and **5** (as determined by modeling on Spartan).