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Synthesis of linearly-fused benzodehydro[12]annulenes

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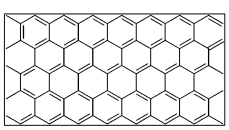
Abstract—This communication describes the preparation of the first linearly-fused benzodehydro[12]annulene systems, which we have called acediynes. These stable antiaromatic materials exhibit absorption properties that closely resemble the spectra of the corresponding acenes.

Theoretical studies have predicted the existence of stable, planar phases of carbon consisting of sp^2- and sp-hybridized carbon atoms.[1] Dubbed graphyne and graphdiyne, these materials were predicted to be large band-gap semiconductors that would form conductive stacks when doped with alkali metals. These materials resided strictly within the realm of theory until recent advances in synthetic methodologies allowed the synthesis of remarkably large oligomers of these systems.[2] The recent theoretical and synthetic studies on graphyne and graphdiyne oligomers have intrigued us with the possibility of applying a similar strategy to graphite substructures such as acenes and phenacenes. For example, separating the aromatic rings of acenes with butadiyne units leads to the acediynes **1**. There are a number of potential advantages to this class of materials: separation of the aromatic rings in this fashion allows the use of bulky solubilizing groups attached to the aromatic six-membered rings, while the antiaromatic dehydroannulene macrocycles might impart favorable electrochemical properties to the materials.[3] We present here our initial studies of the synthesis and characterization of the first acediynes.



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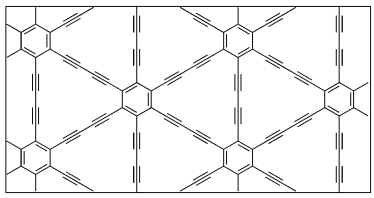
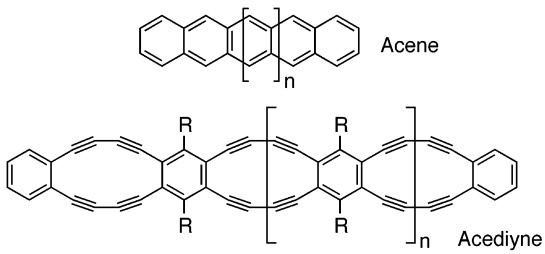


Graphdiyne

The antiaromatic macrocycles that comprise the acediynes are well-known species. The parent compound was first prepared in 1957,[4] and this material was re-investigated in 1999.[5] Solubilized derivatives have also been prepared to determine whether they were suitable for topochemical polymerization.[6] The macrocycles are typically formed by the simple oxidative cyclization of an *ortho*-arenediyne. The most straightforward approach to acediynes would thus involve the oxidative end-capping oligomerization of a suitably solubilized 1,2,4,5-tetraethynylbenzene. However, recent reports of *ortho*-arenediynes undergoing oxidative cyclization to yield complex mixtures of dimer, trimer, and higher cyclic species make such an 'all at once' approach to acediynes untenable.[7] An alternative, stepwise approach involves the initial synthesis of an appropriately substituted phenylenebutadiynylene system (**2**). Desilylation followed by high-dilution oxidative cyclization of this initial polymer will lead to the acediyne.[8] This form of intramolecular cyclization to generate macrocycles of a specific ring size has been exploited with great success in the formation of extended benzodehydroannulenes[9] (Scheme 1).



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Initial approaches to acediynes involving simple oxidative oligomerization of partially-silylated tetrayne **3** yielded inseparable mixtures of lower oligomers along with significant polymeric material. We reasoned that

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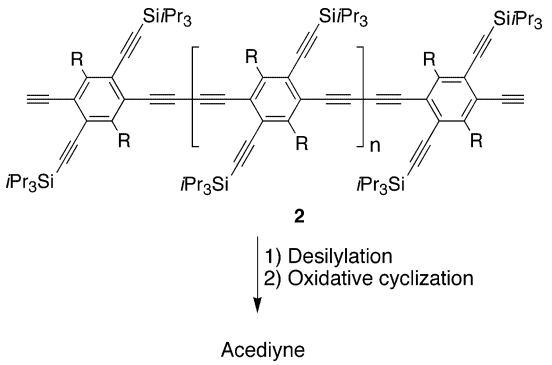
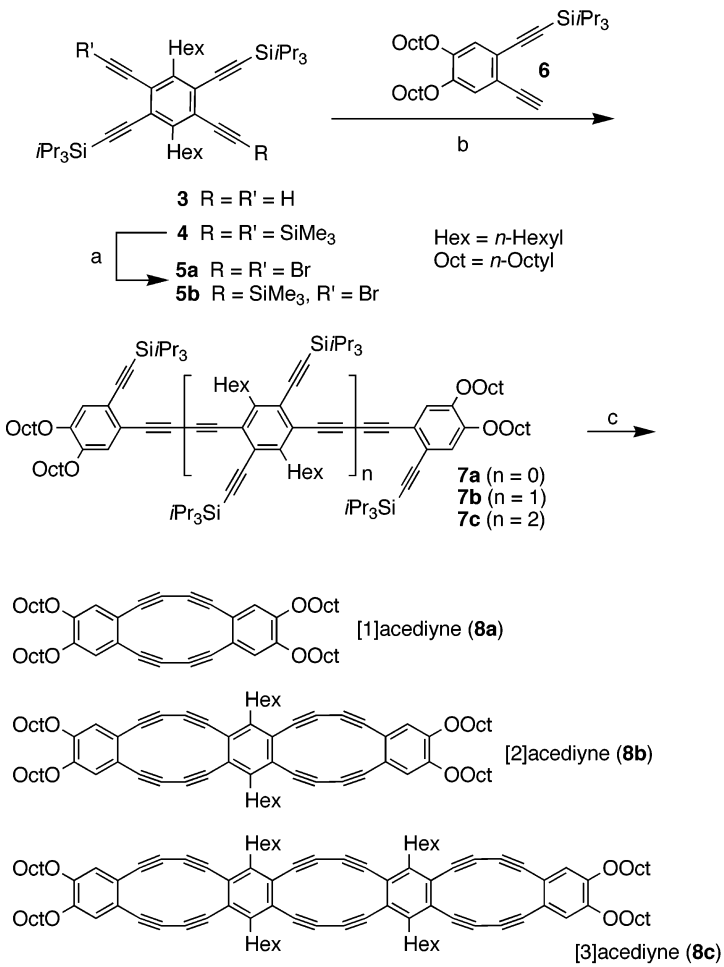


Scheme 1.

inclusion of polar end-cap **6** would simplify separation of the oligomers and decrease the degree of polymerization. Oxidative oligomerization in the presence of this end-cap yielded polymeric materials, along with homocoupled **6**.

Using modified Sonogashira conditions[10] to affect heterocoupling of end-cap **6** to the aromatic tetrayne, the monomer through trimer ([1]acediyne–[3]acediyne) were easily prepared as a mixture which was separated after the final cyclization step as outlined in Scheme 2.

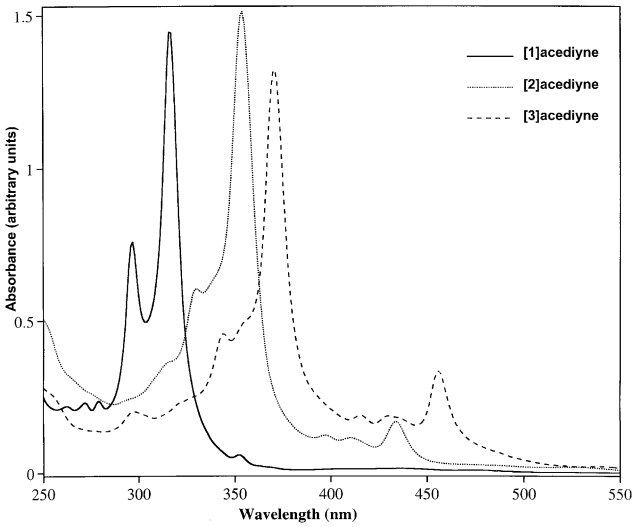
Tetrayne **4**[11] was partially desilylated with catalytic silver nitrate and 3 equiv. of NBS[12] to produce a ~1:1 mixture of monobromide **5a** and dibromide **5b**. Coupling of this mixture to the end-capping reagent **6** under Sonogashira conditions was followed by the removal of any remaining trimethylsilyl groups by treatment with aqueous base during workup. Simple oxidative dimerization (Hay conditions[13]) of the resulting terminal alkynes yielded the expected mixture of acyclic [1][14], [2], and [3]acediyne precursors **7a**–**c**. The organic components of this mixture were separated from metal salts and any remaining baseline or polymeric materials by passing the mixture through a short pad of silica gel. This mixture was then fully desilylated by treatment with fluoride in THF. The final oxidative cyclization was performed in dilute acetone solution. The formation of the brightly colored, cyclic oligomers was easily discerned by thin-layer chromatography, and the reaction was complete within 6 h. The compounds were separated by flash chromatography on silica gel to give the pure [1]acediyne **8a**,[14] [2]acediyne **8b** (31% from **4**) and [3]acediyne **8c** (6% from **4**).[15] The antiaromatic nature of these oligomers was confirmed by examination of their ^{1}H NMR spectra.[16] The singlet corresponding to the aromatic protons of the end-capping unit on **8a**–**c** undergoes a 0.5 ppm upfield (paratropic)



Scheme 2. (a) NBS, $AgNO_3$, acetone, 1 h, rt; (b) $(PPh_3)_2PdCl_2$, CuI, $EtN(iPr)_2$, 40°C, 4 h, then K_2CO_3, MeOH, 20 min then CuCl, TMEDA, acetone, overnight; (c) TBAF, wet THF, 0°C, 20 min then CuCl, TMEDA, acetone, overnight.

shift relative to acyclic **6**, while the benzylic protons of **8b–c** shift upfield by 0.7 ppm with respect to **3**.

The two smallest acediyne oligomers (**8a**, **8b**) are soluble, stable compounds and can be stored for weeks without decomposition. However, [3]acediyne **8c**, with its 29 Å conjugated core, is only sparingly soluble (<0.5 mg/ml in chloroform or *o*-dichlorobenzene). While this material is stable in the solid state, it decomposes slowly in solvents that have not been rigorously deoxygenated.



The presence of fine structure in the optical spectra across the series of oligomers confirms the rigidity of the conjugated backbones. As with the simple acenes,[17] the absorption edge progresses to longer wavelengths as oligomer length increases, and the long-wavelength absorption grows in intensity with respect to the main absorption. A plot of long wavelength cutoff versus inverse oligomer length gives an estimated cutoff for the corresponding infinite polymer of 625 nm (1.98 eV), which is similar in energy to other linear acetylene-based polymers.[18]

In summary, we have synthesized acediynes **8b** and **8c**, the largest molecules based on fused benzodehydro[12]annulenes prepared to date. While these materials are clearly antiaromatic in nature, they are quite stable in the solid state. We are currently investigating more aggressive solubilization strategies that will allow the preparation of the corresponding polymer, which will be the subject of a future report.

Acknowledgements

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14. Compound **7a** arose from excess end-cap reagent **6**, which was carried through subsequent coupling and cyclization steps to yield the [1]acediyne **8a**. Because this is simply a by-product the yield was not calculated.
15. All new compounds were characterized by NMR, EA (where appropriate) and MALDI-MS. Representative spectral data for the acediynes: [1]acediyne **8a**: Yellow crystals (mp 94°C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84–0.88 (m, 12H), 1.14–1.26 (m, 24H), 1.36–1.40 (m, 8H), 1.69–1.74 (m, 8H), 1.76–1.80 (m, 8H), 3.84 (t, $J=7$ Hz, 8H), 6.37 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.08, 22.63, 25.85, 28.92, 29.20, 29.25, 31.76, 69.08, 83.27, 92.18, 113.45, 123.72, 149.67 HRMS (MALDI): calcd for $C_{52}H_{72}O_4$ 760.5425. Found 760.5410. **[2]Acediyne 8b**: Orange crystals, (mp 107°C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84–0.88 (m, 20H), 1.25–1.31 (m, 38H), 1.38–1.44 (m, 12H), 1.68 (quint., $J=7$ Hz, 8H), 2.29 (t, $J=6$ Hz, 4H), 3.84 (t, $J=7$ Hz, 8H), 6.38 (s, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.09, 14.11, 22.51, 22.64,

25.87, 28.82, 28.94, 29.22, 29.28, 29.80, 31.43, 31.77, 34.90, 69.12, 83.36, 88.16, 90.45, 93.55, 113.53, 123.51, 131.42, 141.67, 149.96. HRMS(MALDI): calcd for $C_{78}H_{98}O_4$ 1098.7460, found 1098.7471. **[3]Acediyne 8c**: Red crystals (mp 95°C (dec)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (m, 44H), 1.25 (m, 44H), 1.70 (m, 16H), 2.27 (t, $J=8$ Hz, 8H), 3.84 (t, $J=6.8$ Hz, 8H), 6.39 (s, 4H). HRMS (MALDI): calcd for $C_{104}H_{124}O_4$ 1436.9494, found 1436.9514.

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