

Graphitic Molecules with Partial “Zig/Zag” Periphery

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Polycyclic aromatic hydrocarbons (PAH) represent one of the most intensively investigated classes of compounds.¹ Recently, we have developed a straightforward route to a series of all-benzenoid PAHs with a broad range of sizes and shapes.² In addition to providing real-world examples to test theoretical modeling of the properties of graphite segments,³ these molecules have attracted considerable interest as active components in solar cells, field effect transistors, and other molecular electronic devices.⁴

Because of its hexagonal symmetry, hexa-*peri*-hexabenzocoronene (HBC, **1**, Chart 1) serves as an intriguing homologue of benzene. Inclusion of varying edge structures should be revealing since it is known that periphery and overall size of PAHs are critical factors that determine their electronic structure and chemical reactivity.⁵ Herein, we present our preliminary result, which promises the establishment of a new family of graphitic molecules with “reactive” double bonds. The integration of “zig/zag” edges should influence dramatically not only its electronic properties but also its two- and three-dimensional self-assembly behaviors.

Whereas cyclotrimerization of phenyl-substituted ethynes is restricted to polyphenylene precursors with 6-fold symmetry, Diels–Alder [4 + 2] cycloaddition of tetraphenylcyclopentadienone with diarylacetylenes is a well-established method to construct polyphenylene derivatives.^{6a} Therefore, the key design element here is to incorporate a “zig/zag” edge into the cyclopentadienones. Recently, we found that pyrene-4,5-dione derivatives form unique helical columnar arrangements in single crystals,⁷ and it appears that their Knoevenagel condensation with benzil would give the aimed building block.^{6b,c} Diels–Alder reaction of **4a** with commercially available diphenylacetylene resulted in the corresponding 9,10,11,12-tetraphenyl-benzo[*e*]pyrene (**5a**) in relatively low yield (35%), probably because of the thermal decomposition in the cycloaddition process (240 °C) (see below). Cyclodehydrogenation of the unsubstituted **5a** proceeded smoothly with copper(II) trifluoromethane sulfonate and aluminum(III) chloride to give the desired planar PAH **2a** with one additional “zig/zag” edge. The vanishing solubility of **2a** precludes solution ¹H NMR and ¹³C NMR characterization; however, MALDI-TOF MS (solid-state analyte in TCNQ matrix preparations)⁸ reveals a single species with isotopic distribution in accord with the calculated one for compound **2a**, proving the loss of exactly 10 hydrogen atoms during the formation of five new carbon–carbon bonds.

A UV–visible absorption spectrum of **2a** recorded in 1,2,4-trichlorobenzene clearly shows three types (groups) of bands (α , p (or L_b , L_a^9) and β (B_a , B_b^9)) which are typical for aromatic hydrocarbons (Figure 1).^{1b} The absorption maximum of **2a** ($\lambda_{\max} = 380$ nm) shows a significant bathochromic shift with respect to the corresponding band of **1** ($\lambda_{\max} = 359$ nm) ($0 \rightarrow 0$ band of the $S_0 \rightarrow \beta$ transition, assignments based upon calculations; see below).

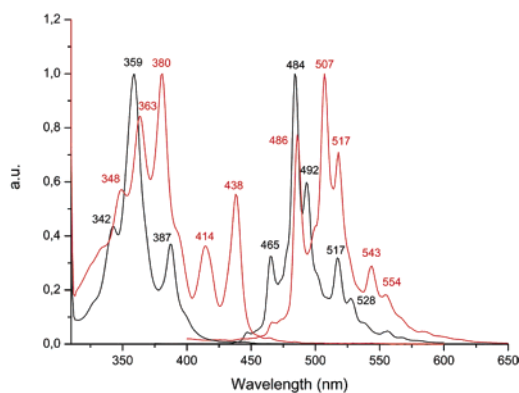
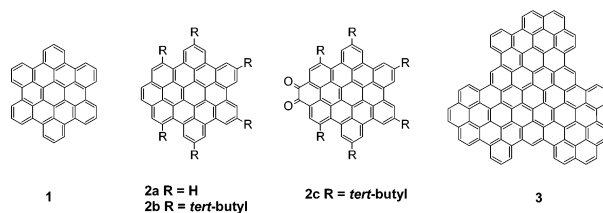


Figure 1. UV–visible absorption and photoluminescence spectra of **1** and **2a** recorded at room temperature in 1.0×10^{-6} M 1,2,4-trichlorobenzene solution. Black line: **1**, red line: **2a**.

Chart 1. Molecular Structure of HBC (**1**) and Target Compounds



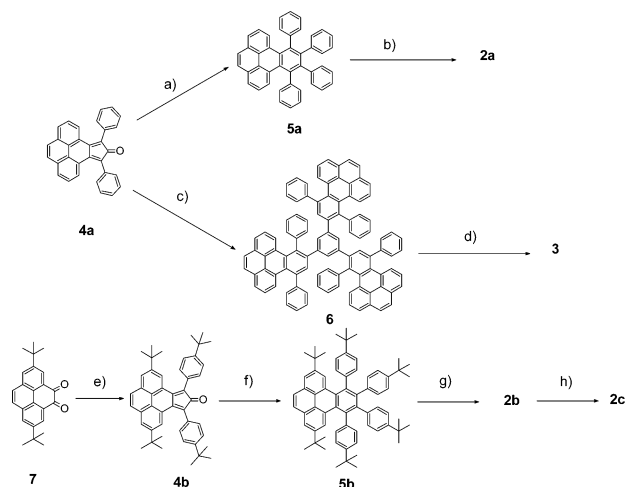
Reducing the symmetry increases the intensity of $0 \rightarrow 0$ band of the α (or L_b) transition (486 nm), which is otherwise very weak (symmetry-forbidden) for the D_{6h} symmetric unsubstituted HBC, as shown in the profile of the emission spectra. Interestingly, there is also a characteristic band at 438 nm that is not found in the all-benzenoid analogue. ZINDO–CIS quantum chemical calculations were carried out to estimate excitation energies and oscillator strengths at the B3LYP/3-21G equilibrium structure of this molecule, and it was found that a net remarkable transition dipole moment is associated with the $0 \rightarrow 0$ band of the $S_0 \rightarrow L_a$ (or $S_0 \rightarrow p$) transition. It is clear that this unusually strong band originates from the strong electronic perturbation induced by the two additional π -centers.

A further step toward “superbenzene” that carries reactive sites in the periphery concerns improving the solubility by introducing *tert*-butyl groups to the parent graphitic molecule.¹⁰ Sufficient solubility is also a prerequisite for the structural investigation and characterization of physical properties.

We achieved hexa-*tert*-butyl-substituted “zig/zag” HBC (**2b**) synthetically in a stepwise manner as outlined in Scheme 1. It should be noted that the yield of Diels–Alder cycloaddition of **4b** with diarylacetylene is much higher (80%) than that of **4a**, probably because *tert*-butyl groups kinetically stabilize the cyclopentadienone. The key step for the synthesis of **2b** is the oxidative cyclodehy-

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Scheme 1. Synthetic Route to “Zig/Zag” PAHs^a

^a Conditions: (a) diphenylacetylene, Ph₂O, 240 °C, 6 h, 35%. (b) Cu(OSO₂CF₃)₂, AlCl₃, CS₂, 25 °C, 20 h, 87%. (c) 1,3,5-Triethynylbenzene, *o*-xylene, 170 °C, 48 h, 70%. (d) FeCl₃, CH₂Cl₂, 25 °C, 10 h, 82%. (e) Di-*tert*-butylbenzil, KOH, EtOH, 80 °C, 15 min, 78%. (f) Di-*tert*-butyldiphenylacetylene, Ph₂O, 240 °C, 6 h, 80%. (g) FeCl₃, CH₂Cl₂, 25 °C, 20 min, 95%. (h) RuO₂/NaIO₄, DMF/H₂O, 48h, 11%.

drogenation of **5b**. Using anhydrous FeCl₃ as oxidant and Lewis acid, we obtained **2b** in nearly quantitative yield after reductive workup. H,H NOESY, H,H COSY, and H,X COSY NMR spectra of **2b** were obtained in THF-*d*₈. The two protons in the “zig/zag” edge were observed at $\delta = 8.64$, i.e., significantly shielded with respect to the aromatic “armchair” protons, which resonate as singlets between 9.1 and 9.5. The solubility of **2b** allows further derivatization to probe the chemical reactivity unique to the “zig/zag” motif. The selective oxidation of the “zig/zag” edge to its corresponding diketo structure was achieved by using ruthenium dioxide/sodium periodate in aqueous *N,N*-dimethylformamide, which provides a potentially versatile building block for giant graphene molecules.

The UV–visible absorption spectrum of **2b** is essentially unchanged with reference to unsubstituted parent compound **2a**, in accord with the relatively weak donor effect of *tert*-butyl groups. A small bathochromic shift by about 6 nm respective to **2a** is probably due to the expected nonplanarity caused by steric congestion.

Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a hexane solution of **2b** at room temperature. It should be noted that the molecule is bent because of the steric interaction of the *tert*-butyl groups (see Supporting Information). The “outer rings” are alternatively bent up and down by approximately 15° each. The unexpected tendency of **2b** to form stable hexane solvates is probably due to the nonplanarity of the molecules, which hinders the formation of the stacking, thus having cavities which are filled by the solvent.

To demonstrate the versatility of our “molecular Lego”, we introduce the polyphenylene dendrimer **6**, which is obtained from a 3-fold Diels–Alder cycloaddition between excess **4a** (4.4 equiv) and commercially available 1,3,5-triethynylbenzene in *o*-xylene at

170 °C in good yield (70%). As the 2D representation of **6** suggests, it can be cleanly cyclodehydrogenated to a graphitic molecule **3** with more extended “zig/zag” character, which can be identified, for example, by its MALDI-TOF MS spectra and solid UV–visible spectra recorded on mechanically “smeared” films on quartz. The absorption maximum of **3** ($\lambda_{\text{max}} = 535$ nm) shows a significant bathochromic shift (45 nm) with respect to its parent PAH without “zig/zag” edge (see Supporting Information). Presumably, the introduction of six *tert*-butyl groups is not enough to solubilize this large PAH,^{11a} and we are currently focusing on the synthesis and characterization of soluble derivatives by attaching long alkyl chains.^{11b}

In conclusion, a new synthetic protocol ensuring novel polycyclic aromatics with partial “zig/zag” periphery and dramatically different electronic properties has been developed. In addition to serving as an interesting theoretical model for graphite, they also provide reactive sites for further functionalization, e.g., preparing its corresponding K-region oxide. Attaching long alkyl chains onto the PAH core is supposed to give liquid crystalline properties.

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Supporting Information Available: Full experimental details, MALDI-TOF mass spectra of compound **2a**, **2b**, and **3**, and quantum chemical calculations of **1** and **2a** (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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