## Synthesis of Large Polycyclic Aromatic Hydrocarbons from Bis(biaryl)acetylenes: Large Planar PAHs with Low $\pi$ -Sextets

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ABSTRACT

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A new synthesis of large PAHs with low Clar sextets was developed. This synthesis involves initial bis(biaryl)acetylene 1, which undergoes initial ICI-aromatization and a subsequent Mizoroki—Heck coupling reaction to give dibenzochrysene derivative 3 that can be transformed into planar PAHs 4 using DDQ-oxidation.

Scholl oxidation of the 1,2-diphenylbenzene units is a powerful tool to access large polycyclic aromatic hydrocarbons (PAHs).<sup>1</sup> Due to the fully populated Clar  $\pi$ sextets,<sup>2</sup> the reported large PAHs such as **I**–**III** (Scheme 1) typically have irreducible highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO– LUMO) energy gaps.<sup>3</sup> To seek large PAHs with low Clar  $\pi$ -sextets,<sup>4</sup> we reported the use of bis(biaryl)diynes **IV** for short syntheses of PAHs **VI** and their heavier congeners,<sup>5</sup> as depicted in Scheme 1. Nevertheless, these PAHs have nonplanar geometries because of the steric interactions around the two cove regions. We envisage that planar PAHs will be beneficial for organic optoelectronic devices due to their strong intermolecular  $\pi - \pi$  interactions.<sup>6</sup>

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Previously, we reported the synthesis of dibenzochrysenes<sup>7,8</sup> based on the 2-fold aromatizations of bis(biaryl)acetylenes.<sup>8</sup> Here, we report further development of this method to achieve the synthesis of planar PAHs **4a**–**4e** with low Clar  $\pi$ -sextets in Figure 1; PAHs **4b** and **4c** are structurally related to the parent skeleton **4a** with two additional benzenes, whereas PAHs **4d** and **4e** have four extra benzenes. An examination of their photophysical properties with increasing benzene arrays is the focus of this investigation.

As depicted in Scheme 2, treatment of bis(biaryl)acetylene **1a** with ICl (1.1 equiv) in cold dichloromethane (DCE, -78 °C, 3 h) afforded iodo derivative **2a** in 82% yield. A subsequent Mizoroki–Heck coupling reaction of species **2a** provided a large dibenzochrysene derivative **3a** 

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Scheme 1. All Benzenoid PAHs and Low Clar Sextets PAHs





Figure 1. Structure of Targeted PAHs (R = t-Bu).

in 71% yield. Species **3a** possesses two nonplanar fjord regions that are subjected to a DDQ-induced oxidative coupling<sup>9</sup> (DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone), giving targeted molecule **4a** in 91% yield. <sup>1</sup>H NMR of PAHs **3a** and **4a** in CDCl<sub>3</sub> show only nine and seven separate aromatic signals over the range -213-333 K that exhibit no dynamic behavior. For species **3a**, we envisage that an alteration at the fjord chiralty is impeded by a strong steric hindrance.

Table 1 highlights the applicability of this new synthesis to additional bis(biaryl)acetylenes 1b-1d, which delivered extended dibenzochrysene species 3b-3d efficiently through a sequential ICl-cyclization and Mizoroki–Heck coupling. For the resulting 3b and 3d, the corresponding DDQ-oxidation in CH<sub>2</sub>Cl<sub>2</sub> (0 °C, 6 h) gave the desired PAHs 4b and 4d in 79% and 85% yields respectively. Nevertheless, the same DDQ-oxidation of PAH 3c under the same conditions effected the coupling of only one fjord region, giving compound 4c' in

Scheme 2. Synthetic Route toward Compound 4a (R = t-Bu)



81% yield. To our delight, the second fusion was subsequently achieved with a DDQ-oxidation in a sealed tube at 70  $^{\circ}C$  (1,2-dichloroethane, 8 h), giving product **4c** in 90% yield.

Scheme 3 depicts the synthesis of large PAH **4e** using dibenzochrysene as the starting building block. Treatment of species **3a** with NBS in CHCl<sub>3</sub>/DMF produced dibromide derivative **1e** in 88% yield; compound **1e** was subsequently transformed into species **2e** (51% yield) *via* Suzuki







<sup>*a*</sup> ICl (1.1 equiv), CH<sub>2</sub>Cl<sub>2</sub>, -78 °C. <sup>*b*</sup> [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (5 mol %), Na<sub>2</sub>CO<sub>3</sub> (4.0 equiv), N,N-dimethylacetamide (0.01 M), 110 °C. <sup>*c*</sup> DDQ (2.1 equiv), CH<sub>3</sub>SO<sub>3</sub>H/CH<sub>2</sub>Cl<sub>2</sub> (1/10, v/v), 0 °C. <sup>*d*</sup> DDQ (1.1 equiv), CH<sub>3</sub>SO<sub>3</sub>H/1,2-dichloroethane (1/10, v/v), 70 °C. <sup>*e*</sup> Yields are given after purification by column chromatography on silica gel.

<sup>(9)</sup> DDQ-oxidation: (a) Zhai, L.; Shukla, R.; Rathore, R. Org. Lett. 2009, 11, 3474. (b) Zhai, L.; Shriya, R.; Wadumethrige, S. H.; Rathore, R. J. Org. Chem. 2010, 75, 4748.

Scheme 3. Synthetic Route toward Compounds 4e (R = t-Bu)



coupling, followed by removal of a silyl group, which subsequently underwent Pt-catalyzed aromatization affording the cyclized product **3e** in 90% yield. For species **3e**, a final DDQ-oxidation enabled a closure of the two fjord regions, giving desired compound **4e** in 78% yield.

The characterization of 3a-3e relies on appropriate analytic methods including elemental analysis, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) high resolution mass spectrometry (HRMS), and <sup>1</sup>H and <sup>13</sup>C NMR spectra. We obtained single crystals of 3c for X-ray diffraction.<sup>10</sup> Crystallographic data of its dibenzochrysene precursor 3c were also acquired to compare their molecular planarity. The unit cells of 3c and 4c contain two independent molecules, Z = 2. Figure 2 shows the ORTEP drawing for molecule 3c that reveals a great distortion from planarity in the fjoid geometry, as revealed by a large dihedral angle 77.8° between the A-E' and E-A' rings. In contrast, the dihedral angle between the A/D and A'/D'benzenes, in the so-called cove areas, is relatively small (51.6°). Species **3c** comprises an  $S_2$  axis with both **A** and **E** rings lying below the E' and A' rings, thus generating a double helicene, defined by rings  $\mathbf{E}' - \mathbf{C}' - \mathbf{B}' - \mathbf{B} - \mathbf{A}$  and A'-B'-B-C-E respectively. Notably, the six carboncarbon distances around the outer rings A, D, and E fall within a narrow range, 1.368-1.416 Å, indicating benzene character. In contrast, we observed large distances (1.60-1.68)Å) for the inner C(1)–C(14), C(2)–C(3), and C(1)–C(15) bonds, near a standard  $C(sp^2)-C(sp^2)$  bond (1.467 Å).<sup>11</sup> Accordingly, 3c is appropriately described by six Clar sextets, with the benzene character located in the six outer rings.

Figure 3 presents an ORTEP drawing of **4c** that confirms our hypothetical structure. The molecular geometry



Figure 2. ORTEP drawing of 3c (left) and bond lengths (right).

is planar, as reflected by the dihedral angle  $(32.9^{\circ})$  between rings **A** and **D** in the cove region, less than that  $(51.6^{\circ})$  of molecule **3c**. Species **4c** consists of an S<sub>2</sub> axis with both the **A'** and **D** rings lying below the **D'** and **A** rings. Examination of the bond lengths indicates that the inner rings **C**, **F**, **C'**, and **F'** are unlikely to have Clar sextet character, as evidenced by the two large C(14)–C(15) (1.464 Å) and C(3)–C(4) (1.460 Å) lengths that approximate a standard C(sp<sup>2</sup>)– C(sp<sup>2</sup>) bond.<sup>11</sup> Molecule **4c** accordingly appears to have six Clar sextets with rings **D** and **E** as two benzene sextets and the **A/B** rings representing a naphthalene group.



Figure 3. ORTEP drawing of 3d (left) and bond lengths (right).

Table 2 summarizes the photophysical properties of 3a-3e and 4a-4e. Compounds 3a-3e have the same UV/vis absorption patterns including three maxima in the  $\beta$ -bands (300-360 nm)<sup>12</sup> and two maxima in the p-bands (365-460 nm) (Figure 4). Here, we observed bath-ochromic shifts for the p-bands increasing with the array size  $3a \rightarrow 3b/3c \rightarrow 3d/3e$ , each with two-benzene alteration. For example, the last maxima of the p-bands appear at 375 nm for 3a, 383/403 nm for 3b/3c, and 409/428 nm for 3d/3e. In the photoluminescence (PL) spectra (Figure s1, Supporting Information (SI)), the emission maxima of 3a-3c are near each other (439-441 nm) but are red-shifted to 453 and 463 nm, respectively, for large arrays 3d and 3e.

Of particular interest are the photophysical properties for planar PAHs 4a-4e derived from 3a-3e. As shown

<sup>(10)</sup> Crystallographic data for compounds 3c and 4c are provided in the Supporting Information.

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Figure 4. UV/vis absorption spectra of compounds 3a-3e.

in Figure 5, we observed significant bathochromic shifts for the absorption maxima of 4a-4e in both  $\beta$ -bands and the *para*-band relative to those of 3a-3e. For example, the last maxima of their *p*-bands are shifted to larger wavelengths up to 86–103 nm. Large bathochromic shifts (50–74 nm) were also observed for the PL spectra of species 4a-4e (Figure s2, SI) relative to those of 3a-3e. Figures 5 and s2 also reveal gradual bathochromic shifts in the last absorption maxima (478–519 nm), as well as the emission maxima (491–537 nm), with increasing sizes  $4a \rightarrow 4b/4c \rightarrow$ 4d/4e (see Table 2). This information reveals that the increasing array size on such planar skeletons significantly affects both UV and PL wavelengths.



Figure 5. UV/vis absorption spectra of compounds 4a-4e.

According to cyclic voltammetry (Figure s3, SI), species 3a-3e show one reversible oxidation (0.75–0.93 V vs Ag<sup>+</sup>/Ag) due to a simultaneous oxidation of two nonplanar half sizes whereas planar PAHs 4a-4e reveal two reversible oxidations. For small PAHs 4a-4c, the two oxidation potentials (0.52–0.54, 0.68–0.71 V), given from the successive oxidation of the two half arrays, are close to each other but recognizable. Large array sizes 4d-4e have two well separated oxidation potentials (0.66–

0.70, 1.08 - 1.17 V); the first oxidation is assigned to a simultaneous oxidation of two half arrays. We estimated the HOMO energy levels from the UV/vis spectra. As shown in Table 2, the electron delocalization of nonplanar 3a-3e appears to be less efficient because variations of their energy gaps  $(E_g)$  are small, within a small range (2.84–2.71 eV). In contrast, a significant decrease in the  $E_g$  values is shown for planar PAHs 4a-4e, within a reasonable range (2.51–2.27 eV). Notably, species 4c bearing two cove regions has  $E_g = 2.42 \text{ eV}$  which is even smaller than that of planar **4b** ( $\tilde{E}_g = 2.48 \text{ eV}$ ) that lacks a cove region. For species 4d and 4e bearing four cove regions, their energy gaps are distinct, 2.42 vs 2.27 eV. These observations reveal that large planar PAHs are not the decisive factor to obtain small  $E_g$  among various geometric isomers.

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PAHs	$\mathrm{Abs}_{\mathrm{max}}(\mathrm{nm})^a$	$PL (nm)^b$	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	$\stackrel{E_{\mathrm{g}}}{(\mathrm{eV})^e} \Phi^{b,f}$
3a 3b	313, 327, 342, 362, 375 316, 326, 345, 369, 383	441 442	$-5.54 \\ -5.51$	$\begin{array}{c} -2.70 \\ -2.67 \end{array}$	$2.84 \ 0.12$ $2.84 \ 0.33$
3c 3d	329, 337, 386, 403 326, 340, 356, 387, 409	$439 \\ 453$	$-5.47 \\ -5.44$	$-2.63 \\ -2.67$	$\begin{array}{c} 2.84 \ 0.20 \\ 2.77 \ 0.18 \end{array}$
3e 4a	332, 345, 407, 428 316, 330, 424, 448, 478	463 491	-5.40 -5.13	-2.69 -2.62	$2.71 \ 0.40$ $2.51 \ 0.61$
4b 4c	332, 348, 424, 449, 482 332, 348, 432, 460, 489	498 506	-5.07 -5.12	-2.59 -2.70	2.48 0.49 2.42 0.17
4a 4e	321, 341, 357, 454, 484, 519	$509 \\ 537$	-5.20 -5.28	-2.78 -3.01	2.42 0.38 2.27 0.21

 $^{a}$  10<sup>-5</sup> M in CH<sub>2</sub>Cl<sub>2</sub>.  $^{b}$  10<sup>-6</sup> M in CH<sub>2</sub>Cl<sub>2</sub>.  $^{c}$  HOMO was calculated from the oxidation potential of CV.  $^{d}$  LUMO was calculated by the sum of HOMO and  $E_{g}$ .  $^{e}$  Calculated from the UV/vis absorption.  $^{f}$  Coumarin 1 as the standard.

In summary, we have developed a new synthesis of large PAHs with low Clar sextets. This synthesis involves initial bis(biaryl)acetylene 1, which undergoes initial ICl-aromatization and a subsequent Mizoroki–Heck coupling reactions to give dibenzochrysene derivatives 3 that can be transformed into planar PAH 4 using DDQ-oxidation. X-ray diffraction studies reveal highly nonplanar skeleta for dibenzochrysene species 3c, but a planar geometry for PAHs 4c. The photophysical properties of 4a-4e including UV/vis, photoluminscence, and cyclic voltammetry indicate that these properties are greatly affected by the increasing array size, whereas those of nonplanar 3a-3e appear to be less sensitive to such size variations.

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Supporting Information Available. Spectral data, NMR spectra, MALDI-Mass, PL, CV measurements of new compounds, and X-ray crystallographic data of compounds **3c** and **4c** are provided in Supporting Information. This materials is available free of charge via the Internet at http://pubs.acs.org.