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Fused Bispentacenequinone and Its Unexpected Michael Addition

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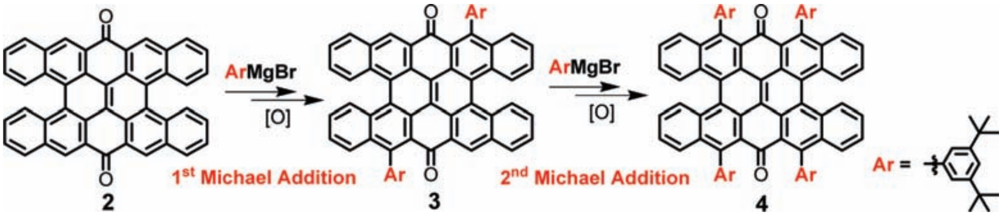
ABSTRACT



Fused bispentacenequinone 2 was synthesized by photocyclization of bispentacenequinone 1. Unusual regioselective Michael addition was observed for 2 when excess aryl Grignard reagent was used. Subsequent acidification and oxidation in air gave diaryl-substituted bispentacenequinone 3. Tetra-aryl-substituted fused bispentacenequinone 4 was obtained from 3 after the second Michael addition followed by oxidation in air.

Polycyclic aromatic hydrocarbons represent a vast library of molecular geometries with properties exploitable for organic opto-electronic materials.[1] Acenes, linearly fused aromatic hydrocarbons, have been the subject of extensive studies owing to their applications for electronic devices such as organic field-effect transistors (OFETs)[2] and organic light-emitting diodes (OLEDs).[3] Our group recently studied the *peri*-fused acenes, which usually exhibit low band gap and can be used as building blocks for near-infrared (NIR) dyes.[4] Syntheses of higher order acenes (ring number $n \geq 5$) and *peri*-fused acenes are challenging because without appropriate substituents they are usually unstable under ambient conditions and insoluble in normal organic solvents. In recent years, many research works have emphasized the chemical modification of acenes to increase solubility and stability and to improve solid-state ordering.[5] Synthesis of soluble and stable *peri*-fused acenes is of interest to challenge synthetic chemistry and to exploit new materials with NIR absorption/emission.

One of the most prominent methods for the synthesis of soluble and stable acenes was the nucleophilic addition of organometallic reagent to the corresponding acenequinones (Figure 1) followed by reduction of the as-formed diol to afford the desired substituted acenes. Anthony and co-workers first synthesized the silylethynyl derivatives of pentacene from pentacenequinone by this method.[6] Later, they also reported the synthesis of functionalized silylethynyl acenes from dithienoacenequinone, hexacenequinone, and

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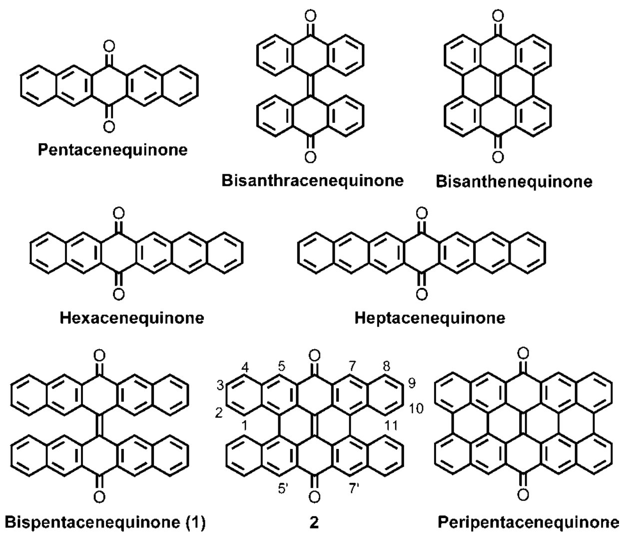

Figure 1. Structures of acenequinones and fused acenequinones.

heptacenequinone.[7] Soluble and stable acenes ($n = 7, 9$) were successfully synthesized by Miller and co-workers from their corresponding acenequinones.[8] The *peri*-fused acenes in principle can also be prepared from the corresponding quinones. In fact, we recently reported the synthesis of bisanthenequinone and bispentacenequinone (**1**) (Figure 1), which were successfully used for the preparation of soluble and stable bisanthene-based NIR dyes[4,9] and cruciform 6,6′-dipentacenyl.[10]

In parallel to these works, we have been working on the synthesis of soluble and stable higher order *peri*-fused acenes by using the corresponding *peri*-fused acenequinone, which could be prepared by photocyclization of the singly linked quinone.[11] In our previous work, we have prepared bisanthenequinone from the bisanthracenequinone using a photooxidative cyclization reaction.[10] Thus, we also expected the occurrence of such photooxidative ring-closing reactions in our bispentacenequinone **1** to give the fused aromatic systems such as **2** and/or peripentacenequinone (Figure 1), which can probably be used for the synthesis of fused bispentacene derivatives. In this work, we report the photocyclization reaction of **1** and an unusual Michael addition reaction of the obtained fused bispentacenequinone **2** during our attempts to prepare fused bispentacenes.

As shown in Scheme 1, we first tested the photocyclization of the bispentacenequinone **1**, which was reported in our previous work.[9] Oxidative photocyclization was conducted in benzene in the presence of I_2 and propylene oxide. Interestingly, only the fused bispentacenequinone **2** was formed with formation of two new C−C bonds. The product **2** precipitated from the benzene solution, and subsequent purification by filtration and column chromatography gave the pure compound **2** as a yellow powder in 59% yield. Extension of the reaction time does not provide further cyclized product such as the fully fused peripentacenequinone. Compound **2** can be regarded as a tetrabenzobisanthenequinone, and it can possibly be used as a building block to prepare tetrabenzobisanthene derivatives with expected long wavelength absorption. Thus, the nucleophilic reaction of compound **2** with excess Grignard reagent of 1-bromo-3,5-di-*tert*-butylbenzene in anhydrous THF was tested. Surprisingly, a diaryl-substituted fused bispentacenequinone **3** was obtained in 50% yield after standard acidification workup and column chromatography in air, which means the aryl Grignard reagent attacked onto the benzene rings instead of the carbonyl groups in **2**! The strucutre of **3** was unambiguously confirmed by NMR spectroscopy, mass spectrometry (see Supporting Information), and single-crystal analysis (vide infra). Such an unusual addition reaction is similar to the Michael 1,4-addition of α,β-unsaturated ketone.[12] Considering that there are similar α,β-unsaturated C=C bonds in the four benzene rings near the −C=O units in **2**, 1,4-conjugation addition could take place to give the intermediate **3a** after treatment with aqueous acid. Compound **3a** is supposed to be very unstable, and it can quickly undergo oxidative dehydrogenation (aromatization) in air. As a result, the disubstituted fused bispentacenequinone **3** is obtained. It is also worth noting that although a large excess of aryl Grignard reagent was used, there were no derivatives with more than two aryl substituents detected. This is reasonable since after addition of two aryl anions the intermediate consists of two negative charges, and addition of third negative charge will be very difficult due to Coulombic repulsion. It is also understandable that the two aryl units in **3** selectively adopt a trans alignment because the Coulombic repulsion is minimized in this configuration. In addition, compound **3** has the same framework as that of **2**. Thus, further Michael addition is possible if this mechanism is true. In fact, treatment of **3** with excess aryl Grignard reagent followed by acidification in air gave the tetraaryl-substituted fused bispentacenequinone **4** in 36% yield presumably via intermediate **4a**. The FT-IR spectra of **2**−**4** (see the Supporting Information) confirmed the existence of the carbonyl group as the typical intense C=O stretching vibration band was observed at 1660 cm^{-1} for **2**, 1667 cm^{-1} for **3**, and 1672 cm^{-1} for **4**.

Considering that the 1,2-addition of the carbonyl group usually takes place when aryllithium and Grignard reagent are used, the observed 1,4-conjugation addition is very unusual. Compared with the singly linked bispentacenequinone **1**, the carbonyl groups in the fused bispentacen-

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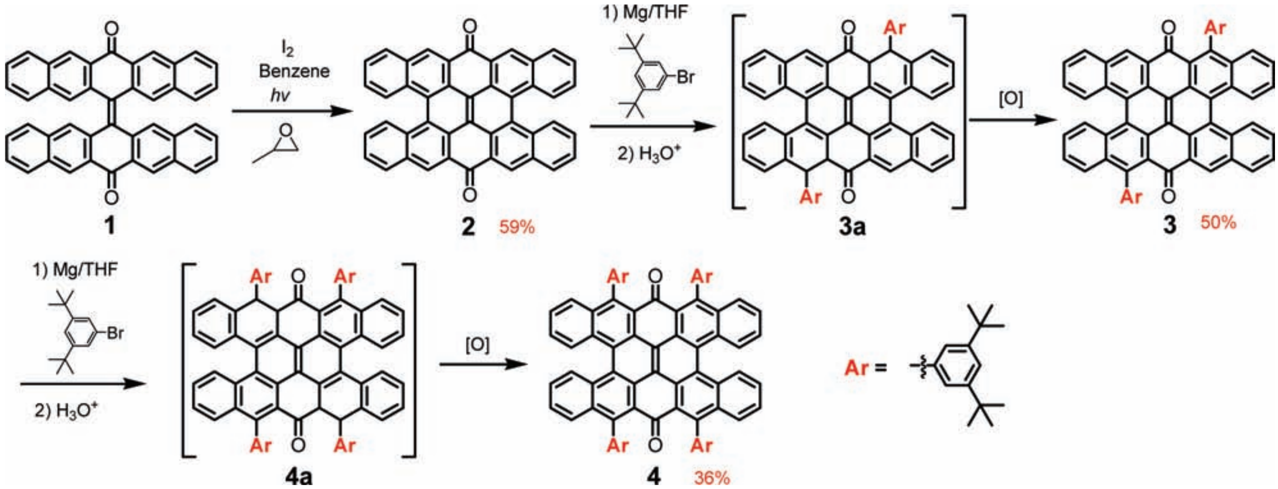
Scheme 1. Synthetic Route toward Compounds **2**−**4**



quinone **2** show lower reactivity presumably due to extended conjugation of the $-\mathrm{C{=}O}$ units with the fused π-system and activation of the α,β-unsaturated C=C bond induced by structural distortion.

To further understand the possible reasons for this unusual reaction, single crystals of **3** suitable for X-ray diffraction analysis were successfully grown by slow diffusion of methanol into a solution of **3** in chloroform, and the single-crystal structure is shown in Figure 2.[13] The two parallel pentacene subunits contort into a intersecting conformation due to steric congestion. The bending of the core is visualized most clearly in Figure 2c. Essentially all of the bending is concentrated in pairs of carbon atoms that act as pivot points (highlighted with gray circles in Figure 2a). A comparison was made between some of the bond lengths in this fused bispentacenequinone **3** and those from the anthracenequinone crystal structure.[14] One of the most interesting features is that the $\mathrm{C_b{-}C_c}$ and $\mathrm{C_d{-}C_e}$ bonds (highlighted with red color in Figure 2a) are shorter in **3** (1.36 Å) relative to the anthracenequinone (1.40 Å). A major contribution from the radialene resonance would explain these unusual bond lengths. The bond lengths for all of these unusual bonds are quite close to an individual C=C bond, and thus, α,β-unsaturated carbonyl structures (highlighted with red color in Figure 2b) are actually constructed. Thus, the low reactivity of the $-\mathrm{C{=}O}$ and the existence of α,β-unsaturated ketones would explain the unexpected Michael addition reactions of **2** and **3**. In addition, we also found that no further reaction occurred between **4** and 1-hexynelithium reagent presumably due to steric hindrance around the carbonyl center.

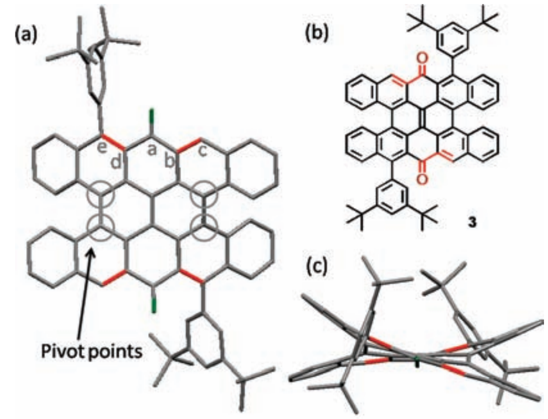


Figure 2. Single-crystal structure of **3**. Hydrogen atoms are removed for clarity. (a) Face-on view with marked pivot points (gray circles). (b) Top view along the *c* axis. (c) Molecular structure of **3** with labeled α,β-unsaturated ketone subunits.

Compounds **2**−**4** are soluble in chlorinated solvents such as chloroform and chlorobenzene, and their UV−vis absorption spectra in chloroform are shown in Figure 3a. Solutions of **2**−**4** in chloroform display a light yellow color, and well-resolved absorption bands between 400 and 510 nm with the peak at 493 nm ($\log \varepsilon = 4.43$, 4.34 and 4.39, respectively; ε, molar extinction coefficient in $\mathrm{M^{-1}\ cm^{-1}}$) were observed. Additional bands in the UV range were also found. Compounds **2**−**4** show similar absorption bands, which indicates that there is only weak electronic coupling between the bispentacenequinone framework and the 3,5-di-*tert*-butylphenyl units. A similar optical band gap around 2.44 eV was deduced for compounds **2**−**4** from the low energy absorption onset. The UV−vis−NIR absorption spectra of **2** and **3** recorded in concentrated sulfuric acid are shown in Figure 3b. Solutions of **2** and **3** in protonated form displayed a deep green color and well-resolved absorption bands between 500

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[13] Single-crystal data for **3**: $C_{72}H_{60}O_2$; triclinic; space group P-1; $a = 10.293(2)$ Å, $b = 15.245(4)$ Å, $c = 21.665(5)$ Å; $\alpha = 87.020(6)°$, $\beta = 86.029(6)°$, $\gamma = 79.479(6)°$; $V = 3331.6(13)$ Å^3; $Z = 2$; $\rho = 1.311$ Mg/m3; $R_1 = 0.0985$, $wR_2 = 0.2767$.

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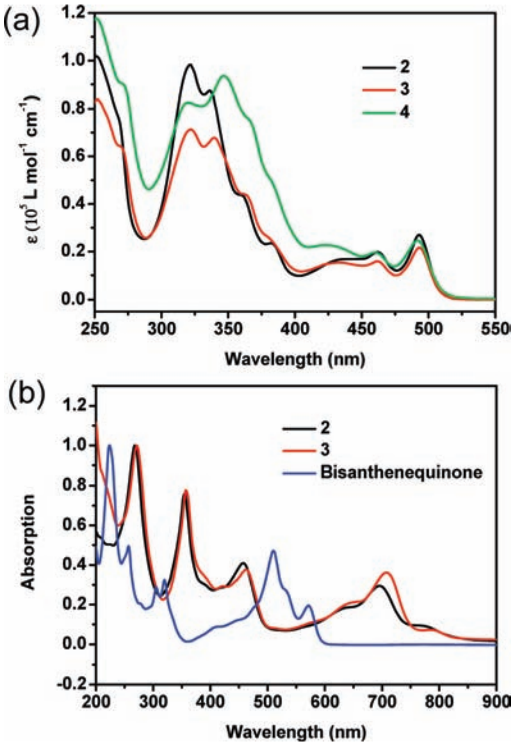

Figure 3. (a) UV−vis absorption spectra of **2**−**4** in chloroform (10^{-5} M). (b) Normalized absorption spectra of **2**,**3**, and bisanthenequinone in concentrated H_2SO_4.

and 850 nm with the maximum peak at 698 and 709 nm, respectively. Compared with the absorption spectrum of bisanthenequinone in concentrated sulfuric acid, there is a red-shift of about 126 and 137 nm for **2** and **3**, respectively. The red-shift indicates that π-conjugation of the bisanthenequinone core is further extended by incorporation of additional four benzo rings and aryl moieties.

The electrochemical properties of compounds **2**−**4** were studied by cyclic voltammetry in chlorobenzene at 70 °C. As shown in Figure 4, for compound **2**, two reversible reduction waves with half-wave potentials at −1.83 and −1.64 V (vs Fc^+/Fc) were observed, indicating that the bispentacenequinone **2** unit can be reversibly reduced into the radical anion and dianion. For compounds **3** and **4**, only one irreversible reduction wave was observed. LUMO energy levels of −3.18, −3.04, and −2.93 eV were estimated for **2**, **3**, and **4**, respectively, based on the onset potential of the first reduction waves.[15] This also indicates that the electron-donating aryl substitution has an obvious effect on the electrochemical property of the fused bispentacenequinone.

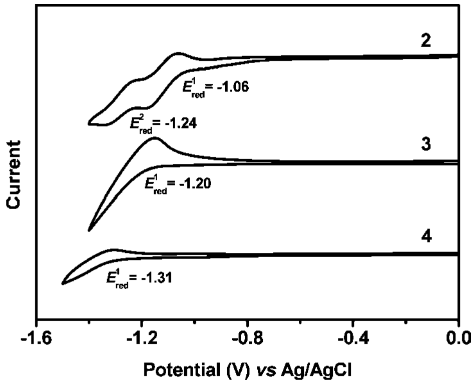

Figure 4. Cyclic voltammograms of **2**−**4** in hot chlorobenzene (70 °C) under nitrogen atmosphere with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s.

In conclusion, a fused bispentacenequinone **2** was prepared in good yield by a photocyclization reaction. An unusual Michael addition reaction of **2** was observed, and diaryl- and tetraaryl-substituted fused bispentacenequinones **3** and **4** were obtained. Crystallographic analysis disclosed that there are α,β-unsaturated ketone structures in the fused bispentacenequinone, which may explain the unusual additions.

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Supporting Information Available: Experimental procedures, characterization data of all new compounds, normalized UV−vis absorption spectra, cyclic voltammetry data, FT-IR spectra, and X-ray crystallographic analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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