

Diels-Alder Additions to 2,2'-Biaceanthrylene

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Abstract: A series of Diels-Alder reactions between the diene 2,2'-biaceanthrylene and several dienophiles is presented. The diene is a cyclopenta-fused polycyclic aromatic hydrocarbon with anthracene units linked by two cyclopentene rings. Depending on the dienophile, the major product was the result of a single addition (dimethyl acetylenedicarboxylate) or double addition (quinone, benzyne) to the diene. Single crystal X-ray analysis of the quinone-derivative shows a propeller-like structure composed of mixed enantiomers. The synthesis and photophysical properties of these compounds is presented.

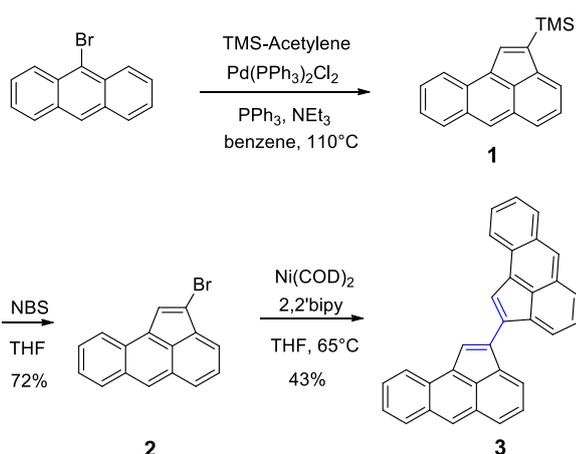
Polycyclic aromatic hydrocarbons (PAHs) are intensely studied because of their potential application as active components in electronic devices.^{1,2} Many small molecule and polymeric materials with a broad range of band gaps and electronic properties have been prepared to take advantages of their extended pi-systems, unique molecular connectivity, and ability to include heteroatom substitutions.^{3,4} Chemical linkages between semiconductor aromatic groups play a pivotal role in establishing material properties including charge transport, optical band gaps, and chemical reactivity.^{5,6} We recently explored a range of new materials that were accessed from cyclopentannulation reactions, which provides opportunities to expand the pi-

conjugated network and to modulate the frontier molecular orbitals to significantly change the optical and electronic properties of traditional PAHs. Furthermore, the annulation chemistry provides access to new functional group connectivities that offer opportunities for additional chemical transformations. The Diels-Alder reaction is one such reaction that has long been employed in PAH chemistry and offers prospects to further tune molecular architectures.⁷⁻¹⁰

In previous work, we employed a palladium-catalyzed cyclopentannulation reaction¹¹⁻¹⁶ with trimethylsilyl-acetylene and 9-bromoanthracene to give aceanthrylene **1**.¹⁷ Subsequent *ipso*-bromination with N-bromosuccinimide gave **2** that could then be homo-coupled with a Nickel-catalyzed Yamamoto cross-coupling to give 2,2'-biaceanthrylene **3**. The five-five ring-linked chromophores provided an opportunity to utilize the adjacent double bonds of the cyclopentene rings as a diene for Diels-Alder reaction chemistry. To investigate the scope of the transformation, we

investigated a series of traditional dienophiles including dimethyl acetylenedicarboxylate, benzoquinone, and *in situ* generated benzyne (Scheme 2). Depending on the substrate utilized, the resulting major

Scheme 1. Preparation of 2,2'-biaceanthrylene **3**.



isolated material was either a 1:1 or a 1:2 adduct, while employing a 1:1 feed ratio of diene to dienophile. Similar differentiation was found in Diels-Alder reaction

chemistry with the similar diacenaphthothiophene based system.¹⁸ For dimethyl acetylenedicarboxylate, the expected 1:1 adduct **4** was preferentially formed with an

aromatic pi-sextet at the central cycloaddition position. The new

aromatic unit limited further cycloaddition chemistry from

proceeding. For reaction with

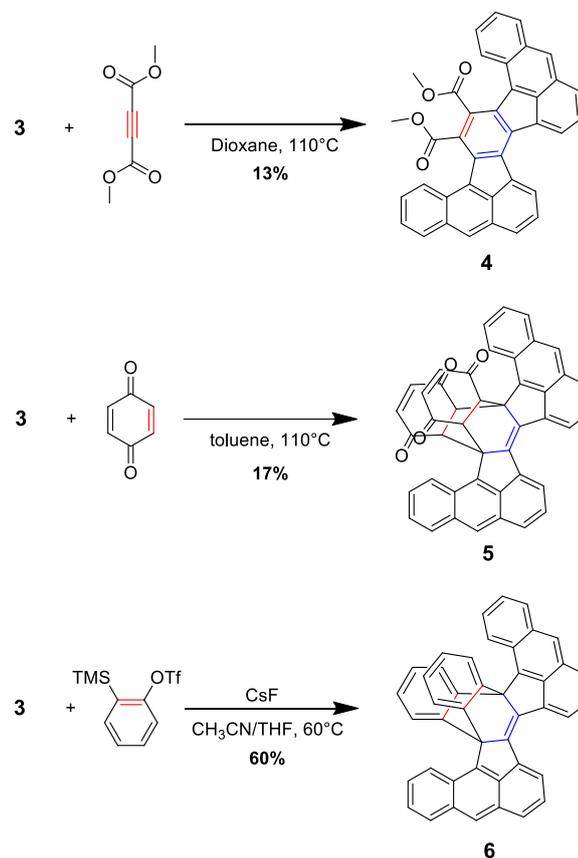
benzoquinone, the 1:2 adduct **5** was isolated as the predominant product in similarly low yield of 17%.

Here, the low yields were attributed to side-products that were not easily identified after chromatographic separation and could be owing to the

higher temperatures required to

consume the starting materials. In contrast, the reaction with benzyne, which was formed in situ from reaction of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate with CsF, was successful at a lower temperature and gave a more reasonable yield of 60% of the 1:2 adduct.

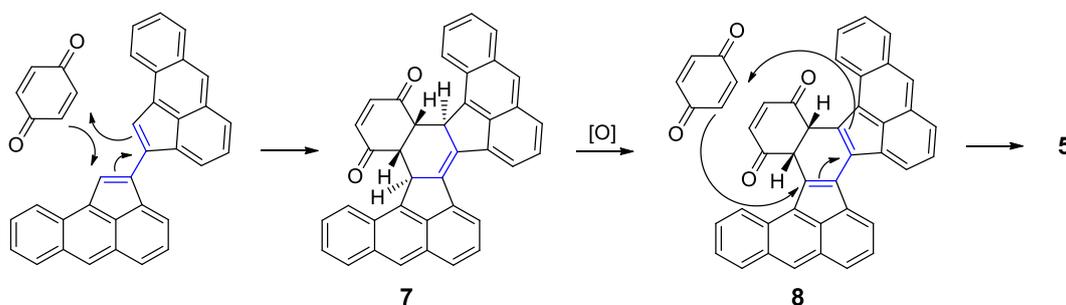
Scheme 2. Diels-Alder additions to **3**.



Results and Discussion

Several synthetic attempts were carried out to differentiate the reaction outcomes and to realize 1:1 adducts for the benzoquinone and benzyne reactions. These attempts included changing the feed ratios of the reactants to a 2:1 ratio of diene **3** to dienophile. However, even with these modifications, the 1:2 diene:dienophile adduct was isolated as the major isolatable species. For the 1:2 adducts to be formed, the 1:1 adduct **7** is re-aromatized to form a diene **8** that can participate in a second Diels-Alder cycloaddition (Scheme 3). Diene **8** possesses pre-aligned diene functionality,

Scheme 3. Mechanism for formation of 1:2 adduct **5**.



and presumably leads to greater reactivity to allow the second equivalent of dienophile to react in preference to the freely rotating diene **3**. The addition of the second equivalent of benzoquinone approached from the *endo*-face and gave two enantiomers in a 1:1 ratio. This structure was

confirmed by obtaining a single-crystal that was solved using X-ray diffraction.¹⁹ The molecules

in the single crystal existed in inverted chirality as well in an exact 1:1 ratio. Further analysis showed

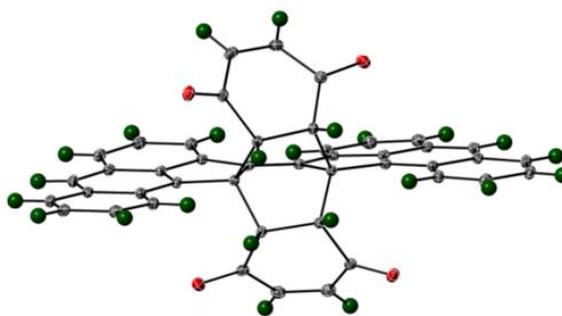


Figure 1. Crystal structure of **5** with thermal ellipsoids drawn at 50% probability.

aceanthrylene segments remain in a planar geometry with the benzoquinone segments lying above and below the aromatic plane. Several attempts were made to oxidize the appendages of **5** to quinone functionality but to no avail. Oxidative chemistry using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as well as a reductive pathway using lithium aluminum hydride followed by aromatization both resulted in the starting hydrogenated ketone **5**.

The absorption properties of compounds **3-6** are shown in Figure 2. A significant change in the long wave absorption is found upon the Diels-Alder addition to **3**. The broad low energy absorption band centered at ~580 nm is replaced with stronger, high-energy bands at ~475 nm for the three Diels-Alder adducts. Compound **4** is the most significantly red-shifted with an onset of 560 nm, while **5** and **6** longest wavelength absorptions are 530 nm and 510 nm, respectively.

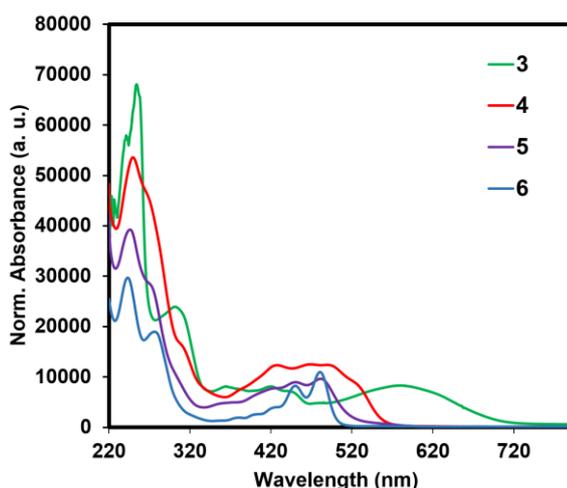


Figure 2. Absorption spectra of **3-6**.

In conclusion, we have successfully employed 2,2'-biaceanthrylene as a diene in Diels-Alder transformations. The 1:1 adduct is the only isolated product for the system that made a pi-sextet at the cycloaddition center. The 1:2 adduct is predominant when a non-aromatic center is formed upon the first cycloaddition and the pre-alignment of a new diene facilitates the

second addition of a dieneophile. The resulting materials' absorptions are blue-shifted in the relationship to the starting diene and is presumably owing to the change in electronic communication between the two aceanthrylene chromophores.

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Supplementary data

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