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Expeditious Synthesis of Contorted Hexabenzocoronenes

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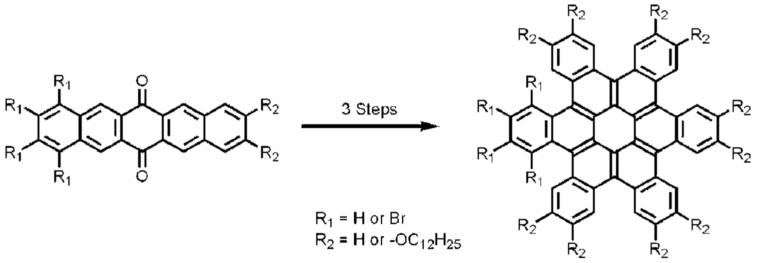
ABSTRACT



Contorted hexabenzocoronenes (HBCs) have been synthesized in an expedited manner utilizing a double Barton-Kellogg olefination reaction and a subsequent Scholl cyclization. The scope of both transformations was investigated using a series of pentacene quinones and double olefin precursors. The utility of these reactions to help create functionalized and oligomeric HBCs in a rapid manner is demonstrated.

Scheme 1. Previously Employed Retrosynthetic Pathway to HBC

Here we detail a new methodology for the synthesis of contorted hexabenzocoronenes (HBCs) that proceeds in high yield and produces highly functionalized molecules capable of further modification. The HBCs (**1**, Scheme 1) investigated here have four carbons (red) annulated around the coronone core (black), which produces a structure that is severely distorted from planarity. We have previously shown that these HBCs are useful in several respects: they behave as semiconductors with relatively high hole mobility when assembled into columnar structures,[1,2] they have unusual self-assembly/reactivity on the surface of crystalline metals,[3] and they are precursors for the synthesis of hemispheric forms of carbon.[4]

Until now the syntheses of these HBCs have been limited for two primary reasons. One, the final step in the synthesis is a photocyclization/oxidation of a double olefin (**2**), shown in Scheme 1. This reaction is intolerant of some functional groups and also ineffective with substituents in the most sterically hindered positions. Two, the double olefin is laborious to form because it requires two sequential olefinations starting from a thioketone (**3**). Here we reveal a method that circumvents these problems by using previously unknown dithioquinones, which are derived from pentacene quinones, to rapidly build up the double olefin skeleton.

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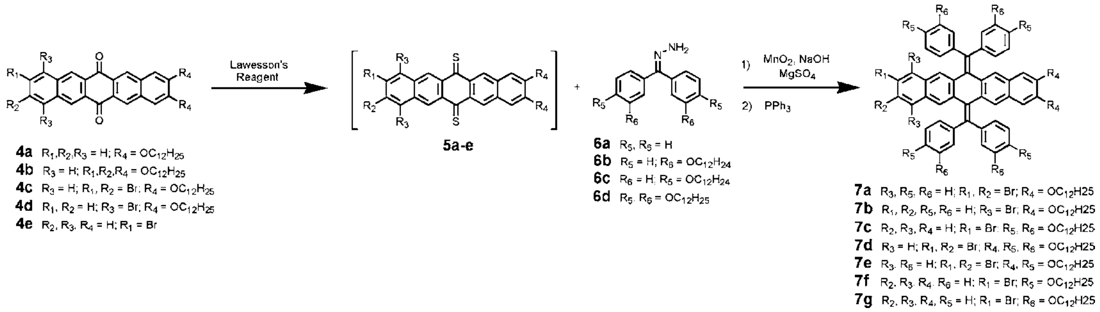
Scheme 2. General Strategy for Barton−Kellogg Modification of Pentacene Quinones



Furthermore, we have employed a Scholl reaction to supplement, and in some cases completely eliminate, the need for the photocyclization. These findings are significant because they allow quick access to HBC structures that can be further elaborated into oligomers and other useful structures.

The Barton−Kellogg reaction is a powerful tool for creating tetra-substituted alkenes by reaction of a thioketone with a diazomethane and subsequent reduction with a triarylphosphine.[5−7] To our knowledge, there are no previous examples of a double Barton−Kellogg on a dithioquinone substrate. This is presumably because the sulfur analogs of benzoquinone,[8] naphthoquinone,[8] and anthraquinone[9] are unstable and form polymeric species through disulfide formation.

Remarkably, we could form dithioquinones (**5a**−**e**) from pentacene quinones (**4a**−**e**) via reaction with Lawesson's reagent in toluene at 80 °C (Scheme 2). Unfortunately, we were unable to isolate the dithioquinones in pure form and therefore opted to prepare them *in situ* and react them directly with two molar equivalents of the diphenyldiazomethane derived from hydrazones **6a**−**d** to produce a double thioepoxide. Reduction of the thioepoxide functionality with triphenylphosphine produced the desired double olefins (**7a**−**g**).

The proper choice of starting pentacene quinone derivative was crucial for the success of the double Barton−Kellogg olefination due to the combination of the starting materials' solubility and electronic structure. These parameters are summarized in Figure 1. The parent pentacene-6,13-dione **8**, as well as symmetrically brominated pentacene quinone derivatives **9** and **10**, were found to be too insoluble to be functionalized with Lawesson's reagent and therefore were not able to undergo the Barton−Kellogg reactions. To combat the insolubility, we installed dodecyloxy chains on the pentacene quinone core to yield **4a** and **4b**. Both compounds were soluble during the reaction with Lawesson's reagent; however, only minor amounts of the bis-thioepoxide products were obtained (<5%). The majority of the mass balance was intractable material that was not characterizable. The low yields may be due to the electron-rich pentacene quinone core that could stimulate poly disulfide formation similar to what has been observed with other quinones.[9] When bromine groups were added to dodecyloxy-containing pentacene quinone cores (**4c** and **4d**), yields rose to as much as 60% for the double olefins **7a**, **7b**, **7d**, and **7e**. (Table 1). This yield refers to the isolated yield of the double olefin from the Barton−Kellogg three-step process in Scheme 2. We suggest that the bromines deactivate the pentacene quinone core and stabilize the dithioquinone toward side reactions.

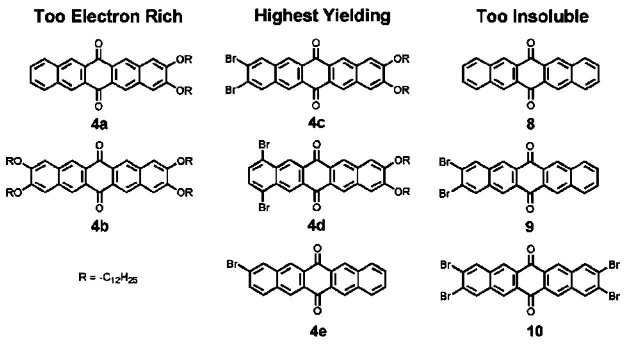


Figure 1. Pentacene quinones that were subjected to Barton−Kellogg reaction conditions.

Table 1. Double Olefin Yields[a]

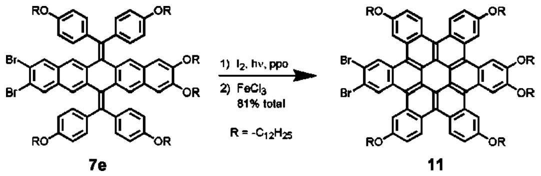
double olefin	% yield
7a	45
7b	57
7c	38
7d	32
7e	29
7f	36
7g	45

[a] Structures shown in Figure 2.

Desymmetrized 2-bromopentacene-6,13-dione (**4e**) was appreciably more soluble than the symmetric analogs **8**, **9**, and **10** and could be successfully modified with Lawesson's reagent without the requirement for solubilizing chains. Reactions ran smoothly with all diphenyldiazomethanes tested to give yields of ~40% for **7c**, **7f**, and **7g** (Table 1). In general, a successfully designed pentacene quinone precursor incorporates either solubilizing substituents that are balanced with withdrawing groups or substituents that desymmetrize the pentacene quinone to help solubilize them.

With several double olefin analogs in hand, we investigated methods to oxidatively close the HBC core. In our previous studies, we utilized a Katz-modified Mallory photocyclization of the double olefins to afford HBC analogs.[10,11] This reaction is problematic because some substrates do not fully close. Moreover, some functionalities are incompatible with the photocyclization conditions. As an example, the resulting mixture obtained from the photocyclization of **7e** contained around 50% HBC **11** (determined by TLC) and 50% of its half-cyclized analogs, even after 18 h of exposure time (Scheme 3). We found that the addition of $FeCl_3$ converted this mixture to the fully closed HBC in less than 20 min. This result builds off of the vast body of research that uses the Scholl reaction to close flat aromatic systems.[12,13] This is the first instance where the Scholl reaction has been employed to close these contorted HBCs.[14]

Scheme 3. Combining a Photocyclization and Scholl Reaction



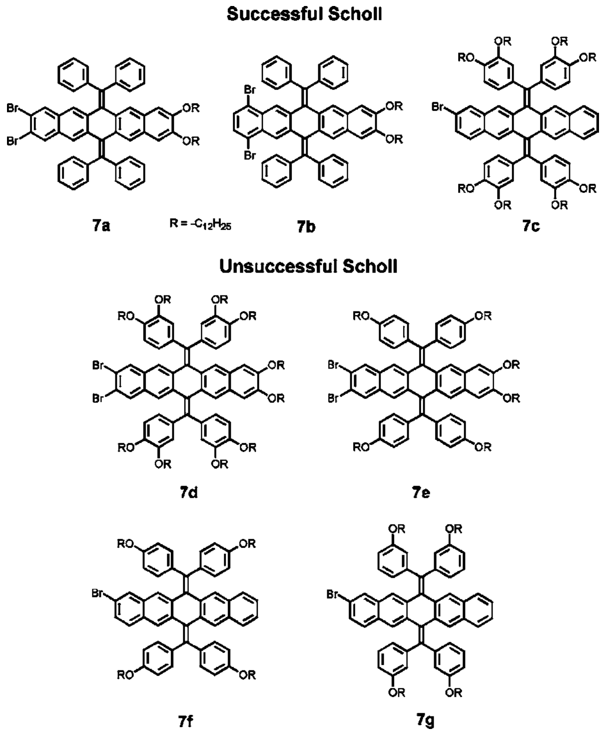
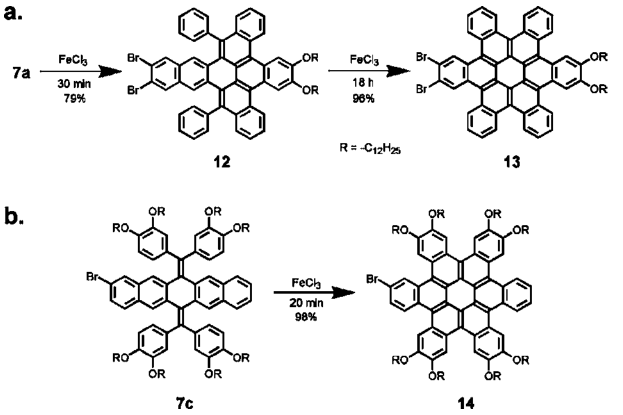


Figure 2. Double olefins that were successfully (top) and unsuccessfully (bottom) closed via the Scholl reaction with $FeCl_3$. Note: Double olefins **7d**, **7e**, and **7f** could be successfully closed by combining the Katz-modified Mallory photocyclization and Scholl reaction. Double olefin **7g** led to an inseparable mixture of isomers during photocyclization. Compound **7c** can be fully closed using photocyclization alone. Compounds **7a** and **7b** are half-closed during photocyclization.

Our attempts at complete closure of double olefin **7e** with the Scholl reaction alone were unsuccessful giving back starting material and some uncharacterizable byproducts after quenching with methanol. This result suggests that the Scholl reaction may only work for systems that have already been partially closed. We screened several other double olefins to test this assumption. While **7d** reacted in a manner similar to **7e** (i.e., undergoing the Scholl reaction only after half-cyclization via the Katz-modified Mallory photocyclization), **7a** was remarkably different. **7a** reacted with $FeCl_3$ for 30 min to give half-cyclized **12** after quenching with methanol (Scheme 4a). The fully closed HBC **13** was only obtained after further subjecting **12** to $FeCl_3$ overnight. Interestingly, when the initial Scholl reaction of double olefin **7a** was prolonged from 30 min to overnight, only a small amount of the fully closed HBC **13** was observed. This suggests that a stable radical cation is formed on the half-cyclized HBC and may require quenching before the second half of the HBC can be oxidatively closed to form HBC **13**.[15] Similar reactivity was seen for double olefin **7b**, with half-cyclized HBC being initially isolated followed by overnight oxidation to give the fully closed HBC. Double olefins based on 2-bromopentacene-6,13-dione (**4e**) were also tested for compatibility with the Scholl reaction. Amazingly, **7c** undergoes complete ring closure to the HBC within 20 min with $FeCl_3$ (Scheme 4b). We assumed this increased reactivity was due to the presence of alkoxy groups para to the ring closure sites, which have been shown in other systems to accelerate ring closures.[16] We therefore prepared double olefins with alkoxy groups meta (**7f**) and para (**7g**) to the closing bonds. Although we were not surprised that the meta alkoxy-containing **7f** did not undergo the Scholl reaction, we were amazed that the para alkoxy-containing **7g** did not lead to closed HBC either. We can only assume double olefin **7c** provides an optimal amount of directing ability and electron density to complete the Scholl reaction. Through these initial studies, there appears to be no hard set rules for the success of the Scholl reaction in taking a double olefin

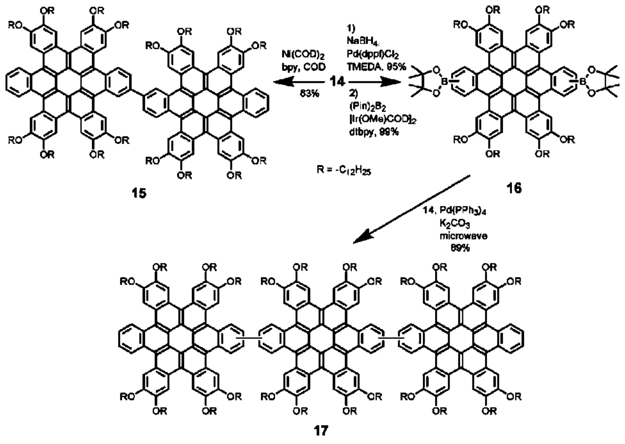
Scheme 4. HBC Closures Solely with Scholl Reactions



to its final closed state. However, the Scholl reaction in conjunction with the Katz-modified Mallory photocyclization is an effective scheme for a higher yielding synthesis of contorted and highly functionalized HBCs.

The new expeditious synthesis of HBC derivatives allowed for the rapid construction of higher ordered electronic structures such as HBC oligomers (Scheme 5). Yamamoto coupling of **14** using Ni(COD)$_2$ gave HBC dimer **15** in 83% yield.[17] To create even longer oligomers, an iridium-catalyzed aryl borylation was employed to install new reactive functionalities.[18,19] First, **14** was hydrodebrominated[20] with NaBH$_4$ to yield the parent HBC, which was borylated with bis(pinacolato)diboron (Pin$_2$B$_2$) by using a [Ir(OMe)COD]$_2$ and 4,4′-ditert-butyl-2,2′-dipyridyl cocatalyst system.[18,19] The borylation is a sterically controlled process; therfore, excess Pin$_2$B$_2$ selectively functionalized the HBC compound twice to give **16** in quantitative yield. Suzuki coupling between **16** and two equivalents of **14** gave the trimer **17** in excellent yield. Dimer **15** and trimer **17** are highly soluble in organic solvents (UV−vis spectra in Supporting Information), which is in contrast to previously prepared trimers of flat HBC analogs.[21] Therefore, similarly soluble yet longer oligomers should also be accessible by continuing the strategy of borylation (i.e., borylated **15** or **17**) followed by Suzuki coupling of **14**. These new oligomeric species should provide interesting materials for testing in electrical devices such as field effect transistors and organic photovoltaics.

Scheme 5. Oligomerization of HBC



In summary, this study details an expedited, versatile synthesis of several HBC analogs. First, we utilize soluble and stable pentacene bis-thioquinone derivatives to prepare double olefin precursors. Second, we reveal the feasibility of the Scholl reaction to help form many of the contorted HBC derivatives. The HBC derivatives included in this publication have high-yielding syntheses and are suitable for fuctionalization through metal-catalyzed reactions to afford many potentially useful materials including oligomeric species.

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Supporting Information Available: Detailed experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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