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Unexpected Phenyl Group Rearrangement during an Intramolecular Scholl Reaction Leading to an Alkoxy-Substituted Hexa-*peri*-hexabenzocoronene

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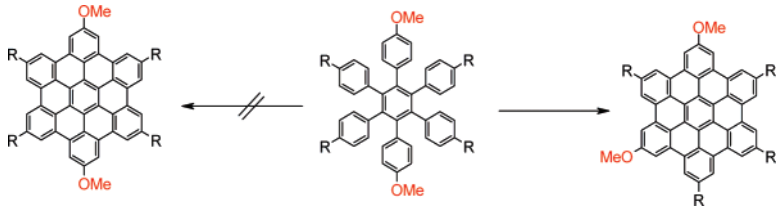
ABSTRACT



A simple dimethoxy-substituted hexa-*peri*-hexabenzocoronene (*m*-dimethoxy HBC) was unexpectedly obtained along with a bis-spirocyclic dienone during an intramolecular Scholl reaction of its para isomer.

Polycyclic aromatic hydrocarbons (PAHs) have aroused increasing scientific interest because of their special electronic and optoelectronic properties.[1−3] Hexa-*peri*-hexabenzocoronene (HBC), which is a disc-like, all-benzenoid PAH, and many of its derivatives have been successfully synthesized via the intramolecular Scholl reaction[4] under mild reaction conditions.[5,6] However, the direct attachment of heteroatom-based substituents to the periphery of the HBC skeleton, which influences the electronic properties,[7] remains a synthetic challenge.[8,9] Our group has reported the synthesis of an arylamine-substituted HBC as a "coaxial" hole-transport material,[7] a permethoxylated HBC as a host molecule for cocrystallization with C_{60},[10] and an "unwrapped" HBC with three neighboring dodecyloxy chains on one side that exhibit good solution processability.[11] On the other hand, the attempted cyclodehydrogenation of hexakis(dodecyloxy)-substituted hexaphenylbenzene only gave a quinoidal compound in 96% yield.[9] This problem was recently circum-

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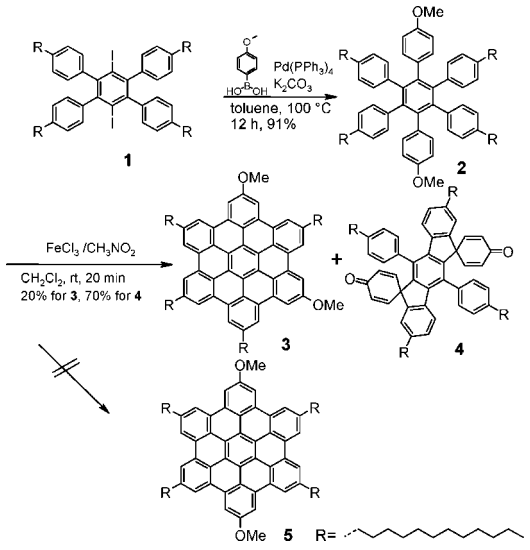
vented by the introduction of electron-withdrawing fluorine atoms on either side of every alkoxy group.[8] Herein, we report the cyclodehydrogenation reaction of compound **2**, the *p*-dimethoxy hexaphenylbenzene, which gives two unexpected products, namely *m*-dimethoxy HBC **3** and the bis-spirocyclic dienone **4**.

Compound **2** was synthesized via a sterically hindered Suzuki cross-coupling reaction[12] between 1,4-diiodo-2,3,5,6-tetraphenylbenzene **1** and 4-methoxyphenyl boronic acid (91%) (Scheme 1). Instead of the expected *p*-dimethoxy HBC

Scheme 1. Synthesis of Compounds **3** and **4**



5, the cyclodehydrogenation reaction of **2** with 20.4 equiv of iron(III) chloride in dichloromethane surprisingly delivered 2,8-dimethoxy-5,11,14,17-tetradodecyl-hexa-*peri*-hexabenzocoronene **3** (20%) as the only HBC product. Its structure was determined using mass spectrometry, ^{1}H NMR, ^{13}C NMR, ^{1}H,^{1}H NOESY and ^{1}H,^{1}H COSY experiments. The major product of the reaction was the bis-spirocyclic dienone **4** (70%), which was purified by recrystallization from a dichloromethane/acetone (1:1) mixture. Its structure was unambiguously determined by single-crystal X-ray diffraction[13] (Figure 1). The formation of the spirocyclic dienone substructure was reported recently in a related cyclodehydrogenation reaction,[14] but the formation of two of these units in the same molecule is unprecedented.

Figure 2a shows the enlarged alkyl α-proton and aromatic areas of the ^{1}H NMR spectrum of **3** in $CDCl_3$. The three alkyl α-proton signals (from 2.79 to 2.35 ppm) and six different aromatic proton signals (six singlets from 7.91 to 7.21 ppm) indicated that the compound is the *m*-dimethoxy

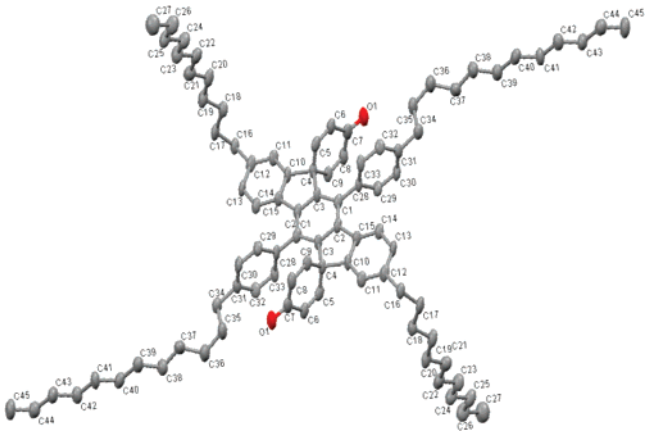


Figure 1. X-ray crystallographic structure of compound **4**.

HBC and not the para isomer, which should exhibit signals for only one type of alkyl α-proton and three aromatic protons, or the ortho system, which would give two alkyl α-proton and six aromatic proton signals. This assignment was supported by the ^{13}C NMR spectroscopy, whereby 24 well-resolved aromatic peaks were recorded in the range of 148−96 ppm. This corresponds exactly to the *m*-dimethoxy HBC **3**. By comparison, 12 and 21 different aromatic carbon signals are expected for the *p*-HBC and *o*-HBC isomers, respectively. The structure of **3** was confirmed using ^{1}H,^{1}H NOESY and ^{1}H,^{1}H COSY experiments. Key correlations are summarized in Figure 2b (see Supporting Information for a detailed explanation of the structure assignment).

Migration of alkyl groups under Friedel−Crafts conditions[15,16] and skeletal rearrangements leading to planar PAHs from "nonplanarizable" oligophenylenes[17] have been observed previously, as has the degenerate rearrangement of biphenyl[18] under Lewis acid catalysis. Nevertheless, to the best of our knowledge, this is the first time that a position-exchange of substituents has been observed during the cyclodehydrogenation process. PM3-calculated[19,20] heats of formation for compounds **3** and **5** indicate that they are nearly isoenergetic (**3** is 0.03 kcal/mol lower in energy than **5**). Thus the driving force for the rearrangement must be exerted at some intermediate stage. Mechanisms for the Scholl reaction[21,22] involving either radical cations or arenium cations have been put forward. Several mechanisms, involving either type of intermediate, can be drawn to account for the forma-

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(13) Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a CH2Cl2/acetone (1:1) solution of compound **4** at room temperature. Crystal structure determination was carried out on a KCCD diffractometer with graphite-monochromated Mo Kα irradiation. The structure was solved by direct methods.

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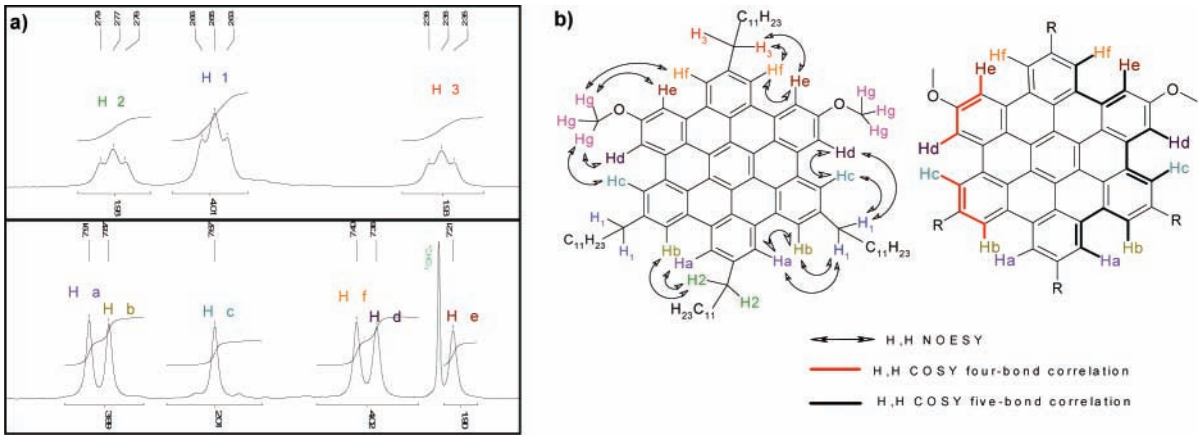
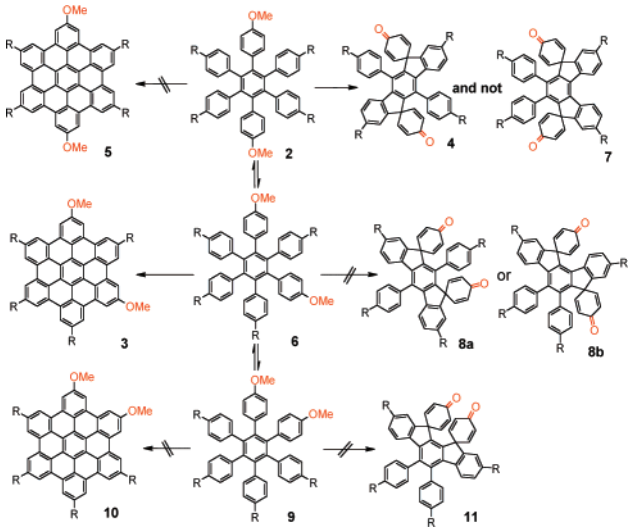


Figure 2. (a) Enlarged alkyl α-proton and aromatic region of ^{1}H NMR spectrum of **3** ($CDCl_3$, room temp, 500 MHz) and structural indication; (b) ^{1}H,^{1}H NOESY and ^{1}H,^{1}H COSY correlations of **3**.

tion of **3** and **4**, which is summarized in the reaction "landscape" shown in Scheme 2. This involves initial interconversion of *p*-HPB **2** to *m*-HPB **6** and their subsequent reaction by different pathways. Whatever mechanisms are considered, several interesting mechanistic questions present themselves.

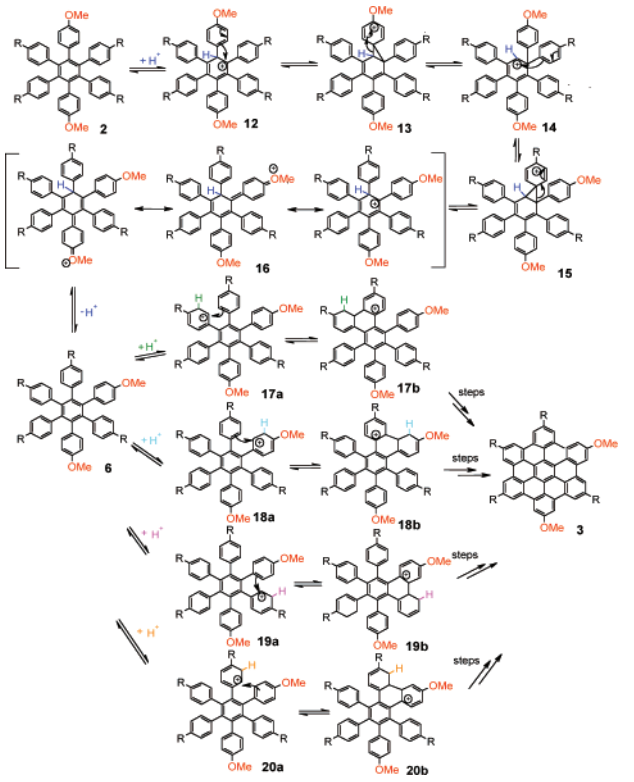
Scheme 2. Proposed Reaction "Landscape"



The first key question is how HBC **3** is formed. This can be answered by invoking Scott's biphenyl rearrangement mechanism to first convert **2** to **6** (Scheme 3).[18] Protonation of **2** on the central ring *ipso* to a 4-methoxyphenyl group affords a cation **12** that can undergo ring closure to give phenonium ion[23] **13**. Opening of **13** leads to cation **14**, which bears two aryl groups on the same carbon atom. Migration of the 4-dodecylphenyl group affords a new phenonium ion **15**, which can open to afford cation **16** and then **6** after deprotonation. Since the formation of **3** and **4** is likely under Curtin−Hammett control,[24] the positions of the equilibria connecting **2** and **6** are probably of little consequence. However, it is worth noting that the positive charge in protonated **6** (i.e., **16**) can be stabilized by both methoxy groups, while the positive charge in protonated **2** (i.e., **12**) can only be stabilized by one methoxy group. Once HPB **6** has been generated, HBC **3** can then form through a Scholl reaction.

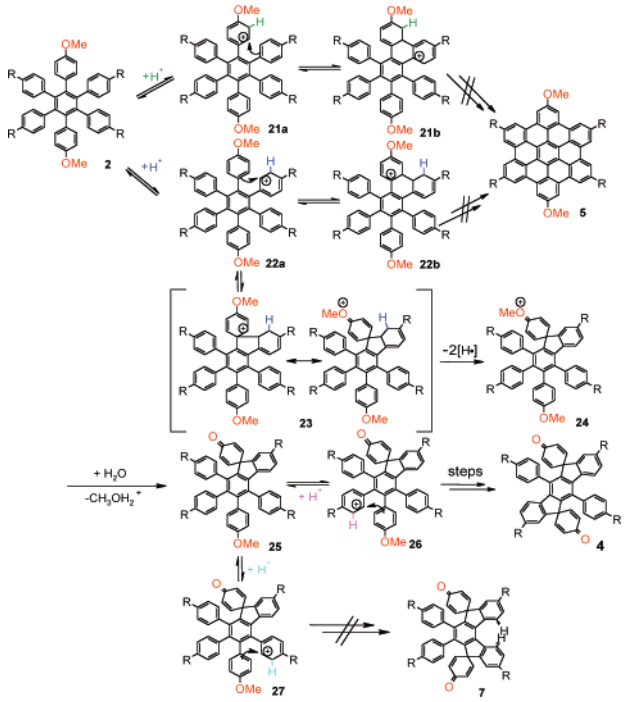
Why does HPB **6** undergo Scholl reaction, but HPB **2** does not? Following an arenium cation mechanism in which the six protonations occur on the 4-methoxyphenyl groups and the 4-dodecylphenyl group meta to both 4-methoxyphenyl groups (i.e., **6** to **17a** and **6** to **18a**), it is evident that the

Scheme 3. Proposed Mechanism for the Methoxyphenyl Migration and the Formation of Compound **3**



cations resulting from six-membered ring closure (e.g., **17b** and **18b**) are all stabilized by direct conjugation with both methoxy groups. By comparison, the pathway from **6** to **3** via cations **19a** and **20a**, proceeds through ring-closed cations **19b** and **20b** (and related cations), which are stabilized by neither methoxy group. More importantly, arenium cation mechanisms leading from **2** to the corresponding *p*-HBC **5** (which did not form) all go through ring-closed cations (e.g., **21b** and **22b**) that are only stabilized by a single methoxy group. (Scheme 4) If the stabilization of positive charge by

Scheme 4. Proposed Mechanism for the Formation of *p*-Dimethoxy HBC **5** and C_{2h}- and C_2-Symmetric Bis-spirocyclic Dienone (**4** and **7**) from *p*-Dimethoxy HPB **2**



the methoxy groups in these systems manifests itself to a significant extent at the transition state, the rate-limiting step, then the rate of reaction leading to **3** should be considerably faster than that leading to **5**.

Why does HPB **2** react to afford bis-spirocyclic dienone **4** instead of participating in a Scholl reaction to give **4**? Again following an arenium cation mechanism, **2** can be protonated either on a 4-methoxyphenyl group to give cation **21a** or on a 4-dodecylphenyl group to give cation **22a** (Scheme 4). Both of these cations can conceivably continue toward HBC **5** by undergoing six-membered ring formation to give cations **21b** and **22b**, respectively. However, cation **22a** can react to form a five-membered ring through attack of the relatively nucleophilic carbon atom situated para to the methoxy group. Presumably, this process (or the first irreversible step following it) is faster than the alternative six-membered ring forming process. The question of why the C_{2h}-symmetric product **4** is produced and its C_2-symmetric isomer **7** is not may have its origin in strain rather than electronic effects (Figure S2). In examining analogous mechanisms leading to **7** and **4**, no significant electronic differences could be identified. However, PM3 calculations predict **7** to be 3.2 kcal/mol higher in energy than **4**. The energy difference is likely due to the additional strain associated with the helical conformation adopted by the indeno[2,1-*b*]fluorene skeleton of **7** compared to the perfectly planar indeno[1,2-*b*]fluorene skeleton of **4**.

If HPB **2** affords bis-spirocyclic dienone **4**, why does HPB **6** not give analogous products (**8a**/**8b**)? Examination of the arenium cation mechanisms leading to such products and those leading to **4** does not reveal any differences that would suggest significantly different rates (Scheme S1). It is worth noting that cations **19a** and **20a**, which are on unproductive pathways from **6** to **3**, are also the first cationic species *on route* to **8a**/**8b**. Consequently, the wholesale difference in reactivity between **2** and **6** is consistent with the following scenario: the rate of conversion of **2** → **4** and those of **6** to analogous products (**8a**/**8b**) are roughly equivalent, and they are intermediate between the rate of conversion of HPB **6** → HBC **3** (fast due to cooperative stabilization of (developing) charge) and that of HPB **2** → HPB **5** (slow).

Under such a scenario, which includes the equilibration of **2** and **6**, the question of whether **6** can further isomerize to **9** arises. Mechanistically, there is nothing to suggest that this would not occur (Scheme S1). If **9** is indeed accessible, the absence of products derived from it could be due either to its formation being unproductive (HBC formation would be expected to be relatively slow for the same reasons as HBC formation from **2**) or the rate of conversion of **6** to **3** being fast enough to preclude its formation altogether.

In summary, the intramolecular Scholl reaction of **2** resulted in the formation of two unexpected products, **3** and **4**, which may mean that the course of the intramolecular Scholl reaction might be subject to some degree of control through the judicious use of substituents.[14] Moreover, two methoxy groups without any extra peripheral decoration were successfully attached directly to the HBC core, albeit with a meta instead of the expected para relationship. The electron-donating character of substituents is expected to influence the electronic or optoelectronic properties of the HBC system. The investigation of these properties is currently underway.

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Supporting Information Available: Experimental details and structure assignment of compound **3**; proposed mechanism for the isomerisaton between **6** and **9**; calculated structures of **4** and **7**; and crystallographic information files (CIF) of compound **4.** This material is available free of charge via the Internet at http://pubs.acs.org.

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