ORGANIC LETTERS

2012
Vol. 14, No. 10
2472–2475

Synthesis of Oxygen-Substituted Hexa-*peri*-hexabenzocoronenes through Ir-Catalyzed Direct Borylation

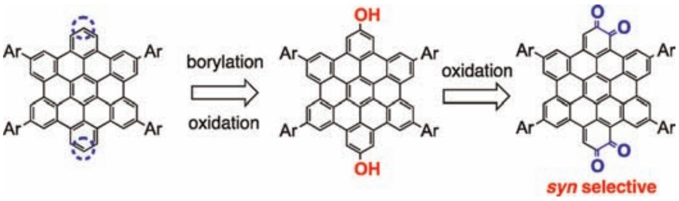
Ryuichi Yamaguchi, Satoru Hiroto, and Hiroshi Shinokubo*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

hshino@apchem.nagoya-u.ac.jp

Received March 22, 2012

ABSTRACT



Direct C−H borylation of hexa-*peri*-hexabenzocoronenes (HBCs) has been achieved under iridium catalysis, which allows efficient synthesis of hydroxy-substituted HBCs by oxidation of the boryl groups. Further oxidation of dihydroxy HBC with phenyliodine bis(trifluoroacetate) (PIFA) afforded tetraoxo-substituted HBC without any regioisomers, which can be considered as a π-extended quinone.

Polycyclic aromatic hydrocarbons (PAHs) such as pyrenes, triphenylenes, and hexa-*peri*-hexabenzocoronenes (HBCs) have attracted much attention as fragments of graphene.[1] The structure and functionality at the edge of graphenes significantly alter the physical properties of graphenes.[2] Consequently, effective functionalization methods of PAHs are required to prepare model compounds for the edge structures for functionalized graphenes.

Among various PAHs, HBCs have been extensively investigated as the building block for liquid crystals and motifs in supramolecules because of their disk-shaped structures, producing a discotic liquid crystalline mesophase efficiently.[3] However, introduction of various functional groups at the peripheral positions of the HBC core has been limited. Introduction of functionalities after the synthesis of the HBC core is generally difficult due to low solubility.[4] Furthermore, the presence of reactive substituents often induces undesired reactions during Scholl oxidation of the hexaphenylbenzene precursors with $FeCl_3$. In particular, the synthesis of alkoxy-substituted HBCs is difficult because of severe side reactions.[5] In addition, hydroxy-substituted HBCs have never been synthesized, although they would serve as precursors for π-extended quinone derivatives and novel self-assembling units with hydrogen bondings between hydroxy groups.

Recently, transition metal catalyzed C−H functionalization has been under considerable development. Among the various methods, C−H direct borylation is a convenient protocol for the introduction of boryl groups to functional π-systems.[6,7] The resulting borylated products are useful substrates for further transformations such as Suzuki−Miyaura coupling and oxidation reactions.

Initially, we attempted to employ tetra-*tert*-butyl HBC as a substrate for C−H functionalization.[8] However, poor solubility of this compound in common organic solvents hampered the conduction of further reactions. To improve

---

(1) (a) Haley, M. M., Tykwinski, R. R., Eds. *Carbon-Rich Compound*; Wiley-VCH: Weinheim, 2006. (b) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997. (c) Feng, X.; Pisula, W.; Müllen, K. *Pure. Appl. Chem.* **2009**, *81*, 2203.

(2) Dutta, S.; Pati, S. K. *J. Mater. Chem.* **2010**, *20*, 8207.

(3) (a) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (b) Hill, J. P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481.

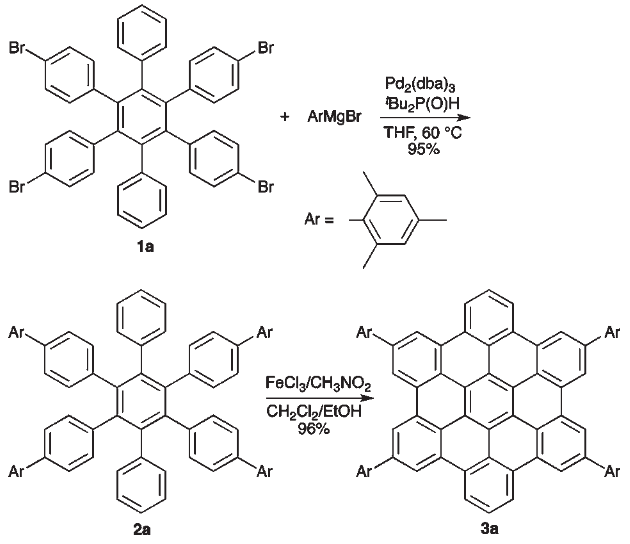
(4) Wasserfallen, D.; Kastler, M.; Pisula, W.; Hofer, W. A.; Fogel, Y.; Wang, Z.; Müllen, K. *J. Am. Chem. Soc.* **2006**, *128*, 1334.

(5) (a) Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, C. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3748. (b) Dou, X.; Yang, X.; Bodwell, G. J.; Wagner, M.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2007**, *9*, 2485. (c) Wadumethrige, S. H.; Rathore, R. *Org. Lett.* **2008**, *10*, 5139. (d) Feng, X.; Pisula, W.; Takase, M.; Dou, X.; Enkelmann, V.; Wagner, M.; Ding, N.; Müllen, K. *Chem. Mater.* **2008**, *20*, 2872.

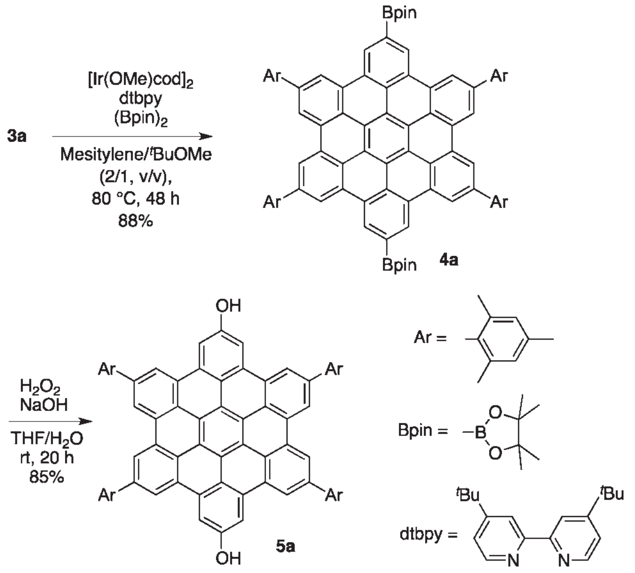
(6) (a) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (b) Miyaura, N. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535. (c) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3.

10.1021/ol300743f © 2012 American Chemical Society
Published on Web 05/02/2012

Scheme 1. Synthesis of Mesityl-Substituted Hexa-*peri*-hexabenzocoronene **3a**



Scheme 2. Ir-Catalyzed Direct Borylation and Oxidation of **3a**



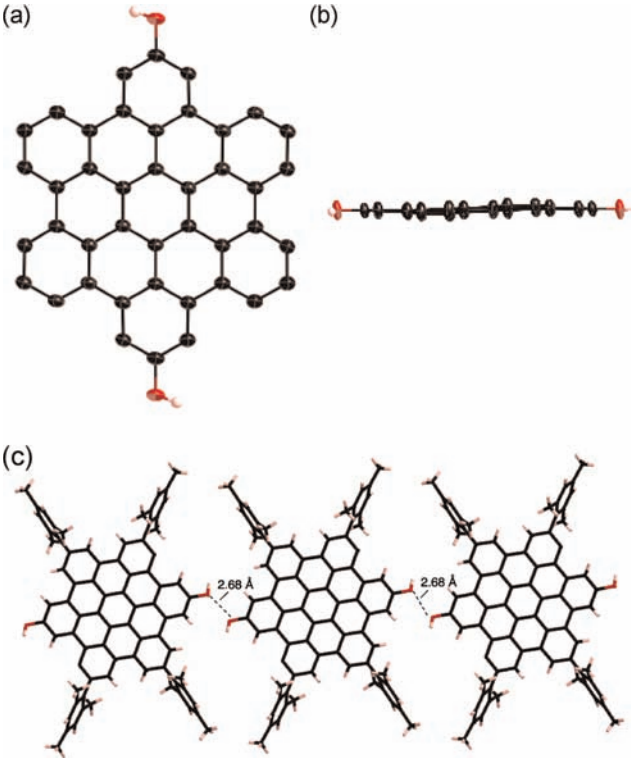


Figure 1. X-ray crystal structure of **5a**. (a) Top view, (b) side view, and (c) packing structure in the crystal. The thermal ellipsoids are scaled to 50% probability level. Mesityl groups are omitted for clarity.

the solubility, more bulky substituents were required at the HBC periphery. The introduction of mesityl groups was achieved by palladium-catalyzed coupling of tetrabromohexaphenylbenzene **1a** with mesitylmagnesium bromide in 95% yield.[9] The Scholl reaction of **2a** with $FeCl_3$ in a CH_2Cl_2/EtOH mixed solvent provided tetramesityl HBC **3a** in 96% yield (Scheme 1), which was highly soluble in organic solvents such as dichloromethane and toluene.

With a soluble HBC in hand, we then investigated the iridium-catalyzed direct borylation of **3a** (Scheme 2). The reaction was performed in the presence of 4.0 equiv of bis(pinacolate)diboron and 6 mol % of $[Ir(OMe)cod]_2$/dtbpy. No reaction proceeded in cyclohexane and 1,4-dioxane, which are often employed as standard solvents for direct borylation. After several trials, we found that a mixed solvent of mesitylene/*tert*-butyl methyl ether (2/1, v/v) was effective in providing fully borylated product **4a** in 88% yield under refluxing conditions.[10] The boryl groups were easily converted into hydroxy groups by oxidation with hydrogen peroxide to furnish **5a** in 85% yield. The structure of **5a** was unambiguously confirmed by X-ray diffraction analysis (Figure 1). The hydroxy groups were incorporated at the least hindered positions. The π-plane of the HBC core was slightly distorted, and the mean

---

(7) Examples of C−H direct borylation of large π-conjugated compounds: (a) Coventry, D. N.; Basanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Marder, T. B.; Perutz, R. N. *Chem. Commun.* **2005**, 2172. (b) Hata, H.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8264. (c) Kimoto, T.; Tanaka, K.; Sakai, Y.; Ohno, A.; Yoza, K.; Kobayashi, K. *Org. Lett.* **2009**, *11*, 3658. (d) Ozawa, R.; Yoza, K.; Kobayashi, K. *Chem. Lett.* **2011**, *40*, 941. (e) Teraoka, T.; Hiroto, S.; Shinokubo, H. *Org. Lett.* **2011**, *13*, 2532. (f) Battagliarin, G.; Li, C.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2011**, *13*, 3012. (g) Crawford, A. G.; Liu, Z.; Mkhalid, I. A. I.; Thibault, M.-H.; Schwarz, N.; Alcaraz, G.; Steffen, A.; Collings, J. C.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Chem.—Eur. J.* **2012**, *18*, 5022.

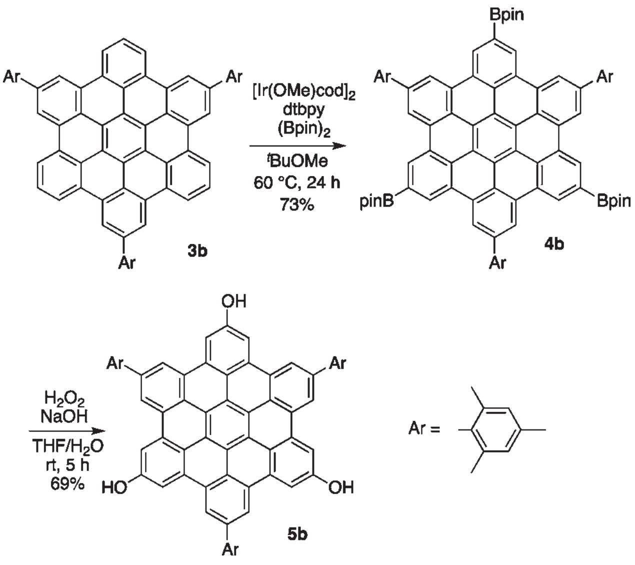
(8) (a) Sadhukhan, S. K.; Viala, C.; Gourdon, A. *Synthesis* **2003**, *10*, 1521. (b) Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Müllen, K. *Chem.—Eur. J.* **2000**, *6*, 1834.

(9) (a) Wolf, C.; Xu, H. *J. Org. Chem.* **2008**, *73*, 162. (b) Li, G. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1513.

(10) Harrisson, P.; Morris, J.; Steel, P. G.; Marder, T. B. *Synlett* **2009**, 147.

plane deviation was calculated to be 0.045 Å. The distance between two oxygen atoms on the adjacent molecules was 2.68 Å, indicating the existence of hydrogen bonding. It is noteworthy that the hydrogen bondings construct a 1D chain network of **5a** in the crystal.

Scheme 3. Ir-Catalyzed Direct Borylation and Oxidation of **3b**



To investigate the generality of the present protocol, the direct borylation of trisubstituted HBC **3b** was examined (Scheme 3).[11] Borylation of **3b** with 6.0 equiv of bis(pinacolate)diboron in *tert*-butyl methyl ether afforded triborylated product **4b** in 73% yield. Treatment of **4b** with H_2O_2/NaOH aq furnished trihydroxy HBC **5b** in 69% yield. The structure was also confirmed by X-ray diffraction analysis, which reveals that HBC **5b** also forms an assembly through hydrogen bondings in the crystal (Figure 2). The structure of **5b** was also slightly distorted, probably as a result of the crystal packing force.

We then attempted further oxidation of **5a** to synthesize dioxo-substituted HBC as a π-extended quinone on the basis of the HBC skeleton. However, the quinone product was not stable enough to be isolated.[12] Instead, oxidation of **5a** with 4.0 equiv of phenyliodine bis(trifluoroacetate) (PIFA) in DMF afforded tetraoxo product **6** in 84% yield without any regioisomers (Scheme 4).[13] The presence of tetraoxo substituents was confirmed by high-resolution mass spectrum. Tetraone **6** was reduced with $NaBH_4$ into tetrahydroxy HBC **7** in 79% yield. The structure of **7** was assigned by the NOESY spectrum and finally confirmed by preliminary X-ray diffraction analysis of acetylated derivative **8** (Figure S29). In tetraacetate **8**, the acetoxy groups were selectively introduced in a syn manner and the π-plane was distorted on one side due to the steric repulsion of four acetoxy groups.[14]

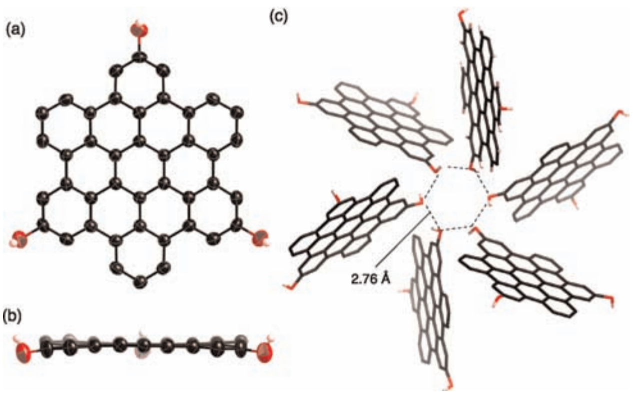


Figure 2. X-ray crystal structure of **5b**. (a) Top view, (b) side view, and (c) packing structure in the crystal. The thermal ellipsoids are scaled to 50% probability level. Mesityl groups are omitted for clarity.

Scheme 4. PIFA Oxidation of **5a**

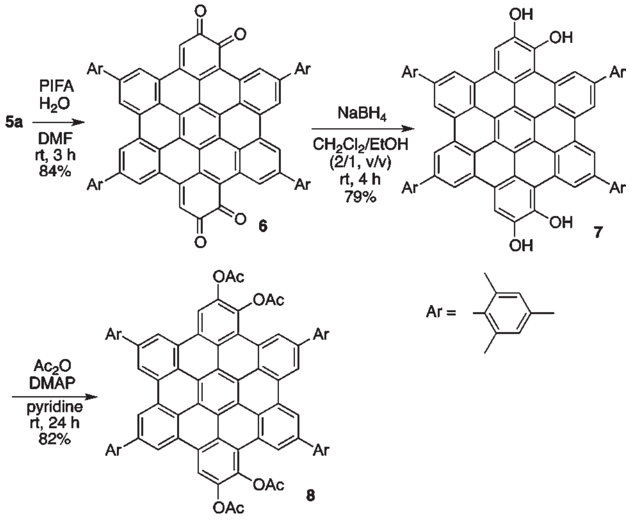


Figure 3 shows UV/vis absorption spectra of **3a**, **5a**, **6**, and **7** in CH_2Cl_2. HBCs **3a**, **5a**, and **7** exhibited typical absorption spectra for aromatic hydrocarbons.[15] Hydroxy groups induce a slight bathochromic shift of absorption spectra due to their electron-donating nature. The broadening of the spectral shape of **7** is probably due to lower symmetry. On the other hand, tetraone **6** exhibited quite a broad absorption spectrum reaching the near-infrared region. The significantly decreased extinction coefficient and the blue shift of the main band around 300 nm can

---

(11) Feng, X.; Wu, J.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2006**, *8*, 1145.

(12) The instability of the possible dioxo-substituted HBC is probably due to its biradical character.

(13) Wu, A.; Duan, Y.; Xu, D.; Penning, T. M.; Harvey, R. G. *Tetrahedron* **2010**, *66*, 2111.

(14) We now speculate that the regioselectivity results from distortion of the HBC core after the introduction of the oxo-substituents.

(15) Kastler, M.; Schmidt, J.; Pisula, W.; Sebastiani, D.; Müllen, K. *J. Am. Chem. Soc.* **2006**, *128*, 9526.

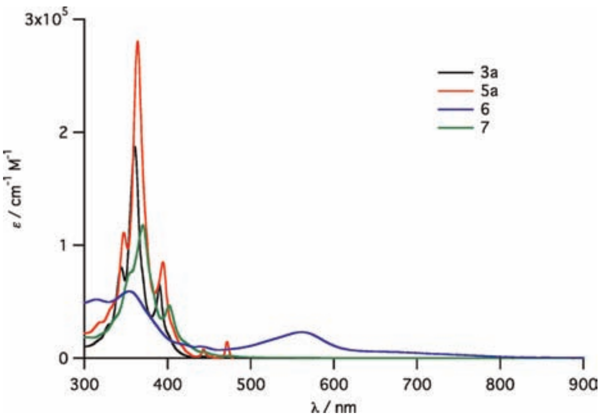


Figure 3. UV/vis absorption spectra **3a**, **5a**, **6**, and **7** in CH_2Cl_2.

be accounted for by the breaking of the π-conjugation of HBC by the carbonyl groups. The observed large bathochromic shift can be accounted for by the intramolecular charge-transfer interaction between the HBC core and the carbonyl moieties on the basis of DFT calculations (Figure S31). The HOMO and LUMO energies of **6** were estimated by electrochemical analysis by cyclic voltammetry (Figure S26). Reversible reduction and oxidation waves were observed at -0.64 and 0.42 V (vs ferrocene/ferrocenium cation), respectively. The gap between the oxidation and reduction potentials is substantially small (1.06 V). The high reduction potential of **6** suggests a prospective feature of **6** as an electron-accepting molecule.

In summary, we have demonstrated that iridium-catalyzed direct borylation of tetraaryl- and triaryl-substituted HBCs proceeded efficiently to afford diborylated and triborylated HBCs in good yields. The borylated HBCs have been successfully converted into hydroxy HBCs, which are difficult to prepare by Scholl oxidation. In addition, π-extended quinone **6** has been synthesized through oxidation of dihydroxy HBC **5a**. The present synthetic method would be useful for modification of HBCs, which allows introduction of various functionalities after construction of the HBC skeleton. Further derivatization of the borylated HBCs and properties of the HBC derivatives are currently under investigation.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 22750036 and 23655033) from MEXT, Japan and the Global COE Program in Chemistry of Nagoya University. H.S. acknowledges the Daiko Foundation for financial support.

Supporting Information Available. General procedures, spectral data for compounds, and CIF files for the X-ray analysis of **5a**, **5b**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.