Carbon Nanostructures

DOI: 10.1002/anie.201108167

Synthesis, Characterization, and Crystal Structure of [6]Cycloparaphenylene**

*Jianlong Xia and Ramesh Jasti**

Hoop-shaped conjugated macrocycles are attracting significant interest from theoretical and synthetic chemists owing to the potential applications of their electronic, optical, and supramolecular properties.[1] Cycloparaphenylenes (CPPs; **1**, Figure 1), in which 1,4-connected phenyl rings form nanosized macrocycles, represent the smallest structural unit of armchair carbon nanotubes (CNTs)[2] and were termed "carbon nanohoops" by Jasti and Bertozzi in 2008.[2a] Although they possess a simple structure, the syntheses of CPPs have been a significant challenge, because the distorted aromatic rings are subjected to a considerable amount of strain energy.

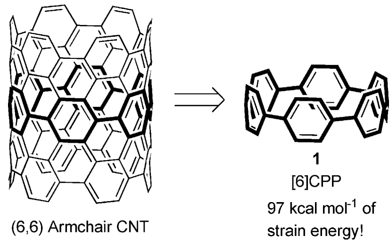
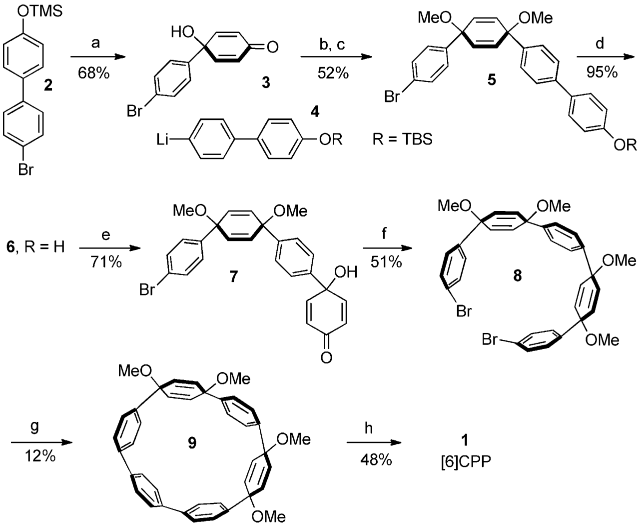


Figure 1. [6]CPP is the shortest-possible subunit of a (6,6) CNT.[3]

To our knowledge, the first synthetic endeavor targeting the CPPs was reported by Parekh and Guha in 1934.[4] Modern cycloparaphenylene research can be traced back to the pioneering work by Vögtle and co-workers,[5] in which they suggested several ingenious strategies for the syntheses of the cycloparaphenylenes. More than seventy years after their original conceptualization, Jasti and Bertozzi reported the first synthesis of the CPPs. Following this seminal work, several clever strategies to the cycloparaphenylenes have been widely explored by Itami and co-workers[6] and Yamago and co-workers.[7] [*n*]CPPs have been successfully synthesized in many sizes ($n = 7$–16) and the shortest sidewall segments of chiral single-walled nanotubes (SWNTs) have also been prepared.[6e] Moreover, Itami has demonstrated the molecular structures of [9]-[6d] and [12]CPP[6c] by X-ray crystallographic analysis.

Computational studies have revealed that the strain energy of the [*n*]CPPs increases with decreasing *n*.[7b,8] For example, the strain energy of [20]CPP is about 29 kcal mol^{-1},[7b] whereas [6]CPP, suggested to be the smallest CPP retaining a benzenoid structure,[9] has a significantly higher strain energy of 97 kcal mol^{-1}.[7b] Owing to the increasing strain energy, the smaller CPPs are extremely challenging synthetic targets. Very recently, we reported the selective synthesis of highly strained [7]cycloparaphenylene using cyclohexadienes as masked aromatic rings.[10] A synthetic strategy to access even smaller cycloparaphenylenes would be a significant addition to this exciting area. Herein, we describe the selective synthesis, crystal structure, and optoelectronic characterization of [6]CPP (**1**), which is the smallest carbon nanohoop synthesized to date. Analysis of the X-ray structure revealed a fascinating packing geometry reminiscent of a carbon nanotube.

To synthesize [6]cycloparaphenylene (**1**), we envisioned macrocycle precursor **9** as the penultimate intermediate in the sequence (Scheme 1). Macrocycle **9** contains two cyclohexadiene units as masked benzene rings to attenuate the strain energy for cyclization. We designed a sequential oxidative dearomatization/addition procedure to prepare dibromide **8** with high diastereoselectivity. The synthesis began with the oxidation of 4-bromo-4′[(trimethylsilyl)oxy]biphenyl (**2**) in the presence of phenyliodine(III) diacetate (PIDA) and water to generate ketone **3**.[10b,11] Deprotonation of alcohol **3** with



Scheme 1. Reagents and conditions: a) PIDA, CH_3CN, THF, H_2O, 16 h; b) 1. NaH, THF, −78 °C, 2 h; 2. **4**, THF, 4 h; c) NaH, CH_3I, THF, 16 h; d) TBAF, THF, 2 h; e) PIDA, CH_3CN, THF, H_2O, 2 h; f) 1. NaH, THF, −78 °C, 2 h; 2. 4-BrPhLi, THF, −78 °C, 4 h; 3. NaH, CH_3I, THF, 16 h; g) 1,4-benzenediboronic acid bis(pinacol) ester, $[Pd(PPh_3)_4]$, Cs_2CO_3, DMF, isopropanol, 120 °C, 18 h; h) 1. sodium naphthalenide, THF, −78 °C, 30 min; 2. I_2, THF, 45 min. THF = tetrahydrofuran, 4-BrPhLi = (4-bromophenyl)lithium, DMF = dimethylformamide, TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl.

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[*] Dr. J. Xia, Prof. R. Jasti
Department of Chemistry, Boston University
24 Cummington St., Boston, MA 02215 (USA)
E-mail: jasti@bu.edu

[**] This work was supported by generous start-up funds from Boston University. The authors gratefully acknowledge Dr. Jeffrey Bacon for his assistance with X-ray crystallography.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108167.

sodium hydride, subsequent addition of TBS-protected aryllithium **4**, and subsequent methylation produced the dimethyl ether **5** in 52 % yield. Removal of the silyl-protecting group of **5** with tetrabutylammonium fluoride (TBAF) proceeded smoothly to generate phenol **6**, which was converted to ketone **7** (71 %) after a second oxidation with PIDA. Ketone **7** was then treated with (4-bromophenyl)lithium under similar conditions as those for ketone **3** to give dibromide **8** in 51 % yield. Aryl lithium additions to both ketones (**3** and **7**) are highly diastereoselective; this finding is consistent with the electrostatic model proposed for similar systems.[10b,12]

With compound **8** in hand, macrocycle **9** was successfully assembled by a Suzuki–Miyaura cross-coupling reaction with 1,4-benzenediboronic acid bis(pinacol) ester utilizing [Pd($(PPh_3)_4$] as a catalyst in a yield of 12 % (Scheme 1). The low yield for this transformation was expected because of the significant strain present in macrocycle **9** (see below, Figure 2). Finally, we examined the reductive aromatization reaction[2,10b] of macrocycle **9** to produce the desired [6]CPP. Macrocycle **9** was subjected to sodium naphthalenide at −78 °C for 30 min and then quenched with I_2 to provide [6]CPP (**1**), the smallest nanohoop to date, as an orange solid in 48 % yield. Interestingly, the proton NMR spectrum of **1** shows a singlet at $\delta = 7.64$ ppm. The signals in the proton NMR spectra of all previously synthesized [*n*]CPPs have shifted upfield with decreasing size. In this case, however, the singlet for [6]CPP is shifted downfield by 0.16 ppm relative to [7]CPP ($\delta = 7.48$ ppm).

To provide conclusive evidence for the molecular structure of macrocycle **9** and [6]CPP (**1**), we have also analyzed these compounds by X-ray crystallography[13] (Figure 2, for the refinement details, see the Supporting Information). A single crystal of **9** suitable for X-ray diffraction was obtained by recrystallization in dichloromethane/hexane at room temperature. The benzene ring (a, as shown in Figure 2) between the two cyclohexadiene units of **9** was shown to have a disordered structure. The terphenyl section of the macrocycle is clearly bent, and the strain of this section of the molecule is the obvious culprit in the low-yielding macrocyclization step. Replacement of the middle benzene ring in the terphenyl section by a cyclohexadiene unit is an attractive future strategy to prepare [6]CPP in improved yields.

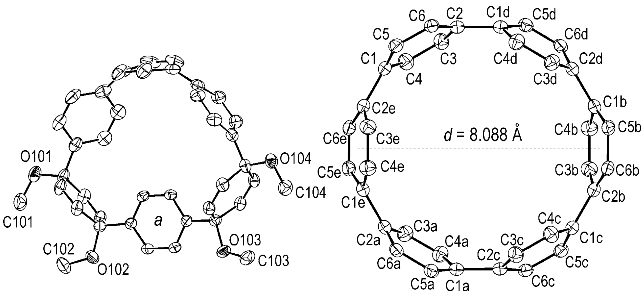

Figure 2. ORTEP drawing of **9** (left) and [6]CPP (**1**, right). Thermal ellipsoids are shown at 50 % probability, minor disorder sites in **9** and all hydrogen atoms are omitted for clarity. The benzene ring between the two cyclohexadiene units in **9** is labeled a. Selected bond lengths of [6]CPP: C1–C4 1.400(2) Å, C1–C5 1.407(2) Å, C1–C2(e) 1.490(2) Å, C2–C3 1.399(2) Å, C2–C6 1.407(2) Å, C2–C1(d) 1.490(2) Å, C3–C4 1.387(2) Å, C5–C6 1.386(2) Å.

Up to now, only [9]-[6d] and [12]CPP[6c] have been characterized by X-ray structure analysis. Confirmation of the molecular structure of [6]CPP by crystallography was a goal from the outset of this project. After careful recrystallization of [6]CPP from a dichloromethane/hexane solution, orange crystals suitable for X-ray diffraction were generated. The ORTEP drawing is depicted in Figure 2. The diameter of this ring is approximately 8.1 Å as estimated from the distance between the two central benzene rings (Figure 2). The bond lengths of C1−C4, C2−C3, and C3−C4 in a representative benzene unit are 1.400, 1.399, and 1.387 Å, respectively. These approximately equivalent bond lengths indicate that a benzenoid structure is preserved in [6]CPP, even though the benzene rings are substantially bent as a result of the geometry of the small cyclic system.

Perhaps more intriguing is the packing pattern of [6]CPP in the crystalline state (Figure 3). Itami has shown that the crystal packing of [12]CPP results in a herringbone pattern, although a tubular type of stacking structure can be seen from an appropriate perspective.[6c] After investigating the crystallographic information file of [9]CPP,[6d] a similar herringbone alignment style was also found in the packing structure of [9]CPP. To our surprise, [6]CPP exhibits a fantastic linear alignment to form a regular nanotube-like structure in the crystalline state (Figure 3, left). The organization of [6]CPP molecules could provide a "bottom-up" approach towards the assembly of structurally uniform (6,6) armchair single-walled carbon nanotubes.[14] Moreover, the presence of a nanosized cavity (Figure 3, right) in such a tubular structure might also pave the way for the application of [6]CPP in novel supramolecular chemistries.[15]

After conclusively validating the structure of [6]CPP, we also examined the optoelectronic properties of [6]CPP by UV/Vis spectroscopy, fluorescence spectroscopy, and cyclic voltammetry. [6]CPP has a dominant absorption maximum at 338 nm (Figure 4, left), similar to the other [*n*]cycloparaphenylenes ($n = 7$–12 and 18).[7b] To gain a further understanding of the absorption spectrum, we carried out time-dependent density functional theory (TD-DFT) calculations for [6]CPP at the B3LYP/6-31G* level of theory with Gaussian 03.[16] The calculation revealed that the HOMO→LUMO transition (491 nm; HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) is forbidden with an oscillator strength of $f = 0$, which has also been found for other [*n*]CPPs.[7b,17] The maximum absorption can be assigned to a combination of HOMO−2→LUMO,

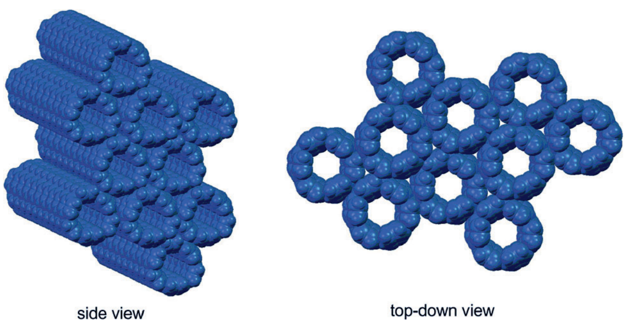

Figure 3. Packing structure of [6]CPP in the crystalline state.

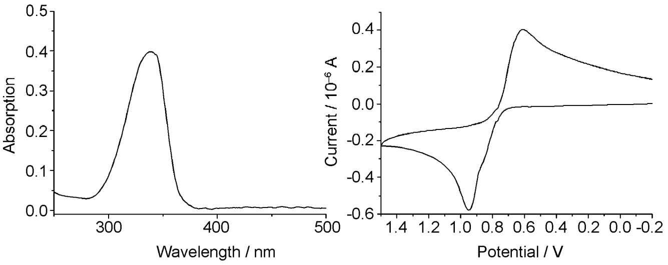

Figure 4. UV/Vis spectrum (left) and cyclic voltammogram (right) for [6]CPP.

HOMO−1→LUMO, HOMO→LUMO+1, and HOMO→LUMO+2 transitions (Table S1 in the Supporting Information). Interestingly, we observed no detectable fluorescence emission from [6]CPP. This behavior is similar to that observed with [7]CPP, which has a quantum yield of 0.007, and this absence of detectable fluorescence emission from [6]CPP can be attributed to the completely forbidden transition.[10b]

The oxidation potential of [6]CPP was studied by cyclic voltammetry in a dichloromethane solution using Bu_4NPF_6 (0.1 M) as the supporting electrolyte (Figure 4, right). The reduction potential could not be detected within the electrochemical window available under this condition.[18] The half-wave oxidation potential of [6]CPP is 0.44 V (vs. the ferrocene/ferrocenium couple). Yamago and co-workers have demonstrated that the oxidation potential of [*n*]CPPs decreases as the size of the CPPs decreases. For example, the half-wave oxidation potential of [8]CPP is 0.59 V (vs. the ferrocene/ferrocenium couple).[7b] This result illustrates that [6]CPP has a higher-energy HOMO and will be easier to oxidize than other [*n*]CPPs of larger size.

In summary, [6]cycloparaphenylene (**1**), the smallest carbon nanohoop to date, has been synthesized for the first time. A two-fold dearomatization/diastereoselective-addition procedure has been designed to assemble the penultimate macrocycle **9**. Reductive aromatization at low temperatures furnishes the highly strained [6]CPP. The structures of macrocycle **9** and [6]CPP have been confirmed by X-ray crystallography. As predicted, [6]CPP retains a benzenoid structure. The stacking structure of [6]CPP in the crystalline state displays a striking linear alignment to form a regular nanotube-like packed structure, which might be useful for a variety of applications in materials science. Our explorations into the properties of these crystalline materials will be reported in due course.

Received: November 21, 2011
Revised: December 15, 2011
Published online: January 27, 2012

Keywords: carbon nanohoop · macrocycles · nanotubes · synthetic methods · X-ray crystal structures

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[12] The *syn*/*anti* ratio for aryllithium addition to ketone **3** was 19:1 consistent with reference [10b]. In the case of aryllithium addition to ketone **7**, we were not able to isolate any of the minor *anti* diastereomer. Based on NMR spectroscopy analysis of the crude material, the diastereomeric ratio (dr) is greater than 10:1.

[13] CCDC 852988 (**9**) and 852989 (**1**, [6]CPP) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] We observe a very weak absorption from 400–550 nm in the UV/Vis spectrum. For a magnification of this region see Figure S1 in the Supporting Information.

[18] Reduction wave(s) could not be observed even when the potential was lower than −2.0 V. This finding is similar to the other [*n*]CPPs reported by Yamago and co-workers (Ref. [7b]).