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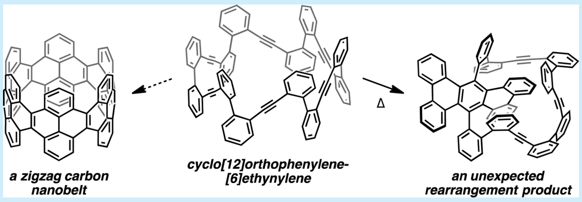
Synthesis, Structure, and Reactivity of a Cylinder-Shaped Cyclo[12]orthophenylene[6]ethynylene: Toward the Synthesis of Zigzag Carbon Nanobelts

Katsuma Matsui,[†] Masako Fushimi,[†] Yasutomo Segawa,*[,†,‡] and Kenichiro Itami*[,†,‡,§]

[†]Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan
[‡]JST, ERATO, Itami Molecular Nanocarbon Project, Chikusa, Nagoya 464-8602, Japan
[§]Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Chikusa, Nagoya 464-8602, Japan

Ⓢ *Supporting Information*



ABSTRACT: Benzannulated cyclacenes (BCs) have been proposed as stable zigzag carbon nanobelts. Density functional theory (DFT) calculations revealed a closed-shell ground state for [12]BC, whereas an open-shell ground state was suggested for [12]cyclacene. The calculated strain energy and frontier molecular orbital energies of [12]BC also implied high stability. An unstrained macrocycle **1**, consisting of orthophenylene and ethynylene moieties, was designed as a potential precursor for [12]BC and synthesized by sequential Suzuki–Miyaura cross-coupling of diphenylacetylene derivatives. While the conversion of **1** into [12]BC is still under investigation, an unexpected rearrangement of the triene moieties in **1**, affording a tribenzo[*f*,*k*,*m*]tetraphene structure, was discovered during the screening of reaction conditions. An attempt was made to rationalize this result by proposing a plausible reaction mechanism that proceeds via intermediates containing cyclobutadiene or Dewar benzene moieties. The proposed mechanism is partially supported by DFT calculations.

Molecules that represent constituent segments of carbon nanotubes (CNTs) are fascinating compounds due to their unique cyclic π-conjugation systems and their application as building blocks in the bottom-up synthesis of structurally uniform CNTs.[1] CNTs can be subdivided into three classes, according to their chiral indices (*n*,*m*).[2] Accordingly, (*n*,*m*)CNTs with $n = m$, $n > m > 0$, and $m = 0$ are called "armchair", "chiral", and "zigzag", respectively, and the corresponding segment molecules for each type of CNT have been targeted by synthetic organic chemists.[1c]

The shortest segments for armchair CNTs are *para*-connected cyclic oligophenylenes, the so-called cycloparaphenylenes (CPPs).[1,3] Although the CPP structure was proposed for the first time in the 1930s,[4] it took almost 80 years to accomplish their synthesis due to a lack of efficient synthetic methods to construct such highly distorted structures. In 2008, Bertozzi and Jasti achieved the synthesis of [*n*]CPPs ($n = 9$, 12, and 18),[5a] and since then, [*n*]CPPs ($n = 5$–16, and 18) have been reported based on synthetic methods developed by Jasti,[5] Itami,[6] and Yamago.[7] As a matter of fact, [5]-, [9]-, [12]-, and [15]CPPs are now commercially available.[8] After the successful synthesis of these CPPs, their size-dependent photophysical properties,[9] guest-encapsulating behavior,[10] adsorption properties,[11] and reactivity with metal complexes[12] were investigated.

Since the discovery of suitable synthetic routes to CPPs, the constituent segments of chiral[13] and zigzag[14] CNTs have also been studied. The simplest zigzag CNT segments are cyclacenes[15] (Figure 1a,b). As the closed-shell structure of cyclacenes does not contain a Clar aromatic sextet (Figure 1c), the open-shell singlet state was predicted to be favored in the ground state.[16] Given that this feature endows cyclacenes with high reactivity, it is not surprising that their synthesis has not yet been accomplished.[15]

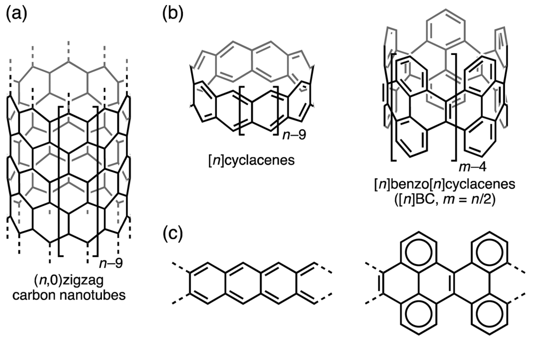


Figure 1. (a) Zigzag CNTs. (b) [*n*]Cyclacenes and [*n*]BCs. (c) Resonance structures of [*n*]cyclacenes (left) and [*n*]BCs (right). Clar aromatic sextets are drawn as circles.

We designed the new cyclacene derivatives [*n*]benzo[*n*]cyclacenes ([*n*]BCs) in which two benzene rings are annulated to each naphthalene moiety of the corresponding [*n*]cyclacenes. Because of this structural modification, these [*n*]BCs include Clar aromatic sextets, and thus, they may accordingly exhibit increased thermal and chemical stability. As [*n*]BCs still exhibit the segment

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structure of (n,0)zigzag CNTs, [n]BCs can also be categorized as *zigzag carbon nanobelts.*[17] In this study, we conducted theoretical calculations on the electronic properties and strain energies of [n]BCs. Moreover, we report the synthesis of a possible precursor for [12]BC and its reactivity including an unexpected rearrangement reaction.

In order to estimate the stability and electronic properties of [n]BCs, density functional theory (DFT) calculations were carried out (Table 1).[18] Because of the steric repulsion at the fjord regions, [n]BCs were slightly distorted in a “waggling”[19] fashion. A closed-shell character was found for the optimized structures of [n]BCs (n = 8, 12, 16, 20, 24, and 28). For example, a strain energy (SE) of 82.6 kcal·mol^{-1} was estimated for [12]BC on the basis of a strain energy calculation method for carbon nanobelts that we developed[17] (see the Supporting Information for details). As this value is comparable to that of [12]cyclacene (110.4 kcal·mol^{-1}),[17] the strain energy of [12]BC should be derived predominantly from the [12]cyclacene framework, and the benzannulation of [12]cyclacene into [12]BC should have a stabilizing effect. The SE of [12]BC per carbon atom is thus 1.03 kcal·mol^{-1}, which is slightly smaller than that of [9]CPP (1.21 kcal·mol^{-1}).[6d] Consequently, the HOMO−LUMO gap increases upon benzannulation ([12]cyclacene, 2.03 eV; [12]BC, 3.14 eV). Therefore, [12]BC should exhibit an increased stability relative to [12]cyclacene (see the SI for other BCs).

Table 1. Strain Energies and Orbital Energies for [12]Cyclacene and [12]BC

compd	strain energy (kcal·mol^{-1})	orbital energy (eV)		
		HOMO	LUMO	energy gap
[12]cyclacene	110.4	−4.48	−2.45	2.03
[12]BC	82.6	−5.15	−2.01	3.14

Our strategy for the synthesis of [12]BC is shown in Figure 2. Based on previously reported reactions, which described the conversion of bis(2-biphenylyl)acetylene into dibenzo[g,p]chrysene,[20] we designed cyclo[12]orthophenylene[6]ethynylene (**1**) as a possible precursor for [12]BC. As the biphenyl moieties in **1** can move flexibly, we envisage that macrocycle **1** should be unstrained. This notion is supported by DFT calculations on a hypothetical homodesmotic reaction, which suggest a strain energy of 0.2 kcal·mol^{-1} for **1**. Thus, we envisioned that **1** might be synthesized selectively by sequential Suzuki−Miyaura cross-coupling reactions of diphenylacetylene derivatives bearing bromo or boryl groups.

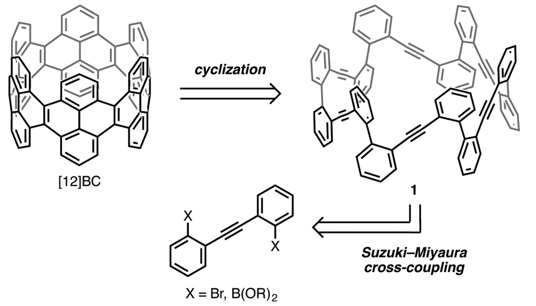

Figure 2. Retrosynthesis of [12]BC.

Macrocycle **1** was synthesized on the basis of this synthetic strategy (Figure 3a). Lithiation, borylation, and hydrolysis of bis(o-bromophenyl)acetylene (**2**) afforded boronic acid **3** quantitatively, and a subsequent Suzuki−Miyaura coupling of **3** with an excess of **2** proceeded in a 1:2 manner to furnish trimer **4** in 52% yield. Borylation of **4** by a dilithiation and treatment with *i*-PrOBpin (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) afforded **5** as a mixture containing small amount of impurities. When **4** and the impure **5** were subjected to the cross-coupling reaction conditions catalyzed by $Pd_2(dba)_3$/X-Phos (dba = dibenzylideneacetone, X-Phos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl), **1** was synthesized in 29% yield. By X-ray crystallography, the dihedral angle of the biphenyl moiety of **4** was found to be 64.5°, which is almost identical to that of the cyclic hexamer **1** (60°). This preorganized structure of **4** should have contributed to the relatively high yield in the macrocyclization.

The molecular structure of **1** was unambiguously determined by X-ray crystallography (Figure 3b). A single crystal of **1** was obtained from vapor diffusion of pentane into a chloroform solution of **1** at room temperature. In the solid state, **1** forms a distorted hexagonal structure with C_2 symmetry, which contains four chloroform molecules in the cavity. Considering that the optimized structure of **1** exhibited C_6 symmetry (Figure 3c), the observed slight distortion of **1** in the solid state should be attributed to packing interactions between **1** and the incorporated chloroform molecules. The CH_2Cl_2 solution of **1** has UV absorption with the peak at 296 nm and weak blue fluorescent (Φ_F = 0.07) as shown in Figure 3d.

Subsequently, we attempted to find suitable reaction conditions to convert cyclic precursor **1** into [12]BC (Figure 4a), starting from previously reported conditions for the transformation of bis(2-biphenylyl)acetylene into dibenzo[g,p]chrysene.[20] Unfortunately, a variety of reaction conditions, including treatment with ICl followed by $PdCl_2(PPh_3)_2$/NaOAc, TFA/TfOH followed by $FeCl_3/MeNO_2$, AuCl/AgOTf, and $PtCl_2$/AgOTf (Ac = acetyl, Tf = trifluoromethanesulfonyl), afforded complex mixtures, and the targeted [12]BC could not be detected by MALDI-TOF MS in any of the obtained reaction mixtures. During our attempts, we discovered that heating **1** in *N*,*N*-dimethylacetamide (DMAc) to 150 °C for 2 days resulted in the unexpected formation of **6** via a formal [2 + 1 + 2 + 1] cycloaddition.[21] Compound **6** was isolated in 9% yield, and the structure was confirmed by X-ray crystallography.

A plausible reaction mechanism for the formation of **6** from **1** is shown in Figure 4b, in which the structures of **1** and **6** are simplified to **A** and **D**,[22] respectively, for the DFT calculations. The [2 + 2] cycloaddition of two alkyne moieties[23] in triyne **A** should occur initially to afford cyclobutadiene **B**. Subsequently, another alkyne moiety should react with the cyclobutadiene moiety to form the Dewar benzene structure **C** via a [2 + 2] cycloaddition.[24] Finally, this Dewar benzene moiety should isomerize via an electrocyclic ring-opening reaction[24] to furnish tribenzo[f,k,m]tetraphene **D**. The structures of **A**−**D** and two transition states ($\mathbf{TS_{BC}}$ and $\mathbf{TS_{CD}}$) could be successfully optimized by DFT calculations, while the optimization of $\mathbf{TS_{AB}}$ failed, probably due to the presence of a radical mechanism.[23] These results indicate that this rearrangement should be highly exothermic (99.0 kcal·mol^{-1}) on account of the aromatic stabilization arising from the formation of a benzene ring, and the calculated energy barriers ($\mathbf{B} \rightarrow \mathbf{TS_{BC}}$: 2.6 kcal·mol^{-1}, $\mathbf{C} \rightarrow \mathbf{TS_{CD}}$: 25.1 kcal·mol^{-1}) are low enough for a reaction to proceed at 140 °C.

In summary, we have proposed [n]BCs as stable zigzag carbon nanobelts. DFT calculations revealed a closed-shell ground state for [12]BC. The strain and the frontier orbital energy values for

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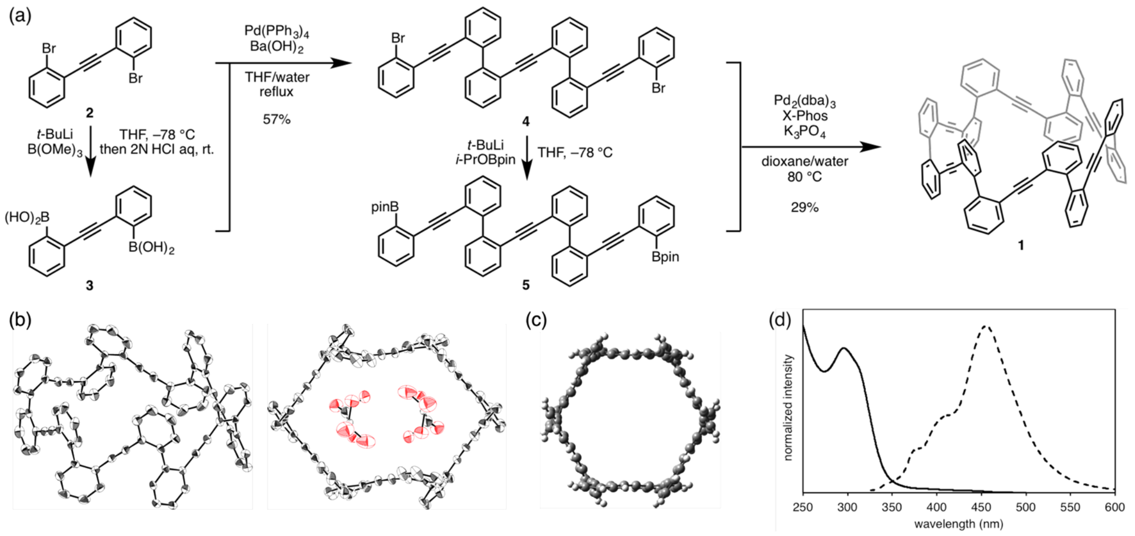

Figure 3. (a) Synthesis of **1**. (b) ORTEP drawing of **1** (left, side view; right, top view) with 50% probability: all hydrogen atoms are omitted for clarity. Key: black, carbon; red, chlorine. (c) Structure of **1** optimized by DFT calculations. (d) UV–vis absorption (solid line) and fluorescence (broken line) spectra of the CH_2Cl_2 solution of **1**.

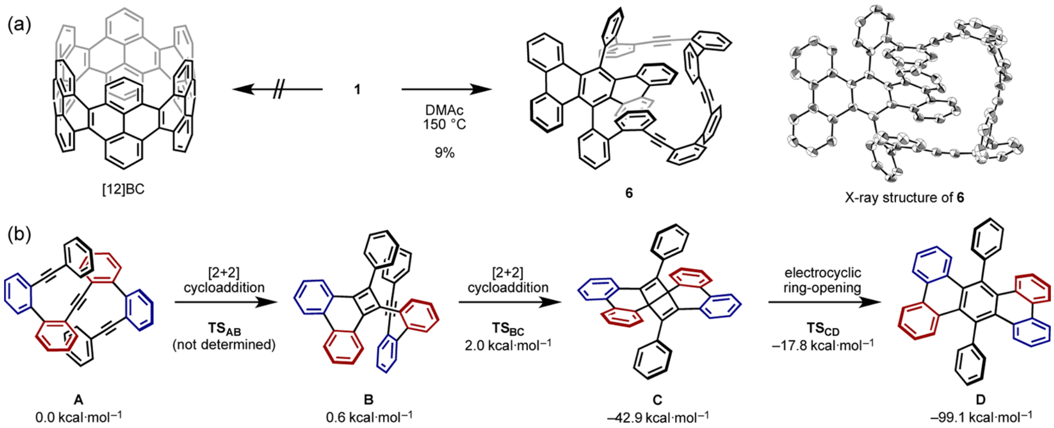

Figure 4. (a) Formation of **6** by the thermal reaction of **1** and ORTEP drawing of **6** with 50% probability: all hydrogen atoms and solvent molecules are omitted for clarity. (b) Plausible mechanism for the sequential transformation of triyne **A** (a simplified model of **1**) into 9,18-diphenyltribenzo[*f*,*k*,*m*]-tetraphene **D** (a simplified model of **6**) with calculated Gibbs free energies relative to that of **A**.

[12]BC implied desirably high stability. Unstrained macrocycle **1** was designed as a potential precursor for [12]BC, and synthesized via sequential Suzuki–Miyaura cross-coupling reactions of the corresponding diphenylacetylene derivatives. For the transformation of **1** into [12]BC, a variety of reaction conditions were tested. Even though these reaction conditions did not afford [12]BC, we observed an unexpected rearrangement of **1** into **6**, which exhibits a tribenzo[*f*,*k*,*m*]tetraphene structure. A plausible reaction mechanism via cyclobutadiene and Dewar benzene intermediates was proposed, which is partially supported by DFT calculations. Further optimizations of the reaction conditions to synthesize [*n*]BCs are currently ongoing on our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02702.

Experimental details and spectra of new compounds (PDF)

X-ray diffraction data for compound **6** (CIF)

Cartesian coordinates of optimized structures (XYZ)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ysegawa@nagoya-u.jp.
*E-mail: itami@chem.nagoya-u.ac.jp.

Notes

The authors declare no competing financial interest.

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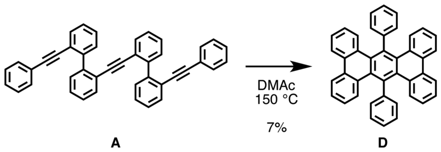
(22) The rearrangement product **D** was also obtained in 7% yield when acyclic triene **A** was treated under the same conditions. See the Supporting Information for details.



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