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Three-Dimensionally Arranged Cyclic *p*-Hexaphenylbenzene: Toward a Bottom-Up Synthesis of Size-Defined Carbon Nanotubes

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Hexa-*peri*-hexabenzocoronene (HBC) is one of the fundamental polycyclic aromatic hydrocarbons (PAHs), which can be synthesized from hexaphenylbenzene (HPB) through oxidative cyclodehydrogenation involving a Lewis oxidant/acid, such as ferric chloride ($FeCl_3$). HBC derivatives have been widely synthesized and studied not only for tuning the electronic properties at the molecular level, but also for controlling the supramolecular behavior in solution and the solid state.[1] With the recent boom in graphene research,[2] bottom-up approaches to access size- and/or shape-defined graphene nanoribbons (GNRs)[3] and nanographenes (NGs)[4] have become appealing because the electronic properties of GNRs and NGs are largely dependent on the size and edge structures (i.e., zigzag or armchair). Therefore, precise synthesis of these materials is required for developing the next generation of nanoscale electronic and spintronic devices.[5] Naturally, the π extension of HBCs in a one-dimensional or two-dimensional manner from the corresponding polyphenylene precursors is a convenient method to build GNRs or NGs with defined sizes and/or shapes, of which several have been synthesized and investigated (Figure 1).[1–4] On the other hand, unlike GNRs and NGs, bottom-up synthesis of three-dimensional PAHs, fragments of fullerenes or carbon nanotubes (CNTs), remains a challenging task.[6] Therefore, we have extended this concept to three dimensions, and for this purpose, three-dimensionally arranged cyclic *p*-hexaphenylbenzenes (*cyclo*-4′,4′′′′-hexaphenylbenzenes (CHPBs), Figure 2) were designed as a step toward CNTs with defined size and chiral indices (*n*,*m*). The as-synthesized CHPBs could serve as fundamental precursors for *cyclo*-2,11-(hexa-*peri*-hexabenzocoronenes) (CHBCs), that is, segments of (*n*,*n*) CNTs with approximately 1.0 nm long side walls. Additionally, CHPBs possess a *cyclo*-*p*-phenylene (CPP)[7] core and, therefore, investigation of the differences between CHPBs and CPPs is also an attractive point. Herein, we report the synthesis and physical properties of [3]CHPBs and the attempts of cyclodehydrogenation thereof for the synthesis of [3]CHBCs, a (9,9)-CNT segment.

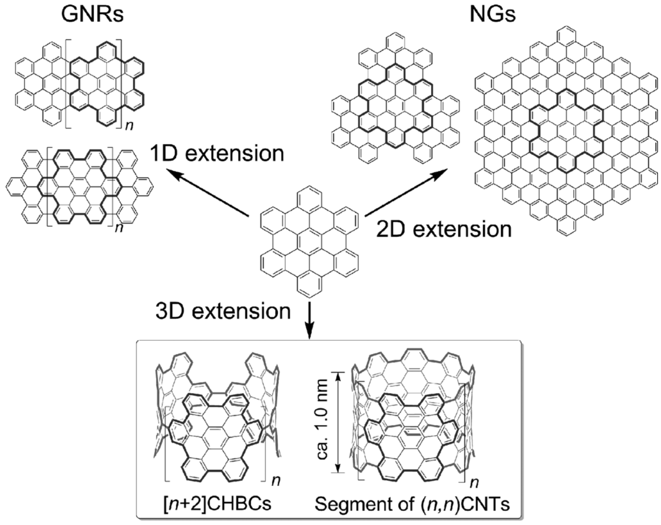

Figure 1. Concept of π extensions of HBC from 1D (GNRs) and 2D (NGs) to 3D (CHBCs and (*n*,*n*)-CNTs segments).

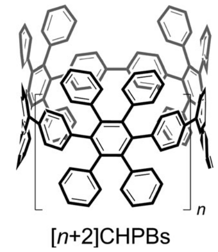

Figure 2. Structure of the CHPBs.

Scheme 1 shows the synthetic procedure for **1a** and **1b**. Diiodo precursor monomers **2a** and **2b**, the key intermediates toward CHPBs, were prepared from 2,3,5,6-tetraphenyl-1,4-benzoquinone[8] in two steps (see the Supporting Information). Macrocyclization of **2a** and **2b** was achieved by Yamamoto coupling reactions.[7h,j,9] We had anticipated that this reaction might afford mixtures of trimers, **3a** and **3b**, and tetramers as major compounds. However, only trimers **3a** and **3b** were obtained in moderate yields (40 and 42%, respectively). This is due to the dihedral angle formed by the two iodophenyl rings of **2**, which is estimated to about 50° by theoretical calculations (see the Supporting Information). For the reductive aromatizations to yield [3]CHPBs **1a** and **1b**, we used low-valent titanium, which can be prepared from the reaction of $TiCl_3$ or $TiCl_4$ with, for example,

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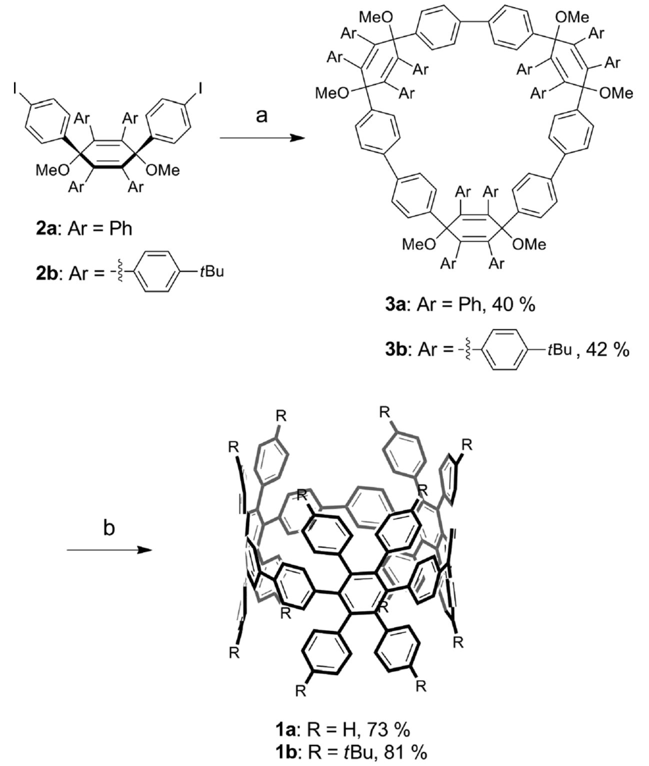


Scheme 1. Reagents and conditions: a) [Ni(cod)$_2$], (cod = 1,5-cyclooctadiene), 1,5-cyclooctadiene, 2,2′-bipyridine, DMF/toluene/THF, 80 °C; b) TiCl$_4$/LiAlH$_4$ (1:4), THF, 80 °C, 3 days.

alkali metals (Li, Na, K), zinc, a zinc–copper couple, or lithium aluminum hydride (LiAlH$_4$).[10] We used a method involving TiCl$_4$ and LiAlH$_4$ to produce [3]CHPBs. LiAlH$_4$ was added to TiCl$_4$ (LiAlH$_4$/TiCl$_4$ = 4:1) in THF. Addition of **3a** or **3b** at 80 °C gave **1a** or **1b** in good yields (73 and 81 %, respectively).

A structure of **1a**, optimized theoretically by using DFT calculations (B3LYP/6-31G*), showed C_3 symmetry with a highly twisted CPP core (Figure 3). The diameter of **1a** is 12.2 Å. Dihedral angles between rings A and B, and rings B and B′ are 51.2° and 78.7°, respectively. Based on this result, the CPP core is not expected to possess extended π conjugation. To estimate the strain energy (ΔH) of **1a**, we used a homodesmotic reaction,[11] which gave a high strain energy of 93.9 kcal mol^{-1} due to the phenyl substitutions at the side positions of the CPP core. This strain energy is 28 kcal mol^{-1} higher than that of [9]CPP (65.6 kcal mol^{-1}) and close to that of [6]CPP (96.0 kcal mol^{-1}).[11b]

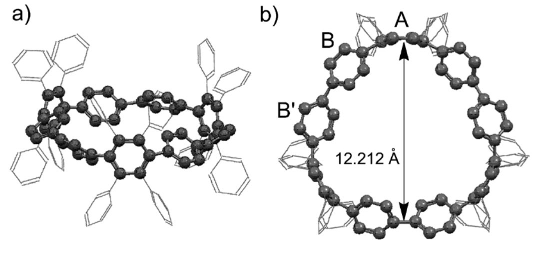


Figure 3. Optimized structure of **1a**; a) side view and b) top view. The CPP core is represented as balls and sticks, and phenyl substitutions are represented as wireframes for clarity.

To investigate the rotation of phenyl rings of **1** in solution, variable-temperature ^{1}H NMR spectra of **1a** were measured, because the flexibility of each phenyl ring may influence the efficiency of the cyclodehydrogenation. In addition, protons a and b (see Figure 4) of the CPP core were expected to separately appear as “inner cavity proton” and “outer cavity proton” at low temperature. However, despite the highly twisted structure of the CPP core, the rotational speed of each benzene ring is still fast and only a broadening behavior of all protons was observed at low temperature.

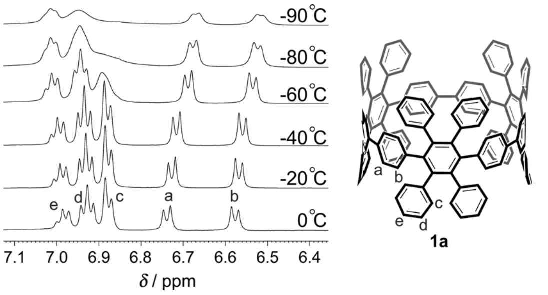


Figure 4. Variable-temperature ^{1}H NMR spectrum of **1a** (500 MHz, solvent: CD$_2$Cl$_2$).

UV/Vis and fluorescence spectra of **1a** and **1b** are shown in Figure 5. Due to the substitution of *tert*-butyl groups, λ_{max} of **1b** appeared at slightly longer wavelength than that of **1a**. Similarly, fluorescence spectra of **1a** and **1b** showed small differences at the onsets of the emissions (**1a**: 365 nm, **1b**: 350 nm) and the first emission maxima (**1a**: 405 nm, **1b**: 400 nm). As expected from theoretical calculations, UV/Vis absorption and fluorescence emission of **1a** and **1b** were observed at shorter wavelengths than for [9]CPP (λ_{max} = 340 nm, λ_{em}≅500 nm).[7a,n] In addition, the highly twisted structure of **1a** and **1b** also affected the redox properties (see the Supporting Information). Cyclic voltammograms of **1a** and **1b** showed similar irreversible oxidation waves at

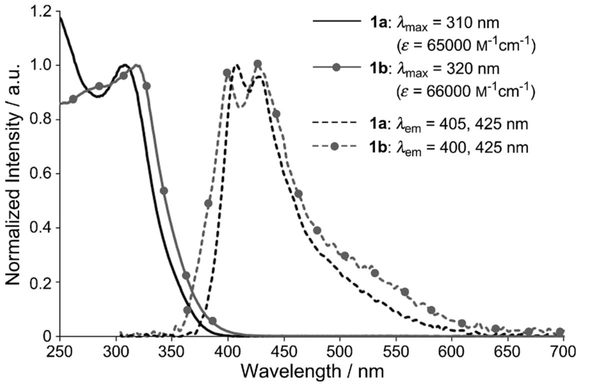


Figure 5. UV/Vis and fluorescence spectra of **1a** and **1b** (CH$_2$Cl$_2$).

1.00 V. These oxidation potentials are higher than those of [9]CPP ($E_{1/2}=0.70$ V (vs. Fc/Fc$^+$)).[7n]

Single crystals of **1a** and **1b** could be prepared by recrystallization from a dichloromethane/acetonitrile mixture and dichloromethane, respectively, and X-ray analysis was performed (Figure 6).[12] In the crystalline state, contrary to what was predicted by the theoretical calculations, the six aryl substitutions of **1a** and **1b** fill the cavity space. Due to the crystal packing force, **1a** and **1b** show C_1 symmetry and the [9]CPP core possesses an ellipsoidal shape. Whereas the cavity of **1a** is filled by its own phenyl rings, two dichloromethane molecules are incorporated in the cavity of **1b** to fill an extra space, because the 4-*tert*-butylphenyl groups are too large to fill the cavity. The diameters of the major and minor axes of **1a** and **1b** are approximately 13.6 and 11.0 Å, and 13.0 and 11.2 Å, respectively. In addition, owing to the highly twisted structures of **1a** and **1b**, no quinoidal distribution in the CPP core was observed as shown in [9]CPP[7j] (see the Supporting Information).

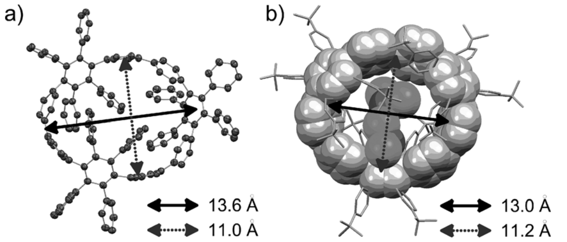


Figure 6. X-ray crystal structures of a) **1a** (ORTEP drawing) and b) **1b** (the CPP core and the dichloromethane molecules are represented by the CPK model and phenyl substitutions are represented as capped sticks for clarity). Protons are omitted for clarity.

Finally, the cyclodehydrogenations of **1a** and **1b** to produce [3]CHBCs **4a** and **4b** were attempted by using several oxidation conditions, such as CH_3SO_3H with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),[13] phenyliodonium bis(trifluoroacetate) (PIFA) with $BF_3{\cdot}Et_2O$,[14] or $FeCl_3$ (Scheme 2). Through optimizations of the cyclodehydrogenation, we found that addition of $FeCl_3$ and heating to reflux in dichloromethane is the best method to yield highly cyclodehydrogenated compounds. Although the cyclodehydrogenation of **1a** afforded partially dehydrogenated and chlorinated compounds, which were identified by MALDI-TOF MS (see the Supporting Information), the reaction of **1b** proceeded more smoothly than that of **1a**, and the corresponding MS signals of **4b** as well as of the monochlorinated **4b** were observed, because the electron-donating nature of *tert*-butyl groups enhances the efficiency of cyclodehydrogenation. In particular, the isotopic signal pattern of the monochlorinated **4b** was in good agreement with the simulated signal pattern (Figure 7). However, together with the corresponding MS signals, several intermediates of **4b**, which are partially dehydrogenated compounds, were also identified. The partially dehydrogenated compounds result from the high ring strain of the [9]CPP core, which may cause interference with the cyclodehydrogenation reaction. Prolonged reaction time and more rigorous conditions (with 1,2-dichloroethane at 100 °C in a sealed tube) did not improve the cyclodehydrogenation, but led to more chlorinated products. Separation and purification of **4b** have so far been unsuccessful. Hence, unfortunately, the exact evidence for the formation of pure [3]CHBC **4b** was not obtained, but our numerous attempts revealed that cyclodehydrogenation of a cyclic π system did proceed. Although **1b** was a colorless solution with a blue emission, after cyclodehydrogenation it exhibited an orange-red color and a yellow-orange emission (in dichloromethane solution), suggesting an effective π conjugation of the ring structures (see the Supporting Information).

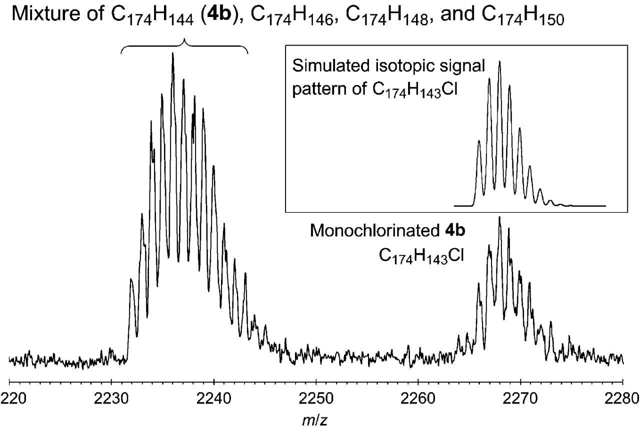
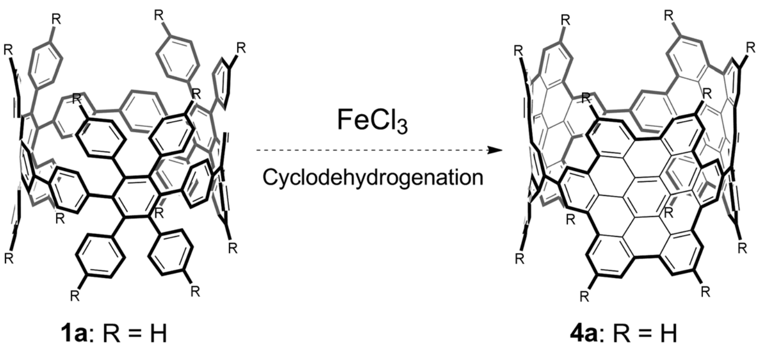


Figure 7. MALDI-TOF MS spectrum of after cyclodehydrogenation of **1b**.



1a: R = H
1b: R = *t*Bu
4a: R = H
4b: R = *t*Bu

Scheme 2. Cyclodehydrogenation reaction of **1a** and **1b**.

In summary, we have described the synthesis and crystal structure determination of [3]CHPBs **1a** and **1b**.[15] Macrocyclization of **2a** and **2b** were achieved by Yamamoto coupling reactions with moderate yield of the products, and reductive aromatizations of **3a** and **3b** were performed by using low-valent titanium to give good yields of the products. The precursor monomer **2** offers further opportunities for the synthesis of a variety of [3]CHPBs derivatives; for example, [3]CHPBs substituted with thiophenes, pyrroles, or other aryl groups could also be synthesized. Compared with nonsubstituted [9]CPP, **1a** and **1b** showed greater HOMO–LUMO gaps, due to high ring strain induced by the aryl substitutions. X-ray crystallography revealed the unique twisted structure of **1a** and **1b**. To overcome the problems related to the cyclodehydrogenation, synthesis of "higher" homologues of **1** with reduced ring strains as well as synthesis of size-defined CNTs, that is, segments of (*n*,*n*) CNTs, is currently underway in our group.

Acknowledgements

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Keywords: carbon nanotubes • cyclodehydrogenation • *cyclo*-*p*-phenylene • polycyclic compounds • hydrocarbons

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[12] a) Crystal data for **1a**: $C_{126}H_{84}\cdot 3\,CH_2Cl_2$, $M_W = 1852.40$, triclinic, space group $P\bar{1}$, $a = 13.3974(4)$, $b = 16.6360(4)$, $c = 24.8473(5)$ Å, $\alpha = 95.0665(13)$, $\beta = 96.3597(13)$, $\gamma = 110.3886(10)°$, $V = 5111.0(2)$ Å^3, $Z = 2$, $\rho = 1.204$ g cm^3, $T = 120$ K. Data were collection with $Mo_{K\alpha}$ radiation (Nonius KCCD diffractometer): 46171 measured reflections, 22839 unique reflections, $R_{merge} = 0.0621$, 18863 observed reflections ($I > 2.0\sigma(I)$). The structure was solved by direct methods (Shelxs), refined by full matrix least squares on F with anisotropic temperature factors for the non-hydrogen atoms. Final $R = 0.0649$, $R_W = 0.0611$, GOF = 0.9208; b) Crystal data for **1b**: $C_{174}H_{180}\cdot 7CH_2Cl_2$, $M_W = 2864.86$, orthorhombic, space group *Pbca*, $a = 25.5816(7)$, $b = 33.8376(9)$, $c = 38.8518(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 33630.9(15)$ Å^3, $Z = 8$, $\rho = 1.132$ g cm^3, $T = 120$ K. Data were collection with $Mo_{K\alpha}$ radiation (Nonius KCCD diffractometer): 64551 measured reflections, 30606 unique reflections, $R_{merge} = 0.0706$, 18372 observed reflections ($I > 2.0\sigma(I)$). The structure was solved by direct methods (Shelxs), refined by full matrix least squares on F with anisotropic temperature factors for the non-hydrogen atoms. Final $R = 0.0501$, $R_W = 0.0661$, GOF = 0.9619. CCDC-892921 (**1a**) and CCDC-892922 (**1b**) 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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[15] The concept, synthesis, properties, and X-ray structure of **1a** were first reported at the 14th International Symposium on Novel Aromatic Compounds (ISNA-14, July 2011; POSTER 12: "*π-Expanded Cycloparaphenylenes: Toward a Bottom-Up Synthesis of Size-Defined Carbon Nanotubes*"). Shortly thereafter Jasti and co-workers reported a tetraphenyl-substituted [12]CPP (see Ref. [7e]).

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