

論文の内容の要旨

Synthesis of Large Curved Nanocarbon Molecules by a Polygon Assembling Strategy

(多角形組立戦略による大型湾曲ナノカーボン分子の合成)

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Introduction

Since the discovery of fullerenes and carbon nanotubes, large nanocarbons with curvature have attracted attention in various fields. The nanocarbons are prepared by physical methods such as arc discharge and laser ablation and are obtained as a mixture of various structures. Recently, bottom-up synthetic methods of nanocarbons became competitive subjects that tackle preparations of "molecular" nanocarbons with uniform and discrete structures. Due to synthetic challenges, nanocarbon molecules are synthesized by developing synthetic strategies that are tailored to each structure. Very recently, a more general synthetic strategy has been developed: in place of sp^2 -carbon atoms, 1,3,5-trisubstituted benzene, so called "phenine", is adopted as trigonal units of nanocarbon molecules, which enables us to utilize biaryl coupling reactions for the synthesis. However, the first-generation "phenine nanocarbons" were commonly synthesized by one-by-one expansions of a core polygon of phenine, *i.e.*, "omphalos", to construct bowl- and saddle-shaped structures. Thus, albeit unique, this method still lacked the synthetic generality to cover large nanocarbon molecules with structural diversity. In this study, a "polygon assembling strategy" was developed: by assembling multiple, preformed polygons via biaryl coupling, large phenine nanocarbons were readily designed. Hoop-shaped and hemispherical nanocarbon molecules were synthesized, and unique curved structures were disclosed in detail.

Hoop-shaped Phenine Nanocarbons

As initial targets of the polygon assembling strategy, phenine [n]cyclo-*p*-phenylenes (**2**, **3** and **4**) were designed. For this target, hexagons of [6]cyclo-*m*-phenylene ([6]CMP) were adopted to assemble hoop-shaped phenine nanocarbon molecules. By using Pt-mediated macrocyclization, borylated [6]CMP (**1**) was assembled to

give a series of hoop-shaped molecules **2-4** with three, four and five [6]CMP in the macrocycles (Figure 1a). The large molecules were confirmed by mass spectrometry with $m/z = 2036, 2716$ and 3394 and by NMR spectroscopy to have highly symmetric time-averaged structures. The structures were unequivocally determined by single-crystal X-ray crystallography (Figure 1b), which revealed severe structural deformations with larger congeners having four and five hexagons (**B** and **C**). The structural deviations from symmetric structures as well as simple NMR spectra indicated the presence of dynamically fluctuating structures in solution.

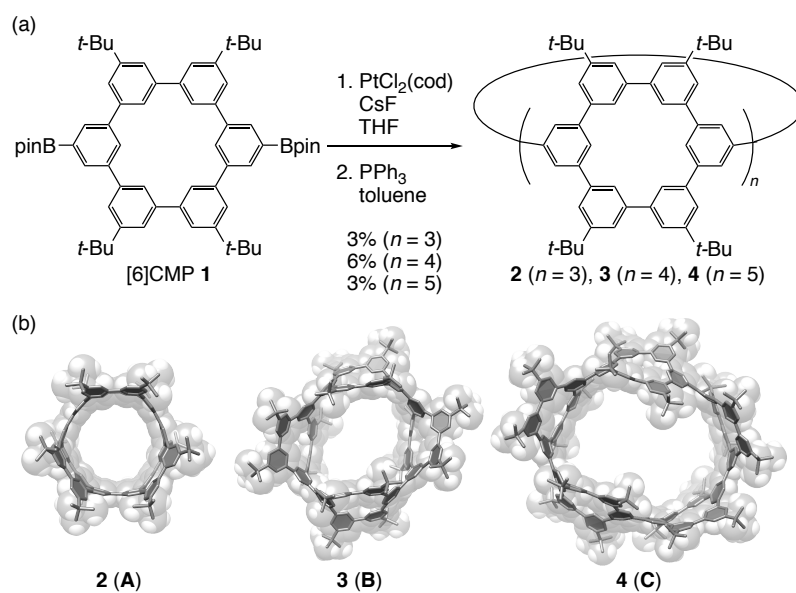


Figure 1. (a) Synthesis of phenine $[n]$ CPPs. (b) Crystal structure of the hoop-shaped phenine nanocarbons **2-4**.

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Hemispherical Phenine Nanocarbon

The next target, a hemispherical phenine nanocarbon (**9**), is a molecule having phenine units mapped on a bisection segment of [60]fullerene. Among possible bisections of [60]fullerene, **5** is the most symmetric structure that possesses pentagons at the periphery. In place of sp^2 -carbons of **5**, we adopted phenine at the vertices in **9**, which should be readily accessed by the polygon assembling strategy. As shown in Figure 2, two different types of pentagons of [5]CMP were designed as an omphalos (**6**) and peripheries (**7**). The omphalos (**7**) with five iodo-substituents were coupled with five periphery units of borylated [5]CMP (**7**) by Suzuki-Miyaura reactions. The resultant star-shaped precursor (**8**) was then converted to the hemispherical phenine nanocarbon (**9**, $\text{C}_{180}\text{H}_{220}$) via

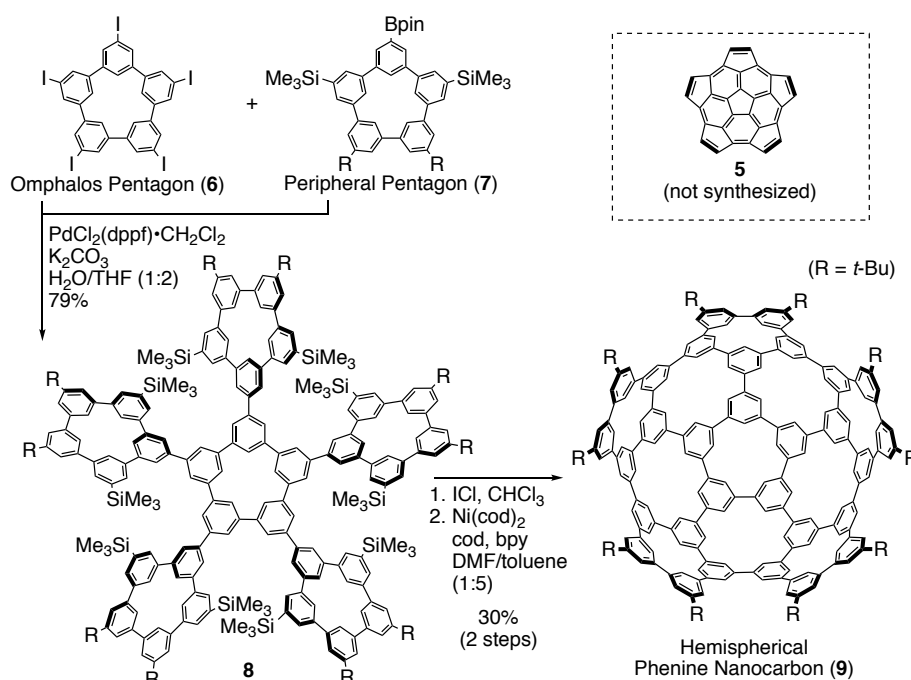


Figure 2. Pentagon-assembling strategy for the hemispherical phenine nanocarbon molecule.

ring-closure coupling at the periphery. The hemispherical molecule was fully identified by spectroscopy and crystallography. Only nine aromatic resonances in the ^1H NMR spectrum were observed to indicate a highly symmetric structure (Figure 2), whereas the crystal structure revealed an ovally deformed shape of the molecule (see Figure 3c). A small energy barrier of $0.12\text{ kcal mol}^{-1}$ for the structural fluctuations was indicated by theoretical calculations, confirming the time-averaged structure as the origins of simple NMR spectra.

Curved Phenine Normal Vectors

Geometric measures are indispensable to quantitatively evaluate the structural characteristics of molecules. For quantitative analysis of curved π -systems, the π -orbital axis vector (POAV) analysis has been established to describe the degree of nonplanarity of sp^2 -carbon atoms (Figure 3a). In this study, curved phenine normal vectors (CPNVs) were newly developed for quantitative geometric analyses of large, curved structures of phenine nanocarbons. Following POAV definitions (Figure 3a), CPNV (\mathbf{v}_p) is defined as a vector having equal angles (θ_{op}) to three radiating vectors ($\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3$) of three biaryl linkages (Figure 3b). Pyramidalization angles (θ) and dihedral angles (ϕ) were then shown as color mappings over the trigonal vertices and chemical bonds both for POAV and CPNV. Although POAV

analyses failed to disclose the origins of nano-scale curvature (see **D**), the CPNV analyses showed that contorted vertices at the central region (CPNV $\theta \sim 12^\circ$) decided the bowl shape. Comparisons of the CPNV analyses of **E** and **F** further revealed that the crystal structure was deformed by twists at biaryl linkages (Figure 3c).

Conclusion

Hoop-shaped and hemispherical phenine nanocarbon molecules were designed and synthesized by the assembly of hexagons and pentagons of [6]- and [5]CMPs. Their large and fluctuating structures were thoroughly revealed by a combination of spectroscopy, crystallography and theoretical calculations. In addition, a geometric measure, CPNV, was introduced to enable visual evaluations of structural characteristics of curved nanostructures. The polygon assembling strategy established in this study will serve as a groundwork for further exploration of a variety of unique curved nanocarbon molecules, such as a phenine analog of C_{60} .

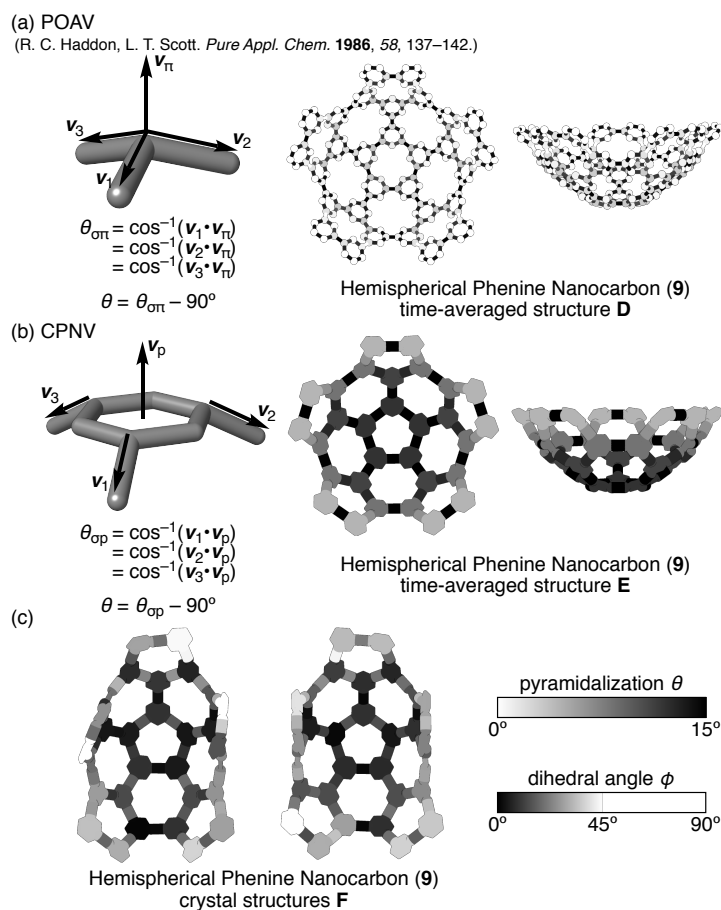


Figure 3. (a) POAV and (b) CPNV analysis of hemispherical phenine nanocarbon **9**. (c) CPNV analysis of the crystal structures of **9**.