

An obtuse-angled corner unit for fluctuating carbon nanohoops

Zhe Sun^{1,4}, Naoya Miyamoto², Sota Sato^{1,3}, Hidetoshi Tokuyama² and Hiroyuki Isobe^{1,3,4*}¹JST, ERATO, Isobe Degenerate π -integration Project and Advanced Institute for Material Research²Graduate School of Pharmaceutical Sciences, Tohoku University³Advanced Institute for Material Research and Department of Chemistry, Tohoku University⁴Department of Chemistry, The University of Tokyo

1 Introduction

The chemistry of carbon nanohoop is heavily relied on the devise of the corner unit to construct the macrocyclic structure. In preceding reports, the corner units commonly possessed directing angles of $\leq 90^\circ$, which enabled the macrocyclization of multiple units up to six. In this report, an obtuse-angled corner unit with oxanorbornadiene possessed a directing angle of 126° and thus allowed for the macrocyclization of larger structures with up to seven units. Structural studies with experimental and theoretical methods revealed a fluctuating structure with an intrinsic non-belt shape.[1]

2 Experiment

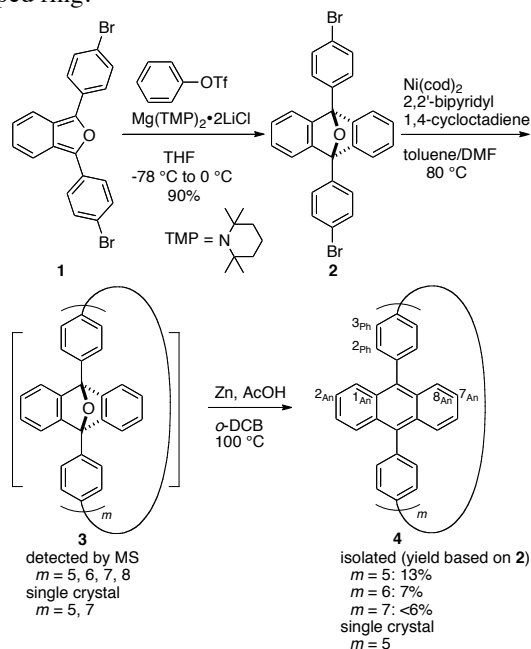
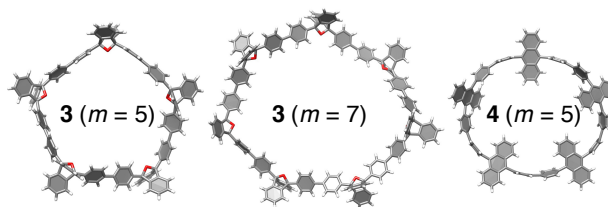
The synthesis of the $[n]$ CPP congeners **4** is shown in scheme 1. Benzyne generated from phenyl trifluoromethanesulfonate and magnesium amide $[\text{Mg}(\text{TMP})_2 \cdot 2\text{LiCl}]$ was adopted for the Diels-Alder reaction with bromophenylated isobenzofuran **1** to afford the corner unit **2** in a good yield.[2] The corner unit **2** was then subjected to the Ni-mediated, Yamamoto-type macrocyclization reaction. The aromatization reaction proceeded under reductive conditions using Zn/AcOH, and $[n]$ CPP congeners containing anthracenylene panels were obtained.

Single crystals of **3** ($m = 5, 7$) and **4** ($m = 5$) were obtained by diffusion of poor solvents (methanol or isopropanol) to the solution of the compounds in good solvents (dichloromethane or chloroform). A single crystal was mounted on a thin polymer tip with cryoprotectant oil and frozen at measurement temperature via flash-cooling. The diffraction analysis of a single crystal with a synchrotron X-ray source was conducted at -178°C at the beamline PF-AR NE3A at the KEK Photon Factory using a diffractometer equipped with an Dectris Pilatus 2M-F PAD detector.

3 Results and Discussion

The crystal structures of macrocycles revealed important structural features of **3** and **4**. As shown in Fig. 1, The directing angles embedded in the macrocyclic structures did not deviate from the original angle in the monomer (126°) and were, on average, 122° and 125° for 5-mer and 7-mer, respectively. Although naive considerations of the geometries may suggest that the directing angle of 126° should match better with internal angles of an equilateral heptagon (129°) than those of an equilateral pentagon (108°), the pentagonal 5-mer was obtained as the major product. To tolerate the mismatch,

the macrocycles possessed contorted structures in which *ipso* carbons and linking carbons were not on a flat plane: from a mean plane of *ipso* and linking carbons, the average distances of the carbon atoms from the plane were measured 1.13 and 1.45 Å for 5-mer and 7-mer **3**, respectively. Upon aromatization from **3** to **4**, the directing angles were widened by 40° to 162° on average, and the aromatized structure was found to be an oval-shaped ring.

Scheme 1: Synthetic route to $[n]$ CPP congeners **4**.Fig. 1: Crystal structures of **3** ($m = 5, 7$) and **4** ($m = 5$).

References

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* isobe@chem.s.u-tokyo.ac.jp