

Stereoisomerism in Nanohoops with Heterogeneous Biaryl Linkages of *E/Z*- and *R/S*- GeometriesParantap Sarkar¹, Zhe Sun^{1,2}, Toshiki Tokuhira³, Motoko Kotani^{1,4}, Sota Sato^{1,2} & Hiroyuki Isobe^{*,1,2,3}¹Advanced Institute for Material Research and Department of Chemistry, Tohoku University²JST, ERATO, Isobe Degenerate π -integration Project and Advanced Institute for Material Research³Department of Chemistry, The University of Tokyo⁴Mathematical Institute, Tohoku University

1 Introduction

Pervading all of chemistry, stereochemistry is an indispensable concept in any field allied with central science of molecules. When embedded in cyclic molecules, the stereochemistry results in an interesting stereoisomerism (cyclosteroisomerism) accompanying isomer degeneracies. The cyclosteroisomerism also emerges in hoop-shaped, sp^2 -carbon networks of cycloarylenes, called nanohoops, and gives rise to unique planar chirality in the persistent belt-shaped structures mimicking single-wall carbon nanotubes (SWNT). In this study, cyclosteroisomerism of a cyclophenanthrylene nanohoop ([8]CPhen_{3,9}) possessing both *E/Z*- and *R/S*-geometries has been clarified^[1]. Experimental investigations of the dynamic behavior of the [8]CPhen_{3,9} further revealed two-stage isomerization processes taking place separately at *E/Z*- and *R/S*-linkages.

2 Experiment

We synthesized [8]CPhen_{3,9} through a combination of several transformations. The stilbene **1**, synthesized via Perkin condensation was subjected to iodine-mediated, photochemical cyclization to afford a phenanthrene derivative **2**. Photochemical conversion of carboxylic acid to iodide with 1,3-diiodo-5,5-dimethylhydantoin was found applicable with **2** to synthesize 9-iodophenanthrene derivative **3**. After unsuccessful attempts of Ullmann coupling under several conditions, we found that a low-temperature condition in nitrobenzene allowed for the site-selective coupling reaction to give 9,9'-biphenanthrenyl derivative **4**. After furnishing 9,9'-biphenanthrenyl with boryl moieties via Miyaura borylation, Pt-mediated macrocyclization and subsequent reductive elimination were performed to afford [8]CPhen_{3,9} (Scheme 1).

A single crystal (ca. 0.10 × 0.07 × 0.01 mm³) suitable for X-ray analysis was obtained from slow diffusion of pentane into *o*-DCB solution of [8]CPhen_{3,9}. A single crystal was mounted on a thin polymer tip with cryoprotectant oil and frozen at -178 °C 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 a Dectris PILATUS 2M-F PAD detector.

3 Results and Discussion

As shown in Figure 1, the crystal structure of [8]CPhen_{3,9} existed as a racemate, and two enantiomeric

structures were determined. The dihedral angles measured with 4-3-3'-4' carbon atoms at the 3,3'-connections (*E,R,E,R,E,R,E,R*)-structure in Figure 1 were 141°, 149°, 166° and 166°, and those with 8a-9-9'-8a' atoms at the 9,9'-connections were -142°, -142°, -143° and -143° (see below for the descriptors and Figure 1 for the atom numbers). Thus, deviations from the coplanar biaryl orientations were 25° at the 3,3'-linkages and 38° at the 9,9'-linkages on average.

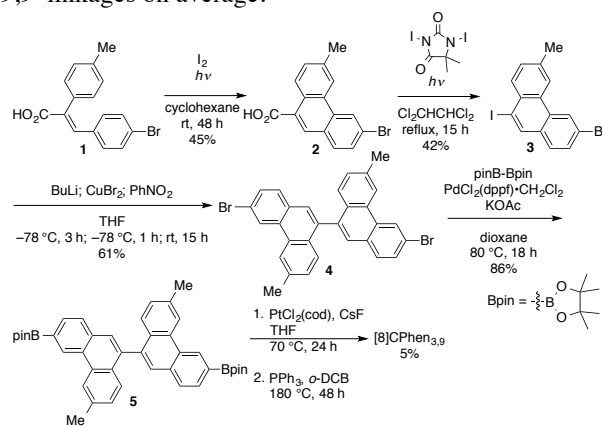
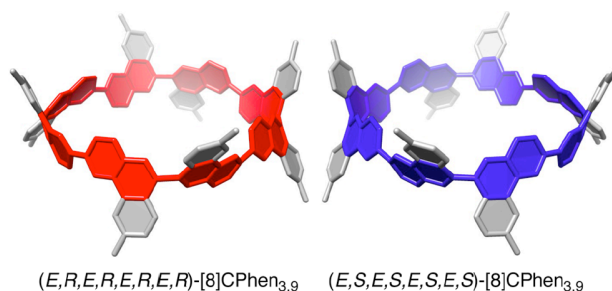
**Scheme 1:** Synthetic route to [8]CPhen_{3,9}.

Figure 1: Crystal structures of [8]CPhen_{3,9}. Naphthylene units identical with those of [8]CaNAP^[2] are colored in red and blue. A minor structural deviation of one phenanthrylene panel was found as a disordered structure, but the major structure with 83% occupancy was adopted as the representative structure for discussion.

References

- [1] P. Sarkar, Z. Sun, T. Tokuhira, M. Kotani, S. Sato, and H. Isobe, *ACS Cent. Sci.* **2**, 740 (2016).
- [2] Z. Sun, P. Sarkar, T. Suenaga, S. Sato and H. Isobe, *Angew. Chem. Int. Ed.* **54**, 12800 (2015).

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