AR-NE3A/2015G097

Stereoisomerism, crystal structures and dynamics of belt-shaped cyclonaphthylenes

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1 Introduction

The chemistry of belt-shaped cyclic array of aromatic panels has increasingly attracted much interest. However, the structural chemistry such as the origin of the belt rigidity has not been clarified. Previously, we disclosed that the belt-shaped structure is realized by linking the biaryl units with methylene moieties in a cyclonaphthylene molecule [1]. In this report, with a series of cyclonapthylenes with various size, we demonstrate that the arylene rotation depends on the hoop size [2].

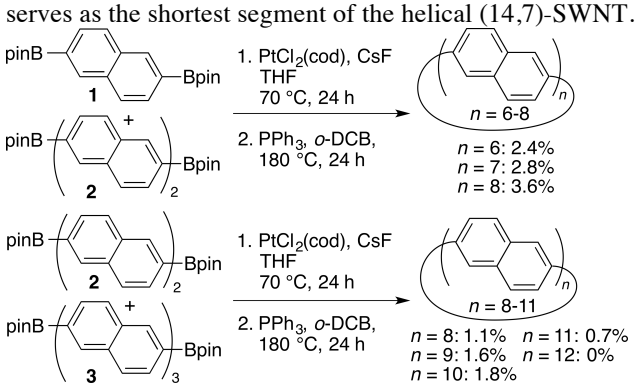
2 Experiment

We synthesized six congeners of [*n*]CaNAP with *n* = 6-11 from two sets of macrocyclization reactions. A similar random synthesis route has been investigated by Yamago to synthesize six [*n*]CPP congeners with *n* = 8-13 *via* a combination of double-panel biphenyl and triple-panel terphenyl precursors [3]. In this study, we prepared three different precursors, naphthalene **1**, binaphthyl **2** and ternaphthyl **3**, and examined two different combinations in the Pt-mediated macrocyclization of diborylated precursors). A combination of single- and double-panel precursors, **1** and **2**, afforded three [*n*]CaNAP congeners with *n* = 6-8 *via* Pt-mediated macrocyclization and subsequent reductive elimination reactions (Scheme1).

A single crystal (ca. 0.13 × 0.04 × 0.02 mm^3) suitable for X-ray analysis was obtained from evaporation of isopropanol and dichloromethane solution of [7]CaNAP. 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 Fig. 1, Six distinct structures of [7]CaNAP were found in two sets of disordered structures in the single crystal grown in a mixture of isopropanol and CH_2Cl_2. In the first disorder set, the major structure of 52%-occupancy was an a^6b^1-conformer and the minor structure of 48%-occupancy was an a^7-conformer. In the second disorder set, four structures of a^6b^1-, b^7-, a^7- and a^1b^6-conformers were located at the occupancies of 33%, 25%, 21% and 21%, respectively. Possessing belt shapes with sp^2-carbon networks, the structures can also be designated with the chiral indices SWNT: a^6b^1/a^1b^6-conformers are (13,8), and a^7/b^7-conformers are (14,7). The bond-filling and atom-filling indices of the a^7/b^7-conformers were 100%, which shows that the structure serves as the shortest segment of the helical (14,7)-SWNT.



Scheme 1: Synthetic route to [n]CaNAPs (n = 6-11).

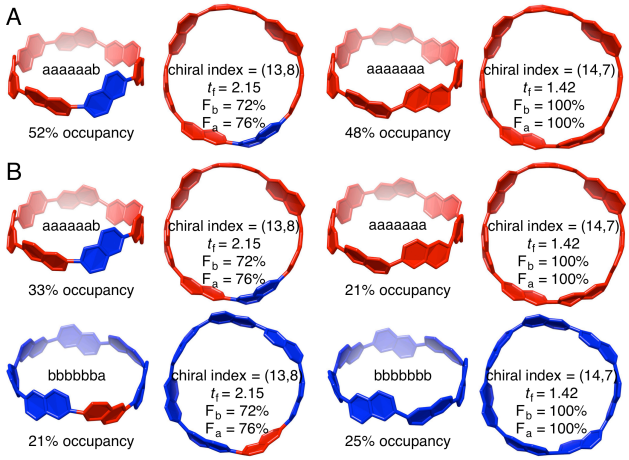


Fig. 1: Crystal structures of [7]CaNAP found in (A) the first disordered structure and (B) the second disordered structure.

References

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