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Belt-Shaped Cyclonaphthylenes

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1 Introduction

The chemistry of cyclophenylenes is enjoying its renaissance while the development of its naphthalene counterpart, cyclonaphthylene, is lagged far behind. Among merely two examples of cyclonaphthylenes in literature, namely [n]CNAP [1] and [9]CN [2], neither has retained a belt-shape that resembles the tubular structure of single-wall carbon nanotubes (SWNTs). Herein, we report a new congener in cyclonaphthylene family linked at 2,6-positions of the naphthalene, namely u-[8]CaNAP (scheme 1), with its belt-shape structure revealed in the crystalline phase. [3]

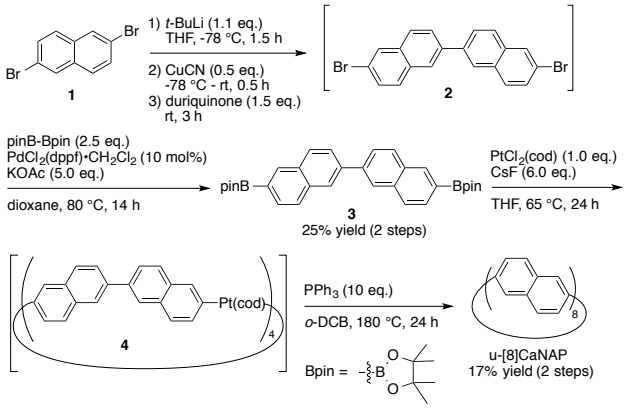
2 Experiment

The synthesis of u-[8]CaNAP is outlined in Scheme 1. 6,6'-Dibromo-2,2'-binaphthyl (**2**) was synthesized by a coupling reaction of 2,6-dibromonaphthalene (**1**) with CuCN/duroquinone through monolithiation. Without further isolation of 2, Miyaura borylation with pinB-Bpin was carried out with $PdCl_2(dppf)•CH_2Cl_2$/KOAc to afford **3** in 25% yield for 2 steps. The macrocyclization was then performed in a two-step sequence, firstly, a square-shaped complex **4** was formed by treating **3** with $PtCl_2(cod)$ and CsF, without purification, **4** was then subjected to reductive elimination by heating with PPh_3. The target compound u-[8]CaNAP was obtained in 17% yield from **3** and purified by preparative HPLC with cholester column.

A single crystal (ca. 0.14 × 0.02 × 0.01 mm^3) suitable for X-ray analysis was obtained from slow diffusion of either isopropanol or hexane into chloroform solution. The 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 crsytal 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 ADSC Q270 CCD detector.

3 Results and Discussion

As shown in Fig. 1, two diastereomers were identified as disordered structures in each of the solvent system used for crystal growth. The structure from isopropanol/$CHCl_3$ was found to be aaaabbab with 70% occupancy and aaaaaabb with 30% occupancy, while from hexane/$CHCl_3$ system, it appeared to be aaabbaab with 48% occupancy and aaaaaabb with 52% occupancy. Due to their tubular nature, the chiral indexes of (13,11) and (14,10) were assigned to them, indicating the molecular structures are chiral and helical. As a result, *P* and *M* enantiomers emerged and they were found to pack alternatively in the crystal structure. All of the structures were slightly distorted to an oval form with the major and minor diameters measured form carbon atoms on opposite sides to be 1.7 and 1.6 nm, which are consistent with those expected for SWNTs.



Scheme 1: Synthetic route to u-[8]CaNAP.

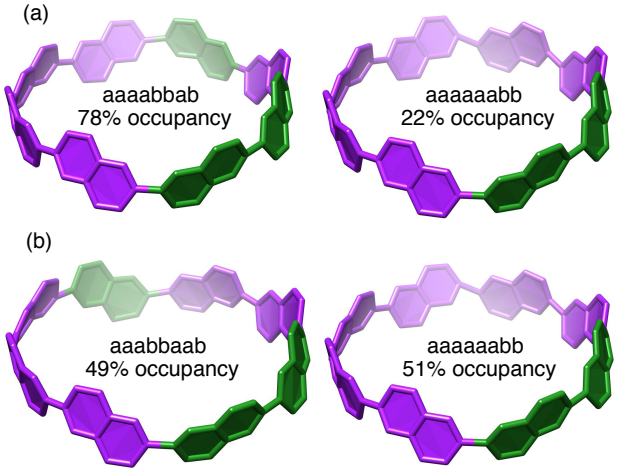


Fig. 1: Crystal structures found in (a) a single crystal grown from isopropanol/$CHCl_3$ and (b) a single crystal grown from hexane/$CHCl_3$.

References

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