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Synthesis and Racemization Process of Chiral Carbon Nanorings: A Step toward the Chemical Synthesis of Chiral Carbon Nanotubes

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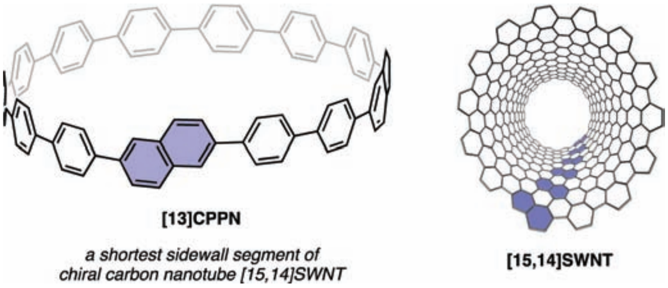
ABSTRACT



A simple and realistic model for the shortest sidewall segments of chiral single-walled carbon nanotubes (SWNTs) has been designed, and one of the chiral carbon nanorings, cyclo[13]paraphenylene-2,6-naphthylene ([13]CPPN, 1) has been successfully synthesized. DFT calculations reveal that the racemization energy of 1 is 8.4 kcal·mol^{-1}. In addition, some important energetic values, such as racemization barriers and strain energies, of other chiral carbon nanorings have been systematically estimated for future molecular design.

Currently, single-walled carbon nanotubes (SWNTs) can only be produced as mixtures in terms of diameter and chirality (armchair, chiral, or zigzag). Therefore, the selective and predictable synthesis of structurally uniform SWNTs has been recognized as a Holy Grail in both nanocarbon chemistry and synthetic chemistry. As proposed by Scott[1] and others,[2] the synthesis of SWNTs through a controlled growth process using a small hydrocarbon template is a logical strategy for providing structurally uniform SWNTs.[3] In order for this template strategy to be enlisted into service, it is necessary to rationally design and synthesize a small hydrocarbon template that corresponds to the target structure of SWNTs (Figure 1).[1,4]

Depending on the way a graphene sheet is rolled up (starting and end points of chiral vector), SWNTs can form armchair, chiral, and zigzag structures. Given that the electric properties of SWNTs are primarily determined by the sidewall structures (metallic for armchair structures and semiconducting for most zigzag and chiral structures), electrical uniformity is critically important for SWNT-based electronics.[5] Recently we have established a modular

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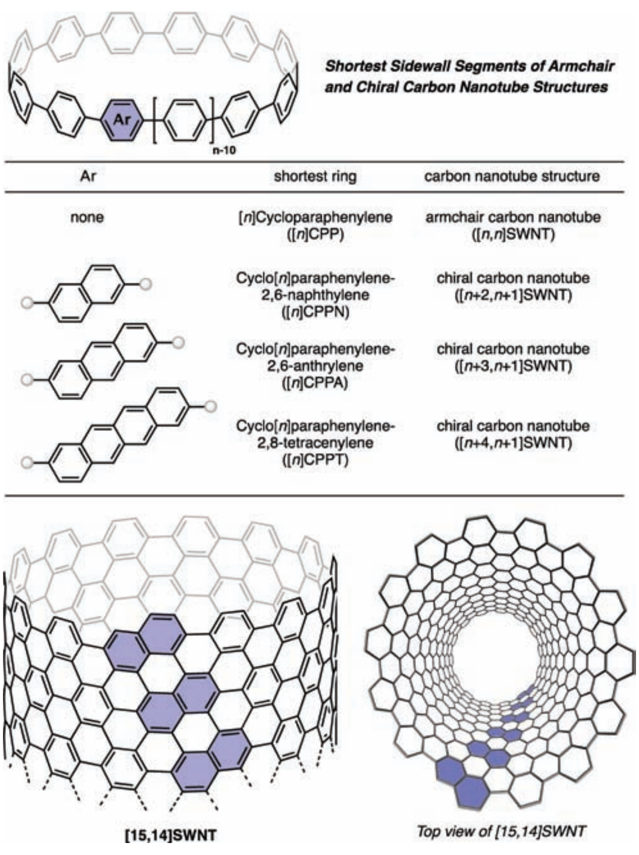

Figure 1. Armchair/chiral carbon nanotubes and their shortest sidewall segments.

and ring-size-selective synthesis of [*n*]cycloparaphenylenes ([*n*]CPPs),[6−10] which represent the shortest sidewall segments of [*n*,*n*]SWNTs (armchair SWNT structures) (Figure 1).[11−13] We now report on the design and the first synthesis of a shortest chiral SWNT structure (chiral carbon nanoring). In addition, a unique racemization process of chiral carbon nanorings has been uncovered by DFT calculations.

Our design of chiral carbon nanorings is straightforward, inserting an acene unit into [*n*]CPP structures. For example, when inserting a naphthalene unit with 2,6-linkage, the resulting cyclo[*n*]paraphenylene-2,6-naphthylene ([*n*]CPPN) will become the shortest segment of an [$n + 2$, $n + 1$]SWNT (Figure 1). Similarly the incorporation of anthrylene-2,6-diyl ([*n*]CPPA) and tetracenylene-2,8-diyl ([*n*]CPPT) will result in the shortest segments of an [$n + 3$, $n + 1$]SWNT and an [$n + 4$, $n + 1$]SWNT, respectively. By inserting these acenes with appropriate linkages, all possible chiral structures of SWNTs can be created. In this work, we report the synthesis of [13]CPPN (**1**), which is the shortest segment of [15,14]SWNT, as a proof-of-principle study (Figure 1).

Following our previous CPP synthesis,[6,7] we synthesized **1** by using L-shaped *cis*-1,4-dihydroxycyclohexane-1,4-diyl to attenuate the buildup of strain energy during the macrocyclization as well as its benzene-convertible nature (Scheme 1). Thus, the 2:1 cross-coupling reaction of L-shaped dibromide **2** and 2,6-diborylated naphthalene **3** occurred in the presence of a $Pd(PPh_3)_4$ catalyst, Na_2CO_3, and n-Bu_4NBr in THF/H_2O to furnish naphthalene-inserted U-shaped dibromide **4** in 72% yield. Compound **3** was synthesized by treating 2,6-dibromonaphthalene with bis(pinacolato)diboron in the presence of a $PdCl_2$(dppf) catalyst and KOAc in DMSO (91%).[14,15] The counterpart U-shaped diboronate **5** was prepared by the Pd-catalyzed 2:1 cross-coupling of **2** and benzene-1,4-diboronic acid, followed by the Pd-catalyzed borylation of the thus-formed dibromide.[7] These U-shaped units **4** and **5** were then cross-coupled in the presence of a $Pd_2(dba)_3$/X-Phos catalyst[15,16] and K_3PO_4 in 1,4-dioxane/H_2O to afford the macrocycle **6** in 35% yield. Finally, the treatment of **6** with $NaHSO_4 \cdot H_2O$ in refluxing *m*-xylene/DMSO under air afforded the target [13]CPPN (**1**) in 25% yield. The structure of **1** was confirmed by ^{1}H NMR, ^{13}C NMR, HH COSY, and MALDI-TOF MS.

Chiral carbon nanorings such as [13]CPPN (**1**) possess helical chirality (e.g., **(*P*)-1** and **(*M*)-1** for **1**; Scheme 2), corresponding to the helical chirality of chiral SWNTs. The racemization of chiral carbon nanorings occurs via the rotation of the inserted acene unit (naphthalene for **1**) around the two C−C bonds that connect it to the neighboring benzene units. For the future realization of enantioselective synthesis of chiral SWNTs, it is important to know the

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(15) dppf = 1,1′-bis(diphenylphosphino)ferrocene. dba = dibenzylideneacetone. X-Phos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

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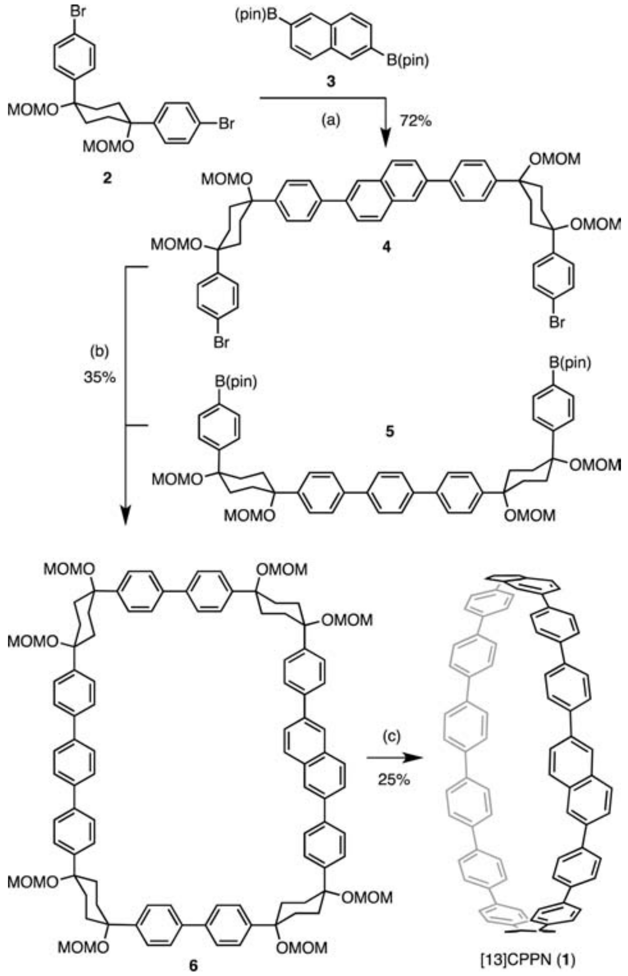
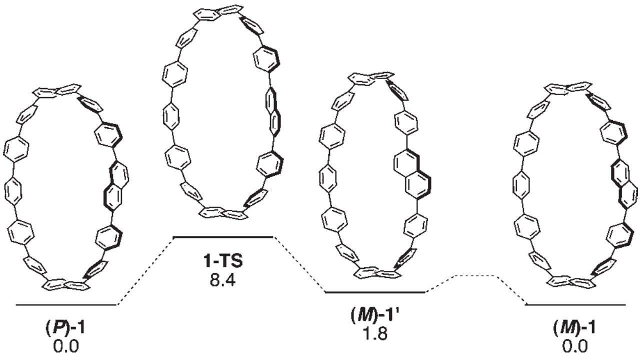
Scheme 1. Synthesis of [13]CPPN (**1**)[a]



[a] Conditions: (a) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$, *n*-Bu$_4$NBr, THF/H$_2$O, 60 °C; (b) Pd$_2$(dba)$_3$, X-Phos, K$_3$PO$_4$, 1,4-dioxane/H$_2$O, 80 °C; (c) NaHSO$_4$·H$_2$O, *m*-xylene/DMSO, reflux under air.

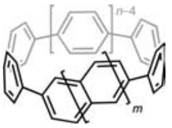
racemization process of chiral carbon nanorings. Therefore, we began by investigating the racemization of **1** using theoretical calculations at the B3LYP/6-31G(d) level of theory. The racemization pathway from **(*P*)-1** to the corresponding enantiomer **(*M*)-1** is shown in Scheme 2. The structure **(*P*)-1**, in which all benzene and naphthalene units are alternately twisted, has the lowest energy among other local minima. Preference for the all-alternating structure is similar to the case of even-numbered [*n*]CPPs.[10] The naphthalene unit and the two neighboring benzene units are perpendicularly aligned (two dihedral angles are ca. 90°) in the transition state (**1-TS**), and the Gibbs free energy of **1-TS** is 8.4 kcal·mol^{-1} higher than that of **(*P*)-1**. Before settling to **(*M*)-1** from **1-TS**, we identified that there exists a local minimum structure **(*M*)-1′**. As a similar rotation in the smaller nanoring [12]CPP occurs with a barrier of 3.8 kcal·mol^{-1} (via the TS with 0° of dihedral angle),[10] the rotation of benzene units for the isomerization of **(*M*)-1′** to **(*M*)-1** should take place through a transition state that is lower in energy than **1-TS**. These results clearly implicate that **1** undergoes rapid racemization at ambient temperature.

Scheme 2. Racemization Pathway from **(*P*)-1** to **(*M*)-1** ($\Delta G^{\ddagger}$, kcal·mol^{-1})



We then calculated the racemization barriers ($\Delta G^{\ddagger}$) of other chiral carbon nanorings, [*n*]CPPN, [*n*]CPPA, and [*n*]CPPT (*n* = 5–13), in order to clarify the effect of ring size and acene unit of the nanorings (Table 1). Although there are small upsets in the racemization energies of [13]CPPN/[12]CPPN and [13]CPPA/[12]CPPA,[17] the $\Delta G^{\ddagger}$ value generally increases (i) as the number of benzene units decreases (as the ring size decreases) or (ii) as the acene unit becomes larger. The transition state for [5]CPPT could not be modeled due to huge ring strain.

Table 1. Racemization Barriers of Chiral Carbon Nanorings[a]



Number of benzene units (*n*)	[*n*]CPPN (*m* = 1)	[*n*]CPPA (*m* = 2)	[*n*]CPPT (*m* = 3)
5	29.6	45.5	–
6	21.2	31.3	44.0
7	17.4	25.7	33.0
8	13.5	19.5	26.3
9	12.5	16.5	21.3
10	9.8	13.5	17.9
11	9.7	12.3	15.4
12	7.7	9.8	12.5
13	8.4	10.0	11.9

[a] $\Delta G^{\ddagger}$/kcal·mol^{-1}, B3LYP/6-31G(d).

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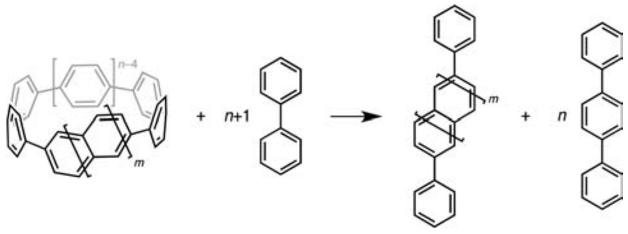
(17) The racemization processes of chiral carbon nanorings having even-number benzene units are slightly different from that of **1**. See the Supporting Information for details.

(18) A homodesmotic reaction is a reaction in which reactants and products contain equal numbers of carbon atoms in corresponding states of hybridization. Moreover, there is matching of the carbon–hydrogen bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. (a) Minkin, V. I. *Pure Appl. Chem.* **1999**, *71*, 1919. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

Table 2. Strain Energies of Chiral Carbon Nanorings Estimated by Hypothetical Homodesmotic Reactions[a]



Number of benzene units (n)	[n]CPPN ($m = 1$)	[n]CPPA ($m = 2$)	[n]CPPT ($m = 3$)
5	89.9	84.4	78.8
6	78.8	75.3	69.3
7	68.8	65.5	62.4
8	62.4	59.1	56.2
9	55.5	53.3	51.2
10	51.4	49.2	47.1
11	46.5	44.9	43.4
12	43.7	42.8	41.4
13	39.9	38.7	37.6

[a] ΔH/kcal·mol^{-1}, B3LYP/6-31G(d).

In addition to the racemization barriers we also estimated the strain energies of these chiral carbon nanorings by DFT calculations. The strain energies were calculated based on the hypothetical homodesmotic reactions,[18] where chiral carbon nanorings and biphenyl are converted to the corresponding linear diphenylacenes and terphenyl (Table 2). Judging from the obtained strain energies (37.6–89.9 kcal·mol^{-1}), the chiral nanorings listed in Table 2 could exist as stable molecules. It should also be mentioned that these strain energies are in the range of those of [6]CPP to [16]CPP. Based on these studies, we are now in a position to rationally design and synthesize a chiral carbon nanoring with target racemization aptitude.

In summary, we have designed a simple and realistic model for the shortest sidewall segments of chiral SWNTs and successfully synthesized one of the chiral carbon nanorings, cyclo[13]paraphenylene-2,6-naphthylene ([13]CPPN, **1**). DFT calculations reveal that the racemization energy of **1** is 8.4 kcal·mol^{-1}. In addition, some important energetic values, such as racemization barriers and strain energies, of other chiral carbon nanorings ([*n*]CPPN, [*n*]CPPA, and [*n*]CPPT) have been systematically estimated for future molecular design. In view of the simplicity, reliability, and modularity, it is likely that our synthetic methodology will be applicable to a range of chiral carbon nanorings. The chirality-controlled synthesis of chiral SWNTs using chiral carbon nanorings as a template are currently ongoing in our laboratory.

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Supporting Information Available. Experimental procedures, characterization data for all new compounds, and details of computational study. This material is available free of charge via the Internet at http://pubs.acs.org.