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Synthesis and Properties of [9]Cyclo-1,4-naphthylene: A π-Extended Carbon Nanoring

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Supporting Information

ABSTRACT: The first synthesis of a π-extended carbon nanoring, [9]cyclo-1,4-naphthylene ([9]CN), has been achieved. Careful structure−property analyses uncovered a number of unique features of [9]CN that are quite different from those of [9]CPP, a simple carbon nanoring.

After many years of efforts,[1,2] the long-awaited chemical synthesis of cycloparaphenylene (CPP), a simple conjugated carbon nanoring consisting solely of benzene rings with para linkages (Figure 1), has been accomplished by the groups of Bertozzi,[3] Itami,[4−8] Yamago,[9,10] and Jasti.[3,11] Currently, the modular,[6] size-selective,[4,6,9,11] and scalable[7,8] synthesis of [*n*]CPPs is possible, and [12]CPP, prepared by the procedure developed in our group, has become commercially available.[12] CPP is an interesting and unique molecular entity not only because of its aesthetic appeal,[7] unique cyclic and curved conjugation,[5] photophysical properties,[3,10,11] and guest-encapsulating properties[7,8,13] but also because it represents the shortest sidewall segment of armchair carbon nanotube structures.[2] In relation to these studies, the groups of Itami[14] and Isobe[15] recently reported the design and synthesis of short sidewall segments of "chiral" carbon nanotubes.

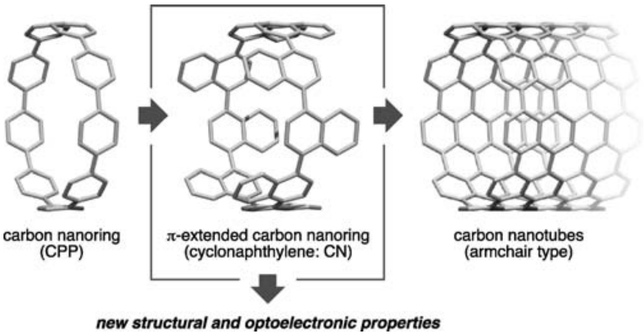

Figure 1. π-Extended carbon nanoring and related materials.

An important next step based on these fundamental studies is the synthesis of π-extended carbon nanorings, which would allow the elucidation of the structural and electronic effects present in the π systems of carbon nanorings (Figure 1). In addition, we expect these π-extended carbon nanorings to be closer precursors of carbon nanobelts[16] and tubes.[17] Herein we report the first successful synthesis of [9]cyclo-1,4-naphthylene ([9]CN) using a Ni-mediated "shotgun" macrocyclization as the key reaction. Interesting structural and photophysical properties of [9]CN are also presented in this paper.

We selected cyclo-1,4-naphthylene (CN),[18] a ring-shaped molecule with 1,4-naphthylene units (Figure 1), as the first target in our campaign to prepare π-extended carbon nanorings. Obviously, the challenge of synthesizing CN lies in the increased strain energy that results from ring closure, as in the case of CPP. For example, the strain energy of [9]CN was estimated to be 50.8 kcal·mol^{-1} by DFT calculations [see the Supporting Information (SI) for details].[19] Encouraged by the previous successful CPP syntheses using a cyclohexadiene (Bertozzi/Jasti)[3,11] or cyclohexane (Itami)[4−8] ring as a bent benzene-convertible unit, we envisioned that a *cis*-1,4-dinaphthyl-1,4-dihydronaphthalene derivative should function as a ternaphthalene-convertible L-shaped unit in the synthesis of CN (Figure 2). We decided to focus on a Ni-mediated shotgun macrocyclization[7,8] to assemble the corresponding L-shaped dibromide units (Figure 2).

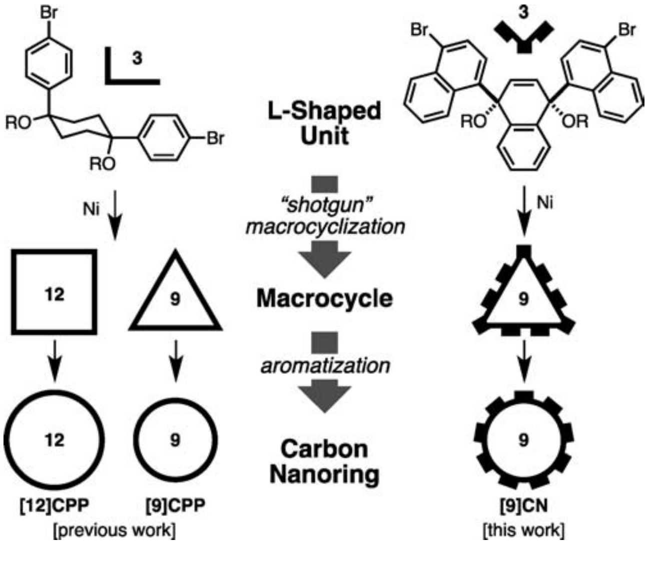

Figure 2. Our strategy for the synthesis of carbon nanorings.

The outcome of our extensive investigations based on this strategy is the first synthesis of [9]CN, which is shown in Scheme 1. The synthesis began with the preparation of the naphthalene-containing L-shaped unit. Thus, 1,4-dibromonaphthalene was treated with *n*-butyllithium to produce 1-bromo-4-

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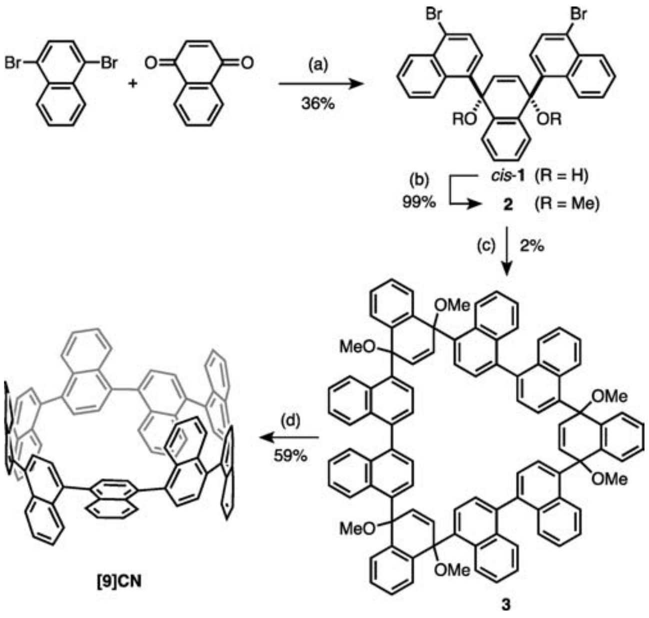
Scheme 1. Synthesis of [9]CN[a]



[a]Reaction conditions: (a) (i) 1,4-Dibromonaphthalene, *n*-BuLi, Et_2O, −78 °C; (ii) 1,4-naphthoquinone, −78 °C to rt. (b) MeI, NaH, THF, 54 °C. (c) $Ni(cod)_2$, 2,2′-bipyridyl, DMF, 85 °C. (d) Li (granular), THF, rt.

lithionaphthalene, which was then reacted with 1,4-naphthoquinone. This double nucleophilic addition yielded the desired cis-configured diol (*cis*-**1**) in 36% yield, along with undesired *trans*-**1** (13%). The stereoselectivity of double addition was determined to be 3:1 (cis/trans) by ^{1}H NMR spectroscopy. To facilitate further synthetic operations, *cis*-**1** was treated with MeI and NaH to give the methoxy-substituted L-shaped dibromide **2**.

The configurations of these molecules were unambiguously confirmed by X-ray crystallography. For example, a suitable single crystal was obtained by slow vapor diffusion of *n*-pentane into a THF solution of **2** at room temperature. In the solid state, the included angle between the two 1-(4-bromo)naphthyl groups of **2** is ca. 71° (see the SI for details). This value is somewhat smaller than that in the cyclohexane-based L-shape unit used in the synthesis of CPPs (ca. 80°). Thus, at this point we predicted that the macrocyclization of monomer **2** would produce the cyclic trimer preferentially.[20] In line with this assumption, the strain energy of the cyclic trimer was estimated by DFT to be only 1.4 kcal·mol^{-1} (see the SI for details).

With the requisite L-shaped monomer **2** in hand, we next investigated the Ni-mediated shotgun macrocyclization of **2** to produce the macrocycle in a single operation.[21,22] Treatment of **2** (1.0 equiv, 8.3 mM) with $Ni(cod)_2$ (2.2 equiv) and 2,2′-bipyridyl (2.2 equiv) in DMF at 85 °C furnished the cyclic trimer **3** in 2% isolated yield after extensive purification using preparative recycling gel-permeation chromatography and preparative thin-layer silica gel chromatography (Scheme 1). It should be noted that no other macrocyclic compound was identified, although many linear oligomers were generated. No reaction occurred under more diluted conditions (1.0 mM **2**), and polymerization became predominant at higher concentrations (64 mM **2**). In the final step of the synthesis, reductive aromatization of macrocycle **3** was investigated. Although a number of reductive conditions such as the use of $SnCl_2$, lithium naphthalenide,[3] or a lithium dispersion were unsuccessful, we found that treating **3** with granular lithium in THF at room temperature successfully afforded [9]CN in 59% yield as a yellow powder (Scheme 1).

The ^{1}H NMR spectrum of [9]CN in THF-d_8 is shown in Figure 3b. Contrary to the simple one-singlet spectra observed for CPPs, many signals appeared in the aromatic region, with one characteristic singlet at high magnetic field (6.28 ppm). We further found that these signals coalesced to three broadened signals (7.03, 7.66, and 8.47 ppm) when a DMSO-d_6 solution of [9]CN was heated to 150 °C. When the heated sample was cooled back to room temperature, we observed a spectrum identical to that acquired before heating. These measurements indicated that the ground-state structure of [9]CN has low symmetry and that the dynamic conformational change (arene rotation) of [9]CN is slow on the NMR time scale at room temperature. Furthermore, we were able to assign these groups of signals to the 2,3- (red), 5,8- (green), and 6,7-positions (blue) of the naphthalene units (Figure 3b) using HH COSY, NOESY, and HMQC methods.

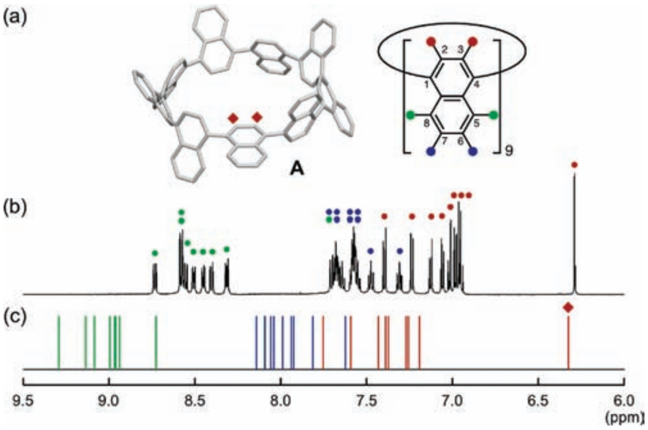


Figure 3. (a) Optimized structure of [9]CN depicted with wireframe. (b) ^{1}H NMR spectrum of [9]CN in THF-d_8. (c) ^{1}H NMR chemical shifts of [9]CN calculated at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level in THF with $SiMe_4$ (0.0 ppm) as a reference.

To gain insight into the structural properties of [9]CN, structure optimization and GIAO calculations on [9]CN were performed. In the most stable conformation of [9]CN, **A** (Figure 3a), all of the pendant fused arenes are located outside the circumference of the nanoring. Since **A** has C_2 symmetry, the 27 H atoms of [9]CN are magnetically nonequivalent. The result of the GIAO calculation on **A** at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level in THF with $SiMe_4$ (0.0 ppm) as a reference is shown in Figure 3c, where the H atoms at the 2,3-, 5,8-, and 6,7-positions of the naphthalene units are colored in red, green, and blue, respectively. Although all the calculated chemical shifts were higher than those observed, the three sets of signals corresponding to these positions (8:18:1) were reproduced quite accurately. The characteristic high-field-shifted singlet signal is assigned to the hydrogens at the 2,3-positions indicated by red diamonds in Figure 3a. The upfield shift of these inner hydrogen atoms should be ascribed to the ring current of the neighboring naphthalene rings.

The striking structural difference between [9]CN and [9]CPP is notable (Figure 4). Because of the sterically demanding naphthyl groups, the average dihedral angle

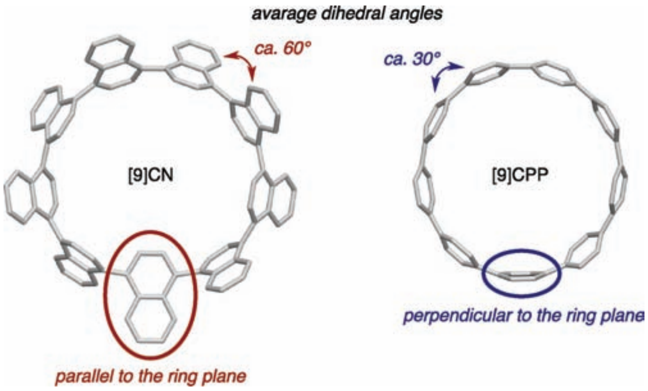


Figure 4. Comparison of the optimized structures of [9]CN and [9]CPP.

between neighboring naphthalene rings in [9]CN is considerably larger (ca. 60°) than in [9]CPP (ca. 30°). Moreover, because these nanorings are both odd-numbered cycloarylenes, it is not possible for all of the arene rings to be alternately twisted; one helical moiety has to be generated in the structure.[5] As a result, one benzene ring in [9]CPP is aligned perpendicular to the plane of the nanoring (Figure 4). In contrast, one naphthalene ring in [9]CN is parallel to the nanoring plane as a result of the larger dihedral angles.

Even more interestingly, it was revealed that [9]CN is inherently a unique chiral molecule according to these structural features. Thus, we investigated the racemization pathway and the activation energy for racemization using DFT [B3LYP/6-31G(d)] to uncover the dynamic behavior of [9]CN (Figure 5). For comparison, we also calculated the racemization process of 1,1′-binaphthyl at the same level of theory.[23] As shown in Figure 5, there are two twisting modes of racemization for 1,1′-binaphthyl between the ground state **C** and its enantiomer **C***: in the higher-energy transition state (**TS1**), the 8- and 8′-hydrogens come close, and in the lower-energy transition state (**TS2**), the 2- and 8′-hydrogens come close. In the case of [9]CN, transition states with similar rotation modes were also identified. One is the transition state for the racemization of [9]CN between the most stable conformation **A** and its enantiomer **A*** ($\mathbf{TS_{rac}}$, blue/green), and the other is that for the isomerization of **A** to conformation **B** ($\mathbf{TS_{AB}}$, green/orange). Very interestingly, it was found that these barriers to interconversion for [9]CN (19.9/21.4 kcal·mol^{-1}) are lower than those for 1,1′-binaphthyl (34.3/25.4 kcal·mol^{-1}). These relatively lower barriers to arene rotation most likely stem from the ring strain of [9]CN. In the transition-state structures ($\mathbf{TS_{rac}}$ and $\mathbf{TS_{AB}}$), the bending enforced by the ring structure alleviates C−H/C−H eclipsing interactions. Although the experimental determination of the racemization barrier by using chiral HPLC or NMR spectroscopy was unsuccessful, a unique effect of ring strain on the rotation mode of the 1,1′-binaphthyl moiety was uncovered from these studies.

Finally, the photophysical properties (UV−vis and fluorescence) of [9]CN in chloroform were measured (Figure 6,

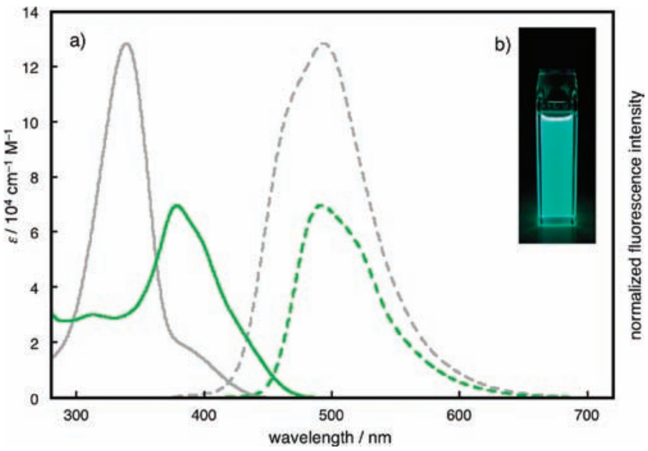


Figure 6. (a) UV−vis absorption (solid lines) and fluorescence spectra (dashed lines) of [9]CN (green) and [9]CPP (gray). (b) Green fluorescence emission of [9]CN (1.12 × 10^{-6} M in chloroform solution).

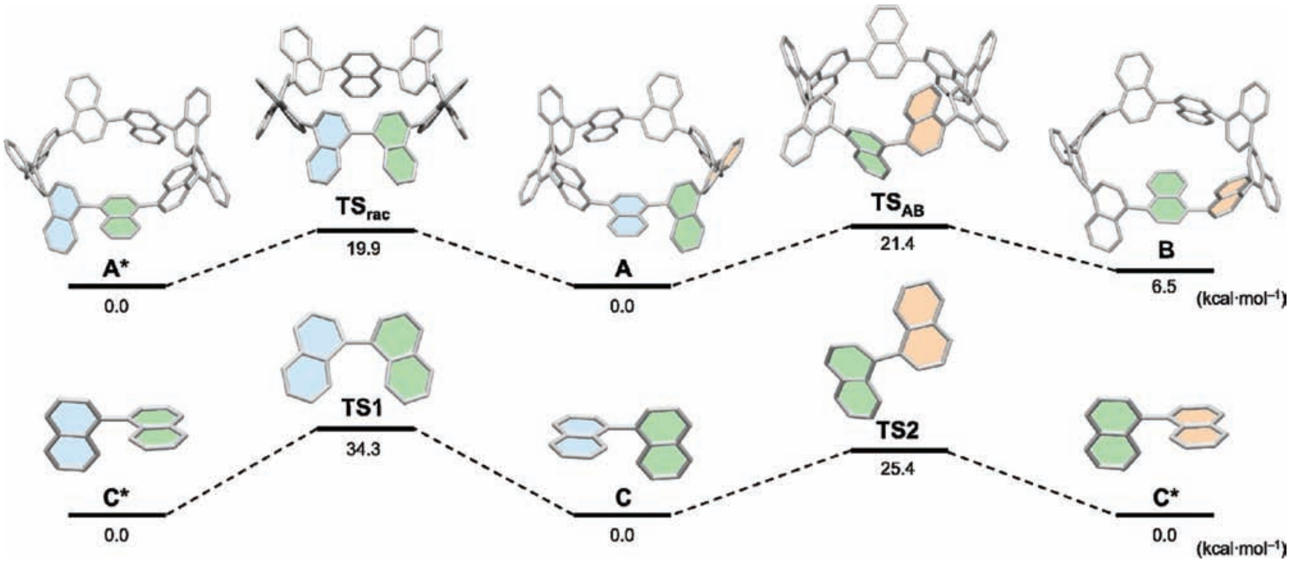


Figure 5. Rotation pathways of (top) [9]CN and (bottom) 1,1′-binaphthyl. Values are relative Gibbs free energies (ΔG) at 298.15 K and 1 atm calculated at the B3LYP/6-31G(d) level. The symbol * represents the enantiomer of the corresponding structure.

green lines). For comparison, the spectra of [9]CPP (gray lines) are also depicted in Figure 6. In the UV−vis spectrum of [9]CN, the absorption maximum (λ_{abs}) was observed at 378 nm with a molecular absorption coefficient (ε) of 6.8×10^4 cm^{-1} M^{-1}. The shape of the spectrum implies that several distinct electronic transitions overlap in the higher-wavelength region above 378 nm. To determine the nature of the excitation of [9]CN, a TD-DFT study was performed at the B3LYP/6-31G(d) level. The molecular structure, spatial distribution, and energies of the representative frontier molecular orbitals (FMOs) of conformer **A** of [9]CN are shown in the SI. It was found that λ_{abs} corresponds to the HOMO−1 → LUMO and HOMO → LUMO+1 π−π^* transitions (431 nm, f_{calc} = 0.823), whereas the HOMO → LUMO transition occurs at a longer wavelength (472 nm) with weak oscillator strength (f_{calc} = 0.165) (see the SI for details). There is a clear red shift in the absorption of [9]CN in comparison with that of [9]CPP, which should be ascribed to the π extension of the arene units. Nevertheless, the fluorescence maxima (λ_{em}) of [9]CN (491 nm) and [9]CPP (494 nm) were found to be quite similar. The absolute fluorescence quantum yield (Φ_F) of [9]CN was determined to be 0.35 using a calibrated integrating sphere (average of 7 measurements).

In summary, the first synthesis of a π-extended carbon nanoring, [9]cyclo-1,4-naphthylene ([9]CN), has been achieved. A nickel-mediated "shotgun" cyclotrimerization of L-shaped units successfully provided a macrocycle that was transformed to [9]CN by reductive aromatization. Careful structure analysis uncovered a number of unique structural features of [9]CN, such as large dihedral angles, slow arene rotation, chirality, and a racemization process, that are quite different from those of [9]CPP, a simple carbon nanoring. Due in part to the π-extension of arene unit, [9]CN has an absorption maximum at a longer wavelength and luminesces with a smaller Stokes shift in comparison with [9]CPP. The synthesis of a series of π-extended carbon nanorings and their transformations to the corresponding carbon nanobelts and nanotubes are the focus of ongoing work in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization of data for all new compounds, crystallographic data for *trans*-**1** and **2** (CIF), and details of photophysical and computational studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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