Cycloarylenes

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# Belt-Shaped Cyclonaphthylenes

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***Abstract:*** *The recent development of cyclo-para-phenylenes has demonstrated the feasibility of radial π systems in nanohoop structures, especially in the crystalline state. However, in contrast to macrocyclic molecules with benzene units, which have a several-decades-long history, macrocycles composed solely of naphthylene units (the smallest acene) have been much less explored. Although two examples of cyclonaphthylenes have been reported to date, neither possesses a radial π system. We herein report the first example of belt-shaped cyclonaphthylenes with curved π systems. The molecule, [8]cyclo-amphi-naphthylene, is linked at the 2,6-positions of the naphthylene units, thus affording belt-shaped molecules. Although the molecular structures are flexible, which allows for rotation of the naphthylene units in solution, they can be rigidified with the aid of methylene bridges to afford persistent molecular structures in solution.*

The chemistry of cyclophenylenes is experiencing a renaissance.[1] The first *ortho*-linked congeners appeared in the 1940s,[2] and a second congener with *meta* linkages was synthesized in the 1960s.[3] The third, most recent entry of *para*-linked cyclophenylenes, [*n*]cyclo-*para*-phenylenes ([*n*]CPPs), revived the field of cycloarylenes in 2008 with the introduction of novel hoop-shaped macrocycles, known as carbon nanohoops.[4–6] The carbon nanohoops with phenylene units connected by single-bond linkages contain unique $sp^2$-carbon networks with radially conjugated π systems, and the accumulation of a wide range of structural variants has enhanced the chemistry of the unique curved π systems.[7] The molecular structures of [*n*]CPPs ($n = 5$–10, 12) in the crystalline state are of particular importance[8] and clearly show the presence of unique belt-shaped $sp^2$-carbon networks that mimic the tubular structures of single-wall carbon nanotubes (SWNTs).[9,10] A complete replacement of the one-hexagon systems of benzene with the two-hexagon systems of naphthalene in the cycloarylene macrocycles took an unexpectedly long time to achieve, and the first cyclonaphthylenes were only synthesized four years ago.[11] The first example of 2,7-linked cyclonaphthylenes (named [*n*]cyclo-2,7-naphthylenes; [*n*]CNAPs) was immediately followed by 1,4-linked congeners (named [9]cyclo-1,4-naphthylenes; [9]CNs),[12] and these are the only two reported examples of cyclonaphthylene congeners to date. As shown in Figure 1a, however, three-dimensional structures of these cyclonaphthylenes failed to reproduce the tubular structures of SWNTs, despite the potential of generating a radial π system from a $sp^2$-carbon network; hence, a belt-shaped molecular structure has not been realized with cyclonaphthylenes.[13] We herein report the first example of belt-shaped cyclonaphthylenes. The new congener was linked at the 2,6-positions (so-called *amphi* positions) to afford [8]cyclo-*amphi*-naphthylene ([8]CaNAP),[14] and two congeners were shown to have belt-shaped nanohoop structures: unbridged [8]CaNAP (u-[8]CaNAP) and bridged [8]CaNAP (b-[8]CaNAP; Figure 1b). Although the belt-shaped structures of u-[8]CaNAP were revealed in the crystalline state, they were not persistent in solution because of rapid rotation of the naphthylene units.[15,16] We thus incorporated four -$CH_2CH_2$- (hereafter denoted methylene) bridges into the nanohoop to afford b-[8]CaNAP and successfully rigidify the belt shape in solution. The UV/Vis absorption maxima of [*n*]CPPs are known to be insensitive to the number of π electrons in the conjugated system.[17] The absorption maxima of the methylene-bridged [8]CaNAP in solution are, however, red-shifted relative to the those of the unbridged structure, which contains the same number of π electrons. The rich structural chemistry of cyclonaphthylene nanohoops may further stimulate interest in cycloarylene chemistry in the near future.

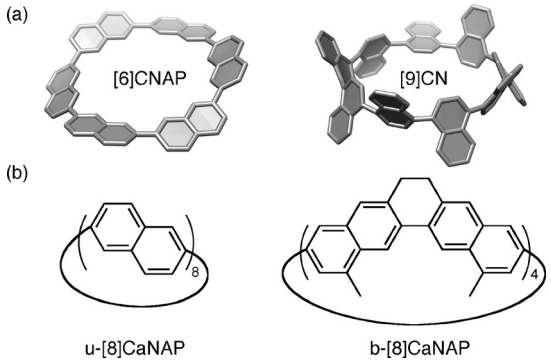


***Figure 1.*** Structures of cyclonaphthylenes. a) Molecular structures of reported cyclonaphthylenes. The structure of [6]CNAP was determined by crystallographic analysis,[11] and the structure of [9]CN was elucidated by spectroscopic and theoretical analyses.[12] Including other examples, the side-view molecular models are consistently displayed with a single-bond linkage at the front. b) Chemical structures of belt-shaped [8]cyclo-*amphi*-naphthylenes in this study.

We first synthesized u-[8]CaNAP from diborylated binaphthyl **1** through macrocyclization via Pt-cornered tetra-

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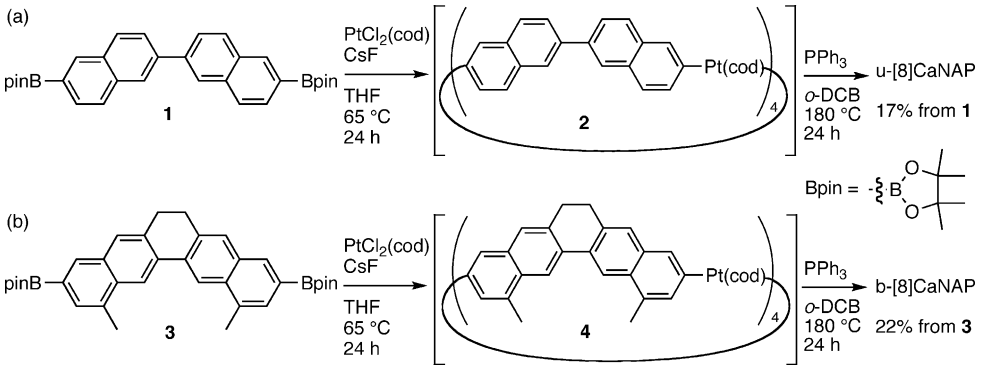


***Scheme 1.*** Synthesis of cyclonaphthylene nanohoops. a) Synthesis of u-[8]CaNAP. b) Synthesis of b-[8]CaNAP. cod = 1,5-cyclooctadiene, *o*-DCB = *ortho*-dichlorobenzene.

meric complex **2** (Scheme 1 a).[6,13] The overall yield of u-[8]CaNAP from **1** was 17 %. The second variant, b-[8]CaNAP, was likewise synthesized in 22 % yield from methylene-bridged binaphthyl **3**[18] with the same Pt-based procedure via **4** (Scheme 1 b).

The belt-shaped structures of u-[8]CaNAP were confirmed by X-ray crystallographic analysis of single crystals. We first describe the possible structures of u-[8]CaNAP. The two possible facial orientations of the eight naphthylene units in the nanohoop lead to a total of $2^8$ adoptable structural combinations. Among these combinations, there are 29 stereoisomers, including 11 sets of enantiomers of belt-shaped structures; excluding the enantiomers, the number of possible diastereomers is 18 (see Figure S1 in the Supporting Information). Note that such a complicated diastereoisomerism allows for the elucidation of dynamic behavior in solution (see below). Experimentally, we found three diastereomeric belt-shaped structures in single crystals (Figure 2). In the single crystal grown from a isopropanol/$CHCl_3$ solvent system, two atropisomers were identified with disordered structures (Figure 2 a). The isomers can be discriminated by the facial orientations of the naphthylene units: the one with 70 % occupancy was the aaaabbab isomer, and the other, with 30 % occupancy, was the aaaaaabb isomer.[19] Interestingly, the structures depended on the solvent system used for the crystal growth, and the aaabbaab and aaaaaabb isomers were found as disordered structures with occupancies of 48 % and 52 %, respectively, in the single crystal obtained from a hexane/$CHCl_3$ solvent system (Figure 2 b). Geometric descriptors for SWNTs can be applied for these structures with tubular $sp^2$-carbon networks,[9,10] and chiral indexes of (13,11) and (14,10) were assigned for these molecular segments of helical SWNTs. As these chiral indexes indicate, the molecular structures in the crystal are chiral and helical, and the molecules in the solid state were found to be racemates of *P* and *M* enantiomers (Figure S5). All of the structures were slightly distorted to an oval form, and the major and minor diameters measured from carbon atoms on opposite sides were 1.7 and 1.6 nm, for both the (13,11) and (14,10) isomers (Figure S4).[13b] These values are close to those expected for SWNTs [1.65 nm for (13,11) and 1.66 nm for (14,10)][9] and among the largest diameters recorded for belt-shaped nanohoops.[8e] The other geometrical parameters of the length index ($t_f$), bond-filling index ($F_b$), and atom-filling index ($F_a$) can also be assigned (Figure 2).

We found that u-[8]CaNAP is flexible in solution because the naphthylene units can rapidly rotate. Despite the presence of diastereomeric structures in the crystals, HPLC analysis of the compounds showed a single peak (Figure S2). The NMR spectra afforded clearer evidence of the structural fluctuation in solution. The $^1$H NMR spectrum of u-[8]CaNAP in $CD_2Cl_2$ showed three resonances in the aromatic region,[20] while the DEPT135 spectrum showed three CH resonances at 25 °C (Figure 3 a, see also Figure S6). Together with the results of the crystallographic and HPLC analyses, the spectra show that u-[8]CaNAP does not have a rigid structure, which should afford a complicated NMR spectrum as a result of its

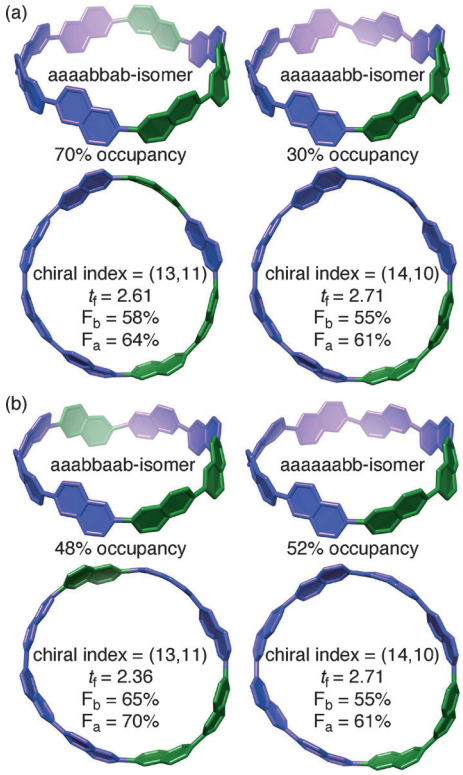


***Figure 2.*** Molecular structures of u-[8]CaNAP from crystallographic analysis. Side and top views of each structure are shown. Naphthylene units are colored differently depending on their facial orientations, and hydrogen atoms are omitted for clarity. Among a set of enantiomers in the racemic crystals, one representative isomer with *P* handedness is shown. The chiral index, length index ($t_f$), bond-filling index ($F_b$), and atom-filling index ($F_a$) are also shown.[10] a) Structures found in a single crystal grown from isopropanol/$CHCl_3$. b) Structures found in a single crystal grown from hexane/$CHCl_3$.

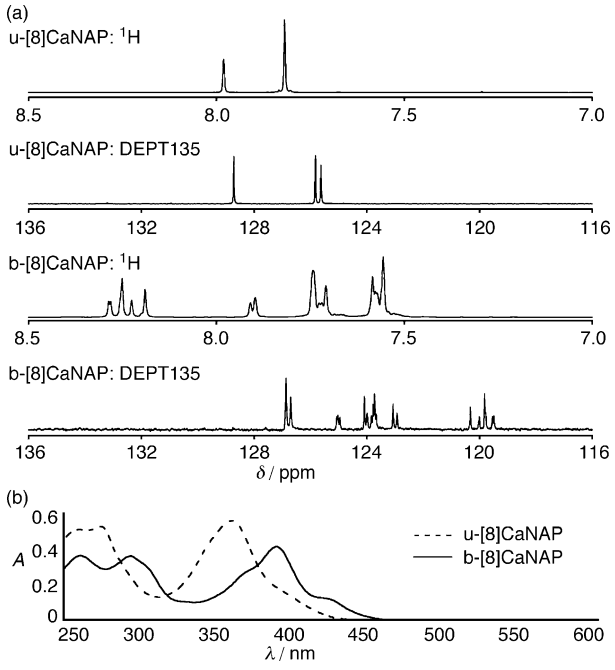


***Figure 3.*** Spectra of u-[8]CaNAP and b-[8]CaNAP. a) $^1$H and DEPT135 NMR spectra in $CD_2Cl_2$ at 25 °C. See the Supporting Information for further details. b) UV/Vis spectra of u-[8]CaNAP and b-[8]CaNAP at $4.1\times10^{-6}$ mol L$^{-1}$ in $CHCl_3$ at 25 °C.

18 possible diastereomers (Figure S1).[21] The naphthylene units of u-[8]CaNAP undergo rotation to afford time-averaged structures with high symmetry. We indeed observed resonance splitting below −30 °C, which indicated restricted rotation at low temperature (Figure S7). Thus, the belt-shaped structures of u-[8]CaNAP do not persist in solution under ambient conditions, and, therefore, the application of SWNT descriptors to the solution-phase structures may not be appropriate.[10]

The solution-phase structure of [8]CaNAP was rigidified by reinforcement of half of the single-bond linkages with methylene bridges to afford b-[8]CaNAP. The structural integrity of b-[8]CaNAP as a macrocycle with four methylene-bridged binaphthyl units was confirmed by mass spectrometry (Figure S9), and the purity was established by HPLC analysis using five different stationary phases (Figure S3).[22] Despite the indication of a single molecular entity from MS and HPLC analyses, NMR analysis afforded complicated spectra. As shown in Figure 3, the $^1$H NMR spectrum of b-[8]CaNAP showed complicated signals in the aromatic region, and the number of aromatic CH resonances in the DEPT135 spectrum was 20 (see also Figure S6). Although four possible diastereomeric atropisomers could emerge from the b-[8]CaNAP molecule (see Figure 4), none of these isomers alone can account for the corresponding spectra. For example, the AAAA isomer with the highest symmetry should show 4 aromatic CH resonances, and the AAAB isomer with the lowest symmetry should show 16 aromatic CH resonances. We did not observe coalescence of the resonances, even when we increased the temperature of the NMR analysis to 150 °C (Figure S8).[23] These observations show that the molecular structures of b-[8]CaNAP are rigidly persistent and that the binaphthyl units in b-[8]CaNAP do not rotate in solution on the NMR timescale. Additional support for this conclusion was obtained from the precursor Pt complex **4** affording simple NMR spectra (Figure S6). Thus, before reductive elimination to b-[8]CaNAP, the bridged binaphthyl units were rapidly rotating, and **4** was detected as a time-averaged structure.

An interesting comparative observation was made of the UV/Vis absorption spectra of u- and b-[8]CaNAP. The longest wavelengths of the absorption maxima for u-[8]CaNAP and b-[8]CaNAP were observed at 360 nm and 390 nm, respectively, with longer wavelength shoulders seen on each band (Figure 3 b). The absorption maxima of [*n*]CPPs are known to be insensitive to the numbers of phenylene units, that is, π electrons, in the macrocyclic systems,[17,24] whereas the present result shows that the absorption maxima are sensitive to conjugation at the single-bond linkages. As was concluded with [9]CN, the red-shift of the absorption maxima may be ascribed to the π extension,[12,25] but importantly, we should also consider the conjugation through the single-bond linkages.[26] Important structural features such as the coplanarity at the linkages may thus be deduced, although only qualitatively, from the UV/Vis analysis of the nanohoops.

Finally, we performed DFT calculations at the B3LYP/6-31G(d,p) level to clarify the structural origin of the atropisomerism in b-[8]CaNAP.[21] The energetics of the stable isomers showed that two belt-shaped isomers, namely, the ABAB and AAAB isomers, were the most stable structures, deviating from each other by

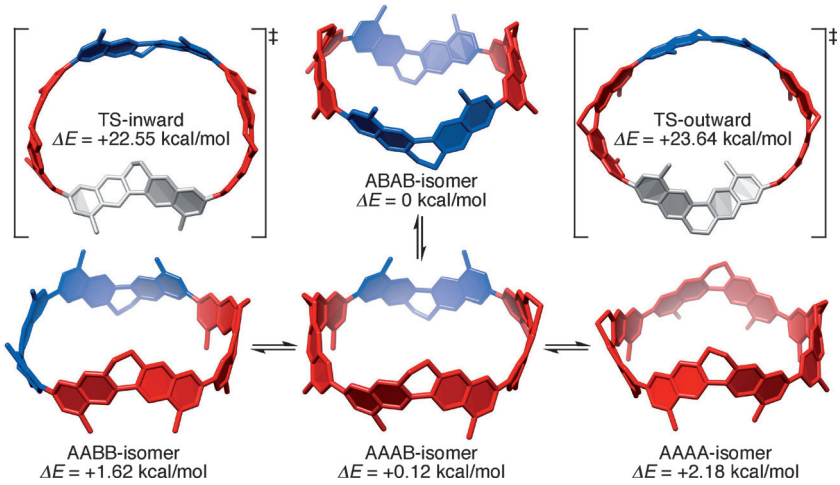


***Figure 4.*** Atropisomerism and equilibrium of b-[8]CaNAP. Structures were obtained from DFT calculations at B3LYP/6-31G(d,p). Along with four structures at the stationary points, two TS structures for the isomerization between the ABAB and AAAB isomers are shown. The relative energies from the most stable structure of ABAB isomer are shown. Binaphthyl units are colored differently depending on the facial orientations, and hydrogen atoms are omitted for clarity. All the structures are assignable with the chiral index of (12,12).[10]

only $+0.12$ kcal mol$^{-1}$ (Figure 4). This result is consistent with the NMR spectroscopic observations, especially with the DEPT135 spectrum. Thus, the energetics predict that the ABAB and AAAB isomers should be considered as two dominant species with a negligible energy difference under ambient conditions. The number of CH resonances expected for the ABAB and AAAB isomers are 4 and 16 based on their point symmetries of $D_{2d}$ and $C_s$, respectively. The prediction of the signal intensities requires the additional consideration of the frequency of occurrence among the $2^4$ possible structural combinations:[21,27] they are 2 for the ABAB isomer and 8 for the AAAB isomer. Consequently, in the absence of isomerization on the NMR timescale, we can expect $4+16$ resonances of comparable signal intensities, which is consistent with the 20 CH resonances observed in the DEPT135 spectrum (see above; Figure 3a and Figure S9).

A transition-state (TS) analysis with the DFT method revealed the molecular structures and the energetics for the isomerization of the ABAB isomer to the AAAB isomer (Figure 4). Depending on the direction of rotation of the arylene unit, two different paths emerge. The inward path rotates the arylene unit by incorporating a methylene bridge in the macrocyclic cavity, and the outward path rotates it in the opposite direction. The energy barriers were $+22.55$ and $+23.64$ kcal mol$^{-1}$ for the inward path and the outward path, respectively, which shows that the former is energetically preferred over the latter. The TS structures show that the rotation of the methylene-bridged binaphthyl units was restricted by the overall ring strain generated upon rotation, which was essentially the same as that observed in previous cases of belt-persistent nanohoops such as [4]cyclochrysenylenes and [4]cycloanthanthrenylenes.[13,21] The energy barrier of over $+20$ kcal mol$^{-1}$ is consistent with the experimental observation of rigid, persistent structures of b-[8]CaNAP.[12,13,21] As a reference, we also performed a theoretical analysis of u-[8]CaNAP (the relative energies of the 18 diastereomeric structures as well as the energetics for the naphthylene rotation are shown in Figures S10 and S11, respectively). Briefly, the barrier of $+10.51$ kcal mol$^{-1}$ measured for isomerization of the aaaaaaaa isomer to the aaaaaaab isomer correlated well with the experimental observations in which the atropisomers were rapidly equilibrating in solution.[28]

In summary, the first belt-shaped cyclonaphthylenes were synthesized, and their structures were revealed by crystallographic and spectroscopic analyses. The interesting structures of *amphi*-linked naphthylene macrocycles allow us to assess their rigidity in solution. Note that the question of the rigidity of CPP congeners can often be answered as "undecidable" due to their high symmetry.[7] The rigidity of the nanohoop structures is reinforced by methylene bridges, which gives rise to the atropisomerism of cyclonaphthylene in solution. An effect of the methylene bridges was also observed in the absorption spectra, which may help the exploration and screening of belt-shaped structures of nanohoops in the near future. The strain-induced atropisomerism revealed by theoretical analysis confirmed the feasibility of this strategy for the development of belt-persistent nanohoops, which also shows the benefit of theoretical analysis for molecular design. A large void space of 1.7 nm diameter in the tubular molecular structures may provide a unique space to be explored in the field of supramolecular chemistry.[29] We hope that the exploration of the structural chemistry of nanohoops will be further stimulated by the present molecular systems that give persistent belts with the smallest acene (naphthalene) units.

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[19] The application of the *E*/*Z* nomenclature is possible for the present structures: a-a (or A-B for b-[8]CaNAP) is connected through an *E* linkage, and a-b (or A-A for b-[8]CaNAP) is connected through a *Z* linkage.
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[23] The highest temperature of 150 °C for the variable-temperature NMR analysis indicates that isomers of b-[8]CaNAP are present as isolable molecules (Refs. [13, 21]). The high energy barrier of 22.55 kcal mol$^{-1}$ from the theoretical analysis (see below) also supports this hypothesis.
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