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Functionalized Carbon Nanohoops: Synthesis and Structure of a [9]Cycloparaphenylene Bearing Three 5,8-Dimethoxynaphth-1,4-diyl Units

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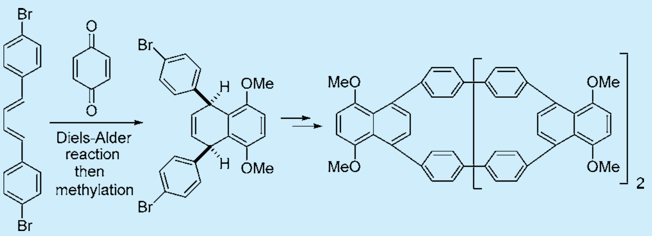
Supporting Information

ABSTRACT: A functionalized [9]cycloparaphenylene ([9]CPP) bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units and two macrocyclic [6]CPP precursors have been synthesized. The Diels–Alder reaction between (*E*,*E*)-1,4-bis(4-bromophenyl)-1,3-butadiene and 1,4-benzoquinone followed by methylation produces *cis*-5,8-bis(4-bromophenyl)-5,8-dihydro-1,4-dimethoxynaphthalene as the key intermediate for the construction of the hooplike structures. The nickel-mediated homocoupling reactions followed by aromatization led to the functionalized [9]CPP.



A synthetic pathway involving a Diels–Alder reaction as a key step for the construction of **1** (Figure 1) as a functionalized [9]CPP and two macrocyclic [6]CPP precursors has been developed. The structures of [*n*]CPPs represent the shortest segments of the repeating hooplike structures of (*n*,*n*)-armchair carbon nanotubes.[1] Since the first report by Jasti, Bertozzi, and co-workers of the synthesis of [9]-, [12]-, and [18]CPP in 2008,[2] development of new synthetic pathways for CPPs has been actively pursued.[3] This is due in part to the possibility of using them as templates for bottom-up synthesis of armchair carbon nanotubes of a uniform diameter, a factor of crucial importance for applications in a variety of nanotechnology fields.[4]

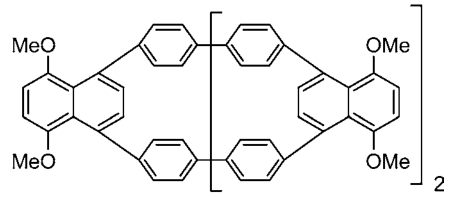


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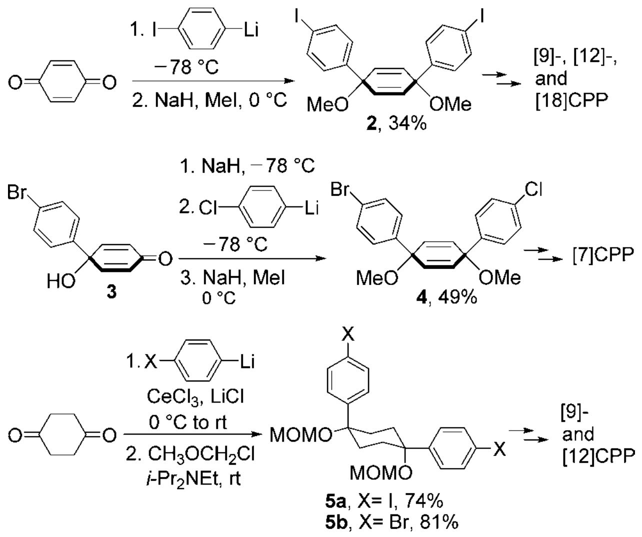
Figure 1. Structure of the functionalized [9]CPP (**1**).

Condensation between 1,4-benzoquinone and 4-iodophenyllithium in the first CPP synthesis (Scheme 1) and related reactions followed by methylation were used to form 3,6-bis(4-haloaryl)-3,6-dimethoxy-1,4-cyclohexadienes, such as **2**, as the CPP precursors.[2,3h,m] The stereoselectivity for the *cis* isomer with the two 4-haloaryl groups on the same side of the cyclohexadienyl ring, essential for the construction of CPPs, is ca. 75%.[3h,m,5] The stereoselectivity for the *cis* isomer was improved to 95% by first deprotonation of the hydroxyl group in **3** to form the corresponding sodium alkoxide followed by treatment with (4-chlorophenyl)lithium to give, after methylation, **4** in 49% yield over two steps.[3f] Condensation between 1,4-cyclohexanedione and 4-halophenylcerium reagents exhibited virtually complete *cis* stereoselectivity leading to **5a** and **5b** as precursors for CPPs.[3c,d]

Scheme 1. Previous Synthesis of CPP Precursors



We envisioned that the versatility and high stereoselectivity of the Diels–Alder reaction could provide exclusively the *cis*

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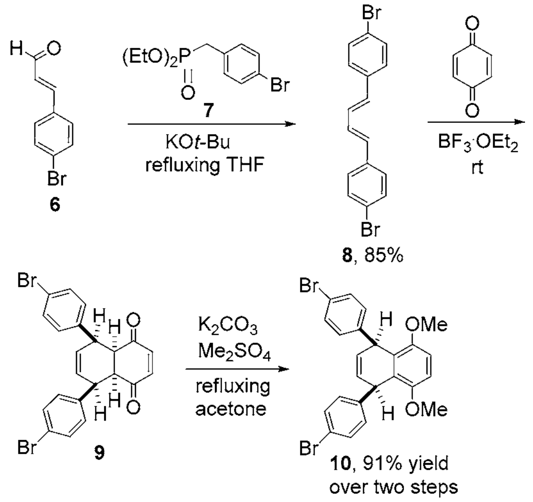
isomer with a wide variety of structural features. In order to explore this synthetic strategy, (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene (**8**) was prepared from 4-bromocinnamaldehyde (**6**) and diethyl 4-bromobenzylphosphonate (**7**) using the Horner–Wadsworth–Emmons reaction as reported previously (Scheme 2).[6] In the presence of $BF_3 \cdot OEt_2$, the Diels–Alder reaction between diene **8** and 1,4-benzoquinone gave, after methylation, the dihydronaphthalene derivative **10** in 91% yield over two steps. The structures of the initially formed *endo* Diels–Alder adduct **9** and the methylated **10** (Figure 2) were established by X-ray structure analyses. The two 4-bromophenyl groups in **10** are *cis* to each other exclusively.

Scheme 2. Synthesis of the CPP Precursor 10 by the Diels–Alder Reaction



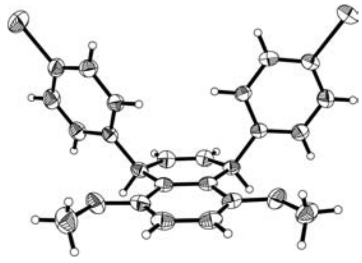
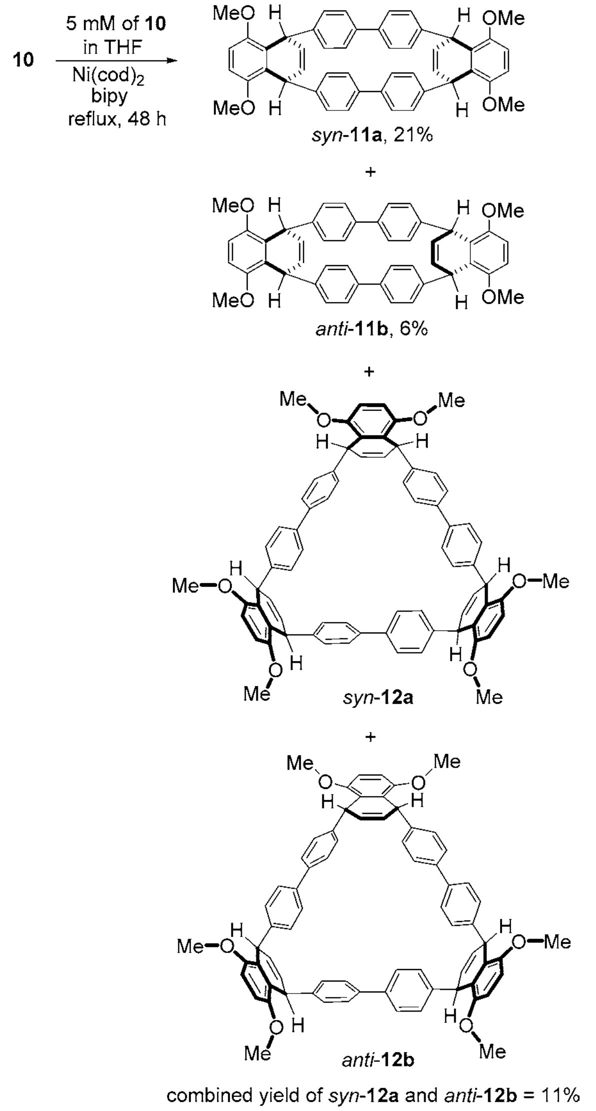


Figure 2. X-ray crystal structure of the CPP precursor **10**.

First employed by Itami and co-workers for the synthesis of [9]- and [12]CPP from **5a** and **5b**[3d,e] and for [7]CPP[3t] and later adopted for the synthesis of aryl-substituted [9]CPPs,[3p] a 1,1′-binaphthalene-containing [12]CPP,[3r] and [5]CPP,[3s] the $Ni(cod)_2$-mediated (cod: 1,5-cyclooctadiene) homocoupling reaction in the presence of 2,2′-bipyridyl (bipy) also found success in producing macrocyclic structures from **10** (Scheme 3). At 5 mM concentration of **10**, the cyclic *syn* dimer **11a** and *anti* dimer **11b** were obtained in 21% and 6% yields, respectively. In addition, the cyclic trimers *syn*-**12a** and *anti*-**12b** were also isolated in 11% combined yield (*syn*-**12a**:*anti*-**12b** = 1:3). At 50 mM of **10**, the cyclic dimers were obtained in 8% combined yield (*syn*-**11a**:*anti*-**11b** = 3:1) and the cyclic trimers were obtained in 18% combined yield (*syn*-**12a**:*anti*-**12b** = 1:3).

Scheme 3. Synthesis of the Cyclic Dimers *syn*-11a and *anti*-11b and the Cyclic Trimers *syn*-12a and *anti*-12b



The X-ray structure of the oval-shaped *syn*-**11a** (Figure 3) indicates that the two biphenyl segments are in close proximity to each other with a distance ranging from ca. 3.42 to 4.10 Å. The two phenyl groups in each of the biphenyl segments are twisted with a dihedral angle of 49°. The ^1H NMR signals of the aromatic hydrogens on the biphenyl segments in *syn*-**11a** and *anti*-**11b** are shifted upfield to δ 6.60 and 6.67, indicating that they are located in a magnetically shielded region of the

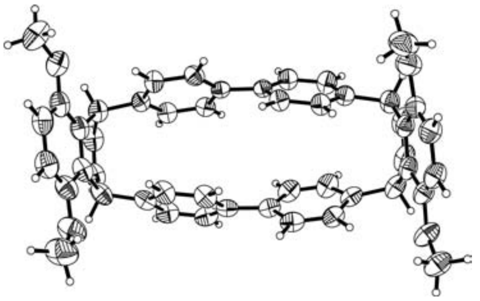


Figure 3. X-ray crystal structure of the cyclic dimer *syn*-**11a**.

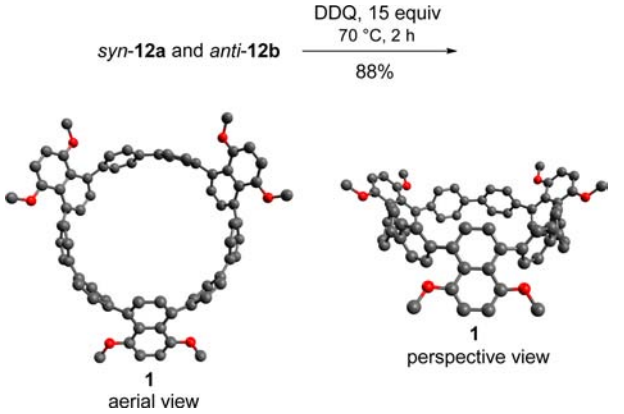
aromatic ring current of the phenyl groups on the opposite side. The presence of three planes of symmetry and a C_3 symmetry in *syn*-**12a** but only a plane of symmetry in *anti*-**12b** allowed the two cyclic trimers to be readily identified by ^{1}H NMR spectroscopy. Only one singlet signal from the methyl groups in *syn*-**12a** was observed, whereas three singlets of equal intensity from the methyl groups in *anti*-**12b** appeared.

The formation of the cyclic dimers *syn*-**11a** and *anti*-**11b** from the Ni(cod)$_2$-mediated homocoupling reactions of **10** is in contrast to the reports that only the cyclic trimer and tetramer from the L-shaped **5a** and **5b** were isolated[3d,e,r] and the cyclic trimers from an aryl-substituted **2**[3p] and a naphthalene derivative was obtained.[3h] The X-ray structure of **10** indicates that the included angle between the two 4-bromophenyl groups is 73.6° in the crystal lattice, smaller than that of **5a** at ca. 80°.[3d] The ^3J coupling constant of 4.7 Hz between the benzylic hydrogens and the alkenyl hydrogens in **10** indicates that the dihydronaphthalene ring is only slightly puckered (<10°) from planarity, correlating to a flattened-boat structure in solution as in crystal lattice. The correlation between the ^3J coupling constant and the extent of puckering in the 1,4-dihydronaphthalene system was established previously.[7] The closer proximity of the two 4-bromophenyl groups in **10** than in **5** may be responsible for channeling the second Ni(cod)$_2$-mediated homocoupling reaction toward the formation of the cyclic dimers *syn*-**11a** and *anti*-**11b**. Perhaps even more importantly, the included angle between the two 4-bromophenyl groups in **10** is unlikely to open wider during the coupling reactions. A wider angle will greatly increase the nonbonded steric interactions with the neighboring methoxy groups. Such constraint is not present in the case of **5**.

The parent [6]CPP was prepared using sodium naphthalide at −78 °C for the reductive aromatization of a cyclic precursor bearing four benzylic methoxy groups.[3o] In addition, the reductive elimination of a cyclic platinum complex to form the parent [6]CPP was also reported.[3q] Our attempts to form the fully aromatized [6]CPP structure by treatment of the cyclic dimers *syn*-**11a** and *anti*-**11b** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[8] at temperatures ranging from 25 to 150 °C were unsuccessful. It was estimated that the strain energy in the parent [6]CPP is ca. 97 kcal/mol,[3g,9] which most likely prevented complete aromatization of *syn*-**11a** and *anti*-**11b**. However, the lower strain energy in [9]CPP (ca. 67 kcal/mol) should make the aromatization process of the cyclic trimers *syn*-**12a** and *anti*-**12b** more easily achievable. It was interesting to observe that *syn*-**12a** and *anti*-**12b** underwent complete aromatization to form the functionalized [9]CPP **1** bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units in excellent yield at 70 °C in 2 h (Scheme 4). The observation that both *syn*-**12a** and *anti*-**12b** produced **1** exhibiting only one set of NMR signals suggests that its various atropisomers are in equilibration.[3h] The milder reaction conditions to promote aromatization to form **1** in excellent yield are in contrast to the elevated temperature (150 °C) and longer reaction time (48 h) that were used to promote aromatization of the cyclic trimer of **5a**/**5b** to form the parent [9]CPP in 24% yield.[3e]

The DFT-optimized structure of **1** indicates that the 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane of the [9]CPP circle at an angle of 133.8° on average with two of the units tilting above the ring and the third tilting below the ring. The three biphenyl moieties of **1** have three unique torsional angles of 19.5°, 36.5°, and −37.5°. The diameter of the ring is calculated to be 12.4 Å as reported previously for the parent [9]CPP.[2] Again, the observation of only one set of NMR signals suggests rapid arene rotations on the NMR time scale.

Scheme 4. Synthesis of 1 and Its Energy-Minimized Structure by DFT Calculations



The UV−vis spectrum of **1** in CH_2Cl_2 (5×10^{-7} M) exhibited the absorption maximum (λ_{abs}) at 362 nm with a molecular absorption coefficient (ε) of 5.2×10^4 cm^{-1} M^{-1}, which lay between those of the parent [9]CPP (340 nm)[2] and [9]cyclo-1,4-naphthalene (378 nm).[3h] However, the fluorescence maximum (λ_{em}) was observed at 512 nm, representing a red shift with respect to those of the parent [9]CPP (494 nm) and [9]cyclo-1,4-naphthalene (491 nm).

In summary, a synthetic pathway leading to the functionalized [9]CPP (**1**) bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units and macrocyclic [6]CPP precursors *syn*-**11a** and *anti*-**11b** has been developed. The use of the Diels−Alder reaction to form **10** unequivocally sets the two 4-bromophenyl groups *cis* to each other, essential for the construction of CPPs and related carbon nanohoops. The high stereoselectivity and versatility of the Diels−Alder reaction between readily available (*E*,*E*)-1,4-diaryl-1,3-butadienes[10] and dienophiles bearing diverse structural features make the synthetic pathway especially attractive for the preparation of CPPs. The presence of three 5,8-dimethoxynaphth-1,4-diyl units in **1** provides additional handles for subsequent synthetic elaborations.[11]

ASSOCIATED CONTENT

Supporting Information

Complete experimental details of new compounds, spectral data, DFT calculations, and crystallographic data (CIF). 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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