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Synthesis of Partially Hydrogenated Cycloparaphenylenes with Bent and Fused Structures Bearing Armchair Carbon Nanotube-like Connections

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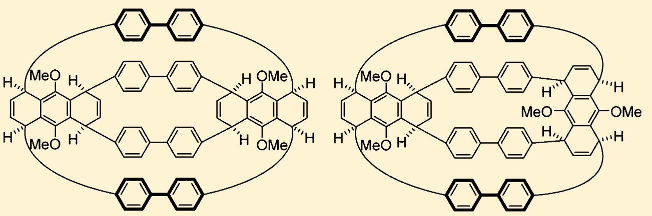
S Supporting Information

ABSTRACT: The Diels−Alder reactions between 2 equiv of (*E*,*E*)-1,4-bis(4-bromophenyl)-1,3-butadiene and 1,4-benzoquinone led to the formation of a key intermediate with all four 4-bromophenyl substituents *cis* to one another. The subsequent nickel-mediated homocoupling reactions then produced partially hydrogenated cycloparaphenylenes, including a molecule bearing two units of tetrahydro[6]cycloparaphenylene (4H[6]CPP) fused together through two 1,4-dimethoxybenzene units in an armchair (6,6)carbon nanotube-like connection. Similarly, two 6H[9]CPPs were connected through three 1,4-dimethoxybenzene units in an armchair (9,9)carbon nanotube-like arrangement. A bent 8H[12]CPP and a bent 12H[18]CPP, which were fused intramolecularly with two and three 1,4-dimethoxybenzene units, respectively, to create the bent structures, were likewise synthesized. A molecule containing a bent 8H[12]CPP fused to a 4H[6]CPP was likewise constructed. The structures of these partially hydrogenated CPPs were established by X-ray structure analysis, NMR spectroscopy, and additional independent synthetic pathways.



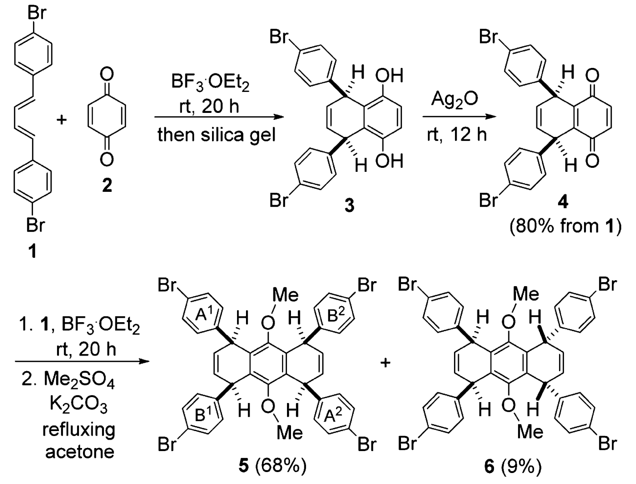
INTRODUCTION

The macrocyclic structures of [*n*]cycloparaphenylenes ([*n*]CPPs) are constructed by connecting *n* units of the benzene ring at *para* positions.[1] They represent the shortest repeating hooplike segments of (*n*,*n*)armchair single-walled carbon nanotubes. Current interest in CPPs is due in part to their potential use as templates for growing armchair carbon nanotubes of a single chirality and diameter for nanotechnology applications.[2] Several synthetic pathways have been developed for the construction of CPPs with various macrocyclic ring sizes.[3] One of the current frontiers of investigation in this area involves preparation of substituted and functionalized CPPs for connection with a nanotube-like arrangement. The 1,4-benzene- and 1,5-naphthalene-bridged [8]CPP dimers were synthesized,[4] and a directly connected [10]CPP dimer was constructed.[5] We now report our development of synthetic pathways leading to fused macrocycles bearing two partially hydrogenated CPP units with armchair nanotube-like connections. Other partially hydrogenated CPPs with bent and multiply fused structures have also been constructed.

RESULTS AND DISCUSSION

We recently reported the use of a Diels−Alder reaction as a key step in the construction of a functionalized [9]CPP bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units and related carbon nanohoops.[6] Specifically, the Diels−Alder reaction between (*E*,*E*)-1,4-bis(4-bromophenyl)-1,3-butadiene (**1**) and 1,4-benzoquinone (**2**) was used to place the two 4-bromophenyl groups *cis* to each other exclusively as shown in **3** for the subsequent macrocyclic ring formation (Scheme 1).[6,7] We have adopted the same strategy in this investigation to produce **3**,[7b] which upon being treated with silver oxide produced 1,4-benzoquinone **4** in 80% yield in two steps. The presence of a 1,4-benzoquinone moiety in **4** allowed a second

Scheme 1. Synthesis of Tetrabromide 5



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Diels–Alder reaction with diene **1** to produce, after methylation, **5** and **6** in an 8:1 ratio as determined by the integration of the ^{1}H NMR spectrum. Isomer **5** with all four 4-bromophenyl groups *cis* to one another was isolated in 68% yield, and a small quantity of isomer **6** with the two sets of the 4-bromophenyl groups *trans* to each other was also isolated for structural elucidation.

A single crystal of **5** was grown for an X-ray structure analysis to establish its stereochemistry. However, the quality of the structural refinement was not sufficient to warrant publication of the final results. Fortunately, we were able to convert **5**, by the lithium–bromine exchanges with *n*BuLi followed by iodination with iodine, to form the corresponding tetraiodide **7** for growing a high-quality single crystal suitable for X-ray structure analysis (Figure 1). A single crystal of **6** was also obtained for X-ray structure analysis.

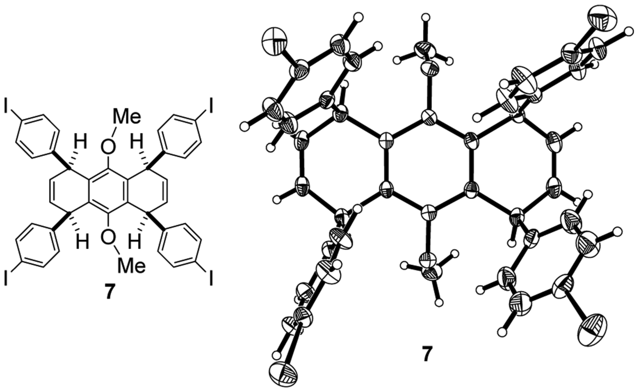


Figure 1. Molecular structure and ORTEP drawing of the crystal structure of tetraiodide **7** prepared from *cis* isomer **5**. A molecule of dichloromethane has been omitted for the sake of clarity.

The formation of **5** as the major product could occur with a preferential *endo* approach of diene **1** toward dienophile **4** from the same side of the two 4-bromophenyl groups and/or with a preferential *exo* approach of **1** toward **4** from the side opposite to the two 4-bromophenyl groups. Although the *endo* approach toward 1,4-benzoquinone (**1**) is the preferred pathway leading to **3**,[6] it appears that the *endo* approach from the same side of the two 4-bromophenyl groups in **4** leading to **5** suffers from more severe nonbonded steric interactions than the *endo* approach from the opposite side, which leads to **6**. This suggests that the *exo* approach from the side opposite to the two 4-bromophenyl groups is likely responsible for the preferential formation of **5**.

Treatment of **5** at a concentration of 1 mM in THF with Ni(cod)$_2$ (cod being 1,5-cyclooctadiene) in the presence of 2,2′-bipyridyl (bpy) promoted the homocoupling reactions[8] to produce the two possible cyclic dimers **8** and **9** in an ∼1:1 ratio in the reaction mixture (Scheme 2). Broad ^{1}H NMR signals in the typical aromatic and methoxy regions were also observed from the crude reaction mixture, indicating that oligomers and/or polymers of **5** were also produced. We were able to use silica gel column chromatography to separate and isolate **8** in 5% yield and **9** in 1% yield. Because of the presence of C_2 symmetry in **5**, the group A 4-bromophenyl substituents are equivalent, as are the group B 4-bromophenyl substituents. On the other hand, the group A and group B substituents are enantiotopic to each other. An initial intermolecular homocoupling reaction between a group A substituent and a group B substituent, such as between A^1 of one molecule and B^1 of a second molecule (A^1–B^1), followed by three intramolecular homocouplings, such as B^1–A^1, A^2–B^2, and B^2–A^2 (not necessarily in this order), would produce **8**. On the other hand, an initial intermolecular homocoupling reaction between two A groups, such as A^1–A^1, or between two B groups followed by three intramolecular homocouplings, such as B^1–B^2, A^2–A^2, and B^2–B^1 (not necessarily in this order), would produce **9**. If the two initial homocoupling reactions involve A^1–A^1 and B^1–B^1, A^1–A^1 and B^2–B^2, or A^1–B^1 and B^1–A^1, then oligomers and/or polymers would be produced.

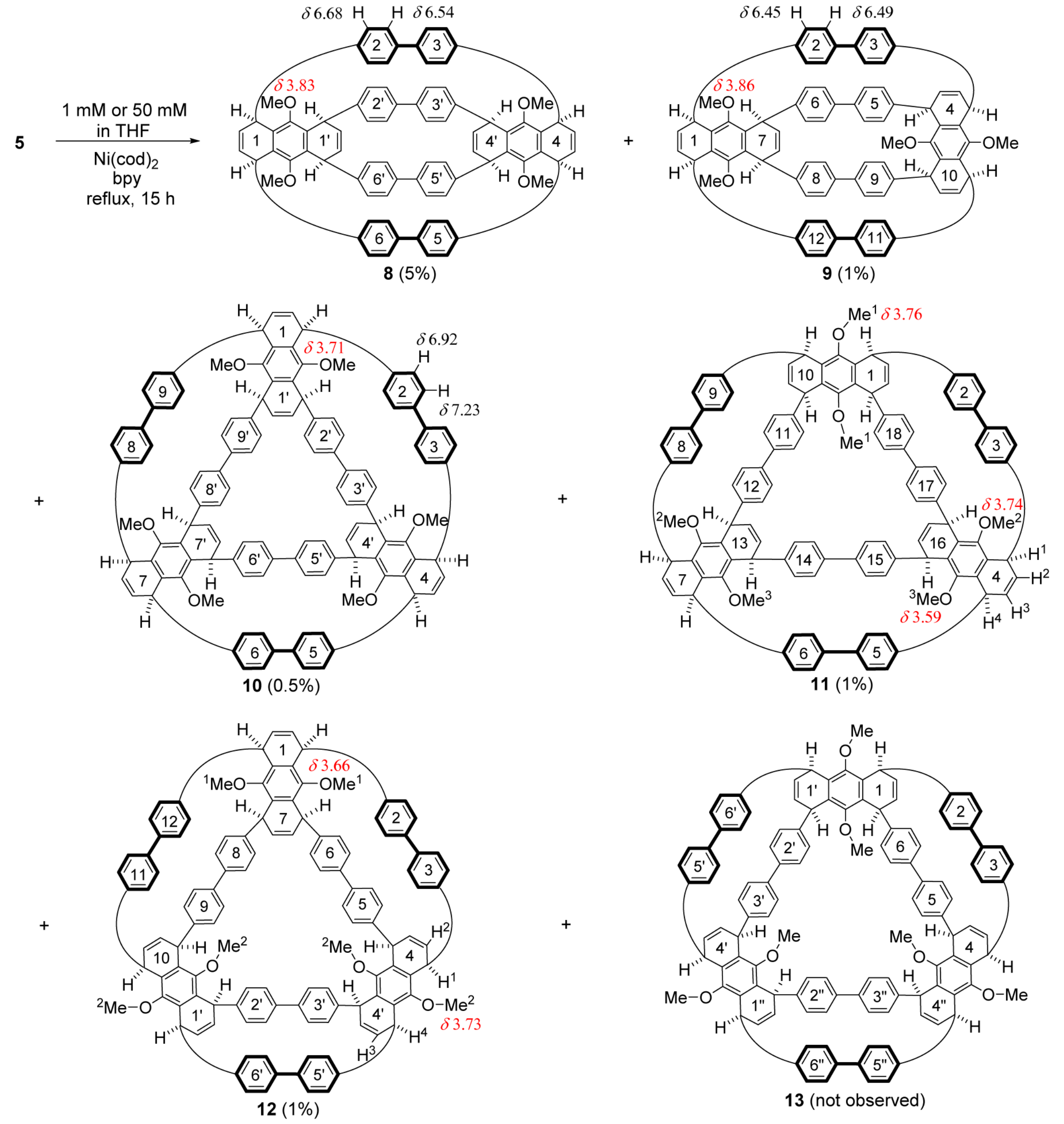
The molecular structure of cyclic dimer **8** contains two tetrahydro[6]CPP (4H[6]CPP) substructures, which are indicated with two sets of sequentially labeled numbers. Compared to earlier reports of structures containing two CPP units,[4,5] the orientations of the two 4H[6]CPP units in **8** are fixed because they are fused to each other through two 1,4-dimethoxybenzene units and aligned with the holes facing each other in an armchair (6,6)carbon nanotube-like connection. The DFT-optimized structure of **8** shows that the two 4H[6]CPP units have an oval shape and the two sets of methoxy groups are parallel to each other (Figure 2). For cyclic dimer **9**, the structure contains a bent 8H[12]CPP unit, which is fused intramolecularly with two 1,4-dimethoxybenzene units. The bent 8H[12]CPP unit is indicated with one set of sequentially labeled numbers. The DFT-optimized structure of **9** shows that the two sets of methoxy groups are perpendicular to each other.

In addition to cyclic dimers **8** and **9**, the Ni(cod)$_2$-mediated homocoupling reactions of **5** at a concentration of 1 mM also produced small quantities of cyclic trimers **10**–**12** (Scheme 2). At 10 mM **5**, the amounts of the cyclic trimers increased as observed previously,[6] and the **8**:**9**:**10**:**11**:**12** mole ratio was determined by ^{1}H NMR spectroscopy to be ∼2:1:1.3:2.7:1. At 50 mM **5**, cyclic trimers **10**–**12** were separated and isolated at levels of 0.5, 1, and 1%, respectively. The fourth possible cyclic trimer, **13**, was not observed.

The molecular structure of cyclic trimer **10** contains two 6H[9]CPP units, which are fused together through three 1,4-dimethoxybenzene units with the holes facing each other with an armchair (9,9)carbon nanotube-like connection. The DFT-optimized structure of **10** shows that the two 6H[9]CPP units have a triangular shape and the three sets of methoxy groups are in a plane parallel to the planes of the two 6H[9]CPP rings with the front ring highlighted in black (Figure 3).

The molecular structure of cyclic trimer **11** contains a bent 12H[18]CPP unit, which is fused intramolecularly with three 1,4-dimethoxybenzene units. The DFT-optimized structure of **11** shows that two sets of the methoxy groups are in a plane parallel to the front and the rear macrocyclic rings and the third set is perpendicular to the plane. The molecular structure of cyclic trimer **12** contains a bent 8H[12]CPP unit, which is fused within itself with a 1,4-dimethoxybenzene unit, and the 8H[12]CPP unit also is fused through two 1,4-dimethoxybenzene units to a 4H[6]CPP unit. The DFT-optimized structure of **12** shows that two sets of methoxy groups are perpendicular to the front and the rear macrocyclic rings and the third set is parallel to the macrocyclic rings. The molecular structure of cyclic trimer **13** has three fused 4H[6]CPP units. The DFT-optimized structure shows that the three sets of the methoxy groups are all perpendicular to the macrocyclic ring structures.

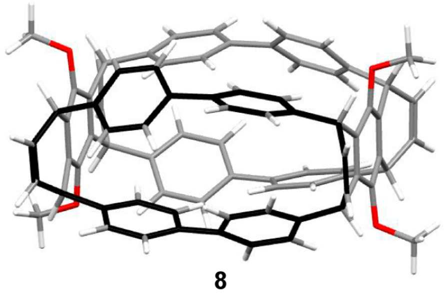
Scheme 2. Synthesis of Bent and Fused Carbon Nanohoops



The molecular structure of cyclic dimer **8** was confirmed by X-ray structure analysis (Figure 4). The two phenyl groups in each of the four biphenyl segments were slightly twisted with dihedral angles between 2° and 7°. This is in contrast to the DFT-optimized structure in which the average dihedral angle was calculated to be 44° and to a one-hoop 4H[6]CPP system in which a dihedral angle of 49° was observed in the crystal lattice.[6]

There are three C_2 axes in **8**, and it belongs to the D_{2h} group. As a result, only five ^{1}H NMR signals were observed with one singlet for the methoxy groups at δ 3.83 and one AB pattern at δ 6.54 and 6.68 for the aromatic hydrogens. The structure of **9** also has three C_2 axes and belongs to the D_{2d} group. It likewise exhibited only five ^{1}H NMR signals with the methoxy signal occurring at δ 3.86 and the AB system appearing at δ 6.45 and 6.49. It is worth noting that the aromatic signals of **8** and **9** are shifted significantly upfield, indicating that they are located in a magnetically shielded region of the aromatic ring currents generated by the phenyl groups of the biphenyl segments in the proximity. In the crystal lattice, the distance between the centers of the bonds joining the two phenyl groups within the same 4H[6]CPP unit is 4.03 Å and across to the other 4H[6]CPP unit is 5.88 Å (Figure S5). The high-resolution mass spectra of **8** and **9** are also consistent with their structural assignments as the cyclic dimers from **5**.

Before the X-ray structure of **8** was obtained, we were unable to assign the two dimeric structures to the isolated samples of **8** and **9** by NMR spectroscopy because they both showed an identical number of signals and very similar chemical shifts. The development of an independent synthetic pathway toward **8** without the possibility of producing **9** was thus initiated. Diene **14** bearing two trimethylsilyl groups as masked iodo groups[9] was used for the Diels–Alder reaction with 1,4-benzoquinone **4** to form **15** as the major isomer in 55% isolated yield (Scheme 3). Treatment of **15** at a concentration of 1 mM with Ni(cod)$_2$ in the presence of bpy produced *syn* dimer **16** and *anti* dimer



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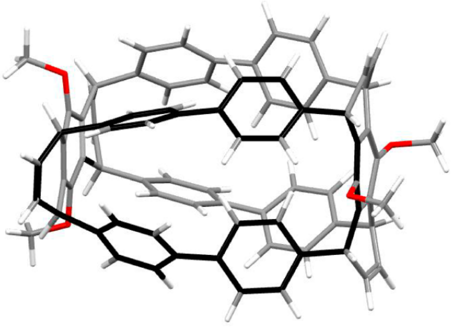

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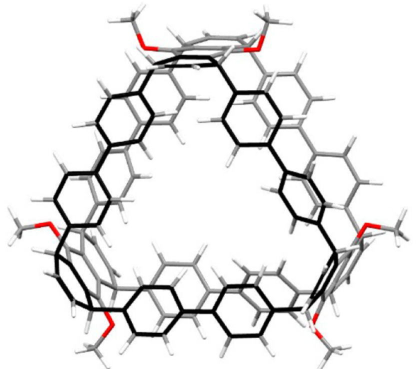
Figure 2. DFT-optimized structures of fused cyclic dimer **8** and bent cyclic dimer **9** with carbons (black and gray), hydrogens (white), and oxygens (red).

17 in a 1:1 ratio, which was determined by ^{1}H NMR spectroscopy. *Anti* isomer **17** was isolated in 30% yield and, upon treatment with ICl at −78 °C, was converted to the corresponding tetraiodide **19**.[9] However, the Ni(cod)$_2$-mediated homocoupling reactions of **19** failed to produce **8**, suggesting that **17** had the *anti* configuration. A small quantity of *syn* dimer **16** was also isolated by preparative TLC for structural elucidation. However, because of difficulty in fully purifying *syn* dimer **16**, the remaining crude *syn* dimer **16** was treated, without further purification, with ICl at −78 °C to form tetraiodide **18**. Crude **18**, upon being exposed to Ni(cod)$_2$, was converted to cyclic dimer **8** in 8% overall yield from **15**, providing an independent confirmation of the structure of **8**.

Cyclic trimer **10** belongs to the D_{3h} group and has a C_3 axis, three C_2 axes perpendicular to the C_3 axis, and a plane of symmetry perpendicular to the C_3 axis between the front and rear 6H[9]CPP units. Again, only five ^{1}H NMR signals were observed with the singlet of the methoxy groups appearing at δ 3.71 and the two doublets of the aromatic hydrogens appearing at δ 7.23 and 6.92. It allowed the structure to be readily differentiated from those of cyclic trimers **11** and **12**. However, cyclic trimer **13** also belongs to the D_{3h} group and can be expected to show only five ^{1}H NMR signals, as well. The ^{1}H NMR signals of the aromatic hydrogens on the three 4H[6]CPP units in **13**, on the other hand, are likely to be shifted more upfield than those assigned for **10** at δ 7.23 and 6.92.

To fully verify that the isolated sample was **10**, a synthetic pathway toward **10** without the possibility of producing **13** was developed (Scheme 4). At a concentration of 50 mM, dibromide **15** was treated with Ni(cod)$_2$ to form, in addition to **16** (8%) and **17** (12%), cyclic *syn* trimer **20** and *anti* trimer **21** in a 1:3 ratio, which was determined by NMR spectroscopy. Cyclic *anti* trimer **21** was isolated in 12% yield. A small quantity of cyclic *syn* trimer **20** was also isolated for structural elucidation, and the majority of **20**, without further purification, was converted, with ICl at −78 °C, to the corresponding hexaiodide. The crude hexaiodide was treated with Ni(cod)$_2$ to produce **10** with ^{1}H NMR signals identical to those of **10**



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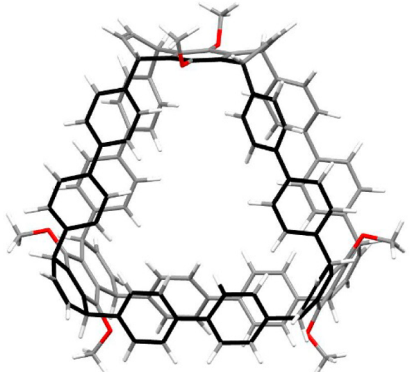

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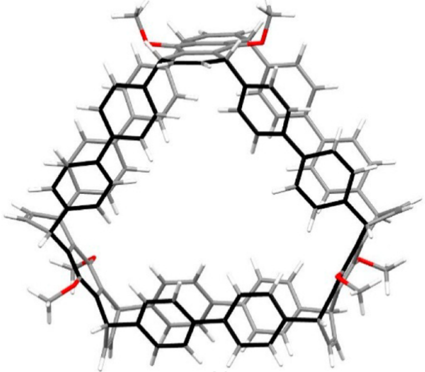

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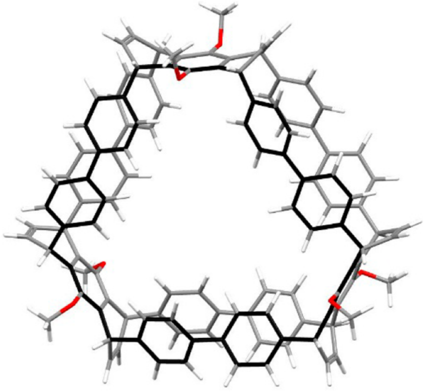

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Figure 3. DFT-optimized structures of cyclic trimers **10**−**13** with carbons (black and gray), hydrogens (white), and oxygens (red).

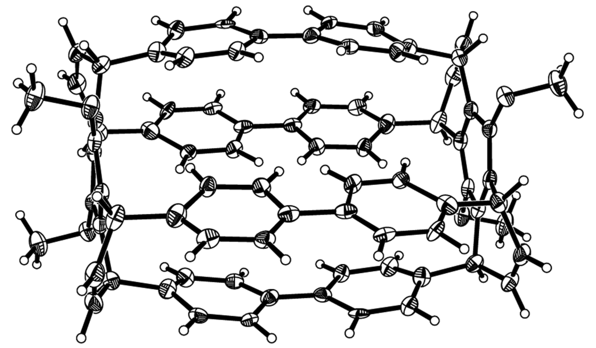
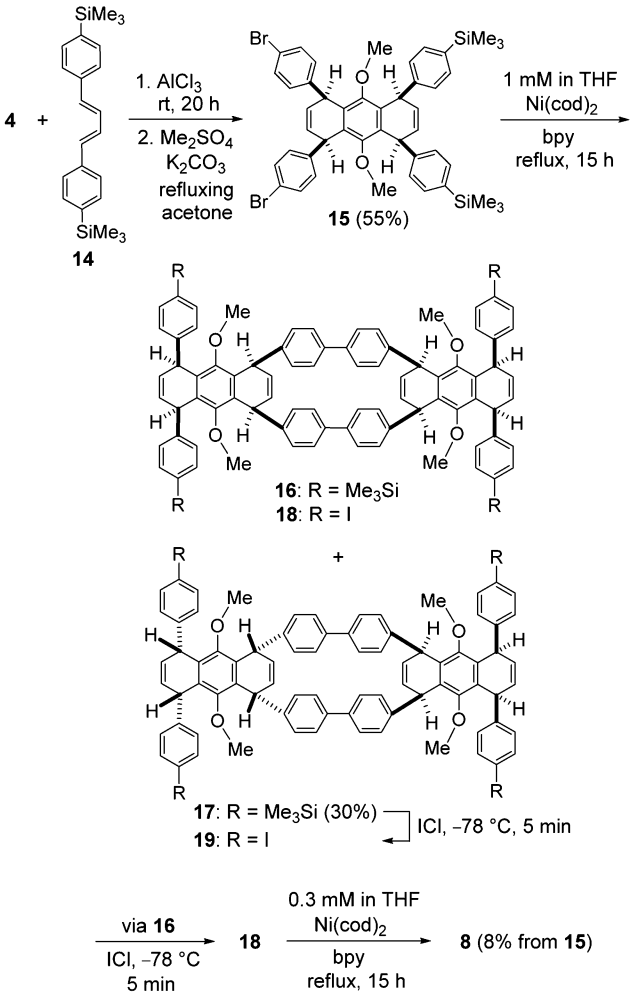
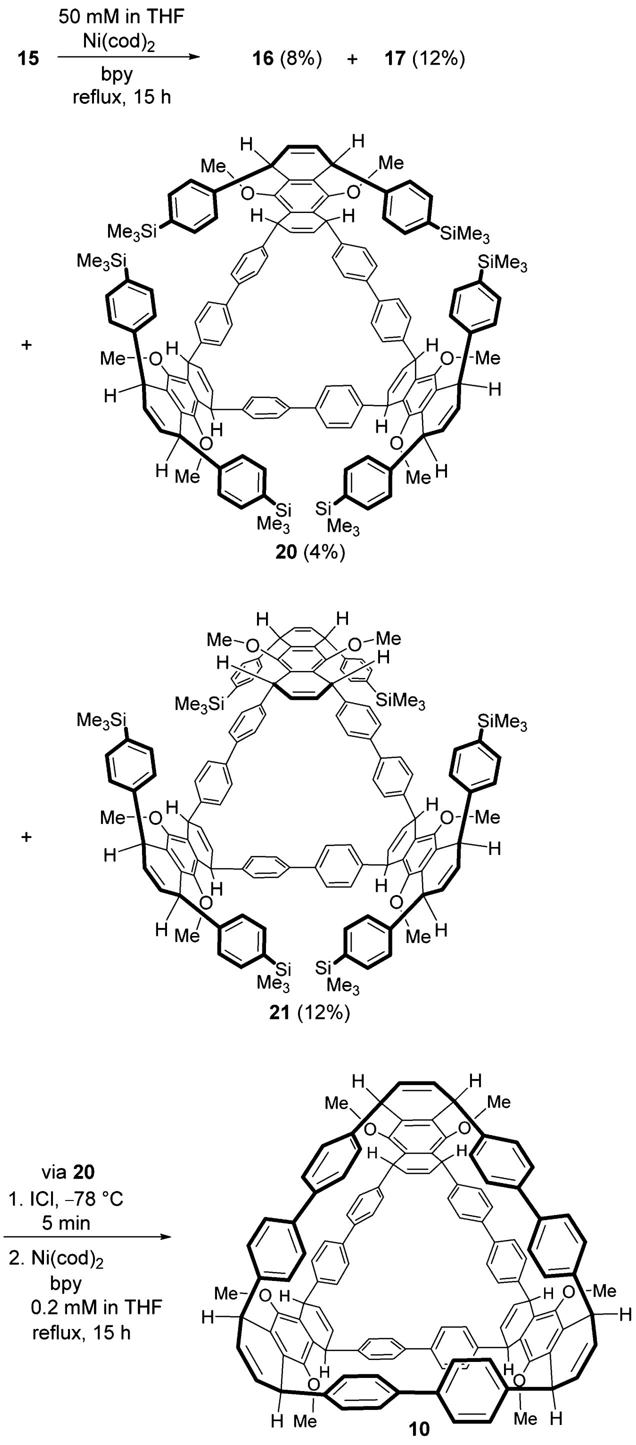


Figure 4. ORTEP drawing of the crystal structure of fused cyclic dimer **8**. A molecule of dichloromethane has been omitted for the sake of clarity.

Scheme 3. Stepwise Synthesis of Fused Carbon Nanohoop 8



Scheme 4. Stepwise Synthesis of Fused Carbon Nanohoop 10



synthesized from **5** directly, supporting the assignment of the structure of **10**.

The molecular structures of cyclic trimers **11** and **12** belong to the C_{2v} group. The two structures could be readily differentiated on the basis of the fact that the ^{1}H NMR spectrum of **11** exhibited three singlets of equal intensity for the three sets of chemically nonequivalent methoxy groups, while **12** showed two singlets in a 2:1 ratio for the two sets of chemically nonequivalent methoxy groups. In addition, upon irradiation of the H^1 and H^4 signals of **11** simultaneously, the H^2 signal became a doublet and the H^3 signal also became a doublet with an AB pattern between them. For **12**, upon irradiation of H^1, H^2 became a singlet, and likewise, upon irradiation of H^4, H^3 became a singlet.

The use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) for the oxidative aromatization reaction of a [9]CPP precursor under mild thermal conditions was found to be successful in producing a fully aromatized [9]CPP derivative bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units.[6] We have attempted to oxidize **10** with DDQ to form two fully aromatized [9]CPP units. Unfortunately, oxidative aromatization with DDQ at temperatures ranging from ambient temperature to 70 °C failed to produce the desired product. Partial removal of the benzylic hydrogens was observed at the initial stage of the oxidative aromatization process at 50 °C. Forcing the reaction to go to completion to form the fully aromatized product resulted in decomposition.

■ CONCLUSIONS

The Diels−Alder reactions between 2 equiv of (*E*,*E*)-1,4-bis(4-bromophenyl)-1,3-butadiene (**1**) and 1,4-benzoquinone (**2**) led to the formation of **5** having all four 4-bromophenyl groups *cis* to one another, which is essential for macrocyclic ring formation. The nickel-mediated homocoupling reactions of **5** produced partially hydrogenated CPPs with bent and fused molecular structures. The two fused 4H[6]CPP units in **8** and the two 6H[9]CPP units in **10** were connected with an armchair carbon nanotube-like arrangement and aligned with the holes facing each other. Other partially hydrogenated CPPs with bent and fused macrocyclic structures in **9**, **11**, and **12** were likewise constructed. The structure of **8** was established by X-ray structure analysis. The other fused and bent structures were established by extensive NMR studies and by the development of independent synthetic pathways. While the synthetic sequence outlined in Scheme 3 was developed to provide an independent confirmation of the structure of **8**, the possibility of using two different 1,3-butadienes for condensation with 1,4-benzoquinone (**2**) provides opportunities to fuse together a variety of macrocyclic ring structures with equal or different ring sizes. The results of this research will be presented in due course.

■ EXPERIMENTAL SECTION

General Experimental Methods. All air- and moisture-sensitive reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. (*E*,*E*)-1,4-Bis(4-bromophenyl)-1,3-butadiene (**1**)[10] and 1,4-bis[4-(trimethylsilyl)phenyl]-1,3-butadiyne[11] were prepared according to the reported procedures. Boron trifluoride diethyl etherate ($BF_3·OEt_2$), 1,4-benzoquinone (**2**), silver(I) oxide (Ag_2O), dimethyl sulfate, bis(1,5-cyclooctadiene)nickel [$Ni(cod)_2$], 2,2′-bipyridyl (bpy), aluminum chloride ($AlCl_3$), iodine chloride (ICl), *n*-butyllithium in hexanes (1.6 M), triethylsilane, [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) [$Pd(dppf)Cl_2$], palladium(II) acetate [$Pd(OAc)_2$], 1,1′-bis(diphenylphosphino)-ferrocene (dppf), copper(II) sulfate ($CuSO_4$), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from chemical suppliers and were used as received. Infrared (IR) spectra of solid samples were recorded on an Fourier transform infrared system equipped with a diamond crystal attenuated total reflectance sampling interface. HRMS spectra were obtained on an FT-ICR mass analyzer coupled with electrospray ionization (ESI).

*Preparation of Dibromide **4**.* To a mixture of 3.64 g of diene **1** (10.0 mmol) and 1.30 g of 1,4-benzoquinone (**2**, 12.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of $BF_3·OEt_2$ (8.10 mmol). The reaction mixture was stirred at rt for 20 h. The reaction mixture was then passed through a short silica gel column, and the column was further eluted with dichloromethane. The combined eluates were concentrated to afford **3** as a brown/yellow solid. Crude **3** was used for the next step without further purification. To crude **3** and 2.78 g of silver oxide (12.0 mmol) under a nitrogen atmosphere was added 100 mL of anhydrous diethyl ether. The reaction mixture was stirred at rt for 12 h and then passed through a short silica gel column. The column was further eluted with diethyl ether (2 × 50 mL), and the combined eluates were concentrated. The residue was recrystallized from diethyl ether to afford 3.76 g of **4** (8.00 mmol, 80% yield) as a brown solid: mp 149−151 °C; IR 1655, 1485, 1293, 1010, 864, 812 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.43 (4 H, d, *J* = 8.4 Hz), 7.15 (4 H, d, *J* = 8.4 Hz), 6.69 (2 H, s), 5.91 (2 H, d, *J* = 2.4 Hz), 4.72 (2 H, d, *J* = 3.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 185.8, 141.4, 140.1, 136.3, 131.7, 130.0, 126.4, 120.8, 39.8; HRMS (ESI) calcd for $C_{22}H_{14}Br_2O_2$ (M^+) 467.9355, 469.9335, 471.9314, found 467.9350, 469.9327, 471.9309. Recrystallization of **4** from chloroform and hexanes produced a single crystal suitable for X-ray structure analysis.

*Preparation of Tetrabromides **5** and **6**.* To a mixture of 3.64 g of diene **1** (10.0 mmol) and 4.70 g of dibromide **4** (10.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of $BF_3·OEt_2$ (8.10 mmol). The reaction mixture was stirred at rt for 20 h. The reaction mixture was then passed through a short silica gel column, and the column was further eluted with dichloromethane (2 × 100 mL). The combined eluates were concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 5.52 g of potassium carbonate in dry acetone (200 mL) was added 2.40 mL of dimethyl sulfate (25.4 mmol) via a syringe, and the reaction mixture was heated at reflux for 3 h. The reaction mixture was then allowed to cool to rt and concentrated. Distilled water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue (8:1 **5**:**6** as determined by ^1H NMR spectroscopy) was purified by flash column chromatography (silica gel, 1:4 dichloromethane/hexanes) to separate **5** and **6**. Recrystallization from chloroform produced 5.86 g of tetrabromide **5** (6.80 mmol, 68% yield) as a white solid and a sample of **6** suitable for X-ray structure analysis. **5**: mp 174−176 °C; IR 1485, 1009, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.22 (8 H, d, *J* = 8.4 Hz), 6.81 (8 H, d, *J* = 9.0 Hz), 6.08 (4 H, d, *J* = 3.6 Hz), 4.80 (4 H, d, *J* = 3.0 Hz), 3.52 (6 H, s); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 152.1, 142.6, 131.17, 131.15, 129.2, 128.1, 119.9, 60.4, 40.4; HRMS (ESI) calcd for $C_{40}H_{30}Br_4O_2$ (M^+) 859.8953, 861.8933, 863.8912, found 859.8940, 861.8930, 863.8901. **6**: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36 (8 H, d, *J* = 8.8 Hz), 7.06 (8 H, d, *J* = 8.8 Hz), 5.86 (4 H, d, *J* = 2.8 Hz), 4.82 (4 H, d, *J* = 2.8 Hz), 2.97 (6 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.7, 143.6, 131.5, 131.0, 129.6, 127.3, 120.1, 60.2, 41.0; HRMS (ESI) calcd for $C_{40}H_{30}Br_4O_2$ (M^+) 859.8953, 861.8933, 863.8912, found 859.8906, 861.8868, 863.8885.

*Preparation of Tetraiodide **7**.* To 1.01 g of **5** (11.7 mmol) in 250 mL of dry THF at −78 °C was added dropwise 32.2 mL of a 1.6 M solution of *n*-butyllithium (51.5 mmol) in hexanes. After 2 h at −78 °C, a solution of 14.8 g of iodine (58.3 mmol) in 100 mL of THF was added dropwise. Then the reaction mixture was stirred at rt for 12 h. Distilled water (100 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 50 mL) and dichloromethane (100 mL). The combined organic layers were dried over magnesium sulfate and concentrated. Recrystallization of the residue from dichloromethane and hexanes produced a single crystal of **7** suitable for X-ray structure analysis: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42 (8 H, d, *J* = 8.4 Hz), 6.68 (8 H, d, *J* = 8.4 Hz), 6.07 (4 H, d, *J* = 3.2 Hz), 4.78 (4 H, d, *J* = 2.8 Hz), 3.52 (6 H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 143.3, 137.1, 131.0, 129.5, 128.0, 91.4, 60.4, 40.5.

*Preparation of Cyclic Dimers **8** and **9** and Cyclic Trimers **10**−**12**.* To an oven-dried 2 L flask were added 1.26 g of tetrabromide **5** (1.46 mmol) and 1.00 g of bpy (6.40 mmol). Then the flask was flushed with nitrogen and placed in a glovebox, and 1.77 g of bis(1,5-cyclooctadiene)nickel (6.43 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox before 1.5 L of THF was added via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h before it was allowed to cool to rt. The reaction mixture was then passed through a short silica gel column, and the column was further eluted with dichloromethane (3 × 150 mL). The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel, 1:5 to 2:1 dichloromethane/hexanes) to produce, in the sequence of appearance from the column, 0.039 g of **8** (0.036 mmol, 5% yield) as a white solid and 0.008 g of **9** (0.007 mmol, 1% yield) as a white solid. At 50 mM **5** (1.96 g, 2.27 mmol), in the sequence of appearance from the column after **8** and **9**, 0.014 g of **12** (0.009 mmol, 1% yield) as a white solid, 0.012 g of **11** (0.007 mmol, 1% yield) as a white solid, and 0.006 g of **10** (0.004 mmol, 0.5% yield) as a white solid were isolated. **8**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 6.94 (8 H, dd, J = 4.1, 2.5 Hz), 6.68 (16 H, d, J = 7.9 Hz), 6.54 (16 H, d, J = 8.2 Hz), 5.17 (8 H, m), 3.83 (12 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 151.4, 139.8, 139.7, 133.9, 132.0, 127.7, 126.8, 62.0, 38.3; HRMS (ESI) calcd for $C_{80}H_{60}O_4$ (M$^+$) 1084.4486, found 1084.4509. Recrystallization of **8** from dichloromethane and hexanes produced a single crystal suitable for X-ray structure analysis. **9**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 6.71 (8 H, dd, J = 3.8, 1.8 Hz), 6.49 (16 H, d, J = 8.3 Hz), 6.44 (16 H, d, J = 7.7 Hz), 5.09 (8 H, dd, J = 3.6, 1.7 Hz), 3.86 (12 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz, from gHMBCAD) 151.9, 139.3, 130.2, 128.3, 127.0, 61.5, 38.8 (the signals from C2 and C8 were not observed); HRMS (ESI) calcd for $C_{80}H_{60}O_4$ (M$^+$) 1084.4486, found 1084.4494. **10**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.23 (24 H, d, J = 8.4 Hz), 6.92 (24 H, d, J = 7.8 Hz), 6.11 (12 H, d, J = 2.4 Hz), 4.78 (12 H, d, J = 2.4 Hz), 3.71 (18 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.7, 142.8, 138.3, 130.6, 127.8, 127.4, 126.5, 60.2, 40.5; HRMS (ESI) calcd for $C_{120}H_{91}O_6$ (MH$^+$) 1627.6810, found 1627.6895. **11**: ^{1}H NMR (CDCl$_3$, 600 MHz, 25 °C) δ 7.33 (8 H, d, J = 7.8 Hz), 7.14 (8 H, d, J = 8.4 Hz), 7.05 (8 H, d, J = 8.4 Hz), 6.91 (8 H, d, J = 8.4 Hz), 6.88 (8 H, d, J = 7.8 Hz), 6.87 (8 H, d, J = 7.8 Hz), 6.84 (4 H, dd, J = 4.5, 3.3 Hz), 6.06 (4 H, dd, J = 10.2, 3.6 Hz), 6.03 (4 H, dd, J = 10.2, 3.6 Hz), 5.24 (4 H, m), 4.73 (8 H, m), 3.746 (6 H, s), 3.745 (6 H, s), 3.61 (6 H, s) [at −20 °C, the three CH_3O signals appear at δ 3.76 (6 H, s), 3.74 (6 H, s), and 3.59 (6 H, s)]; ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.9, 152.8, 151.3, 143.2, 142.8, 140.6, 138.0, 137.8, 137.5, 133.9, 132.9, 130.8, 129.9, 127.8, 127.7, 127.6, 127.5, 126.4, 126.3, 126.1, 125.8, 61.8, 60.6, 59.7, 40.8, 40.6, 38,8; HRMS (ESI) calcd for $C_{120}H_{91}O_6$ (MH$^+$) 1627.6810, found 1627.6744. **12**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.20 (8 H, d, J = 8.4 Hz), 7.09 (8 H, d, J = 8.4 Hz), 6.91 (8 H, d, J = 7.2 Hz), 6.895 (4 H, m), 6.89 (8 H, d, J = 8.4 Hz), 6.88 (8 H, d, J = 8.4 Hz), 6.83 (4 H, m), 6.82 (8 H, d, J = 9.0 Hz), 5.98 (4 H, d, J = 2.4 Hz), 5.26 (4 H, m), 5.23 (4 H, m), 4.68 (4 H, d, J = 2.4 Hz), 3.73 (12 H, s), 3.66 (6 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.9, 151.7, 143.4, 140.6, 140.4, 138.5, 137.7, 137.4, 134.2, 133.8, 133.0, 130.4, 127.69, 127.65, 127.58, 127.2, 126.8, 126.2, 126.1, 125.6, 61.9, 60.0, 40.9, 38.8, 38.7; HRMS (ESI) calcd for $C_{120}H_{91}O_6$ (MH$^+$) 1627.6810, found 1627.6680.

*Preparation of 1,3-Butadiene **14**.* To a mixture of 1,4-bis[4-(trimethylsilyl)phenyl]-1,3-butadiyne (1.00 g, 2.89 mmol), 2.00 mL of triethylsilane (12.5 mmol), Pd(dppf)Cl$_2$ (0.063 g, 0.086 mmol), Pd(OAc)$_2$ (0.020 g, 0.089 mmol), dppf (0.160 g, 0.289 mmol), and CuSO$_4$ (0.138 g, 0.865 mmol) were added 10 mL of toluene and 10 mL of water.[12] The reaction mixture was heated at reflux under air for 24 h before it was allowed to cool to rt. The solvent was removed in vacuo; the residue was passed through a short silica gel column (5 cm), and the column was eluted with dichloromethane (50 mL). The combined eluates were concentrated in vacuo, and the residue was washed with methanol and pentane. After 2 h in vacuo, 0.650 g of **14** (1.85 mmol, 64% yield) was obtained as a white solid: mp 146−148 °C; IR 1245, 1109, 838 cm^{-1}; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.49 (4 H, d, J = 8.0 Hz), 7.42 (4 H, d, J = 8.0 Hz), 6.99 (2 H, m), 6.67 (2 H, m); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 140.0, 137.7, 133.7, 132.9, 129.5, 125.7, −1.14; HRMS (ESI) calcd for $C_{22}H_{30}Si_2$ (M$^+$) 350.1881, found 350.1887.

*Preparation of Dibromide **15**.* To a flask containing 3.50 g of diene **14** (10.0 mmol), 4.70 g of dibromide **4** (10.0 mmol), and 0.34 g of anhydrous AlCl$_3$ (2.5 mmol) was added 200 mL of anhydrous dichloromethane. The reaction mixture was stirred at rt for 20 h and then passed through a short silica gel column. The column was eluted with dichloromethane, and the eluates were concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 5.52 g of potassium carbonate (40 mmol) in dry acetone (200 mL) was added 2.4 mL of dimethyl sulfate (25.4 mmol) via a syringe, and the reaction mixture was heated at reflux for 3 h. The reaction mixture was allowed to cool to rt and concentrated. Distilled water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel, 1:4 to 1:2 dichloromethane/hexanes) to produce 4.67 g of **15** (5.50 mmol, 55% yield) as a yellow solid: mp 97−98 °C; IR 1487, 1248, 839 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.27 (4 H, d, J = 8.4 Hz), 7.17 (4 H, d, J = 8.4 Hz), 6.95 (4 H, d, J = 8.4 Hz), 6.79 (4 H, d, J = 8.4 Hz), 6.11 (2 H, d, J = 3.6 Hz), 6.02 (2 H, d, J = 2.8 Hz), 4.81 (2 H, d, J = 2.8 Hz), 4.80 (2 H, d, J = 3.2 Hz), 3.54 (6 H, s), 0.23 (18 H, s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 152.3, 144.6, 142.7, 137.4, 133.1, 131.5, 131.0, 130.6, 129.2, 128.2, 127.7, 126.8, 119.7, 60.3, 41.2, 40.2; HRMS (ESI) calcd for $C_{46}H_{48}Br_2O_2Si_2$ (M$^+$) 846.1554, 848.1534, 850.1513, found 846.1595, 848.1573, 850.1546.

*Preparation of Cyclic Tetrasilanes **16** and **17**.* To an oven-dried 1 L flask were added 0.570 g of dibromide **15** (0.671 mmol) and 0.25 g of bpy (1.6 mmol). The reaction flask was flushed with nitrogen and then placed in a glovebox before 0.44 g of bis(1,5-cyclooctadiene) nickel (1.6 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox. THF (700 mL) was added via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h before it was allowed to cool to rt. The reaction mixture was passed through a short silica gel column, and the column was eluted with dichloromethane (100 mL). The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel, 1:6 to 1:3 dichloromethane/hexanes) to produce 0.220 g of crude **16** as a white solid and 0.137 g of **17** (0.0994 mmol, 30% yield) as a white solid. A fraction of **16** was further purified by preparative TLC to afford a more pure sample of **16** for structural elucidation. **16**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.47 (8 H, d, J = 8.4 Hz), 7.34 (8 H, d, J = 8.4 Hz), 6.83 (4 H, dd, J = 4.5, 2.7 Hz), 6.67 (8 H, d, J = 8.4 Hz), 6.54 (8 H, br), 5.97 (4 H, d, J = 2.4 Hz), 5.03 (4 H, m), 4.95 (4 H, d, J = 2.4 Hz), 3.46 (12 H, s), 0.25 (36 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.0, 145.9, 140.0, 138.6, 137.6, 134.2, 133.5, 133.3, 130.7, 127.4, 127.0, 126.1, 61.0, 42.1, 38.4, −0.86; HRMS (ESI) calcd for $C_{92}H_{96}O_4Si_4$ (M$^+$) 1376.6380, found 1376.6472. **17**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.49 (8 H, d, J = 7.8 Hz), 7.33 (8 H, d, J = 7.8 Hz), 6.86 (4 H, dd, J = 4.2, 3.0 Hz), 6.65 (8 H, d, J = 8.4 Hz), 6.51 (8 H, br d), 6.01 (4 H, d, J = 2.4 Hz), 5.01 (4 H, m), 4.95 (4 H, d, J = 1.8 Hz), 3.55 (12 H, s), 0.26 (36 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 151.8, 145.8, 139.9, 138.5, 137.6, 134.2, 133.4, 133.1, 130.6, 127.4, 127.0, 126.0, 60.9, 42.0, 38.3, −1.0; HRMS (ESI) calcd for $C_{92}H_{96}O_4Si_4$ (M$^+$) 1376.6380, found 1376.6412.

*Experimental Procedure for Iodination of **16** and the Subsequent Nickel-Mediated Homocoupling Reactions to Form **8**.* One-third of the crude **16** was dissolved in 20 mL of dichloromethane under a nitrogen atmosphere and cooled to −78 °C. To the solution at −78 °C was added dropwise 0.2 mL of a 1 M solution of ICl in dichloromethane. After 5 min at −78 °C, the reaction was quenched with a saturated sodium thiosulfate solution and the mixture diluted with 30 mL of water. The reaction mixture was extracted with dichloromethane (3 × 20 mL), dried over sodium sulfate, and concentrated to afford crude **18** as a white solid. To crude **18** in a 250 mL flask was added 0.41 g of bpy (0.26 mmol), and the flask was flushed with nitrogen. The flask was then placed in a glovebox before 0.73 g of bis(1,5-cyclooctadiene)nickel (0.26 mmol) was added. The flask was fitted with a condenser and a rubber septum and removed from the glovebox before 100 mL of THF was added via cannula under a nitrogen atmosphere. The reaction mixture was heated at reflux for 15 h before it was allowed to cool to rt. The reaction mixture was then passed through a short silica gel column, and the column was eluted with dichloromethane (100 mL). The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel, 1:5 dichloromethane/hexanes) to produce 0.009 g of **8** (8% yield from **15**). **18**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.65 (8 H, d, J = 8.0 Hz), 7.06 (8 H, d, J = 8.4 Hz), 6.83 (4 H, dd, J = 4.2, 2.2 Hz), 6.65 (8 H, d, J = 8.4 Hz), 6.46 (8 H, br d), 6.05 (4 H, d, J = 2.0 Hz), 5.00 (4 H, br), 4.92 (4 H, d, J = 2.0 Hz), 3.53 (12 H, s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 151.6, 144.5, 139.7, 138.5, 137.4, 134.6, 133.1, 130.2, 129.9, 127.8, 127.3, 126.1, 91.8, 61.1, 41.3, 38.3. Cyclic dimer **8** produced from **18** showed ^{1}H NMR signals identical to those of the sample produced directly from **5**.

*Experimental Procedure for Iodination of **17** and the Subsequent Nickel-Mediated Homocoupling Reactions.* The same procedure for iodination of **16** was applied to **17**. Iodination of **17** with ICl produced crude **19**, which was treated with Ni(cod)$_2$ and bpy for the nickel-mediated homocoupling reactions. However, only oligomers and/or polymers were produced. **19**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.64 (8 H, d, *J* = 8.8 Hz), 7.05 (8 H, d, *J* = 8.0 Hz), 6.85 (4 H, dd, *J* = 4.6, 2.6 Hz), 6.66 (8 H, d, *J* = 8.8 Hz), 6.46 (8 H, d, *J* = 7.6 Hz), 6.03 (4 H, d, *J* = 2.8 Hz), 5.00 (4 H, m), 4.91 (4 H, d, *J* = 2.8 Hz), 3.57 (12 H, s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 151.6, 144.6, 139.6, 138.5, 137.4, 134.7, 133.0, 130.0, 129.7, 127.7, 127.3, 126.1, 91.4, 61.0, 41.3, 38.2.

*Preparation of Cyclic Hexasilanes **20** and **21**.* To an oven-dried 200 mL flask were added 1.42 g of dibromide **15** (1.67 mmol) and 0.57 g of bpy (3.65 mmol). Then the flask was flushed with nitrogen and placed in a glovebox before 1.01 g of bis(1,5-cyclooctadiene)nickel (3.67 mmol) was added. The flask was fitted with a condenser and a rubber septum and then removed from the glovebox before 30 mL of THF was added via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h before it was allowed to cool to rt. The reaction mixture was passed through a short silica gel column, and the column was eluted with dichloromethane. The combined eluates were concentrated, and the residue was purified by flash column chromatography (silica gel, 1:5 to 1:1 dichloromethane/hexanes) to produce 0.090 g of **16** (0.065 mmol, 8% yield) as a white solid, 0.132 g of **17** (0.096 mmol, 12% yield) as a white solid, 0.140 g of **21** (0.068 mmol, 12% yield) as a white solid, and crude **20** (4% NMR yield) as a white solid. **20**: ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.44 (12 H, d, *J* = 8.4 Hz), 7.27 (12 H, d, *J* = 8.4 Hz), 7.18 (12 H, d, *J* = 7.8 Hz), 7.03 (12 H, d, *J* = 8.4 Hz), 6.08 (6 H, d, *J* = 3.6 Hz), 6.00 (6 H, d, *J* = 3.0 Hz), 4.99 (6 H, d, *J* = 3.0 Hz), 4.96 (6 H, d, *J* = 3.0 Hz), 3.22 (18 H, s), 0.08 (54 H, s); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 153.0, 144.8, 143.7, 138.2, 137.2, 133.1, 132.1, 131.4, 128.5, 128,4, 127.9, 127.2, 126.5, 61.4, 41.5, 41.4, −1.02; HRMS (ESI) calcd for C$_{138}$H$_{145}$O$_6$Si$_6$ (MH$^+$) 2065.9651, found 2065.9652. **21**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.37 (4 H, d, *J* = 8.0 Hz), 7.34 (4 H, d, *J* = 8.4 Hz), 7.33 (4 H, d, *J* = 8.4 Hz), 7.26 (4 H, d, *J* = 8.4 Hz), 7.21 (4 H, d, *J* = 8.0 Hz), 7.135−7.107 (12 H, m), 7.09 (4 H, d, *J* = 8.4 Hz), 6.99 (4 H, d, *J* = 7.6 Hz), 6.89 (4 H, d, *J* = 7.6 Hz), 6.87 (4 H, d, *J* = 8.0 Hz), 6.14−6.02 (12 H, m), 4.95 (6 H, d, *J* = 3.6 Hz), 4.90 (2 H, d, *J* = 2.8 Hz), 4.86−4.83 (4 H, m), 3.57 (6 H, s), 3.55 (6 H, s), 3.19 (6 H, s), 0.18 (18 H, s), 0.07 (18 H, s), 0.01 (18 H, s); ^{13}C NMR (CDCl$_3$, 100 MHz) δ 152.9, 152.6, 152.4, 144.6, 144.45, 144.38, 143.5, 142.98, 142.95, 138.6, 138.5, 138.0, 137.1, 137.0, 133.08, 133.03, 133.01, 131.8, 131.58, 131.53, 131.1, 130.7, 130.5, 129.0, 128.7, 128.3, 128.1, 128.0, 127.77, 127.71, 126.99, 126.92, 126.69, 126.60, 126.57, 126.4, 61.1, 60.8, 60.5, 41.5, 40.9, 40.7, −1.03, −1.07, −1.12; HRMS (ESI) calcd for C$_{138}$H$_{144}$O$_6$Si$_6$ (M$^+$) 2064.9573, found 2064.9574.

*Experimental Procedure for Iodination of **20** and the Subsequent Nickel-Mediated Homocoupling Reactions To Form **10**.* Crude **20** was dissolved in 20 mL of dichloromethane under a nitrogen atmosphere and cooled to −78 °C. To the solution at −78 °C was added dropwise 0.15 mL of a solution of 1 M ICl in dichloromethane. After 5 min at −78 °C, the reaction was quenched with a saturated sodium thiosulfate solution and the mixture diluted with 30 mL of water. The solution was extracted with dichloromethane (3 × 20 mL), dried over sodium sulfate, and concentrated to afford a crude mixture of the corresponding tetraiodide. To the crude tetraiodide in a 250 mL flask was added 0.030 g of bpy (0.19 mmol), and the flask was flushed with nitrogen before it was placed in a glovebox. Then, 0.050 g of bis(1,5-cyclooctadiene)nickel (0.18 mmol) was added. The flask was fitted with a condenser and a rubber septum before it was removed from the glovebox. THF (100 mL) was added via cannula under a nitrogen atmosphere, and the reaction mixture was heated at reflux for 15 h before it was allowed to cool to rt. The reaction mixture was passed through a short silica gel column, and the column was eluted with dichloromethane (50 mL). The combined eluates were concentrated in vacuo. The ^{1}H NMR spectrum of the residue showed that cyclic trimer **10** was produced.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02789.

X-ray crystallographic file for **4**, X-ray crystallographic file for **6**, X-ray crystallographic file for **7**, and X-ray crystallographic file for **8** (CIF)

NMR spectra, tables listing crystal data and structure refinement and bond lengths and angles for **4** and **6**−**8**, and computational coordinates and energetic details of DFT calculations (PDF)

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Notes

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■ REFERENCES

(1) (a) Yamago, S.; Kayahara, E.; Iwamoto, T. *Chem. Rec.* **2014**, *14*, 84−100. (b) Darzi, E. R.; Jasti, R. *Chem. Soc. Rev.* **2015**, *44*, 6401−6410. (c) Segawa, Y.; Yagi, A.; Matsui, K.; Itami, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 5136−5158. (d) Hammer, B. A. G.; Müllen, K. *Chem. Rev.* **2016**, *116*, 2103−2140.

(2) (a) Jasti, R.; Bertozzi, C. R. *Chem. Phys. Lett.* **2010**, *494*, 1−7. (b) Fort, E. H.; Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 16006−16007. (c) Bodwell, G. J. *Nat. Nanotechnol.* **2010**, *5*, 103−104. (d) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. *Nat. Chem.* **2013**, *5*, 572−576. (e) Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature* **2014**, *512*, 61−64. (f) Sisto, T. J.; Zakharov, L. N.; White, B. M.; Jasti, R. *Chem. Sci.* **2016**, *7*, 3681−3688.

(3) (a) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646−17647. (b) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112−6116. (c) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 757−759. (d) Liu, Y.-Y.; Lin, J.-Y.; Bo, Y.-F.; Xie, L.-H.; Yi, M.-D.; Zhang, X.-W.; Zhang, H.-M.; Loh, T.-P.; Huang, W. *Org. Lett.* **2016**, *18*, 172−175. (e) Li, S.; Huang, C.; Thakellapalli, H.; Farajidizaji, B.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.*

2016, *18*, 2268−2271. (f) Golder, M. R.; Colwell, C. E.; Wong, B. M.; Zakharov, L. N.; Zhen, J.; Jasti, R. *J. Am. Chem. Soc.* **2016**, *138*, 6577−6582. (g) Kuroda, Y.; Sakamoto, Y.; Suzuki, T.; Kayahara, E.; Yamago, S. *J. Org. Chem.* **2016**, *81*, 3356−3363.

(4) Xia, J.; Golder, M. R.; Foster, M. E.; Wong, B. M.; Jasti, R. *J. Am. Chem. Soc.* **2012**, *134*, 19709−19715.

(5) Ishii, Y.; Matsuura, S.; Segawa, Y.; Itami, K. *Org. Lett.* **2014**, *16*, 2174−2176.

(6) Huang, C.; Huang, Y.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2014**, *16*, 2672−2675.

(7) (a) Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2015**, *17*, 3470−3473. (b) Farajidizaji, B.; Thakellapalli, H.; Li, S.; Huang, C.; Baughman, N. N.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Chem. - Eur. J.* **2016**, *22*, 16420−16424.

(8) Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244−3248.

(9) (a) Golling, F. E.; Quernheim, M.; Wagner, M.; Nishiuchi, T.; Müllen, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 1525−1528. (b) Beinhoff, M.; Karakaya, B.; Schlüter, A. D. *Synthesis* **2003**, 0079−0090. (c) Sekiguchi, R.; Takahashi, K.; Kawakami, J.; Sakai, A.; Ikeda, H.; Ishikawa, A.; Ohta, K.; Ito, S. *J. Org. Chem.* **2015**, *80*, 5092−5110.

(10) Davis, M. C.; Groshens, T. J. *Synth. Commun.* **2010**, *41*, 206−218.

(11) Matsuda, T.; Kadowaki, S.; Murakami, M. *Chem. Commun.* **2007**, 2627−2629.

(12) Luo, F.; Pan, C.; Wang, W.; Ye, Z.; Cheng, J. *Tetrahedron* **2010**, *66*, 1399−1403.