

Synthesis of [n]- and [n.n]Cyclophanes by Using Suzuki–Miyaura Coupling

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Reaction of the bis-9-BBN adduct of several dienes with 1,3-dibromobenzene via Suzuki coupling leads to a series of [n]metacyclophanes ranging in size from 10 to 17 atom members. In each case, two carbon-carbon bonds are formed in one reaction vessel. However, when the bis-9-BBN adduct of 1,5-hexadiene is coupled with a variety of aryl dihalides, larger [*n.n*]cyclophanes were formed in preference to the [n]cyclophanes. Four carbon–carbon bonds are formed in this instance. Singlecrystal X-ray analyses of these [n.n]cyclophanes reveal interestingly shaped molecules with large cavities.

Introduction

Cyclophanes are bridged aromatic compounds that have been investigated since the 1950s for the unique interactions of the π -electron systems of the benzene rings and for their potential as molecular hosts.¹ The first directed synthesis of a cyclophane was the preparation of [2.2]paracyclophane performed by Cram and Steinberg.² Since that time, the field has evolved to include supramolecular systems capable of molecular recognition in which cyclophanes serve as host molecules.³ [n]-Metacyclophanes have been prepared in a variety of ways primarily, it appears, through rearrangement chemistry.⁴ For example, [5]metacyclophane, the smallest [n]cyclophane known, was synthesized by Bickelhaupt and coworkers by base-induced rearrangement of a strained dichloropropellane.⁵ In another approach, Vögtle and co-

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workers used flash vacuum pyrolysis in the extrusion of SO₂ to form a series of medium-sized [n]metacyclophanes.⁶ An additional, flexible synthesis for all-carbon systems was developed by Kumada and co-workers in which several metacyclophanes and (2,6)pyridinophanes were prepared via the Ni(II) catalyzed coupling of a bis-Grignard reagent with aromatic dihalides.⁷ A great deal is known about the smaller all-carbon [*n*.*n*]cyclophanes, particularly the [2.2]cyclophanes. Perhaps the most successful approach to the synthesis of small [n.n]cyclophanes has been sequential Wurtz couplings of halogenated aromatics and SO₂ extrusion of dithiacyclophanes.⁸

Our interest in cyclophane chemistry stems from our investigations of silicon-containing cage compounds. In this work, we demonstrated that three sequential carboncarbon bonds form to make a silicon-containing cage compound using Suzuki-Miyaura coupling⁹ of an aryl tribromide with the 9-BBN adduct of methyltriallylsilane.¹⁰ At that point, we decided to pursue the study of all-carbon systems using Suzuki-Miyaura coupling and found that we could prepare [6.6]metacyclophane (an 18membered ring) in 5% yield from 1,5-hexadiene and 1,3dibromobenzene.¹¹ This rather surprising result, in which four carbon-carbon bonds were formed in the reaction, prompted us to investigate the synthesis of all-carbon cyclophanes further. Herein we report the synthesis of a series of all-carbon [n]metacyclophanes as well as the

[#] The synthesis of the [*n*.*n*]cyclophanes was taken, in part, from the M.S. theses of Beverly B. Smith (1997) and David Cartrette (1997), Western Carolina University.

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 a Key: (i) 2.5 M 9-BBN in THF, room temperature, 3 h; (ii) Pd(PPh_3)_4, NaOH, 1,3-dibromobenzene, THF, reflux overnight.

synthesis and X-ray crystal structures of several [*n*.*n*]-cyclophanes.

Results and Discussion

Synthesis of [n]Metacyclophanes. Our strategy for preparing these large- ring systems relies on making multiple carbon-carbon bonds in a single reaction vessel with homogeneous catalysis. We chose to use Suzuki-Miyaura coupling, the palladium-catalyzed coupling of an alkyl borane with an aryl halide, to make sequential carbon-carbon bonds for two reasons. The conditions of the reaction are mild, when the appropriate base is used, so a wide variety of functional groups can be tolerated and the starting reagents, dienes and aryl halides, are readily available. A homologous series of these cyclophanes ranging from [7]metacyclophane (3a) to [14]metacyclophane (3e) has been prepared in fair yields (Scheme 1). For instance, treatment of 1,5-heptadiene (1a) with 2.1 equiv of 9-BBN in THF provides the bis-9-BBN adduct of heptadiene (2a). Subsequent reaction of 2a with 1,3-dibromobenzene, NaOH, and 0.3 mol % Pd- $(PPh_3)_4$ in refluxing THF overnight resulted in a 17% vield of [7]metacyclophane (3a). As with all the cyclophanes prepared in this study, there are undoubtedly polymeric side products that have formed, but these were not characterized.

An interesting feature of the ¹H NMR spectrum of **3a** is the strong shielding effect exhibited by the π cloud of the benzene ring on the methylene chain. This effect is particularly apparent with the hydrogens of the fourth carbon on the seven carbon bridge, which appears as a broad singlet at $\delta = -0.15$ ppm. Each of the homologues in the series shows this upfield shift, which predictably diminishes as the bridge length increases.

Synthesis and Crystal Structures of [6.6]Cyclophanes. We are limited in constructing the [n]metacyclophanes using Suzuki coupling to dienes containing seven carbon atoms or more; when the bis-9-BBN adduct of 1,5-hexadiene was combined with 1,3-dibromobenzene only the [6.6]metacyclophane was isolated and none of the [6]metacyclophane could be detected.¹⁰ Thus, in an analogous series of reactions, treatment of 1,5-hexadiene (4) with 2.1 equiv of 9-BBN in THF affords the bis-9-BBN adduct of hexadiene. Reaction of this bis-adduct with 1,4-dibromobenzene, NaOH, and 0.3 mol % Pd-(PPh₃)₄ in refluxing THF overnight provided the desired [6.6]paracyclophane (5) in 6% yield (Scheme 2).

Crystal structure determination of [6.6]paracyclophane (5) indicates that the benzene rings are parallel to each other (Figure 1). The center-to-center distance of the rings is 6.257 Å and the width of the cavity is 6.682 Å. Interestingly, when Cram and co-workers first reported the synthesis of [6.6]paracyclophane via the acyloin

SCHEME 2. Synthesis of [6.6]Cyclophanes^a



^a Key: (i) 2.1 equiv of 9-BBN in THF, room temperature, 3 h;
(ii) Pd(PPh₃)₄, NaOH, dibromoarene, THF, reflux overnight.

condensation the crystal structure was not determined. In fact, refinement for the data set of **5** proved to be very difficult. Close inspection of the ORTEP of **5** in Figure 1 reveals that the thermal ellipsoids representing the carbons in the methylene chain are quite large, indicating a significant amount of vibration in the molecule.

When 3,5-dibromotoluene was coupled with **4**, the [6.6]-(3,5)toluenophane (**6**) was isolated in 5% yield. The toluene ring planes of **6** are parallel (angle between bestfit planes = 0°) (Figure 1). The center-to-center distance of the rings is 7.907 Å and the width of the cavity is 6.736 Å. Neither 2,6-dibromotoluene nor 2,6-dibromomesitylene, when subjected to the same reaction conditions, provided any of the corresponding [6.6]metacyclophanes. This result is not surprising considering the steric obstacles to overcome during the coupling.

Incorporation of a heteroatoms into a cyclophane system was accomplished by Suzuki-Miyaura coupling of 4 with 2,6-dibromopyridine to provide [6.6](2,6)pyridinophane (7) in 6% yield. As with cyclophanes 5 and 6, the aromatic rings of 7 are parallel (Figure 2), but in this instance, the system has the unusual arrangement of four unique molecules per unit cell (P1 space group). The N-N distances between the undistorted pyridine rings are 6.244, 6.265, 6.549, and 6.557 Å (cavity length) and the corresponding cavity widths are 7.326, 7.258, 4.879, and 4.864 Å. Predictably, the longer N-N distances correspond to shorter cavity widths. The ORTEP representation of 7 clearly shows the preferred anti conformation of the cyclophane. Likewise, the [2.2](2,6)pyridinophane adopts an anti conformation. In contrast, the [3.3](2,6)pyridinophane, as inferred from ¹H NMR studies, exhibits syn geometry.12

In an analogous reaction, this time with 3,5-dibromopyridine as the coupling partner, we anticipated formation of [6.6](3,5)pyridinophane; however, none of this isomeric cyclophane was detected. This outcome is not terribly surprising since, aside from entropic factors, nucleophilic substitution is electronically unfavorable at the bromine-bearing carbons. It was Malenfant and Fréchet's elegant work in the solid-phase synthesis of oligothiophenes¹³ that prompted us to investigate incor-

^{(12) (}a) For [3.3](2,6)pyridinophane see: Shinmyozu, T.; Hirai, Y.; Inazu, T. *J. Org. Chem.* **1986**, *51*, 1551–1555. (b) For [2.2](2,6)pyridinophane see: Pahor, N. B.; Calligaris, M.; Randaccio, L. *J. Chem. Soc., Perkins Trans. 2* **1978**, 38–42.

⁽¹³⁾ Malenfant, P. R. L.; Fréchet, J. M. J. Chem. Commun. 1998, 2657–2658.

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FIGURE 1. X-ray crystal structures of compounds **5** (left) and **6** (right). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms were omitted for clarity in **6**.



FIGURE 2. X-ray crystal structure and packing diagram of compound 7. The asymmetric unit consists of four molecular halves generating four independent molecules per unit cell. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms were omitted for clarity.



FIGURE 3. X-ray crystal structure and packing diagram of **8**. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms were omitted for clarity.

porating sulfur atoms into cyclophanes. Thus, we attempted a palladium-catalyzed coupling of 2,5-dibromothiophene with the bis-9-BBN adduct **4** in the hopes of preparing [6.6]thiophenophane. Once again, however, none of the desired cyclophane could be isolated, presumably due to the electronic influence of the heteroatom in the ring. In each case, with both 3,5-dibromopyridine and 2,5-dibromothiophene, all of the aryl dihalide starting material was consumed in the reaction.

The largest cyclophane system that we prepared also proved to have the most interesting crystal structure. Coupling of 2,7-dibromofluorene with the bis-9-BBN adduct of **4** afforded the cyclophane [6.6](2,7)fluorenophane (**8**) in 1% yield. The crystal structure of **8** clearly depicts a box-shaped molecule with a cavity that spans 11.20 Å. The fluorene rings of **8** are in an anti, parallel arrangement and each ring is bent with a 0.11 Å mean deviation from the least-squares plane defined by C(1)-C(13) (Figure 3). The average distance between the fluorene rings is 5.09 Å with the closest center-tocenter distance being 4.07 Å. Overall, each fluorene ring in **8** bends inward by about 0.51 Å. Deformation of this portion of the smaller [2.2](2,7)fluorenophane is also obvious, but in this instance, the fluorene moieties bend outward with separations ranging from 2.79 Å at the side to 3.82 Å at the center.¹⁴ Not only is there significant intramolecular attraction between the fluorene moieties in **8**, but there is also considerable intermolecular $\pi - \pi$ interaction; the separation between the fluorene moieties of the [6.6](2,7)fluorenophane molecules is approximately 3.93 Å. In addition, the intramolecular strain in [2.2](2,7)fluorenophane, as evidenced by the increased CH₂-CH₂ bond length (1.56 Å), is greater than that found in 8, whose relatively strain-free CH2-CH2 bond distances range from 1.51 to 1.52 Å.

⁽¹⁴⁾ Haenel, M. W.; Irngartinger, H.; Krieger, C. Chem. Ber. 1985, 118, 144–163.

Typically, the aromatic moieties of organic [*n.n*]cyclophanes bend outward when connected by short bridging units due to repulsion of these bridging units with the overlapping aromatic rings.¹⁵ However, when the bridging units of a polycyclic aromatic hydrocarbon consist of silver ions, the aromatic rings of the metallocyclophane bend inward.¹⁶ The bridging silver ions permit a strainfree geometry leading to favorable $\pi - \pi$ overlap between the two aromatic systems. In the case of **8**, the two sixcarbon bridges are long enough to provide a favorable environment for intramolecular interaction between the π -orbitals of the fluorene rings. To the best of our knowledge, no other organic [*n.n*]cyclophane has displayed this attractive, intramolecular interaction.

Conclusion

We have demonstrated that Suzuki-Miyaura coupling provides a rapid route to novel [n]metacyclophanes and [n.n]cyclophanes. When the bis-9-BBN adduct of 1,5hexadiene is used in the coupling dimerization is preferred to formation of the [n]cyclophane due simply to geometric constraints. These [n.n]cyclophanes possess longer all-carbon bridges than previously reported cyclophanes containing the same aromatic moiety. Due to competing reactions, such as oligomerization, the yields of the [n]- and [n.n] cyclophanes are low. Nonetheless, these large rings were prepared by making two or four carbon-carbon bonds in a single step from readily available starting materials under mild conditions. By incorporating substituents into the cyclophane precursors, the synthesis of even more interesting ring systems, possibly via self-assembly, exists.

Experimental Section

General. All reactions were performed in oven-dried glassware under a nitrogen atmosphere unless otherwise stated. All reagents were purified before use. The 9-BBN was titrated by using Brown's method (see: Brown, H. C. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975). ¹H and ¹³C NMR spectra were obtained on a 400, 300, or 200 MHz NMR spectrometer. Flash chromatography was performed on silica gel60, 230–400 mesh ASTM obtained from Baxter Scientific. Atlantic Microlabs Inc., Norcross, GA, performed elemental analyses.

General Procedure for the Preparation of [n]- and [n.n]Cyclophanes. [7]Metacyclophane (3a).¹⁷ To a solution of 26.0 mL of 0.3 M 9-BBN (7.80 mmol) in THF in a 50-mL, round-bottom flask was added 1,6-heptadiene (0.50 mL, 3.71 mmol) at room temperature. After the mixture was stirred for 3 h, the bis-9-BBN adduct was cannulated into a second roundbottom flask that contained Pd(PPh₃)₄ (0.129 g, 0.11 mmol), NaOH (0.37 g, 9.28 mmol), 1,3-dibromobenzene (0.45 mL, 3.71 mmol), and 400 mL of dry THF. The reaction mixture was refluxed overnight, cooled to room temperature, then cooled in an ice bath upon which time 5 mL of 30% H_2O_2 was added and stirring was continued for 30 min. The reaction mixture was then poured into 100 mL of hexanes and extracted with 1 M HCl (50 mL), saturated aqueous NaHCO₃ (50 mL), and brine (50 mL). The organic layer was separated, concentrated, and chromatographed on SiO₂ (0.5% Et₂O/hexanes) to afford

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 Maekawa, M.; Ohta, T. Angew. Chem., Int. Ed. 2000, 39, 4555–4557.
 (17) For [7]MCP see: (a) Fujita, S.; Hirano, S.; Nozaki, H. Tetra-

3a in 17% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.22 (t, J = 7.47 Hz, 1H), 6.97 (d, J = 7.39 Hz, 2H), 2.70 (s, 4H), 1.46 (br s, 8H), -0.15 (br s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 142.8, 131.5, 129.4, 125.0, 37.5, 31.3, 29.5.

[8]Metacyclophane (3b).¹⁸ **3b** was prepared from the bis-9-BBN adduct of 1,7-octadiene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **3b** in 6% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (s, 1H), 7.22 (t, J = 7.47 Hz, 1H), 6.94 (dd, J = 7.48, 1.57 Hz, 2H), 2.61 (t, J = 6.06 Hz, 4H), 1.53 (m, 4H), 1.29 (m, 4H), 0.67 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 130.5, 129.3, 125.6, 36.1, 30.3, 26.9, 23.8.

[9]Metacyclophane (3c).¹⁹ **3c** was prepared from the bis-9-BBN adduct of 1,8-nonadiene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **3c** in 13% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 1H), 7.21 (t, J = 7.71 Hz, 1H), 6.98 (dd, J = 7.52, 1.34 Hz, 2H), 2.71 (t, J = 6.41 Hz, 4H), 1.68 (m, 4H), 1.15 (m, 6H), 0.86 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 141.5, 130.2, 128.5, 126.2, 35.0, 26.9, 26.2, 25.6, 24.9.

[10]Metacyclophane (3d).²⁰ **3d** was prepared from the bis-9-BBN adduct of 1,9-decadiene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **3d** in 9% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (t, J = 7.52 Hz, 1H), 7.14 (s, 1H), 7.00 (dd, J = 7.49, 1.52 Hz, 2H), 2.68 (t, J = 6.22 Hz, 4H), 1.70 (m, 4H), 1.21 (m, 4H), 1.13 (m, 4H), 0.96 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 130.3, 128.6, 125.9, 35.3, 28.3, 26.9, 26.2, 25.6.

[14]Metacyclophane (3e). 3e was prepared from the bis-9-BBN adduct of 1,13-tetradecadiene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **3e** in 7% yield as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 7.25 (m, 1H), 7.18 (m, 2H), 6.94 (d, J =7.16 Hz, 1H), 2.59 (t, J = 6.33 Hz, 4H), 1.57 (m, 4H), 1.28 (m, 20H); ¹³C NMR (75 MHz, CDCl₃) δ 128.5, 128.3, 125.8, 125.6, 36.1, 35.8, 31.6, 31.4, 29.8, 29.7, 29.6, 29.5, 29.43, 29.42, 28.9. Anal. Calcd for C₂₀H₃₂: C, 88.16; H, 11.84. Found: C, 88.02; H, 11.76.

[6.6]Paracyclophane (5). 5 was prepared from the bis-9-BBN adduct of 1,5-hexadiene and 1,4-dibromobenzene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **5** in 6% yield as a colorless solid. Evaporative recrystallization from methanol provided crystals suitable for X-ray analysis. Mp 90–92 °C; ¹H NMR (300 MHz, CDCl₃) δ 6.96 (s, 8H), 2.52 (m, 8H), 1.51 (m, 8H), 1.13 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 139.5, 128.4, 34.8, 30.2, 29.3. Anal. Calcd for C₂₄H₃₂: C, 89.94; H, 10.06. Found: C, 89.82; H, 10.08.

[6.6](3,5)Toluenophane (6). 6 was prepared from the bis-9-BBN adduct of 1,5-hexadiene and 3,5-dibromotoluene. The organic layer was separated, concentrated, and chromatographed on SiO₂ (100% hexanes) to afford **6** in 5% yield as a colorless solid. Evaporative recrystallization from pentane provided crystals suitable for X-ray analysis. Mp 81.5–83 °C; ¹H NMR (200 MHz, CDCl₃) δ 6.81 (s, 6H), 2.55 (t, J = 7.2 Hz, 8H), 2.32 (s, 6H), 1.62 (m, 8H), 1.33 (m, 8H); ¹³C NMR (50 MHz, CDCl₃) δ 142.8, 137.7, 127.2, 125.2, 35.0, 30.5, 27.5, 21.4. Anal. Calcd for C₂₆H₃₆: C, 89.59; H, 10.41. Found: C, 89.63; H, 10.38.

[6.6](2,6)Pyridinophane (7). To a solution of 44.3 mL of 0.4 M 9-BBN (17.73 mmol) in THF was added 1,5-hexadiene (1.00 mL, 8.44 mmol) at room temperature. After the mixture

⁽¹⁵⁾ See ref 1b for a more detailed discussion.

hedron Lett. **1972**, *13*, 403–406. (b) Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nozaki, H. Tetrahedron **1975**, *31*, 2219–2227.

⁽¹⁸⁾ For [8]MCP see: Tamao, K.; Kodama, S.-I.; Nakatsuka, T.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 4405–4406.

⁽¹⁹⁾ For [9]MCP see: (a) Marchesini, A.; Bradamante, S.; Fusco, R.; Pagani, G. *Tetrahedron Lett.* **1971**, *12*, 671–674. (b) Tamao, K.; Kodama, S.-I.; Nakatsuka, T.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 4405–4406.

⁽²⁰⁾ For [10]MCP see: (a) Fujita, S.; Hirano, S.; Nozaki, H. *Tetrahedron Lett.* **1972**, *13*, 403–406. (b) Tamao, K.; Kodama, S.-I.; Nakatsuka, T.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 4405–4406.

was stirred for 3 h, the bis-9-BBN adduct was cannulated into a second round-bottom flask that contained Pd(PPh₃)₄ (0.488 g, 0.422 mmol), NaOH (2.617 g, 65.43 mmol), 2,6-dibromopyridine (2.00 g, 8.44 mmol), and 400 mL of dry THF. The reaction mixture was refluxed overnight, cooled to room temperature, and then cooled in an ice bath. Five milliliters of 30% hydrogen peroxide was then slowly added to consume any unreacted 9-BBN. The reaction mixture was warmed to room temperature, diluted with 500 mL of ethyl ether, and extracted with 1 N HCl (3 \times 100 mL). The organic layer was discarded. The acid wash was made basic with 1 N NaOH and extracted with ethyl ether (3 \times 50 mL). The ether wash was dried with MgS0₄ for approximately 15 min, filtered, and finally concentrated on a rotary evaporator. The residue was chromatographed on SiO₂ (67% diethyl ether/33% hexanes) to afford 7 in 6% yield as a colorless solid. Evaporative recrystallization from pentane provided crystals suitable for X-ray analysis. $R_f = 0.64$ (67% diethyl ether/33% hexanes); mp 90-91 °Č; ¹H NMR (200 MHz, CDCl₃) δ 7.41 (t, J = 7.7 Hz, 2H), 6.85 (d, J = 7.7 Hz, 4H), 2.69 (t, J = 6.9 Hz, 8H), 1.72 (m, 8H), 1.19 (m, 8H); ¹³C NMR (50 MHz, CDCl₃) δ 161.9, 136.3, 120.5, 38.1, 29.4, 28.9. Anal. Calcd for C22H30N2: C, 81.94; H, 9.38, N, 8.69. Found: C, 81.92; H, 9.36, N, 8.66.

[6.6](2,7)Fluorenophane (8). To a solution of 49 mL of 0.4 M 9-BBN (19.44 mmol, 2.1 equiv) in THF was added 1,5hexadiene (1.10 mL, 9.26 mmol) at room temperature. After the mixture was stirred for 3 h, the bis-9-BBN adduct was cannulated into a second round-bottom flask that contained Pd(PPh₃)₄ (0.535 g, 0.463 mmol, 0.05 equiv), NaOH (2.870 g, 71.75 mmol, 7.75 equiv), 2,7-dibromofluorine (3.00 g, 9.26 mmol, 1 equiv), and 400 mL of dry THF. The reaction mixture was refluxed overnight, cooled to room temperature, then cooled in an ice bath at which time 5 mL of 30% H₂O₂ was added and stirring was continued for 30 min. The reaction mixture was then poured into 100 mL of hexanes and extracted with 1 M HCl (50 mL), saturated aqueous NaHCO₃ (50 mL), and brine (50 mL). The organic layer was separated, concentrated, and chromatographed on SiO₂ (10% CH₂Cl₂/hexanes) to afford 8 in 1% yield as a colorless solid. Evaporative recrystallization from methylene chloride provided crystals suitable for X-ray analysis. $R_f = 0.15$ (10% CH₂Cl₂/hexanes); mp 238.5–241 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.61 (d, J = 7.9 Hz, 4H), 7.12 (d, J = 7.9 Hz, 4H), 7.01 (s, 4H), 3.30 (s, 4H), 2.65 (m, 8H), 1.56 (m, 8H), 1.25 (m, 8H); ¹³C NMR (50 MHz, CDCl₃) δ 143.6, 140.9, 139.6, 127.5, 125.9, 119.4, 36.5, 34.5, 30.9, 26.3. Anal. Calcd for C38H40: C, 91.88; H, 8.12. Found: 91.74; H, 8.20.

Solid-State Structures of 5-8. Crystallographic analysis of 5: $C_{24}H_{32}$, fw = 320.50, monoclinic crystal system, $P2_1/n$ (No. 14), a = 10.8250(12) Å, b = 5.9661(10) Å, c = 16.481(3)Å, $\beta = 100.000(12)^\circ$, V = 1048.2(3) Å³, Z = 2 (molecule situated about the inversion center at (0.5, 0.5, 0.5). $D_{\text{calc}} = 1.015 \text{ Mg/}$ m³, μ = 0.056 $\rm mm^{-1}$ (no absorption correction needed). Data collected on a Rigaku AFC8 diffractometer equipped with Mercury CCD area detector. Frames of 0.5° in ω were measured in duplicate for 30 s to a $2\theta_{max}$ value of 46.0°. Structure solution was by direct methods and refinement was based on F^2 (both from SHELXTL-Plus). Final residuals of R_1 = 0.1040 for 1099 observed data ($I > 2\sigma(I)$) and $wR_2 = 0.2357$ on all 1440 unique data were obtained. The crystals used in this study were waxy in appearance and of very poor quality. Numerous samples were studied, and the results reported represent the best sample analyzed. Crystal data for 6:

colorless blocks of $C_{26}H_{36}$; monoclinic, space group $P2_1/n$, with $a = 11.9063(11), b = 5.5631(5), c = 16.833(2) \text{ Å}, \alpha = 90^{\circ}, \beta = 16.833(2) \text{ Å}, \alpha = 10^{\circ}, \beta = 10^{\circ}, \beta$ 100.646(7)°, $\gamma = 90°$, V = 1095.8(2) Å³, z = 2, $\mu = 0.059$ mm⁻¹, $\rho_{\text{calc}} = 1.056 \text{ g/cm}^3$, M = 348.55. 2390 reflections were collected; 1678 independent reflections with R(int) = 0.0173 and 1634 with $I > 2\sigma(I)$. The numbers of parameters was 119. The final $wR(F^2) = 0.1424$, while the conventional R(F) = 0.0475 for 1634 reflections. For all data, $wR(F^2) = 0.1635$ and R(F) =0.0529. The goodness of fit was 1.094. Crystal data for 7: colorless blocks of $C_{22}H_{30}N_2$; triclinic, space group $P\overline{1}$, with a = 8.7420(7) Å, b = 12.9751(11) Å, c = 17.3626(14) Å, $\alpha = 12.9751(11)$ 90.138(6)°, $\beta = 90.773(6)°$, $\gamma = 91.771(7)°$, V = 1968.3(3) Å³, z = 4, μ = 0.063 mm⁻¹, ρ_{calc} = 1.088 g/cm³, M = 322.48. 8366 reflections were collected; 6896 independent reflections with R(int) = 0.0145 and 6465 with $I \stackrel{>}{>} 2\sigma(I)$. The number of parameters was 471. Four crystallographically independent molecules were in each unit cell. A small amount of disorder was modeled for the alkane chains in one molecule. The final $Rw(F^2) = 0.1703$, while the conventional R(F) = 0.0562 for 6465 reflections. For all data, $wR(F^2) = 0.1982$ and R(F) =0.0690. The goodness of fit was 1.029. Crystal data for 8: colorless plates of $C_{38}H_{40}$; monoclinic, space group $P2_1/n$, with a = 14.537(2) Å, b = 5.5063(9) Å, c = 19.003(3) Å, $\alpha = 90^{\circ}$, β = 111.711(13)°, $\gamma = 90°$, V = 1413.2(4) Å³, z = 2, $\mu = 0.065$ mm^{-1} , $\rho_{calc} = 1.167 \text{ g/cm}^3$, M = 496.7. 2953 reflections were collected; 2067 independent reflections with R(int) = 0.0187and 1965 with $I > 2\sigma(I)$. The numbers of parameters was 173. The final $Rw(F^2) = 0.1170$, while the conventional R(F) =0.0428 for 1965 reflections. For all data, $wR(F^2) = 0.1296$ and R(F) = 0.0524. The goodness of fit was 1.057. For **6**, **7**, and **8** data were collected on a Seimens P4 diffractometer at 294 K. Structures were solved by direct methods and refined by fullmatrix least-squares on F^2 with Siemens SHELXTL version 5.03.

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Supporting Information Available: ¹H and ¹³C NMR spectra for the [*n*]cyclophanes **3a**–**e** and [6.6]cyclophanes **5**–**8** and X-ray structure tables for the [6.6]cyclophanes **5**–**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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