Carbon Nanorings

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Concise Synthesis and Crystal Structure of [12]Cycloparaphenylene**

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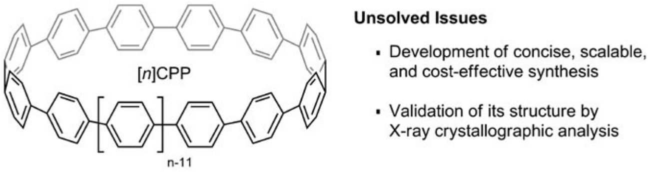
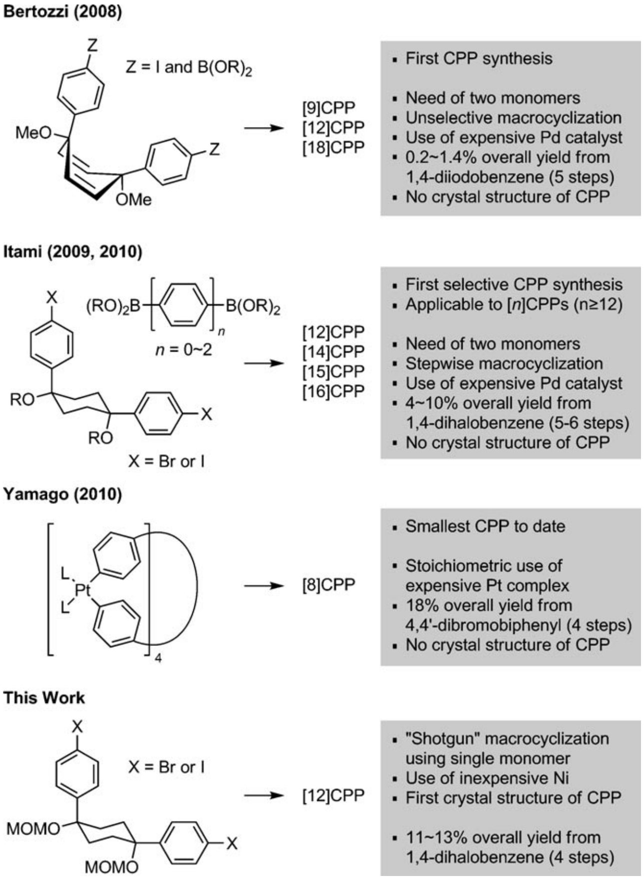
Cycloparaphenylene (CPP) represents the shortest sidewall segment of armchair carbon nanotube structures, and thus has greatly captivated scientists (Scheme 1).[1–3] Even though the bottom-up chemical synthesis of this simple molecular entity had been recognized as a Holy Grail in synthetic chemistry,[1,4] three groups including our own have recently succeeded in synthesizing some [*n*]CPPs.[5–8] Although these studies from the three research groups established the synthetic viability of the long-awaited CPPs, important issues remain unresolved (Scheme 1). For example, any synthetic route must be more concise, cost-effective, and scalable to provide CPP in useful quantities and to ensure that this interesting molecular entity is studied further. In addition, the molecular structure of CPP must be concretely validated by X-ray crystallographic analysis. We herein report a concise nickel-based synthesis of [12]CPP and the first X-ray crystal structure of [12]CPP.



Scheme 1. Unsolved issues in CPP chemistry.



Scheme 2. Key features of the reported synthetic methods of CPPs.

Some of the key features of the previous methods of making CPPs are summarized in Scheme 2. Both the group of Bertozzi[5] and ours[6] utilized the palladium-catalyzed Suzuki–Miyaura coupling of terphenyl-convertible bent monomers[9] to access the macrocycles, which were converted into CPPs by aromatization reactions.[10] Bertozzi and co-workers[5] took a pseudo "shotgun" approach,[11] which involves using a one-pot multicomponent cyclization of small monomers, to access the macrocycle. This shotgun method however often suffers from low yield and lack of control over the ring structure.[11] Indeed, three different macrocycles were obtained in their synthesis.[5] Our group[6] took a stepwise approach[11] in the palladium-catalyzed cross-coupling reaction and only one intermediate macrocycle was synthesized en route to [12]CPP. More recently, we have reported a new strategy using cyclohexane-inserted U-shaped units for the modular and size-selective synthesis of [*n*]CPPs (demonstrated for $n = 14$–16).[7] The use of the cyclohexane unit is important in our CPP synthesis not only because the L-shaped structure of cyclohexane attenuates the build-up of strain energy during the macrocyclization but also because

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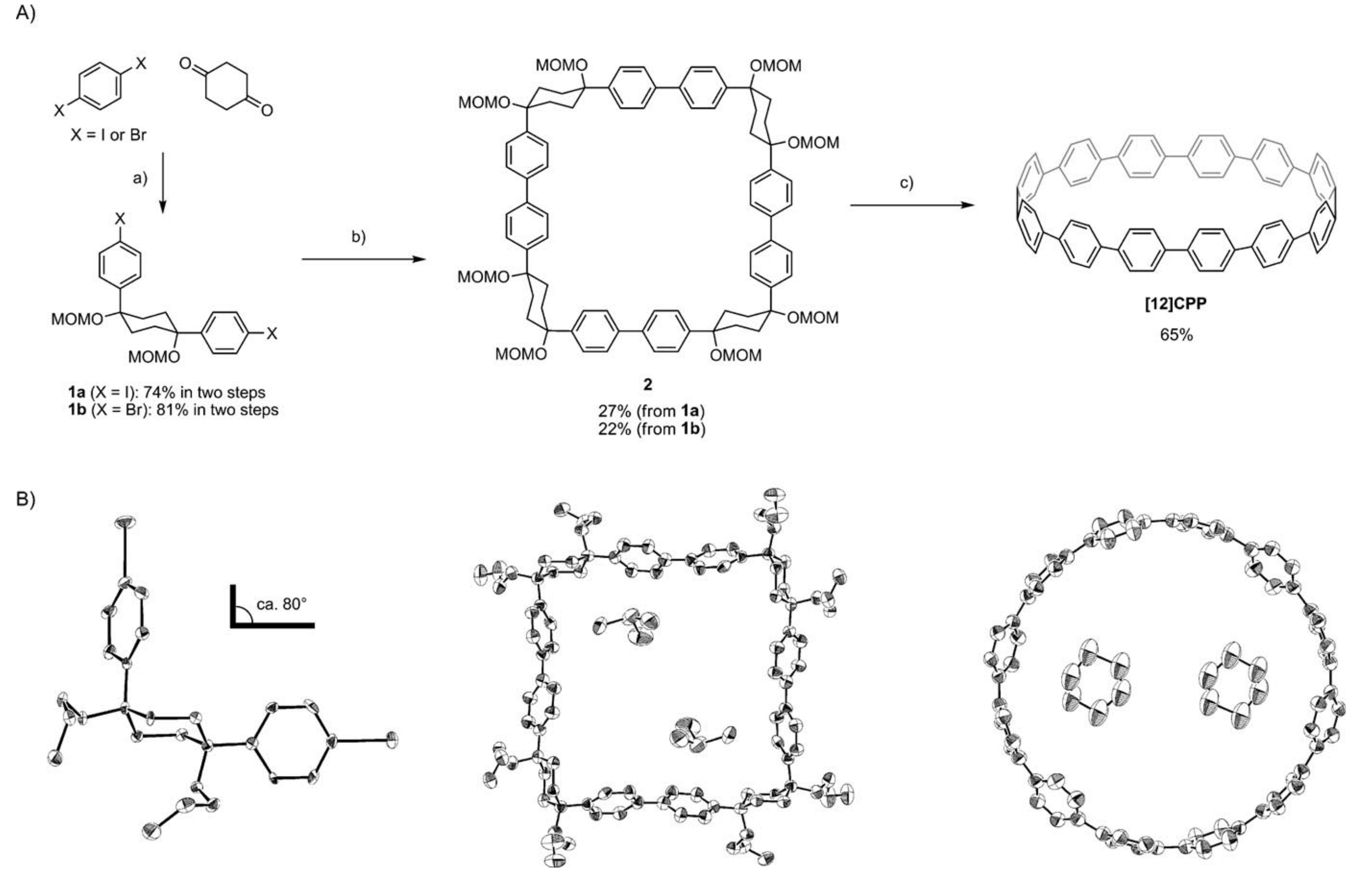
the ring-flipping aptitude of cyclohexane provides a strategic basis for accessing both even- and odd-numbered [*n*]CPPs. The disadvantages of our palladium-based synthetic methods include the necessity to prepare two cross-coupling partners and the requirement for stepwise reactions to access the macrocyclic precursors for [*n*]CPPs.[6,7] Yamago et al. reported the synthesized [8]CPP through the application of Bäuerle's cycloarene synthesis[12] that uses platinum-containing macrocycles.[8] Even though this procedure allowed the synthesis of the smallest CPP to date, the stoichiometric use of expensive platinum complexes is a bane for large-scale synthesis.[10]

Although we were aware of a number of unsuccessful examples of the shotgun approach in the synthesis of shape-persistent macrocycles,[11] we dared to investigate a one-pot shotgun macrocyclization using the simplest diphenylcyclohexane monomer as a key step for a more concise CPP synthesis (Scheme 2). In particular, we postulated that a nickel-promoted one-pot macrocyclization of the L-shaped *cis*-1,4-bis(4-halophenyl)cyclohexane monomer (**1a** or **1b**) might proceed to give the box-shaped macrocycle **2** directly (Scheme 3 A).[13] We expected that this shotgun approach to macrocycle construction using a single monomer and an inexpensive nickel promoter would streamline the synthesis of [12]CPP significantly. Notably, however, no nickel-mediated homocoupling reaction has been utilized in the synthesis of relatively large macrocycles, and this is presumably because of the mechanistic complexity[13] in aryl–aryl bond formation.[14] Nevertheless, we were encouraged by the X-ray crystal structure of **1a** (Scheme 3 B),[15] which revealed its nearly ideal "included" angle (ca. 80°, see the Supporting Information).

The requisite L-shaped monomers (**1a** and **1b**) were prepared by a two-step reaction from 1,4-dihalobenzene (Scheme 3 A). The twofold addition of 4-halophenylcerium reagents, prepared from 1,4-dihalobenzene, *n*BuLi, $CeCl_3$, and LiCl, to cyclohexane-1,4-dione furnished *cis*-1,4-bis(4-halophenyl)cyclohexane-1,4-diol in high yields. The formation of both the monoaddition product and the unfavorable *trans* isomer was suppressed under these cerium-based carbonyl addition conditions.[16,17] The resultant diols were protected with MOM groups to give **1a** and **1b** in 74 % and 81 % overall yields, respectively, from 1,4-dihalobenzene. By using this method, we synthesized in total 50 g of the L-shaped monomers (**1**).

With the requisite L-shaped monomers **1** in large quantities, we next investigated the nickel-mediated shotgun macrocyclization of **1** to produce the box-shaped macrocycle **2** in one step. We began by employing the original procedure of Semmelhack et al. using $[Ni(cod)_2]$ as a promoter.[18] How-



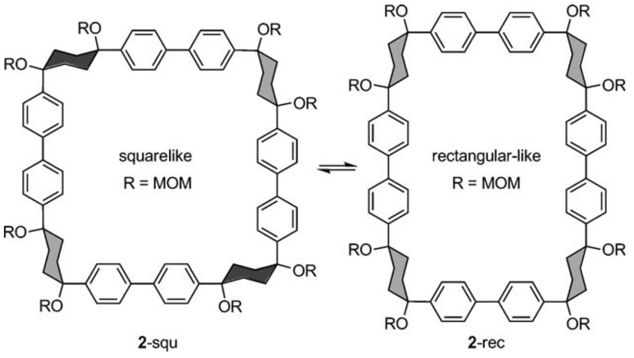
Scheme 3. A) Concise synthesis of [12]CPP. Reaction conditions: a) 1. 1,4-$X_2C_6H_4$ (X = I or Br), *n*BuLi, THF, 2. $CeCl_3$, LiCl, 3. cyclohexane-1,4-dione, 4. CH_3OCH_2Cl, iPr_2NEt, CH_2Cl_2; b) $[Ni(cod)_2]$, bpy, (with or without cod), THF; c) $NaHSO_4 \cdot H_2O$, *m*-xylene/DMSO, under air. B) X-ray crystal structures of **1a**, **2**·$2CHCl_3$, and [12]CPP·2 cyclohexane. Thermal ellipsoids are shown at 50 % probability and hydrogen atoms and minor parts of disordered moiety are omitted for clarity. bpy = 2,2′-bipyridyl, cod = 1,5-cyclooctadiene, DMSO = dimethyl sulfoxide, MOM = methoxymethyl, THF = tetrahydrofuran.

ever, the desired macrocycle **2** was not obtained under these reaction conditions. Similarly, procedures using NiCl$_2$, triphenylphosphine, and zinc dust did not furnish **2** at all.[19] After extensive investigations (see the Supporting Information), we determined that **1a** (1.0 equiv) underwent a shotgun macrocyclization in the presence of [Ni(cod)$_2$] (2.0 equiv), cod (1.7 equiv), and 2,2′-bipyridyl[20] (0.5 equiv) in THF (16 mmol of **1a**) at 60 °C and **2** was isolated in a 27 % yield. For the macrocyclization of **1b** we found that **2** could be obtained in a 22 % yield when the additional cod was excluded from the reaction. Gratifyingly, these reaction conditions were amenable to relatively large-scale reactions (see the Supporting Information). Notably, we synthesized, in total, 5 g of **2** using these methods. Although the yield could be improved, this nickel-based shotgun method already outperforms our palladium-based stepwise method in terms of overall yield and cost.[10]

Finally, we investigated the aromatization of the fully MOM-protected macrocycle **2**. We previously reported that the treatment of a partially MOM-protected macrocycle with *p*-toluenesulfonic acid under microwave irradiation afforded [12]CPP.[6] During our subsequent work on the modular synthesis of [*n*]CPPs, we established non-microwave reaction conditions for converting the fully MOM-protected macrocycles into the corresponding CPPs. The latter method worked nicely in the present synthesis of [12]CPP. Treatment of macrocycle **2** with NaHSO$_4$·H$_2$O (20 equiv) in refluxing *m*-xylene/DMSO under air gave [12]CPP in a 65 % yield. By using this method, we synthesized in total 0.5 g of [12]CPP (Scheme 3 A).

In addition to improving the synthesis of [12]CPP, we also strove to validate the molecular structures of [12]CPP and the macrocyclic precursor **2** as well as to advance our understanding of them by using X-ray crystallography (Scheme 3 B). A single crystal of **2** was obtained from a chloroform solution by the slow addition of *n*-hexane vapor at 25 °C. As shown in Scheme 3 B, a squarelike D_2 symmetric structure of **2** that contains disordered chloroform molecules in the cavity was identified. Interestingly, this squarelike shape of **2** is different from the more rectangular structure that we previously identified in the partially MOM-protected macrocycle (similar to the right-hand structure shown in Scheme 4).[6]

In solution, two conformations (**2**-squ and **2**-rec, Scheme 4) are likely to be in a rapid equilibrium through the flipping of cyclohexane rings.[21] Indeed, the hydrogen atoms on the MOM groups in **2** were observed as two singlet peaks ($\delta = 3.43$ ppm, 4.46 ppm in CDCl$_3$) by ^{1}H NMR spectroscopy at 20 °C. Upon cooling to −30 °C, splitting of these singlet peaks was observed.[22] We estimated representative thermodynamic values of the chair-flipping process in **2** to be $\Delta H^{\ddagger} = 11.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -3.4$ cal mol^{-1} K^{-1} by performing variable-temperature NMR experiments on the CDCl$_3$ solution of **2** using the coalescence method (Figure 1; see the Supporting Information). Interestingly, these values are comparable to that of the chair-flip barrier of cyclohexane ($\Delta H^{\ddagger} = 11$ kcal mol^{-1}).[23] Notably a cyclohexane ring can undergo rapid chair-flipping even within the macrocyclic structure.



Scheme 4. Equilibrium of two different conformations of **2**.

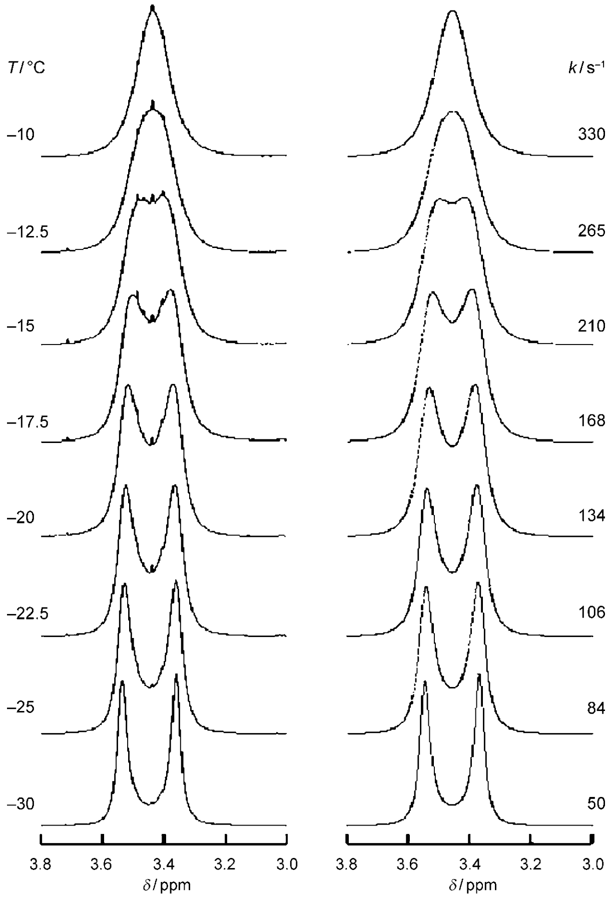
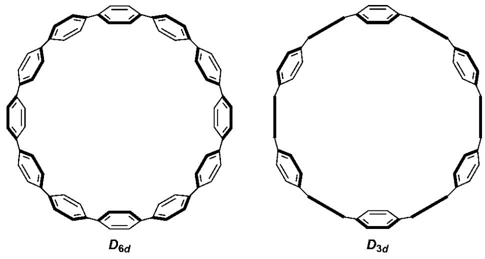


Figure 1. Experimental ^{1}H NMR spectra of **2** (500 MHz, CDCl$_3$) at different temperatures (left) and simulated spectra computed with the specific rate constant, *k* (right).

The structure determination of the CPP molecules by X-ray crystal structure analysis remains a great challenge because of some of their intrinsic properties, such as their high solubility in most organic solvents and their tendency to incorporate guest molecules within the ring. After extensive investigation, we succeeded in obtaining the first X-ray crystallographic structure of [12]CPP. Recrystallization of [12]CPP from chloroform/cyclohexane gave pale yellow crystals of [12]CPP·2cyclohexane.

The ORTEP drawing is shown in Scheme 3B. Two cyclohexane molecules were found to be highly disordered, thus indicating that they might drift into the cavity of [12]CPP even in the crystalline state. In the crystalline form, the center of symmetry of [12]CPP is at the center of the ring. The diameter of this ring is approximately 16.5 Å as estimated by taking the average of the intramolecular atom distances between two diagonal ipso carbon atoms (e.g. C(1)–C(1)*, see the Supporting Information). The small degree of variation between the twelve measured atom distances (16.24–16.84 Å) supports the high circularity of [12]CPP. Notably, the observed conformation is not the most stable D_{6d} symmetrical form that was calculated by DFT methods, but is close to the D_{3d} structure, the energy of which is 3.7 kcal mol^{-1} higher than that of D_{6d} form (Scheme 5).[2a] Crystal-packing forces are most likely responsible for the emergence of D_{3d}-like structure.



Scheme 5. Two optimized structures of [12]CPP.

Although one of the benzene rings in half of [12]CPP was found to be disordered as a result of the rotation of the C–C axis, the disorder was appropriately solved and the intrinsic structural parameters can be discussed using these crystallographic data.[15] Summarized in Table 1 are the average bond lengths of [12]CPP in the crystalline state. The results show that within the range of experimental error the C_{ipso}–C_{ortho} and C_{ortho}–C_{ortho} bond lengths are almost the same, that is approximately 1.39 Å, and the C_{ipso}–C_{ipso} bonds exhibit single-bond character, suggesting no considerable bond alternation in the benzene rings of [12]CPP. Thus, it should be emphasized that the benzenoid character is reasonably preserved in [12]CPP, even though each benzene ring in the crystal structure of [12]CPP is slightly folded as a result of the inherent ring strain of the cyclic system. We also found that these bond lengths are similar to those of the optimized D_{3d} structure of [12]CPP. From these structural data, the benzenoid structure of [12]CPP has been firmly validated.

Table 1: Average bond lengths of [12]CPP in crystalline state and the optimized D_{3d} structure of [12]CPP.

	X-ray	D_{3d}[a]
C_{ipso}–C_{ipso}	1.481 Å	1.485 Å
C_{ipso}–C_{ortho}[b]	1.394 Å	1.407 Å
C_{ortho}–C_{ortho}[b]	1.381 Å	1.391 Å

[a] B3LYP/6-31G(d) level of theory. See, reference [2a]. [b] Bond lengths including disordered C_{ortho} atoms are not included.

The packing mode of [12]CPP molecules in the crystal is also interesting. As shown in Figure 2A, [12]CPP molecules align in a herringbone manner. This type of packing has been observed in a number of planar π-conjugated molecules. It should be mentioned that there are no significant intermolecular interactions between [12]CPP molecules. More strikingly, in addition to the herringbone packing, the [12]CPP molecules align nicely to form a tubular structure (Figure 2B). The emergence of such a surprising channel structure obviously provides various possibilities in CPP chemistry. For example, the preorganized tubular alignment of CPP molecules might pave the way for the formation of carbon nanotube structures by oxidative assembly of CPP molecules in their crystalline state. In addition, CPP molecules might incorporate guest molecules or metal ions thus realizing their one-dimensional alignment.

In summary, we have established a concise and cost-effective synthesis of [12]CPP. A shotgun method for the macrocycle construction using a single L-shaped diphenylcyclohexane monomer and an inexpensive nickel complex was developed. During this study, we successfully validated the molecular structures of L-shaped monomer **1a**, box-shaped macrocycle **2**, and [12]CPP by X-ray crystallography. The benzenoid structure of [12]CPP has been firmly validated by studying the bond lengths. Most excitingly, it was found that [12]CPP molecules crystallize in a tubular and a herringbone structure. Further studies on the properties of [12]CPP will be outlined in due course.

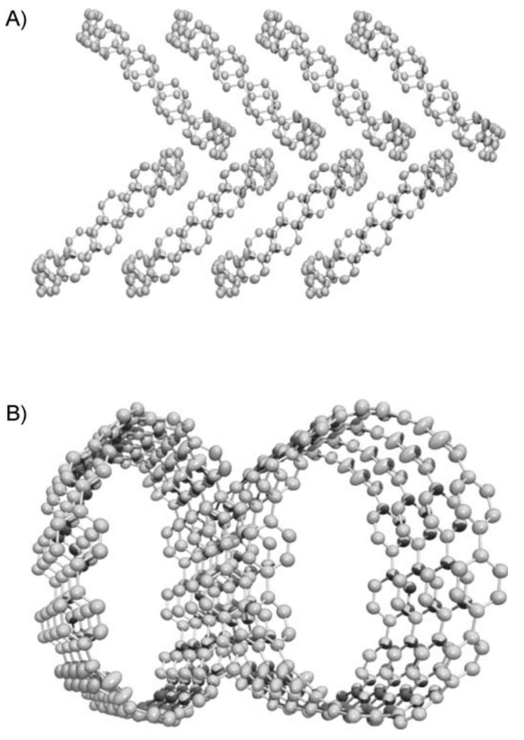


Figure 2. A) Herringbone packing of [12]CPP molecules. B) Tubular alignment of [12]CPP molecules (hydrogen atoms and solvent molecules are omitted for clarity).

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