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Theoretical Studies on the Structures and Strain Energies of Cycloparaphenylenes

Yasutomo Segawa, Haruka Omachi, and Kenichiro Itami*

Department of Chemistry, Graduate School of Science, Nagoya University,
Nagoya 464-8602, Japan

itami@chem.nagoya-u.ac.jp

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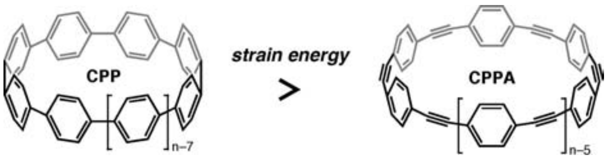
ABSTRACT



The structures and strain energies of cycloparaphenylenes (CPPs) have been determined by DFT calculation at the B3LYP/6-31G(d) level of theory. Fifteen stable conformations of [12]CPP were found as local minimum structures. It was also found that benzene rings of [12]CPP can rotate rather freely at room temperature. The strain energies of [*n*]CPP (*n* = 6−20) were estimated on the basis of the homodesmotic reaction using CPP, biphenyl, and *p*-terphenyl. It was also found that CPPs have higher strain energy in comparison to cycloparaphenyleneacetylenes (CPPAs).

Cycloparaphenylenes (CPPs) are the cyclic oligoarenes composed of solely *para*-substituted benzenes (Figure 1). For nearly one century, CPPs have attracted significant attention of scientists because of their simple and beautiful structure.[1] Adding to their sheer aesthetic appeal, CPPs represent the shortest sidewall segment of armchair carbon nanotube structures and can be envisioned as potential precursors or seeds in the preparation of structurally uniform armchair carbon nanotubes.[2] Despite extensive trials of synthetic chemists,[3] however, it was only very recently that some CPPs have finally been synthesized by the groups of Bertozzi,[4] Itami,[5] and Yamago.[6] These syntheses capitalize on the ability of *cis*-2,5-cyclohexadiene-1,4-diyl (Bertozzi), *cis*-cyclohexane-1,4-diyl (Itami), and *cis*-diarylplatinum (Yamago) to attenuate the buildup of strain energy during otherwise problematic macrocyclization steps.

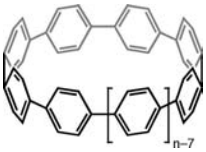


Figure 1. Structures of [*n*]cycloparaphenylenes.

Although further studies (synthesis and application) of these interesting aromatic carbon nanorings are much expected, some of the fundamental structural issues and questions need to be addressed. Of particular importance are the strain energies of CPPs in view of planning synthetic strategy. Comparing the strain energies of CPPs with those of other related carbon nanorings is also very important. Since the three groups (Bertozzi, Itami, and Yamago) reported strain energies different from each other, the stability and synthetic viability of CPP are still elusive. We herein report our systematic computational study on the structures

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[1] Reviews on aromatic carbon nanorings and belts: (a) Yao, T.; Yu, H.; Vermeij, R. J.; Bodwell, G. J. *Pure Appl. Chem.* **2008**, *80*, 533. (b) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250. (c) Scott, L. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 4133.

[2] (a) Steinberg, B. D.; Scott, L. T. *Angew. Chem., Int. Ed.* **2009**, *48*, 5400. (b) Fort, E. H.; Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2009**, *131*, 16006. (c) Bodwell, G. J. *Nat. Nanotechnol.* **2010**, *5*, 103.

[3] Representative attempts: (a) Parekh, V. C.; Guha, P. C. *J. Indian Chem. Soc.* **1934**, *11*, 95. (b) Friederich, R.; Nieger, M.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 1723.

[4] Synthesis of [9]-, [12]-, and [18]CPP: Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646.

[5] Selective synthesis of [12]CPP: Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112.

[6] Synthesis of [8]CPP: Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 757.

10.1021/ol1006168

and strain energies of [n]CPP ($n = 6-20$).[7] Comparison of strain energies of CPPs with those of cycloparaphenylene-acetylenes (CPPAs) is also described.

In this study, we began by optimizing possible conformations of [12]CPP by DFT calculation at the B3LYP/6-31G(d) level,[8] which led to the finding of 15 stable conformations of [12]CPP (Figure 2a). In structure **1**,[9] all benzene rings are alternately twisted with dihedral angles around 33°. This value is smaller than that of biphenyl (39°) calculated at the B3LYP/6-31G(d) level of theory.[10,11] The molecular structure and the spatial distribution of HOMO and LUMO of **1** are shown in Figure 3. Both HOMO and LUMO delocalize over the ring.

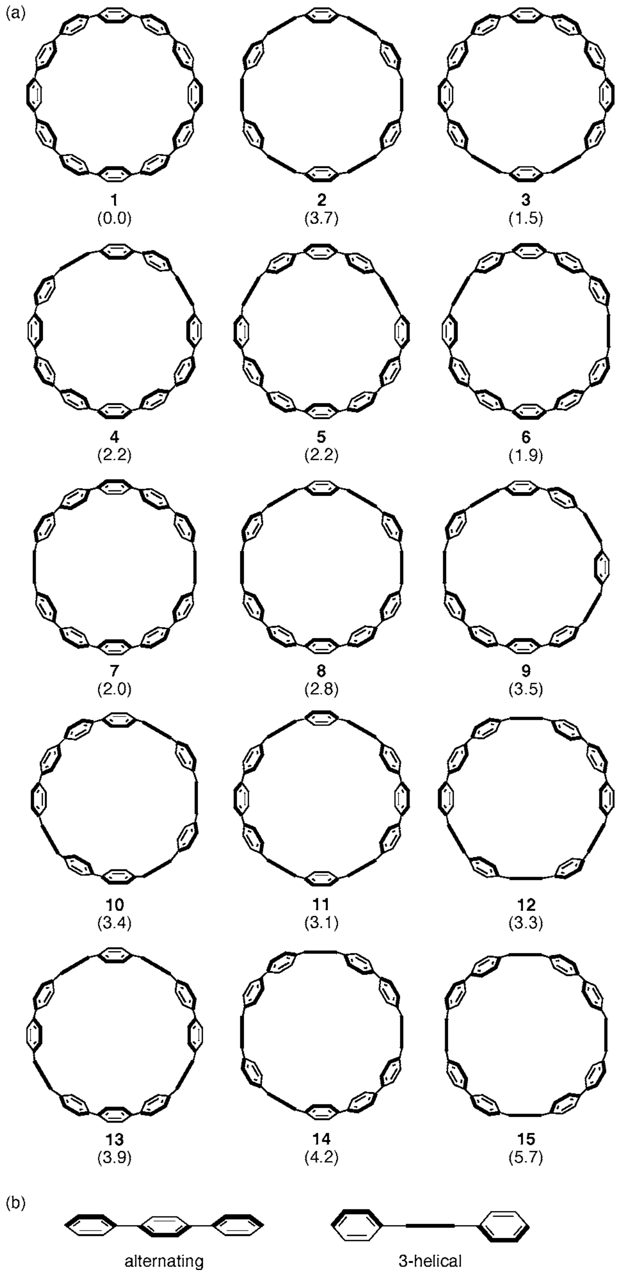

Figure 2. (a) Fifteen conformations of [12]CPP (**1**−**15**) (ΔG in kcal•mol^{-1}, based on **1**) and (b) two conformations of p-terphenyl.

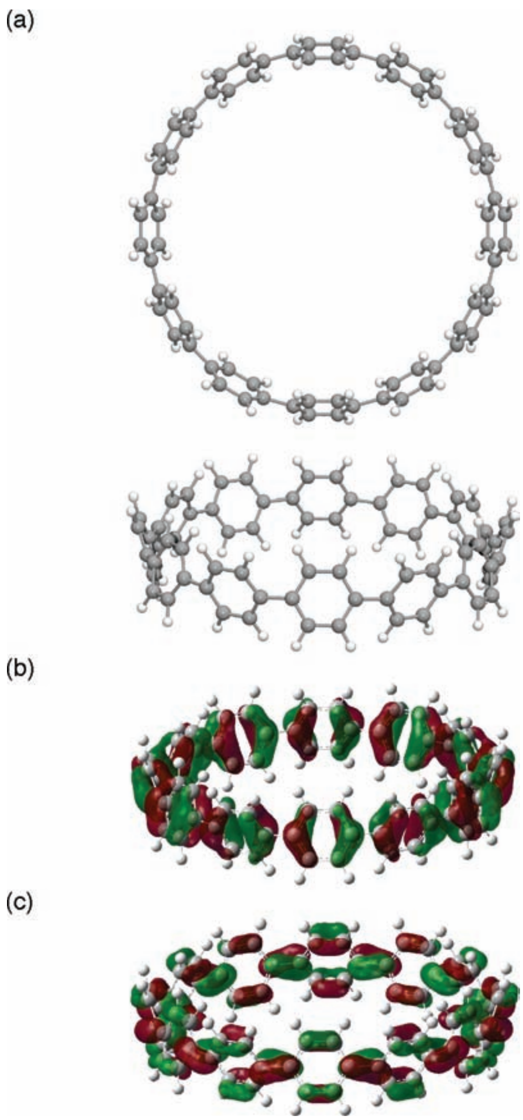

Figure 3. (a) Molecular structure (top view and side view), (b) HOMO, and (c) LUMO of **1**.

We also found another stable conformation (**2**), in which alternate benzene rings are parallel to the central C_3 axis while the intervening rings are twisted (Figure 2a). The relationship

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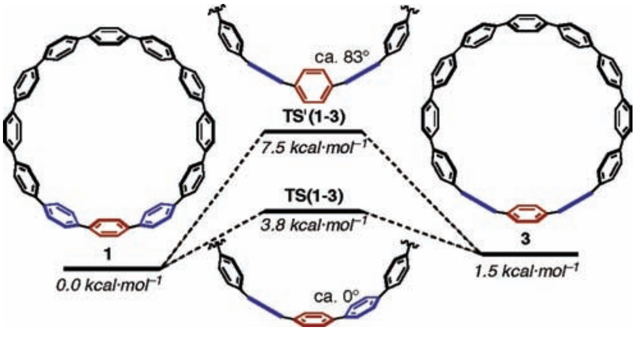
(7) Before being synthesized, [n]CPP ($n = 2-6$) have been theoretically investigated. For example, CPPs smaller than [5]CPP prefer to have the quinodimethane structure rather than the benzenoid structure. As the number of benzene rings increases, the benzenoid form becomes favorable. Thus, CPP having ≥5 benzene rings can be considered as "true" cycloparaphenylenes. Theoretical studies: (a) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274. (b) Jagadeesh, M. N.; Maker, A.; Chandrasekhar, J. *J. Mol. Model.* **2000**, *6*, 226. (c) Basu, S.; Ghosh, P.; Mandal, B. *Mol. Phys.* **2008**, *106*, 2507. Synthesis of small-ring CPP analogues (quinodimethane structures): (d) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342. (e) Kammermeier, S.; Herges, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 417. (f) Kammermeier, S.; Jones, P. G.; Herges, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2200. (g) Tsuji, T.; Okuyama, M.; Ohkita, M.; Imai, T.; Suzuki, T. *Chem. Commun.* **1997**, 2151.

between **1** and **2** is an expansion of two stable conformations of *p*-terphenyl, an alternating and a 3-helical one (Figure 2b).[12] Combination of the alternating and 3-helical moieties produced 13 stable structures of [12]CPP (**3**−**15**). The structures **1**−**15** are rotamers of each other. All structures gave local minima with no imaginary frequency. A structure having 4- or higher-helical moiety was not found as a local minimum. The structures with two 3-helical moieties (**3**−**7**) have reasonable stability comparable to the all-alternating **1** ($\Delta G = 1.5{-}2.2$ kcal·mol^{-1}, $\Delta H = 1.7{-}2.5$ kcal·mol^{-1}). The other structures with six (**2**) or four (**8**−**15**) 3-helical moieties have higher energy compared tothat of **1** ($\Delta G = 2.8{-}5.7$ kcal·mol^{-1}, $\Delta H = 2.9{-}5.2$ kcal·mol^{-1}). Various symmetrical characters such as D_{2d} (**1**), C_{2h} (**2**), D_4 (**15**), C_{2h} (**7**), C_{2v} (**11**), C_2 (**4**, **12**), C_s (**3**, **5**, **8**, **13**), or C_1 (**6**, **9**, **10**, **14**) were found in these structures. The structures **1**, **2**, **6**, and **9** have slightly distorted symmetry such as D_{6d}, D_{3d}, C_2, and C_2, respectively. Stabilization energy of **1** from **1′**, which was optimized with D_{6d} symmetrical limitation, was not small in ΔG (1.7 kcal·mol^{-1}) but negligible in ΔH (0.1 kcal·mol^{-1}). A D_{12d} symmetrical structure **16** (see Supporting Information), in which all benzene rings are parallel to C_{12} axis, has 25.7 kcal·mol^{-1} higher energy compared to that of **1**, and imaginary frequencies were observed. Among these structures, the all-alternating structure (**1**) turned out to be the most stable conformation for [12]CPP.

For [12]CPP, we calculated the rotation barrier of a benzene ring based on the most stable **1** (Scheme 1). It is known that biphenyl has two transition states in the rotation of a benzene ring with dihedral angles of 0° and 90° [rotation barrier ($\Delta G^{\ddagger}$): 0°, 2.0 kcal·mol^{-1}; 90°, 2.4 kcal·mol^{-1} at B3LYP/6-31G(d) level].[10] In the case of [12]CPP, two transition states were obtained in the formation from **1** to **3**. The rotation barrier of **TS(1−3)** in which two dihedral angles are ca. 0° was calculated to be 3.8 kcal·mol^{-1} higher than that of **1**. The other TS with dihedral angle of ca. 83° (**TS′(1−3)**) has 7.5 kcal·mol^{-1} higher energy than **1** has. These values imply that the perpendicular alignment of neighboring benzene rings increases the ring strain. We also found other transition states (**TS3−4**, **TS′3−5**, and **TS′2−8**) with $\Delta G^{\ddagger}$ values of 3.4, 8.1, and 10.3 kcal·mol^{-1}, respectively (see Supporting Information). These results indicate that benzene rings in [12]CPP can rotate rather freely at room temperature. This is consistent with the observation of one singlet in ^{1}H NMR (δ 7.61, $CDCl_3$) and two signals in ^{13}C NMR (δ 127.3, 138.5, $CDCl_3$) for [12]CPP.[5]

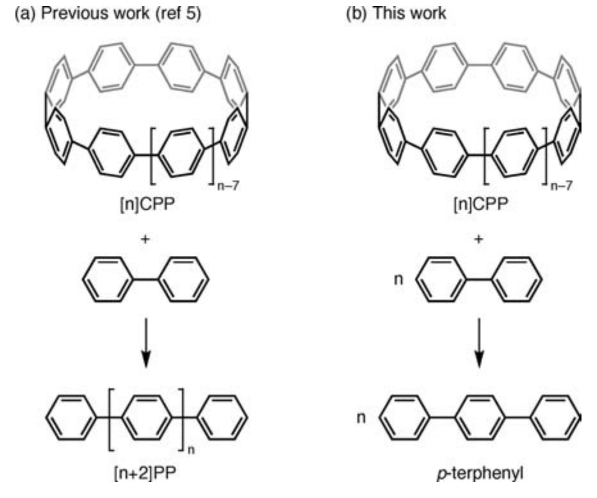
Scheme 1. Rotation of a Benzene Ring through **TS(1−3)** or **TS′(1−3)** (ΔG, Based on **1**)



We next optimized all possible conformations of [*n*]CPP ($n = 6{-}11$) smaller than [12]CPP. As in the case of [12]CPP, all-alternating structures were the most stable ones for even-number [*n*]CPP ($n = 6, 8, 10$). For odd-number [*n*]CPP ($n = 7, 9, 11$), the conformation that has one 3-helical moiety gave lowest energy value in every case. For CPPs higher than [12]CPP, we optimized all-alternating structures having $D_{(n/2)d}$-symmetry for [*n*]CPP ($n = 14, 16, 18, 20$) or structures having one 3-helical moiety for [13]CPP and [15]CPP. The analysis of these CPP structures (see Supporting Information) revealed that the average dihedral angle of two neighboring benzene rings decreases as the diameter of the CPP decreases. These dihedral angles range from 27° ([6]CPP) to 35° ([20]CPP).

Finally, the strain energies of [*n*]CPP ($n = 6{-}16, 18, 20$) were estimated. A hypothetical homodesmotic reaction is suitable for this purpose.[13] In the previous reports, homodesmotic reactions, where linear oligoparaphenylene ([$n + 2$]PP) is produced from [*n*]CPP and biphenyl (Itami, Scheme 2a)[5] or polyparaphenylene is produced from CPP (Bertozzi),[4] were used for estimating the strain energies of CPP.[14−16] In

Scheme 2. Hypothetical Homodesmotic Reactions for the Calculation of Strain Energies of [*n*]CPP



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(8) Frisch, M. J. et al., *Gaussian03W, Revision E.01*; Gaussian Inc.: Wallingford, CT, 2004. See Supporting Information for full reference.

(9) The structure **1** was reported as the most stable conformation by Bertozzi.[4]

(10) Karpfen, A.; Choi, C. H.; Kertesz, M. *J. Phys. Chem. A* **1997**, *101*, 7426.

(11) We also confirmed this reported value (39°).

(12) Honda, K.; Furukawa, Y. *J. Mol. Struct.* **2005**, *735*−*736*, 11.

(13) Homodesmotic reaction is a reaction in which reactants and products contain equal numbers of carbon atoms in corresponding states of hybridization. Moreover, there is matching of the carbon-hydrogen bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. (a) Minkin, V. I. *Pure Appl. Chem.* **1999**, *71*, 1919. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

this study, we adopted more the simplified homodesmotic reaction shown in Scheme 2b. In this method, reference molecules are only biphenyl and *p*-terphenyl so that considering many possible conformations of [$n + 2$]PP can be avoided.

By using the heat of formation (ΔH) of optimized structures of [*n*]CPP, biphenyl, and *p*-terphenyl, the strain energies of [*n*]CPP were obtained (Table 1). As expected, the strain energy decreases as the diameter of CPP increases. However, it should be noted that [20]CPP still has a high strain energy of 28.4 kcal•mol^{-1}. The strain energies are inversely proportional to both *n* and diameter, which indicates the limit of strain energy for [∞]CPP is 0 kcal•mol^{-1} (see Supporting Information). We also confirmed that the strain energies calculated by the present homodesmotic reaction (Scheme 2b) are almost identical to those determined by the previous homodesmotic reaction (Scheme 2a), proving that the present simple method works well, and that the shortened π-system, *p*-terphenyl, is enough for estimating the π-stability of cyclic and linear paraphenylenes (see Supporting Information).

Table 1. Strain Energies and Diameters of [*n*]CPP

n in [*n*]CPP	strain energy[a]	diameter (Å)
6	96.0	8.4
7	84.0	9.5
8	72.2	11.1
9	65.6	12.3
10	57.7	13.9
11	53.7	15.1
12	48.1	16.6
13	45.5	17.9
14	41.0	19.4
15	39.2	20.6
16	35.6	22.1
18	31.7	24.9
20	28.4	27.6

[a] ΔH, kcal•mol^{-1}.

In order to compare CPPs with other existing carbon nanorings in terms of ring strain, we chose [*n*]cycloparaphenyleneacetylenes ([*n*]CPPA) as reference molecules.[17] The strain energies of [*n*]CPPA are taken from the work of Krishna.[17b] The correlation of the strain energies of [*n*]CPP and [*n*]CPPA versus the diameters of the rings is shown in Figure 4. Clearly CPPs have higher strain energies (ca. 20 kcal•mol^{-1}) in comparison to those of CPPAs. We believe that these high strain energy values of CPPs speak well for the years (>75 years) required for chemists to achieve the bottom-up organic synthesis of CPPs.

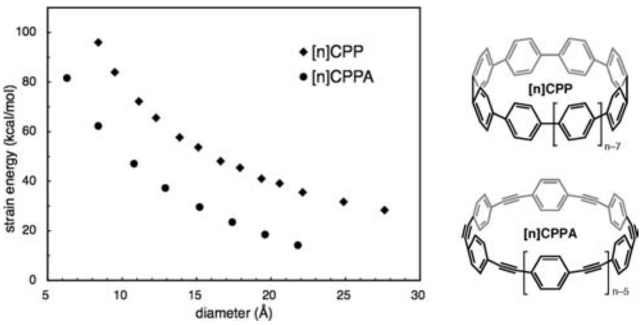

Figure 4. Correlation of strain energies of [*n*]CPP and [*n*]CPPA versus the diameters of the rings.

In summary, the structures and strain energies of CPPs have been determined by DFT calculation at the B3LYP/6-31G(d) level of theory. Fifteen stable conformations of [12]CPP were found as local minimum structures. The rotation barrier of a benzene ring in [12]CPP indicates that benzene rings can rotate rather freely at room temperature. Based on our structural study as well as on the new homodesmotic reactions using CPP, biphenyl, and *p*-terphenyl, the strain energies of [*n*]CPP ($n = 6-20$) were determined to be 96−28 kcal•mol^{-1}. It was also found that CPPs have higher strain energy in comparison to those of CPPAs. The present study should help us not only to plan a new synthetic strategy but also to understand the structural, electronic, and physical properties of CPPs.

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Supporting Information Available: Optimized structures and Cartesian coordinates of optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) We previously reported the strain energy of [12]CPP to be 55 kcal•mol^{-1}.[5] However, this value turned out to be incorrect, because it was based on a structure of [12]CPP with higher energy.

(15) Bertozzi reported the strain energies of [9]-, [12]-, and [18]CPP to be 47, 27, and 5 kcal•mol^{-1}, respectively.[4] Because an infinite polymer was used as a reference molecule, the strain enegies might be underestimated.

(16) The strain energies reported by Yamago were not based on homodesmotic reaction.[6]

(17) Synthesis: (a) Kawase, T.; Darabi, H. R.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2664. DFT calculation: (b) Ali, M. A.; Krishnan, M. S. *Mol. Phys.* **2009**, *107*, 2149.