

Communication

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Synthesis of Oligoparaphenylene-Derived Nanohoops Employing Anthracene Photodimerization-Cycloreversion Strategy

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Supporting Information Placeholder

ABSTRACT: The century-old, yet synthetically underexplored anthracene photodimerization/cycloreversion reactions have been employed as the key steps to access highly strained aromatic hydrocarbons. Herein, we report the chemical syntheses of oligoparaphenylene-derived nanohoops in 5 steps or less, featuring a rigid dianthracene synthon. The newly synthesized nanohoops display intriguing experimental and computational properties.

The highly strained, non-planar aromatic hydrocarbons are aggressively pursued synthetic targets for decades because of their unusual structures and distinct properties. The seemingly counterintuitive bond connections and forced geometries present considerable synthetic challenges which have, in turn, inspired creative molecular designs and impressive synthetic solutions.¹ In particular, significant progress has been reported recently on the syntheses of cycloparaphenylenes (CPP's) and related non-planar oligoparaphenylenes.² To date, most successful synthetic approaches have employed three types of craftily designed L-shaped synthons³ in order to overcome these molecules' non-trivial strain energy (Scheme Ia).

We envision that the rigid yet reversible dianthracene scaffold,⁴ when appropriately functionalized, would serve as a new X-shaped building block toward strained aromatics such as non-planar oligoparaphenylenes (Scheme 1b). Particularly, this strategy complements aforementioned synthetic approaches by (1) establishing a dual-arched core structure with around 50-degree bent angle, and (2) enabling late-stage ring expansion via photodimer cycloreversion. Although the century-old anthracene photodimerization has been extensively studied with versatile applications including polymers and molecular switches,⁵ the reaction's synthetic uses remain limited⁶ largely due to a number of technical hurdles associated with the photodimers such as isomer separation and poor solubility.⁴ Here we disclose the preparation and crystal structure of a dianthracene-derived dual-curve oligoparaphenylene molecule (1) exhibiting attractive optoelectronic properties and synthetic utility toward nanohoop 2.

Scheme 1. Synthetic Design



Our study commenced with the [4+4] photodimerization of 2,6-dibromoanthracene (3, Scheme 2). The reaction cleanly generated a mixture of two barely soluble stereoisomers under the irradiation of a xenon lamp. Refluxing benzene was found optimal for best dissolving the starting material

Scheme 2. Synthesis of 1 Employing A Dianthracene-derived Key Synthon



Reagents and conditions: (a) benzene, xenon lamp, 80 °C, 24 h (4a/4b 65:35), then recrystalized in CHCl₃; (b) Pd(OAc)₂, S-Phos, B₂pin₂, K₃PO₄, 1,4-dioxane, 80 °C, 20 h; (d) benzene, xenon lamp, 30 °C, 12 h (5a/5b 20:80), then recrystalized in EtOAc; (e) 7, Pd(OAc)₂, dppf, K₂CO₃, Ag₂O, PhMe/H₂O, 80 °C, 24 h; (f) Ni(cod)₂, 2,2'-bipyridyl, THF, 65 °C, 24 h; (g) sodium napthalenide, THF, -78 °C, 1 h, then quenched with I₂.

and the products, and one of the photodimers was more soluble in hot chloroform than the other one. Thus the less soluble isomer **4a** was isolated by recrystalization with 35% yield. Palladium-catalyzed Miyaura borylation⁷ of **4a** smoothly afforded tetraborate **5a** (84% yield), the stereochemistry of which was unambiguously confirmed to be head-to-head (H-H) by X-ray crystallography.⁸ The head-to-tail (H-T)dimer **5b** can be obtained from **3** by reversing the order of photodimerization and borylation steps. The quantitative dimer formation from bis-borylated anthracene **6** favored the less hindered **5b** over **5a** likely due to increased sterics, thus recrystalization with ethyl acetate allowed isolation of the H-Tisomer **5b** with 54% yield.

With pure isomers **5a** and **5b** in hand, Suzuki crosscoupling⁹ with Jasti's cyclohexadiene-derived synthon 7^{10} stitched four new C-C bonds in a single step with good efficiency. In both reactions, greater than 80% yield per bond formation can be achieved.

The macrocycle-closing step was expected to be most challenging and crucial, since molecular strain builds up significantly. Similar steps in CPP (and related compounds) syntheses were reported employing coupling strategies, albeit with low to moderate yields.^{2a} It turned out that treatment of the tetrabromides 8a/8b with nickel-mediated Yamamoto coupling conditions¹¹ led to contrasting results. Although trace signal of desired mass can be observed by MALDI-TOF analysis of the complex crude reaction mixture from the H-H isomer 8a, isolation of either mono- or bis-cyclized products were unsuccessful. In sharp contrast, treatment of the H-T isomer **8b** with Ni(cod)₂/2,2'-bipyridyl furnished exclusively the desired double cyclization with 95% yield of 9b (>97% yield per bond formation!). To the best of our knowledge, this result represents the highest yield among similar strained macrocycle formations, still less in the case of forming two

highly strained rings in a single step. Final reduction of $\mathbf{9b}$ with freshly made sodium napthalenide^{3a} effectively afforded the target molecule $\mathbf{1}$ as a yellow solid.



Figure 1. ORTEP drawing of **1** with the thermal ellipsoids shown at a 50% probability.

The X-ray crystallography analysis of a single crystal of 1^8 confirmed the propeller-like dual-curve structure that deviated somewhat from C2 symmetry (Figure 1). With four bridge-head sp³ carbons connecting a total of sixteen benzene rings on both sides, the furthest ipso-carbons within a single molecule 1 were 2.8 nm apart, and the width of one macrocycle was measured 0.85 nm. In comparison, the diameters of [6]- and [7]CPP's are 0.79 nm and 0.95 nm, respectively.¹² The oligoparaphenylene subunits became heavily yet unevenly bent, with torsional angles between adjacent benzene rings broadly ranging from 7.2° to 43.6° (24.8° on average). Notably, the two "propeller blades" were almost orthogonal to each other, exhibiting a 75° dihedral angle between the two furthest C(ipso)-C(ipso) bonds. The average bond lengths for $C(sp^2)-C(sp^2)$ within a benzene unit and C(ipso)-C(ipso) were 1.39 Å and 1.48 Å, respectively, which were in accordance with the CPP's.¹² In the crystalline state, a unit cell of racemic 1 contained a pair of opposite enantiomers which alternatively packed on top of each other with good alignment (Figure S11).

Next, the synthetic utility of **1** was explored by inducing cycloreversion of its dianthracene core (Scheme 3). The

Scheme 3. Synthesis of 2 via Cycloreversion



Reagents and conditions: (a) 8-watt 254 nm UV lamp, CH_2Cl_2 , 25 °C, 3h; (b) toluene, 110 °C, 12 h; (c) o-dichlorobenzene, 175 °C, in dark, 18 h.

concurrent ring expansion should afford the anthraceneincorporated aromatic macrocycle 2, a new nanohoop potentially applicable for bottom-up syntheses of carbon nanotubes (CNT).¹³ The challenging aspect for the ring expansion is that neither 1 nor 2 has polar functional groups, therefore excessive by-product formation or incomplete starting material conversion would complicate product purification. The photo-induced cycloreversion^{6b} of 1 under 254 nm UV light led to decomposition into a complex mixture. This result was echoed by the absence of the characteristic UV-Vis absorption of the dianthracene unit in 1 (cf. Figure 3), likely due to its extended conjugated structure. We then investigated thermally induced conditions, 4c,6a and 1 was found intact after hours in refluxing toluene. After an extensive survey of solvents with higher boiling points, we established that heating 1 in o-dichlorobenzene at 175 °C for 18 h in dark cleanly produced the desired product 2 with 72% isolated yield.

Compound **2** was characterized by NMR and mass spectrometry, showing only simple ¹H and ¹³C NMR spectra.¹⁴ With the incorporation of two **2**,6-disubstituted anthracene units, the nanohoop **2** was expected to generate stereoisomers as a result of rotation of the anthracene units.¹⁵ In order to gain further structural information of **2**, we performed preliminary density functional theory (DFT) calculation with Gaussian o9 package (Figure **2**),¹⁶ showing two thermodynamically favored conformers corresponding to the sidewall



Figure 2. DFT-calculated conformers and rotation barriers (kcal/mol) of **2**.

fragment of chiral(18,14) and armchair(16,16) CNT's, respectively. The two conformers exhibited minimal energy difference (o.8 kcal/mol) based on their computationally optimized geometries. Notably, the calculated energy barriers to interconvert between the two conformers were less than 10 kcal/mol. This result indicated rapid rotations of the anthracene units at ambient temperature, thus was consistent with the observed NMR spectra of **2**.

Molecules 1 and 2 exhibited intriguing photophysical properties compared with structurally related CPP's (Figure 3). The octaparaphenylene-containing 1 was paired with [8]CPP, highlighting the effect of interrupted vs. cyclic conjugated aromatic loops. 1 showed an absorbance maximum at 336 nm, consistent with the CPPs' common λ_{max} between 336 nm and 340 nm.¹² A shoulder peak was observed spanning from 350 nm to 450 nm, which can be assigned to transitions including HOMO→LUMO and HOMO-1→LUMO/HOMO→LUMO+1 (Table S12).¹⁴ The fluorescence emission of 1 was blue-shifted with a much higher quantum yield of 0.59 and a much shorter singlet lifetime of 2.4 ns.¹⁷

The anthracene-incorporated nanohoop **2** was compared to [16]CPP based on similar diameters, thus showcasing the effect of anthracene as a photophysically functional moiety.¹⁸ The absorbance maximum of **2** was slightly blue-shifted to 329 nm, with shoulder peaks at 395 and 418 nm that corresponded to DFT calculated transitions involving HOMO, LUMO, and adjacent molecular orbitals (Tables S13 and S14).¹⁴ **2** showed red-shifted, dual maxima at 441 and 464 nm, consistent with a smaller calculated HOMO/LUMO gap.¹⁹ The lower quantum yield of **2** may be related to non-radiative pathways of the photo-excited state due to the rotation of the anthracene units (*cf.* Figure 2).



Figure 3. Photophysical data and DFT calculated HOMO/LUMO gap. ^{*a*}Ref. 12; ^{*b*}Ref. 18; ^{*c*}Ref. 19; ^{*d*}Average gap calculated based on optimized conformers A and B of **2**. See the Supporting Information.

In conclusion, chemical syntheses of highly strained oligoparaphenylene molecules 1 and 2 has been achieved with 27% yield over 4 steps and 20% yield over 5 steps, respectively. Key synthetic features include a rigid anthracenephotodimer synthon, late-stage ring expansion through cycloreversion, and high-yielding macrocycle formation using Yamamoto coupling. Both 1 and 2 display attractive properties experimentally and theoretically, suggesting their potential utility as organic optoelectronic materials and building blocks for bottom-up carbon nanotube synthesis. Further synthetic applications of the anthracene photodimerization/ cycloreversion strategy are under investigation and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.xxxxxx.

Experimental, spectral, and computational details (PDF)

- Crystallographic data for 1 (CIF)
- Crystallographic data for 5a (CIF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) (a) Scott, L. T. Angew. Chem. Int. Ed. 2004, 43, 4994. (b) Pascal, R. A., Jr. Chem. Rev. 2006, 106, 4809. (c) Tahara, K.; Tobe, Y. Chem. Rev. 2006, 106, 5274. (d) Merner, B. L.; Dawe, L. N.; Bodwell, G. J. Angew. Chem. Int. Ed. 2009, 48, 5487. (e) Eisenberg, D.; Shenhar, R.; Rabinovitz, M. Chem. Soc. Rev. 2010, 39, 2879. (f) Gingras, M. Chem. Soc. Rev. 2013, 42, 968. (g) Golder, M. R.; Jasti, R. Acc. Chem. Res. 2015, 48, 557. (h) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. Chem. Soc. Rev. 2015, 44, 6616. (i) Yamago, S.; Kayahara, E.; Hashimoto, S. Cycloparaphenylenes and carbon nanorings. In Polycyclic Arenes and Heteroarenes: Synthesis, Properties, and Applications; Qian, M., Ed.; John Wiley & Sons: Chichester, UK, 2015; pp 143-162. (j) Hammer, B. A. G.; Müllen, K. Chem. Rev. 2016, 116, 2103. (k) Segawa, Y.; Ito, H.; Itami, K. Nat. Rev. Mater. 2016, 1, 15002. (l) Segawa, Y.; Yagi, A.; Matsui, K.; Itami, K. Angew. Chem. Int. Ed. 2016, 55, 5136.

(2) (a) For a recent comprehensive summary, see: Lewis, S. E. Chem. Soc. Rev. 2015, 44, 2221. (b) Kayahara, E.; Patel, V. K.; Mercier, A.; Kündig, E. P.; Yamago, S. Angew. Chem. Int. Ed. 2016, 55, 302. (c) Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S. J. Am. Chem. Soc. 2016, 138, 338. (d) Sisto, T. J.; Zakharov, L. N.; White, B. M.; Jasti, R. Chem. Sci. 2016, 7, 3681. (e) Golder, M. R.; Colwell, C. E.; Wong, B. M.; Zakharov, L. N.; Zhen, J.; Jasti, R. J. Am. Chem. Soc. 2016, 138, 6577. (f) Sakamoto, H.; Fujimori, T.; Li, X.; Kaneko, K.; Kan, K.; Ozaki, N.; Hijikata, Y.; Irle, S.; Itami, K. Chem. Sci. 2016, 7, 4204. (g) Lu, D.; Wu, H.; Dai, Y.; Shi, H.; Shao, X.; Yang, S.; Yang, J.; Du, P. Chem. Commun. 2016, 52, 7164. (h) Sun, Z.; Suenaga, T.; Sarkar, P.; Sato, S.; Kotani, M.; Isobe, H. Proc. Natl. Acad. Sci. U.S.A. 2016, 113, 8109.

(3) (a) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. J. *Am. Chem. Soc.* **2008**, *1*30, *1*7646. (b) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. Angew. Chem. Int. Ed. 2009, 48, 6112. (c) Yamago, S.; Watanabe, Y.; Iwamoto, T. Angew. Chem. Int. Ed. 2010, 49, 757. Recent effective methods for nanohoop syntheses include but not limited to: (d) Tran-Van, A.-F.; Huxol, E.; Basler, J. M.; Neuburger, M.; Adjizian, J.-J.; Ewels, C. P.; Wegner, H. A. Org. Lett. 2014, 16, 1594. (e) Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. Org. Lett. 2015, 17, 3470. (f) Mitra, N. K.; Meudom, R.; Corzo, H. H.; Gorden, J. D.; Merner, B. L. J. Am. Chem. Soc. 2016, 138, 3235.

(4) (a) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145. (b) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43. (c) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2001**, *30*, 248.

(5) (a) Tung, C.-H.; Wu, L.-Z.; Zhang, L.-P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, *39*. (b) Bringmann, S.; Brodbeck, R.; Hartmann, R.; Schäfer, C.; Mattay, J. *Org. Biomol. Chem.* **2011**, *9*, 7491. (c) Zhu, L.; Al-Kaysi, R. O.; Bardeen, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 12569. (d) Kory, M. J.; Worle, M.; Weber, T.; Payamyar, P.; van de Poll, S. W.; Dshemuchadse, J.; Trapp, N.; Schluter, A. D. *Nat. Chem.* **2014**, *6*, 779. (e) Murray, D. J.; Patterson, D. D.; Payamyar, P.; Bhola, R.; Song, W.; Lackinger, M.; Schluter, A. D.; King, B. T. *J. Am. Chem. Soc.* **2015**, *137*, 3450.

(6) (a) Takaguchi, Y.; Tajima, T.; Ohta, K.; Motoyoshiya, J.; Aoyama, H. *Chem. Lett.* **2000**, *29*, 1388. (b) Gao, D.; Meier, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 186. (c) Benard, C. P.; Geng, Z.; Heuft, M. A.; VanCrey, K.; Fallis, A. G. *J. Org. Chem.* **2007**, *72*, 7229. (d) Liang, C.-K.; Desvergne, J.-P.; Bassani, D. M. *Photochem. Photobiol. Sci.* **2014**, *13*, 316. (e) Fukuhara, G.; Iida, K.; Kawanami, Y.; Tanaka, H.; Mori, T.; Inoue, Y. *J. Am. Chem. Soc.* **2015**, *137*, 15007. (f) Li, P.; Wong, B. M.; Zakharov, L. N.; Jasti, R. *Org. Lett.* **2016**, *18*, 1574.

(7) Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. Angew. Chem. Int. Ed. 2007, 46, 5359.

(8) CCDC 1492176 (for compound **5a**) and 1492177 (for compound **1**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

(9) (a) Martin, R.; Buchwald, S. L. Acc. Chem. Res. 2008, 41, 1461. (b) Fu, G. C. Acc. Chem. Res. 2008, 41, 1555.

(10) Darzi, E. R.; Sisto, T. J.; Jasti, R. J. Org. Chem. 2012, 77, 6624.

(11) (a) Nelson, T. D.; Crouch, R. D. Org. React. 2004, 63, 265. (b) Omachi, H.; Segawa, Y.; Itami, K. Acc. Chem. Res. 2012, 45, 1378. (c) Kayahara, E.; Patel, V. K.; Yamago, S. J. Am. Chem. Soc., 2014, 136, 2284. (d) Myśliwiec, D.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Stępień, M. J. Am. Chem. Soc. 2015, 137, 1643. (e) Yamamoto, T.; Wakabayashi, S.; Osakada, K. J. Organomet. Chem. 1992, 428, 223. (f) Ohlendorf, G.; Mahler, C. W.; Jester, S.-S.; Schnakenburg, G.; Grimme, S.; Höger, S. Angew. Chem. Int. Ed. 2013, 52, 12086.

(12) Darzi, E. R.; Jasti, R. Chem. Soc. Rev. 2015, 44, 6401.

(13) (a) Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat. Commun.* **2011**, *2*, 492. (b) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. *Nat. Chem.* **2013**, 5, 572. (c) Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature* **2014**, *512*, 61. (d) Liu, C.; Cheng, H.-M. *J. Am. Chem. Soc.* **2016**, *138*, 6690.

(14) See the Supporting Information for details.

(15) (a) Omachi, H.; Segawa, Y.; Itami, K. Org. Lett. 2011, 13, 2480.
(b) Hitosugi, S.; Nakanishi, W.; Isobe, H. Chem. Asian J. 2012, 7, 1550.
(c) Sun, Z.; Sarkar, P.; Suenaga, T.; Sato, S.; Isobe, H. Angew. Chem. Int. Ed. 2015, 54, 12800.

(16) Frisch, M. J. *et al* Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

(17) For a report on interrupted CPP molecules showing blueshifted fluorescence and higher quantum yield than their parent CPP, see: Li, P.; Sisto, T. J.; Darzi, E. R.; Jasti, R. *Org. Lett.* **2014**, *16*, **18**2.

(18) (a) Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle, S.; Itami, K. *Org. Biomol. Chem.* **2012**, *10*, 5979. (b) Yagi, A.; Venkataramana, G.; Segawa, Y.;. Itami, K. *Chem. Commun.* **2014**, 50, 957.

(19) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. J. Am. Chem. Soc. 2011, 133, 8354.

