

Synthesis, Structure, and Aromaticity of a Hoop-Shaped Cyclic Benzenoid
[10]Cyclophenacene

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Having thus far remained hypothetical,^{1,2} hoop-shaped cyclic benzenoid compounds have attracted the interest of chemists for half of a century³ for their aromaticity,⁴ potential utilities in materials science,¹ and their structures themselves that have challenged synthetic chemists for a number of years.² Comprising a part of the structure of a carbon nanotube (CNT), they are now also the subject of interest of a broader scientific community.⁵ We report herein the first synthesis of the hoop-shaped benzenoid, specifically, carbon-capped derivatives of [10]cyclophenacene **1** (Figure 1b) and its derivatives **4** and **5**. The synthesis was achieved in three or four steps by rationally designed chemical modification of [60]fullerene. Single-crystal X-ray crystallographic analysis afforded a high-precision structure (± 0.02 Å) of this CNT substance. Note that the structural information on the CNTs has been obtained largely by scanning tunneling microscopic measurements, which are not precise enough to discuss the C–C bond lengths.⁶

A 40 π -electron cyclic benzenoid **A**, [10]cyclophenacene ($C_{40}H_{20}$), can be generated by rolling a polyphenanthrene-type graphite ribbon⁷ and hence represents the shortest armchair (5,5) CNT. The nature of this cyclic benzenoid may be described by certain resonance structures such as those shown in Figure 1a,⁸ and previous theoretical studies predicted it to be aromatic.⁴ This latter point has yet to be proven by experiments.

There are a priori two rational synthetic approaches to the hoop-shaped benzenoid molecules,^{1,2} one by rolling a flat precursor⁹ and the other by detracting of the conjugated system of fullerenes or CNTs. None have thus far been successful. Our approach shown in Figure 2 relies on an organocopper reaction that converts the [60]fullerene exclusively and quantitatively into a cyclopentadiene compound **2**.¹⁰ Repetition of the reaction on the bottom 50 π -electron part of **2** should directly produce the desired cyclic 40 π -electron system in three steps overall from [60]fullerene. However, it did not take place at all: The copper reagent deprotonates **2** to generate the corresponding cyclopentadienyl anion, which is entirely unreactive toward further addition reactions. To circumvent this problem, we temporarily protected the acidic hydrogen atom in **2** with a cyano group, which was later removed after the second penta-addition was achieved. In this synthetic sequence, the electronegative cyano protective group also acts to increase the electrophilicity of the 50 π -electron system (the first reduction potential of **2**, -1.48 V (Fc/Fc⁺); that of **3**, to -1.35 V (Fc/Fc⁺) in tetrahydrofuran (THF)).

The synthesis started with penta-methylated [60]fullerene **2**, which was synthesized in 92% isolated yield from [60]fullerene.¹¹ It was treated first with ^tBuOK and then with *p*-toluenesulfonyl cyanide (TsCN) to obtain the cyano fullerene **3** in 63% yield. Treatment of **3** with a phenylcopper reagent afforded the [10]cyclophenacene $C_{60}(\text{CN})\text{Me}_5\text{Ph}_5\text{H}$ (**4**) in 14% isolated yield.¹²

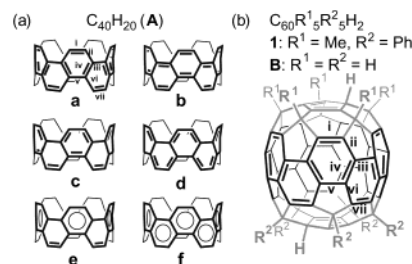


Figure 1. [10]Cyclophenacene and its carbon-substituted derivatives. (a) Some representative resonance structures of the parent compound $C_{40}H_{20}$ (**A**; C_{5v} symmetry). Hydrogen atoms are omitted for clarity. (b) Structure of $C_{60}R^1_5R^2_5H_2$ (**1** and **B**). The [10]cyclophenacene system is made darker than the rest for clarity.

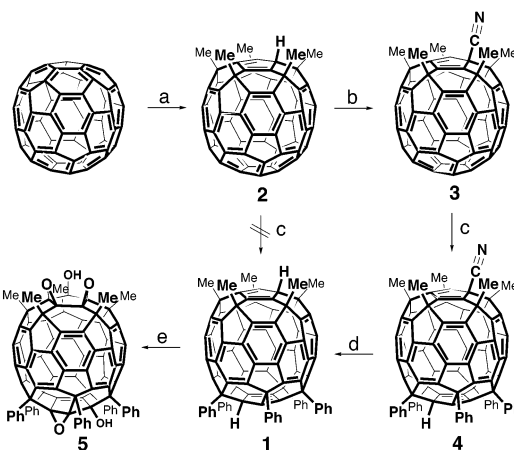


Figure 2. Synthesis of [10]cyclophenacene derivatives. Reaction conditions, a: (1) MeMgBr (30 equiv), CuBr·SMe₂ (30 equiv), *N,N'*-dimethylimidazolidinone (DMI, 30 equiv) in THF, (2) NH₄Cl/H₂O, 92%. b: (1) ^tBuOK (1.1 equiv) in THF, (2) TsCN (1.2 equiv) in PhCN, 63%. c: (1) PhMgBr (30 equiv), CuBr·SMe₂ (30 equiv), DMI (30 equiv) in THF, (2) NH₄Cl/H₂O, 14%. d: (1) Li⁺[C₁₀H₁₀][−] (30 equiv) in PhCN, (2) NH₄Cl/H₂O, 82%. e: (1) KH in THF, (2) under air in THF, 42%. For **1**, **4**, and **5**, isomers always formed as to the relative stereochemistry of the top and the bottom pentagons (only one isomer is shown in Figure 2).

The cyanide group in **4** was reductively removed by treatment with lithium-naphthalenide to obtain $C_{60}\text{Me}_5\text{Ph}_5\text{H}_2$ (**1**) in 82% yield. This compound was found not to give any of the EPR signals (solid, at 4 K). In agreement with its closed shell, aromatic (vide infra) character, the 40 π -electron system was found to be chemically stable. Treatment of **1** with potassium hydride followed by exposure to molecular oxygen afforded the penta-oxygenated product $C_{60}\text{Me}_5\text{Ph}_5\text{O}_3(\text{OH})_2$ (**5**) that gave single crystals suitable for X-ray analysis. The absorption spectra of the [10]cyclophenacene molecules (**1**, **4**, and **5** in cyclohexane) are similar to each other, showing a maximum at ca. 260 nm with broad absorption that extends to ca. 500 nm. The compounds **1** and **5** are strongly luminescent, emitting bright yellow light (ca. 560 nm and ca. 620

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Table 1. Experimental Data (Standard Deviation in Parentheses) Obtained by X-ray Crystallographic Analysis and Theoretical Optimized Structures of Model Compounds **A** (C₄₀H₂₀) and **B** (C₆₀H₁₂)

compounds	bond length (Å) ^{a,b}						
	i	ii	iii	iv	v	vi	vii
5	1.37(2)	1.44(2)	1.43(1)	1.40(2)	1.43(1)	1.45(1)	1.36(1)
A							
(HF)	1.35	1.44	1.43	1.38			
(B3LYP)	1.37	1.44	1.45	1.42			
(PM3)	1.36	1.43	1.44	1.40			
B							
(HF)	1.35	1.44	1.43	1.38			
(B3LYP)	1.37	1.45	1.44	1.39			
(PM3)	1.37	1.44	1.44	1.40			

^a i, iii, v, vii: Average lengths of five equivalent bonds. ii, iv, vi: Average lengths of 10 equivalent bonds. Calculated data for **A** and **B** refer to the geometry optimized structures (C_{2h} symmetry and D_{5d} symmetry, respectively) obtained by the hybrid density functional method (B3LYP), the Hartree–Fock ab initio method (HF) using the 6-31G* basis set, and the semiempirical PM3 method. ^b See Figure 1 for the numbering of the C–C bonds (i–vii).

nm) with quantum efficiency of 0.10 in cyclohexane (irradiation at 366 nm, rhodamin B as standard; see Supporting Information).

X-ray crystallographic structures were obtained for **5** (Table 1). Whereas the double bonds on the edge are short (bonds i and vii, 1.36(2) and 1.37(2) Å, respectively), bond alternation in the equator region is very small (iii, v = 1.43(1) and iv = 1.40(2) Å). This experimental structure obviously does not conform to the “ideal graphitic structure”, which was assumed in most of the previous theoretical studies of CNTs,¹³ but rather similar to the Kekulé structure (a) in Figure 1a. The geometries of the model compounds C₄₀H₂₀ (**A**) and C₆₀H₁₂ (**B**) were optimized with quantum mechanical calculations and found to reproduce the experimental data very well (Table 1). Note that, in contrast to the [10]cyclophenacenes, there is distinctive bond alternation in [60]fullerene (1.36 vs 1.47 Å),¹⁴ in 1,3-butadiene (1.35 vs 1.47 Å),^{15,16} and in 20 π -electron cyclic *cis*-polyacetylene (1.36 vs 1.46 Å, B3LYP/6-31G*-optimized, see Supporting Information).

Nucleus independent chemical shift (NICS)¹⁷ is a useful measure of the magnetic shielding effect of the aromatic ring current. Analysis of the NICS values for six-membered rings of cyclophenacene in the model compounds **A** and **B** indicates that the hoop-like 40 π -electron system is aromatic (NICS = –8.62 and NICS = –11.46 to –11.99, respectively) and the other rings in **B** are nonaromatic (NICS = –1.27 to 0.30). The center of gravity (CG; NICS = –7.25 and NICS = –11.58) is predicted to be subject to an aromatic shielding effect (a value experimentally provable by ³He NMR experiments).¹⁸

The synthesis of the [10]cyclophenacene compounds, which represent the shortest (5,5) CNT, provided the first information on the structure as well as chemical and physical properties of the hoop-shaped cyclic benzenoid. The compounds were found to be stable and aromatic, and luminescent (**1** and **5**). This last property is intriguing in view of the recent reports on luminescent CNT.¹⁹ Finally, the bifunctional nature of compounds (cf. **1**) suggests their use as linkers in a metal/fullerene alternating polymer²⁰ through formation of η^5 -metal fullerene complexes.²¹

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Supporting Information Available: Synthetic procedure, crystallographic data, and computational details of [10]cyclophenacene (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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