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Communication

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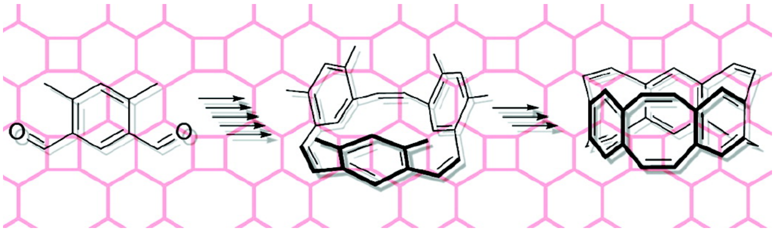

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Synthesis of [6.8]$_3$Cyclacene: Conjugated Belt and Model for an Unusual Type of Carbon Nanotube

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Hoop shaped molecules consisting of annelated, unsaturated rings are of interest with respect to their conjugation, their spectroscopic properties, their cavities and as possible structural motifs for carbon nanotubes. [6]$_n$Cyclacenes[1] (**2** ($n = 8$)) which are built from n linearly annelated benzene rings have been discussed in the literature since 1954[2,3] and can, as well as cyclo[n]phenacenes (**3** ($n = 10$)), be regarded as subunits of carbon nanotubes.[4] However, their synthesis is still lacking, although the challenge has been undertaken by several groups.[5–7] Their results have shown that there are two main obstacles in the synthesis of **2**. The bending of a linear chain of annelated benzene rings into a hoop shape as the first has been overcome by the preparation of belt-like precursors through Diels–Alder reactions with 7-oxanorbornane[5,7] or cyclohexane derivatives.[6] The anticipated high reactivity of [6]$_n$cyclacenes due to a small singlet–triplet gap predicted by quantum chemical calculations[8] is the second obstacle to which we also ascribe the failures to convert the belt-like precursors to fully conjugated systems. This assumption was supported by a recent synthesis of a derivative of the cyclo[10]phenacene **3** (Figure 1) for which, unlike the [6]$_n$cyclacenes, a large singlet–triplet gap is expected. It was accomplished by selective reduction of the north and south pole of C_{60}.[9]

Both obstacles, the bending problem and the singlet–triplet gap, can be circumvented by incorporating such conjugated ring systems that naturally adopt a boat-like conformation.[3c] Especially favorable should be eight-membered (cyclooctatetraene) rings in conjunction with four- and six-membered rings, the former allowing for conjugation and fulfilling the boat shape requirement. Thus, we started to explore the synthesis of [4.8]$_n$ and [6.8]$_n$cyclacenes[3c] and found a rather simple access to the [4.8]$_3$cyclacene derivative **4** (Figure 1).[10] In connection with this work and supported by quantum chemical calculations,[11] we report herein the synthesis of [6.8]$_3$cyclacene **1** (Figure 1) as the first purely hydrocarbon cyclacene and model for a new type of carbon nanotube.

Our stepwise synthesis of **1** commenced with the readily available 4,6-dimethylisophthalaldehyde **5**[12] (Scheme 1). Selective reduction of one of the aldehydic groups with $NaBH_4$ and subsequent treatment of the monoalcohol with HBr in boiling HOAc afforded the benzylic bromide **6** in 65% yield (two steps). **6** was quantitatively converted to the phosphonium salt **7** by refluxing with triphenylphosphine in toluene. The three benzene rings were assembled in a cyclic fashion by an intermolecular Wittig cyclization reaction of **7**, achieving the hexamethyl[2$_3$]-*meta*-cyclophanetriene **8** in 7% yield as the first key intermediate. In the choice of method, we followed Wennerström[13] who had obtained the unsubstituted [2$_3$]-*meta*-cyclophanetriene in 28% yield. The lower yield in our case was presumably caused by the steric hindrance stemming from the methyl groups. The corresponding tetra- up to octameric *meta*-cyclophane-*n*-enes could be isolated as minor products.

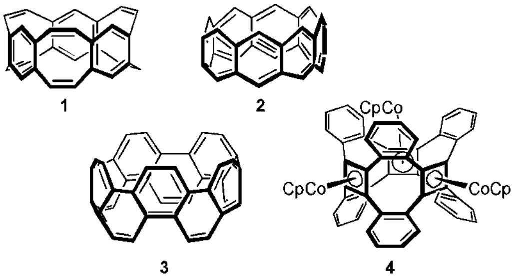
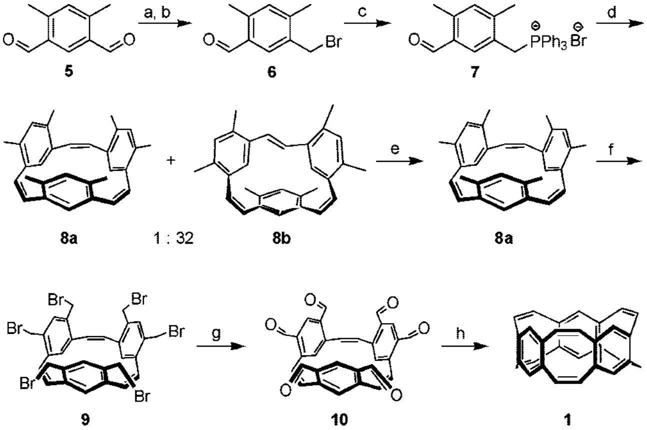


Figure 1. [6.8]$_3$Cyclacene (**1**), [6]$_8$cyclacene (**2**), cyclo[10]phenacene (**3**), and CpCo-capped hexabenzo[4.8]$_3$cyclacene (**4**).

Scheme 1[a]



[a] Reagents and conditions: (a) $NaBH_4$, EtOH, rt; (b) HBr, HOAc, reflux, 65% (two steps); (c) PPh_3, toluene, reflux, 99%; (d) LiOEt/EtOH, DMF, −10 °C, 7%; (e) *hν*, benzene, 5 °C, 85%; (f) NBS, dibenzoylperoxide, CCl_4, reflux, 40%; (g) IBX, DMSO, 65 °C, 37%; (h) $TiCl_3(DME)_{1.5}$, Zn−Cu, DME, reflux, 8%.

The hexamethyl[2$_3$]-*meta*-cyclophanetriene **8** was obtained as a mixture of the *all-Z*, **8a**, and *E,Z,Z* isomer **8b**. This mixture could be converted to pure *all-Z* isomer **8a** in 85% yield by irradiation of a benzenic solution of **8a**/**8b** with a mercury high pressure lamp ($\lambda = 254$ nm). The NMR spectrum of **8a** points toward a C_{3v} symmetrical structure, although in the solid state the molecular structure of **8a** is twisted to a (noncrystallographic) C_2 symmetry (Figure 2). In solution, a fast equilibrium between these twisted conformations is observed as mentioned above with no coalescence down to −90 °C. NBS bromination of **8a** in CCl_4 afforded the hexakis(bromomethyl) derivative **9** in 40% yield. X-ray crystallographic investigation of single crystals of **9** revealed a similar C_2 symmetrical conformation to that of **8a**, while in solution a fast equilibrium resulting in an average C_{3v} symmetry is seen from the NMR spectrum. This species opened the door to the second key intermediate, the hexaaldehyde **10**. Oxidation of the bromomethyl groups in **9** was achieved in 37% yield by reaction with 2-iodoxybenzoic acid (IBX) in DMSO.[14] The conformation of **10** in the solid state (X-ray) and its fast equilibrium in solution (NMR) was

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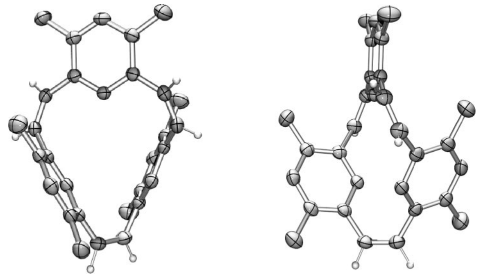

Figure 2. X-ray structure of **8a** (50% probability ellipsoids; front and side view; apart from the olefinic ones, hydrogen atoms are omitted for clarity).

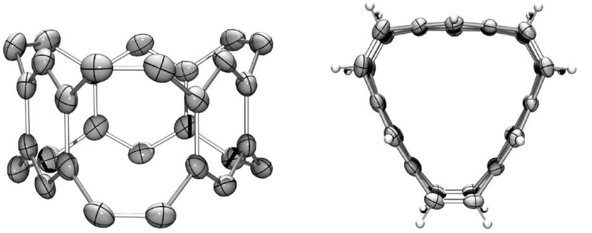

Figure 3. X-ray structure of **1** (50% probability ellipsoids; in the left-hand structure hydrogen atoms are omitted for clarity).

again found to be similar to those of **8a** and **9**. The final 3-fold intramolecular ring closure of **10** to **1** was achieved by a McMurry coupling using low valent titanium ($TiCl_3$−DME complex, Zn−Cu couple)[15] in refluxing DME in 8% yield.

The anticipated D_{3h} symmetrical structure of **1** was confirmed by its analytical data and from X-ray measurements on single crystals (Figure 3). Its structural parameters are close to those theoretically predicted.[11] The carbon skeleton of **1** is reminiscent of Boekelheide's $[2_6]$(1,2,4,5)cyclophane (deltaphane) which consists of three isolated benzene rings bridged by ethano groups.[16] In $[6.8]_3$cyclacene **1**, the mean angle between the plane of the double bond and that of the adjacent aromatic rings amounts to 71.9°. This indicates about 31% conjugation for the cyclacene torus.[17] The UV/vis spectrum of **1** shows an absorption maximum at 220 nm ($\log \epsilon = 4.69$) with two shoulders at 278 and 290 nm ($\log \epsilon = 3.40$ and 3.32, respectively). Fluorescence is observed with a maximum at 370 nm corresponding to a Stokes shift of 80 nm. The UV absorptions are very similar to those of dibenzo[*a.e*]cyclooctatetraene (244, 274, and 304 nm), and a comparison of the NMR spectra shows an upfield shift (0.7−0.8 ppm) of the aromatic protons in **1** compared to the latter. $[6.8]_3$Cyclacene **1** represents the smallest and most strained member of the $[6.8]_n$cyclacene family. Smaller bending angles can be anticipated for larger $[6.8]_n$cyclacenes,[11] and they should be of great interest regarding their conjugation properties. The synthetic path leading to $[6.8]_3$cyclacene **1** offers a general route to $[6.8]_n$cyclacenes starting from hexamethyl-substituted *all-Z*-$[2_n]$-*meta*-cyclophane-*n*-enes.

Structural alternatives to classical fullerenes and carbon nanostructures comprising ring sizes of three- to nine-membered have been considered and theoretically investigated.[18] Slanina calculated a stable cuboctahedron-like C_{48} structure composed of four-, six-, and eight-membered rings.[18c] An expansion of the $[6.8]_n$cyclacenes in the direction of the principal molecular axis leads to carbon nanotubes whose molecular pattern comprises four-, six-, and eight-membered rings.[19] This is a yet unknown type of carbon nanotube but would be a very interesting target to investigate.

In conclusion, we accomplished the synthesis of $[6.8]_3$cyclacene **1** as the first fully conjugated purely hydrocarbon cyclacene. Due to its unsaturated character, it offers conjugation around the belt-like torus consisting of annelated six- and eight-membered rings. It is the smallest and most strained member of the $[6.8]_n$ series.[11] Our synthesis offers a general path to $[6.8]_n$cyclacenes, thus the higher and as anticipated less strained and stronger conjugated members of the $[6.8]_n$cyclacene series are within reach. Furthermore, our work gives first insight into the molecular structures of $[2_3]$-*meta*-cyclophanetrienes.

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Supporting Information Available: Experimental procedures, characterization of all key compounds, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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