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Synthesis of [6.8]₃Cyclacene: 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]_nCyclacenes¹ (2 (n = 8)) which are built from nlinearly 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]_ncyclacenes due to a small singlet-triplet gap predicted by quantum chemical calculations⁸ 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]_ncyclacenes, 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 NaBH₄ 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[2₃]-*meta*-cyclophanetriene **8** in 7% yield as the first key intermediate. In the choice of method, we followed Wennerström¹³ who had obtained the unsubstituted [2₃]-*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*-nenes could be isolated as minor products.

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



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) NaBH₄, EtOH, rt; (b) HBr, HOAc, reflux, 65% (two steps); (c) PPh₃, toluene, reflux, 99%; (d) LiOEt/EtOH, DMF, -10 °C, 7%; (e) *hv*, benzene, 5 °C, 85%; (f) NBS, dibenzoylperoxide, CCl₄, reflux, 40%; (g) IBX, DMSO, 65 °C, 37%; (h) TiCl₃(DME)_{1.5}, Zn-Cu, DME, reflux, 8%.

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 $(\lambda = 254 \text{ nm})$. The NMR spectrum of **8a** points toward a $C_{3\nu}$ 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 CCl₄ 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



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 lefthand 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 (TiCl3-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 [2₆](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 ϵ = 4.69) with two shoulders at 278 and 290 nm (log ϵ = 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]₃Cyclacene 1 represents the smallest and most strained member of the [6.8], 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]₃cyclacene 1 offers a general route to [6.8]_ncyclacenes starting from hexamethylsubstituted *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 C48 structure composed of four-, six-, and eight-membered rings.^{18c} An expansion of the [6.8]_ncyclacenes in the direction of the principal molecular axis leads to carbon nanotubes whose molecular pattern comprises four-, six-, and eightmembered 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]₃cyclacene 1 as the first fully conjugated purely hydrocarbon cyclacene. Due to its unsaturated character, it offers conjugation around the beltlike 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]_ncyclacenes, 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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