Macrocycles

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carbo-Naphthalene: A Polycyclic *carbo*-Benzenoid Fragment of α-Graphyne

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Abstract: *A ring carbo-mer of naphthalene, $C_{32}Ar_8$ (Ar = p-n-pentylphenyl), has been obtained as a stable blue chromophore, after a 19-step synthetic route involving methods inspired from those used in the synthesis of carbo-benzenes, or specifically devised for the present target, like a double Sonogashira-type coupling reaction. The last step is a $SnCl_2$/HCl-mediated reduction of a decaoxy-carbo-decalin, which is prepared through successive [8+10] macrocyclization steps. Two carbo-benzene references are also described, $C_{18}Ar_6$ and o-$C_{18}Ar_4$(C≡C-SiiPr$_3$)$_2$. The carbo-naphthalene bicycle is locally aromatic according to structural and magnetic criteria, as revealed by strong diatropic ring current effects on the deshielding of ^1H nuclei of the Ar groups and on the negative value of the DFT-calculated NICS at the center of the C_{18} rings (−12.8 ppm). The stability and aromaticity of this smallest fused molecular fragment of α-graphyne allows prediction of the same properties for the carbon allotrope itself.*

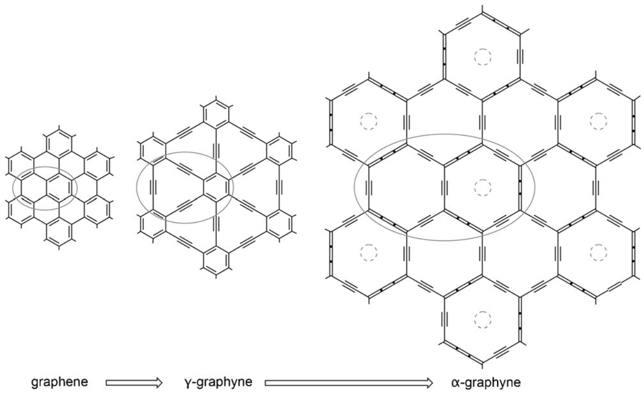
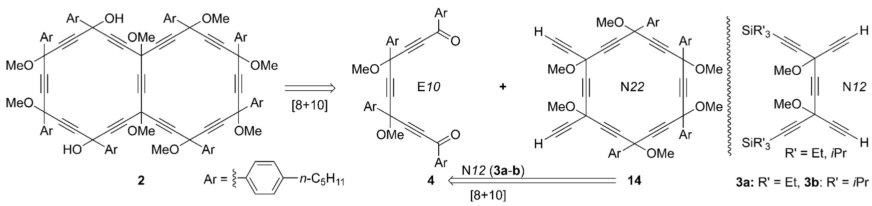


Figure 1. Progressive *carbo*-merization of graphene and its smallest fused fragment. Isolated *carbo*-meric Clar sextets are denoted by dotted circles.

In the chemical design of two-dimensional carbon networks,[1] expanded graphenes containing both sp^2- and sp-hybridized carbon atoms, termed "graphynes",[2] remain essentially investigated at the theoretical level.[3] Besides putative variants (α-, β-, 6,6,12-graphynes), the existence of graphdiyne is today demonstrated,[4] and γ-graphyne has been approached through several polycyclic molecular fragments.[5] The most homogeneous variant is α-graphyne (with only two types of C−C bonds), that is, the total *carbo*-mer of graphene (Figure 1),[6] or a layer of α-graphityne.[2,3b,7] Whereas acyclic and unicyclic molecular fragments of α-graphyne have been exemplified by *carbo*-oligoacetylenes[8] and *carbo*-benzenes,[6,9] a first fused bicyclic fragment is envisaged in a *carbo*-naphthalene.

With a view to securing both stability and solubility, the selected target was octa(*p*-*n*-pentylphenyl)-*carbo*-naphthalene (**1**). Consideration of classical methods used for the synthesis of *carbo*-benzenes from hexaoxy-[6]pericyclynes[10] suggests that **1** could be generated from decaoxy-[4,4,0]peribicyclynes, or *carbo*-decalins, such as **2** (Scheme 1).[11] The latter was thus regarded as an ultimate



Scheme 1. Retrosynthesis of the *carbo*-decalin **2**. For alternative schemes, see the Supporting Information.

C_{32} cycloadduct of a dinucleophile N*n* with a dielectrophile E*m* for $m = 32-n$. While tentative routes for $n = 14$ proved unsuccessful (see the Supporting Information), for $n = 22$, the use of N*12* (**3a**,**b**) and E*10* (**4**) in successive [8+10] cyclization steps turned out to be productive via the intermediate pericyclyne N*22* (**14**).

The pentayne **3b** (R′ = *i*Pr) was obtained through a procedure previously implemented for **3a** (R′ = Et),[9b] via intermediates **I** and **II**,[12] and **III**–**VI** as described in the Supporting Information. The diketone **4** was targeted from the triyne **5**, which was prepared following procedures described for Ar = Ph via intermediates **VII**–**XI**, which are also described in the Supporting Information.[10b] Conversion

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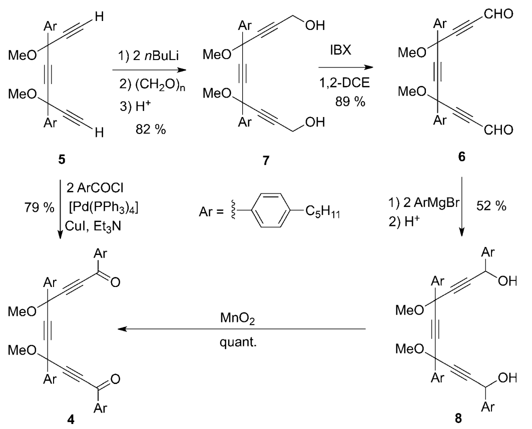
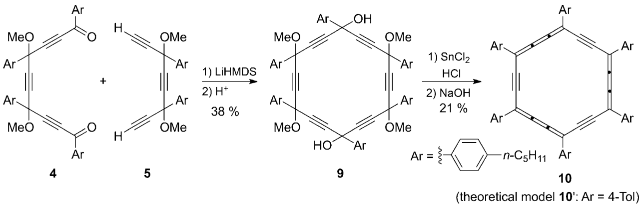
of **5** into **4** was first achieved by adaptation of a known method for Ar = Ph,[10b] through the key dialdehyde **6** and via the diols **7** and **8**, in 37 % yield over four steps (Scheme 2). An alternative method consists of a Sonogashira-like coupling reaction of **5** with ArCOCl. The reaction conditions described for simple terminal alkynes[13] proved compatible with the functional substrate **5**, thus allowing access to **4** in one step and 79 % yield.

In the presence of LiHMDS, cycloaddition of **5** with **4** gave the [6]pericyclynediol **9** in 38 % yield (Scheme 3). Treatment of **9** with $SnCl_2$/HCl led to the *carbo*-benzene **10** (monocyclic reference of **1**) in 21 % yield.



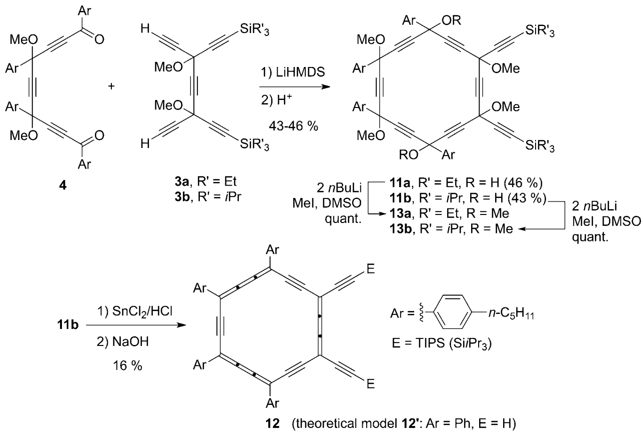
Scheme 2. Synthesis of the diketone **4** (E*10* in Scheme 1). For the synthesis of **5**, see the Supporting Information.



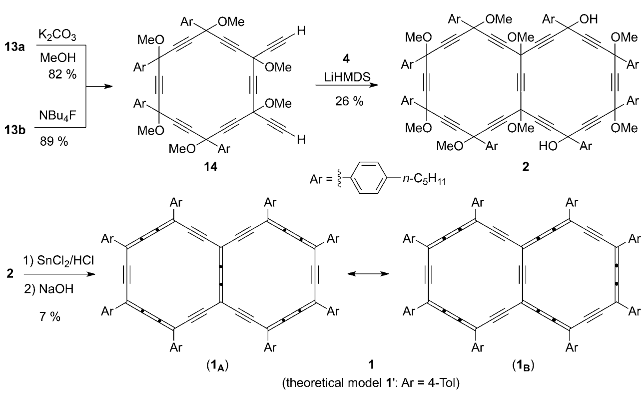
Scheme 3. Synthesis of the hexaaryl-*carbo*-benzene **10**. HMDS = hexamethyldisilazide.

Under similar reaction conditions, the pentanynes **3a**,**b** reacted with **4** to give the [6]pericyclynediols **11a**,**b** in about 45 % yield (Scheme 4). Treatment of **11b** with $SnCl_2$/HCl afforded the *o*-dialkynyl-*carbo*-benzene **12** in 16 % yield. O-Methylation of **11a**,**b** to the ethers **13a**,**b**, and subsequent proto-desilylation gave the diethynyl [6]pericyclyne **14** (Scheme 5). Treatment of **14** with LiHMDS and the diketone **4** afforded the *carbo*-decalin **2** in 26 % yield (theoretical mixture of 130 diastereoisomers). Reductive aromatization of **2** gave **1**, which was isolated in 7 % yield as a poorly soluble blue solid.[14] This solid proved stable enough to be kept exposed to air and light at room temperature for several weeks, and in solution for a few days.

The ^{1}H NMR spectrum of **1** displays two sets of doublets for the *ortho* and *meta* nuclei of the α-,β-Ar groups at lower field (δ = 9.87, 9.48, and 8.03, 7.89 ppm) than the corresponding doublets of **10** (δ = 9.38 and 7.80 ppm) and **12** (δ = 9.37,



Scheme 4. Synthesis of the *o*-dialkynyl-*carbo*-benzene **12**.



Scheme 5. Ultimate steps to the *carbo*-naphthalene **1**.

9.35 ppm and δ = 7.81, 7.71 ppm; Figure 2). This extra deshielding can be attributed to the combined effects of two C_{18} and one C_{30} diatropic ring currents, and the most deshielded signals (δ = 9.87 and 8.03 ppm) are thus assigned to the α-Ar groups closer to the ring junction. More insight into the magnetic aromaticity of **1**, **10**, and **12** was gained by calculation of the nucleus-independent chemical shift (NICS)[15] at the center of the C_{18} rings of the truncated models **1'**, **10'**, and **12'**, respectively (Schemes 3–5). According to the corresponding NICS(0) index at the B3PW91/6-31 + G** level of theory, each C_{18} ring of **1'** appears slightly less magnetically aromatic (δ = −12.8 ppm) than the nonfused C_{18} rings of **10'** (δ = −13.5 ppm) and **12'** (δ = −13.9 ppm). On the basis of B3LYP calculations, an opposite trend was reported for the NICS(0) values in the parent series of naphthalene (δ = −9.9 ppm) and benzene (δ = −9.7 ppm).[15]

In spite of the poor solubility and absence of ^{13}C-^{1}H scalar coupling, the ^{13}C NMR spectrum of **1** was assigned through a crosscheck of consistent data in $CDCl_3$ solution, solid state (CP/MAS), and gas phase (GIAO-B3PW91/6-31 + G**). The central C(sp) and bridgehead C(sp^2) nuclei of the bicycle junction were thus assigned at δ = 104.8 and 79 ppm, respectively (see the Supporting Information).

While **10** and **12** exhibit classical UV/Vis absorption profiles of *carbo*-benzenes, with one main absorption band at $\lambda_{max} = 483.5 \pm 2.5$ nm,[9d] the spectrum of **1** presents two main

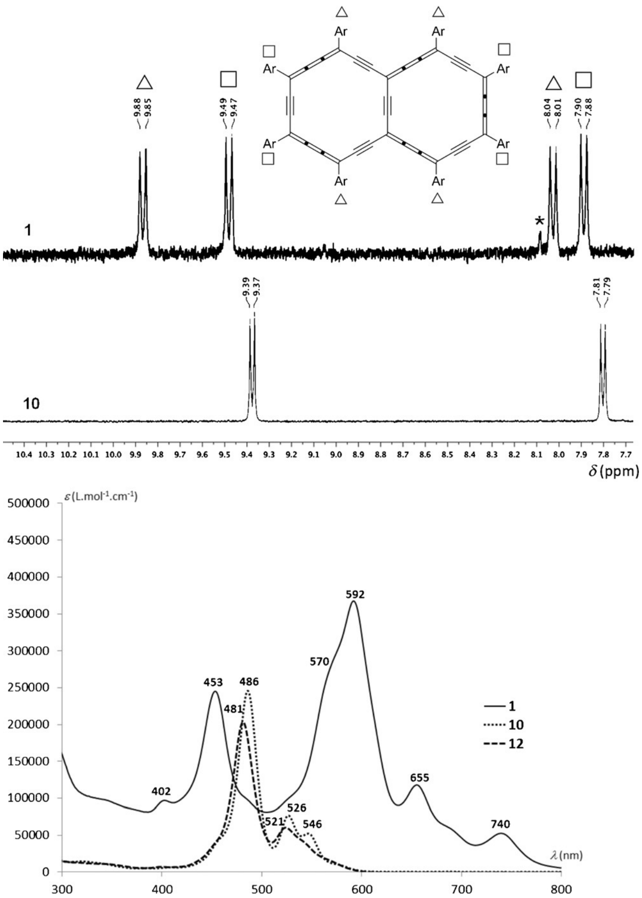


Figure 2. Top: Low-field region of the ^{1}H NMR spectra of **1** and **10** (400 MHz, $CDCl_3$). Bottom: UV/Vis spectra of **1** ($c=1.8\times10^{-6}$ mol L^{-1}), **10** ($c=2.9\ 10^{-6}$ mol L^{-1}), and **12** ($c=4.0\times10^{-6}$ mol L^{-1}; $CHCl_3$).

bands at $\lambda=453$ and 592 nm, with a high extinction coefficient $\varepsilon(592\text{ nm})=382\,000$ L mol^{-1} cm^{-1} (Figure 2). In cyclic voltammetry (see the Supporting Information), **1** is found slightly less readily reduced ($E_p=-0.80$ V/SCE) than **12** ($E_{1/2}=-0.65$ V/SCE).

Crystals of **1** and **10** deposited from chloroform solutions were submitted to XRD analysis (Figure 3).[16] Just as the C_{18} ring of **10**, the C_{32} bicycle of **1** is almost planar, with a maximum deviation of about 0.09 Å, and vanishing dihedral angles with the Ar ring mean planes (ca. 2–8° vs. up to 16° in **10**). The C(sp^2)−C(sp) and C(sp)−C(sp) bond lengths of **1** are similar to those of **10** (1.37–1.42 Å, 1.20–1.25 Å), and are consistent with those found in the DFT-calculated models **1′** and **10′**. All the C_{18} rings in **1**, **1′**, **10**, **10′**, and **12′** exhibit the same mean bond length (1.333 ± 0.001 Å) and standard deviations (0.080 ± 0.007 Å), thus showing that *carbo*-naphthalene and *carbo*-benzene rings have comparable structural aromaticity (see Section S10 in the Supporting Information).[17] Analysis of the bond length alternation also indicates that the valence bond forms $\mathbf{1_A}$ and $\mathbf{1_B}$ have identical weights (Scheme 5).

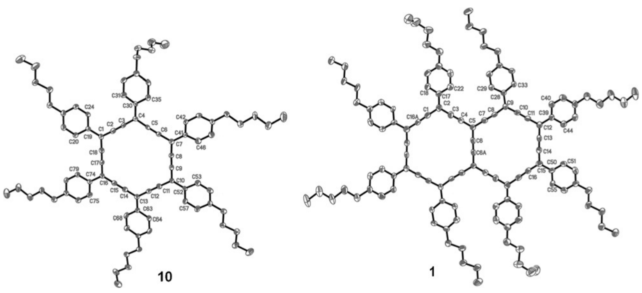


Figure 3. XRD molecular views of **10** and **1**.[16] Thermal ellipsoids shown at 50% probability.

The availability, stability, and structural and aromatic character of the *carbo*-naphthalene C_{32} bicycle are reminiscent of those of the C_{10} naphthalene bicycle, thus opening prospects for the synthesis of larger *carbo*-benzenoid fragments. In spite of the limitation of the long-initiated organic synthetic approach to infinite carbon allotropes,[18] the results also give support to the existence of the α-graphyne allotrope.

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