

Macrocycles

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-npentylphenyl), 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 SnCl₂/ 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 $o-C_{18}Ar_4(C \equiv C-SiiPr_3)_2$. 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.

In the chemical design of two-dimensional carbon networks,^[1] expanded graphenes containing both sp²- and sphybridized 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.



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

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 N12 (**3a,b**) and E10 (**4**) in successive [8+10] cyclization steps turned out to be productive via the intermediate pericyclyne N22 (**14**).

The pentayne **3b** $(\mathbf{R}' = i\mathbf{P}\mathbf{r})$ was obtained through a procedure previously implemented for **3a** $(\mathbf{R}' = \mathbf{E}\mathbf{t})$,^[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 $\mathbf{Ar} = \mathbf{Ph}$ 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 ArCOCI. 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 SnCl₂/HCl led to the *carbo*-benzene **10** (monocyclic reference of **1**) in 21% yield.



Scheme 2. Synthesis of the diketone **4** (E10 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 SnCl₂/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 ¹H 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 $\delta = 7.81$, 7.71 ppm; Figure 2). This extra deshielding can be attributed to the combined effects of two C₁₈ and one C₃₀ diatropic ring currents, and the most deshielded signals ($\delta = 9.87$ 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 $(NICS)^{\left[15\right]}$ 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 ($\delta = -12.8$ ppm) than the nonfused C₁₈ rings of **10'** ($\delta = -13.5$ ppm) and **12'** ($\delta = -13.9$ ppm). On the basis of B3LYP calculations, an opposite trend was reported for the NICS(0) values in the parent series of naphthalene $(\delta = -9.9 \text{ ppm})$ and benzene $(\delta = -9.7 \text{ ppm})$.^[15]

In spite of the poor solubility and absence of ¹³C-¹H scalar coupling, the ¹³C NMR spectrum of **1** was assigned through a crosscheck of consistent data in CDCl₃ solution, solid state (CP/MAS), and gas phase (GIAO-B3PW91/6-31 + G**). The central C(sp) and bridgehead C(sp²) nuclei of the bicycle junction were thus assigned at $\delta = 104.8$ 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 $\lambda_{\text{max}} = 483.5 \pm 2.5 \text{ nm}$,^[9d] the spectrum of **1** presents two main







Figure 2. Top: Low-field region of the ¹H NMR spectra of 1 and 10 (400 MHz, CDCl₃). Bottom: UV/Vis spectra of 1 ($c=1.8 \times 10^{-6} \text{ mol L}^{-1}$), **10** ($c=2.9 \times 10^{-6} \text{ mol L}^{-1}$), and **12** ($c=4.0 \times 10^{-6} \text{ mol L}^{-1}$; CHCl₃).

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

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(sp²)–C(sp) and C(sp)–C(sp) bond lengths of **1** are



Figure 3. XRD molecular views of 10 and $1.^{\mbox{\tiny [16]}}$ Thermal ellipsoids shown at 50% probability.

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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 C₁₈ 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*-naph-thalene 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 **1**_A and **1**_B have identical weights (Scheme 5).

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



Towards α-graphyne: A ring *carbo*-mer of naphthalene, C₃₂Ar₈ (Ar = *p*-*n*-pentylphenyl), was obtained as a stable blue chromophore in 19 steps. The two *carbo*benzenes *o*-C₁₈Ar₄(C=C-Si/Pr₃)₂ and C₁₈Ar₆ are also described. The *carbo*naphthalene bicycle is locally aromatic according to structural and magnetic criteria. The stability and aromaticity of this smallest fused molecular fragment of α-graphyne allows prediction of the same properties for the carbon allotrope itself.