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Technomimetic molecules: synthesis of a molecular wheelbarrow

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Abstract—A molecular analog of a wheelbarrow is synthesized following a strategy based on sequential double Knoevenagel and Diels–Alder reactions.

Recent advances in the imaging and manipulation of single molecules[1] has stimulated much interest in the synthesis of molecules exhibiting unique electronic properties such as amplification or rectification,[2] but also very special mechanical properties like the possibility to grow atomic-sized wires of gold on a surface of copper[3] or to observe a molecular rotor in a supramolecular bearing.[4]

In the field of single molecule manipulation it is a challenge, in a bottom-up approach, to design, synthesize and manipulate a molecule which would at the same time undergo translation and rotation motions.[5] In the case of a macroscopic wheelbarrow, pushing the wheelbarrow results in the rotation of the wheel. We report here the design and synthesis of a molecular analog of a wheelbarrow represented in Figure 1. Its skeleton is made of polycyclic aromatic hydrocarbons (PAHs)[6] which, due to their rigidity, are easily manipulated by the tip of the scanning tunneling microscope (STM). In addition they are relatively resistant to the deposition techniques.[7]

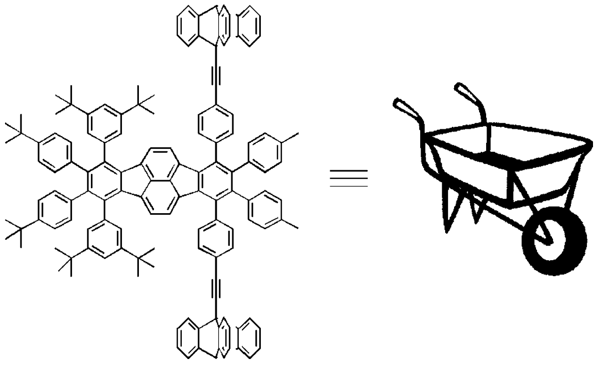

Figure 1. Chemical structure of a molecular wheelbarrow and its macroscopic analog.

The wheelbarrow is constituted of two legs (3,5-di-*tert*-butyl phenyl groups) and two wheels (ethynyl triptycene groups) connected to a polycyclic aromatic hydrocarbon platform.

The left side is equipped with two legs: it has been shown that the 3,5-di-*tert*-butyl phenyl groups are held in a conformation in which the phenyl groups are nearly perpendicular to the main aromatic board. Moreover, the *tert*-butyl groups connected to the PAHs are used to increase organic solubility and are easily observed by STM techniques, inducing a good contrast in the image. The two 4-*tert*-butyl phenyl groups play the role of handles for subsequent manipulation with the tip of the microscope. The right side corresponds to the axle with two 9-triptycenyl groups acting as wheels. We opted for two wheels instead of one for obvious synthetic reasons. Figure 2 shows one of the possible conformations of **1** obtained by semiempirical calculation[8] and the two three-cogged wheels which can freely rotate along the axle due to the acetylenic spacers.

The synthesis of the molecular wheelbarrow **1** is outlined in Scheme 1. Our strategy is based on the repetition of a double Knoevenagel–Diels–Alder reaction sequence on an α-diketo fragment. The first sequence allows the connection of the two 3,5-di-*tert*-butyl phenyl legs, while the second sequence provides the

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Keywords: polyaromatic hydrocarbons; triptycene; single molecule; Sonogashira coupling.

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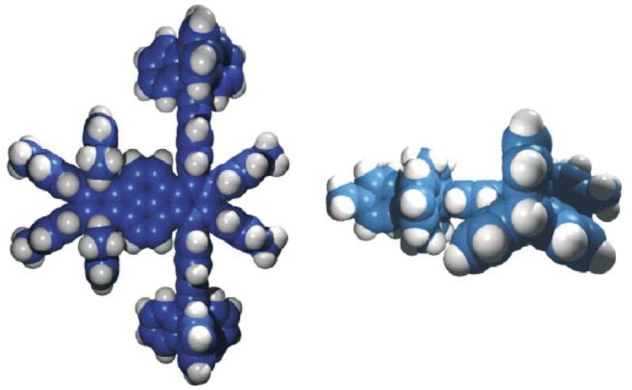
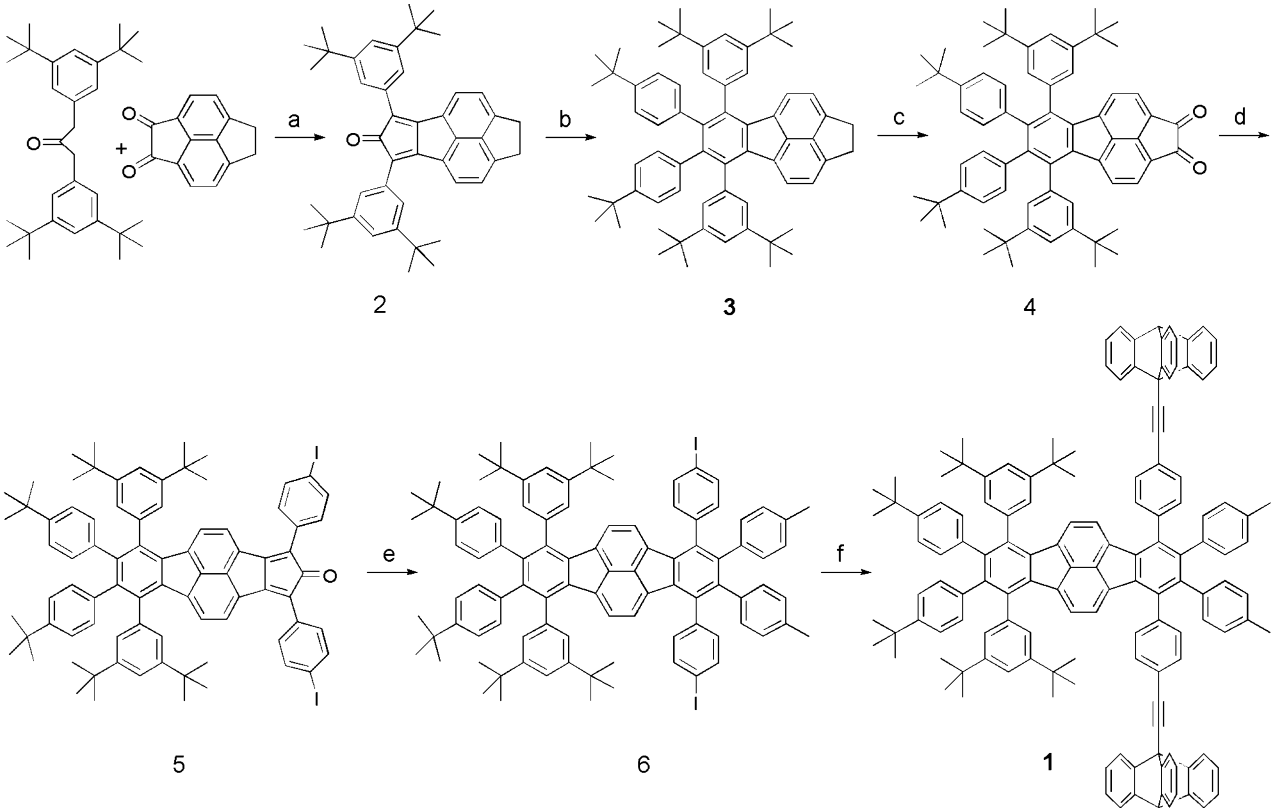


Figure 2. The CPK model showing the minimum energy conformation of the molecular analog **1**. Top view (left) and side view (right). Methyl groups have been omitted for clarity.

precursor for wheels connection. Finally, a double Sonogashira coupling yields the molecular wheelbarrow. The starting cyclopentadienone **2** was obtained via a first double Knoevenagel reaction of 1,3-bis(3,5-di-*tert*-butyl phenyl) propan-2-one with diketopyracene (step a) following a described procedure.[9] The Diels–Alder reaction of **2** with di-(4-*tert*-butyl phenyl)acetylene (step b) provided, after CO extrusion and aromatization, ethane-bridged **3** with a 97% yield. The ^{1}H NMR spectrum of **3** clearly showed the 2:1 ratio between the different types of *tert*-butyl groups. Oxidation of the ethane bridge of the pyracene in **3** with benzeneseleninic anhydride (step c) yielded the diketo fragment **4** necessary for the connection of the second axle.[10] This is the key step of our strategy.

Halogens are introduced at this stage for subsequent coupling in order to connect the triptycene wheels. The double Knoevenagel condensation of **4** with 1,3-di(4-iodophenyl)-propan-2-one (step d) gave the diiodide derivative of cyclopentadienone **5** with a quantitative yield, due to the strong acidic character of the protons involved in the reaction. The Diels–Alder reaction of **5** with di-(4-tolyl)acetylene provided, after CO extrusion and aromatization, the precursor **6** with 30% yield (step e). This low yield may be due to steric hindrance between the overcrowded alkyne and the *tert*-butyl groups of the substrate but the methyl groups are necessary to improve the solubility of this family of molecules in organic solvents.

The two wheels were then simultaneously covalently attached to the axle by a double coupling of 9-ethynyltriptycene with **6** under classical Sonogashira conditions (step f).[11] Pd(PPh$_3$)$_4$, CuI and **6** were suspended under argon in a 1:1 degassed mixture of freshly distilled THF and piperidine. Two equivalents of 9-ethynyltriptycene, obtained following a published procedure,[5] were added



Scheme 1. *Reagents and conditions*: (a) EtOH, 20 h, Ar, 20°C, 90%; (b) di(4-*tert*-butylphenyl)acetylene, diphenylether, 16 h, Ar, reflux, 97%; (c) (C$_6$H$_5$SeO)$_2$O, chlorobenzene, 62 h, Ar, reflux, 60%; (d) 1,3-bis(4-iodophenyl)propan-2-one, KOH, EtOH, Ar, reflux, 100%; (e) di(4-tolyl)acetylene, diphenylether, 16 h, Ar, reflux, 30%; (f) 9-ethynyltriptycene, Pd(PPh$_3$)$_4$ 10 mol%, CuI 20 mol%, piperidine–THF (1:1), 24h, Ar, 20°C, 46%.

with a syringe under argon and the mixture was kept at 20°C for 24 hours. The double coupling afforded **1**[12] in 46% yield after column chromatography (SiO_2, eluent: cyclohexane/0–20% CH_2Cl_2, $R_f = 0.31$) as an orange solid.

The synthesis of a polyaromatic hydrocarbon designed by analogy with a wheelbarrow has been achieved. Studies are currently in progress to image and manipulate **1** with an STM tip. We are hoping to reproduce the mechanical behavior of a wheelbarrow at the molecular level, i.e. to convert the translation movement of the tip into the rotation of the wheels.

Acknowledgements

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12. All new compounds were fully characterized by ^1H NMR, ^{13}C NMR, UV–vis and MS. Compound **1**: Orange solid λ_{max} (CH_2Cl_2)/nm (ε dm^3 mol^{-1} cm^{-1}) 230 (55500), 246 (39250, sh), 276 (17550, sh), 319 (22100), 425 (8040), 450 (9450). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm), 7.84 (m, 6H, Tript), 7.7 (d, 4H, $J_{b-a} = 8$Hz), 7.49 (m, 6H, Tript), 7.42 (d, 4H, $J_{a-b} = 8$Hz), 7.19 (m, 4H), 7.14 (m, 12H, Tript), 7.08 (m, 4H), 6.9 (d, 4H, $J = 8$ Hz), 6.8 (m, 6H), 6.7 (d, 4H, $J = 9$ Hz), 6.4 (d, 2H, $J = 8$ Hz), 6.18 (d, 2H, $J = 7$Hz), 5.5 (s, 2H, Tript), 2.2 (s, 6H, Me), 1.8 (s, 36H, 3,5-di-*tert*-butyl-phenyl), 1.1 (s, 18H, 4-*tert*-butyl-phenyl); ^{13}C NMR (75 MHz, CD_2Cl_2) δ (ppm), 150.13, 148.28, 148.01, 145.47, 144.69, 144.50, 140.77, 139.32, 138.17, 137.86, 137.30, 136.80, 136.67, 131.97, 131.19, 131.03, 130.44, 127.81, 126.24, 125.96, 125.59, 125.43, 125.24, 125.05, 124.86, 124.55, 123.84, 123.68, 123.45, 122.58, 122.49, 121.48, 120.04, 93.03 (alkynes), 34.81 (4 CMe_3), 34.09 (2 CMe_3), 31,23 (12 CMe_3), 31,05 (6 CMe_3), 21.00 (2 CH_3); HR–FAB$^+$–MS (*m*-NBA/*m*/*z*) 1801.9500 (M+H$^+$, calculated for $C_{140}H_{121}$: 1801.9468).