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Diels−Alder Reactivity of Polycyclic Aromatic Hydrocarbon Bay Regions: Implications for Metal-Free Growth of Single-Chirality Carbon Nanotubes

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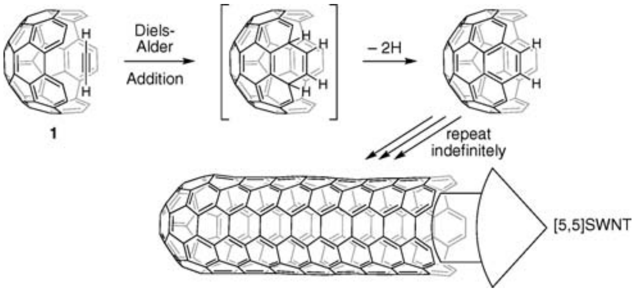
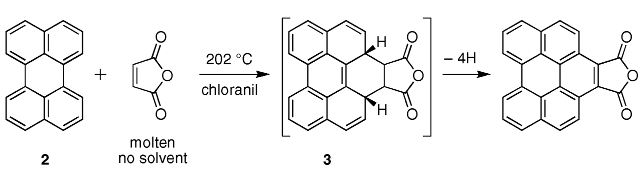
Single-chirality carbon nanotubes (CNTs) of predefined diameter and [*M*,*N*] index will someday be accessible by rational chemical synthesis "from the ground up," in the same way that Lipitor, Nylon, and countless other man-made substances are routinely synthesized today by organic chemists. In principle, one might achieve this objective by "growing" a nanotube using well understood chemical reactions, starting from a suitably constituted small hydrocarbon template.[1] The Diels−Alder addition of acetylene to a [5,5]nanotube end-cap (e.g., **1**), for example, would transform the "bay regions" around the armchair rim of the molecule into new benzene rings, and successive Diels−Alder reactions could continue indefinitely, because the molecule can never run out of bay regions (Scheme 1). The highly exothermic aromatization of each newly formed six-membered ring by loss of two hydrogens would be expected to occur spontaneously, even at moderate temperatures and in the absence of oxidizing agents.[2]

Scheme 1. Proposed Application of the Diels−Alder Reaction to a Chemical Synthesis of Carbon Single-Walled Nanotubes (SWNTs)



Disregarding, for now, the fact that acetylene is a feeble dienophile in Diels−Alder reactions, even with relatively reactive dienes,[3] most organic chemists would dismiss this strategy as unrealistic, because the bay regions of polycyclic aromatic hydrocarbons (PAHs) are notoriously resistant to Diels−Alder addition reactions, even when confronted with potent dienophiles. To coerce perylene (**2**) to react with maleic anhydride, for example, Clar and Zander resorted to using molten maleic anhydride as the solvent at reflux (202 °C), with chloranil added to aromatize the new ring (Scheme 2).[4] Notwithstanding the perceived obstacles to implementing the idealized proposal in Scheme 1, we contend that such a strategy may still be viable.

Scheme 2. A Diels−Alder Addition to the Bay Region of Perylene



The energetic cost of temporarily and simultaneously disrupting the aromaticity of two benzene rings undoubtedly accounts for the reluctance of PAHs to engage in bay region Diels−Alder cycloadditions. That cost can be approximated as the difference in the aromatic stabilization energies (Δ_{ASE})[5] between the starting material and the initially formed cycloadduct. In the example illustrated (Scheme 2), the initially formed cycloadduct (**3**) contains a residual phenanthrene moiety, the ASE of which is quite large but falls below that of the starting perylene (**2**). Phenanthrene itself has never been seen to undergo a bay region Diels−Alder reaction, presumably because the large ASE of the molecule would drop down to zero in the initially formed cycloadduct.

It occurred to us that the smaller Δ_{ASE} of the perylene Diels−Alder reaction (Scheme 2), relative to that of the imaginary phenanthrene Diels−Alder reaction, might point to even smaller Δ_{ASE} values for bay region Diels−Alder reactions of longer PAHs that begin to resemble strips from the side walls of armchair CNTs. Simply counting the resonance structures[6] of progressively longer PAHs and the cycloadducts that they could give in this series lends support to this intuitively reasonable hypothesis. Hückel molecular orbital and semiempirical (AM1) MO calculations on the same starting materials and cycloadducts reinforce this conclusion, but such theoretical treatments give only crude estimates of activation energies (Hammond postulate). We have therefore calculated the transition state energies for cycloadditions of acetylene to the bay regions of PAHs in the "periacene" series[7] phenanthrene → perylene → bisanthene → tetrabenzocoronene. Figure 1 shows the activation energies obtained by subtracting the calculated energies of the starting materials from the calculated energies of the transition states (B3LYP/6-31G*). Higher levels of theory would be expected to yield quantitatively more reliable estimates of the activation energies, but our hypothesis is clearly validated by theory.

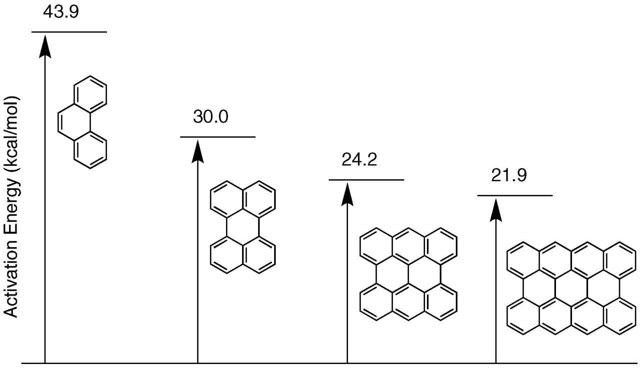


Figure 1. Activation energies calculated for Diels−Alder additions of acetylene to aromatic hydrocarbon bay regions (B3LYP/6-31G*).

To test this hypothesis experimentally, we synthesized 7,14-dimesitylbisanthene (**4**), a simple derivative of the third PAH in this series.[8] The methyl groups *ortho* to the biaryl bonds in **4** were incorporated to force the appendages out-of-plane, thereby enhanc-

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ing solubility, and also to block any cycloadditions at the central rings of the two anthracene subunits. Both objectives were achieved, and we were pleased to confirm the relatively easy transformation of **4** into the Diels−Alder cycloaddition products **5** and **6** when **4** is heated with diethyl acetylenedicarboxylate in toluene for 24 h at 120 °C (all starting material consumed, Figure 2a). The second cycloaddition occurs somewhat more slowly than the first[9] but can easily be pushed to completion. For comparison, perylene (**2**) was heated with diethyl acetylenedicarboxylate at the same concentration in toluene. In this case, the cycloaddition is clearly more difficult (<50% conversion, even after 72 h at 150 °C). The 1:1 cycloadduct (**7**) is formed, but we see no evidence for the 2:1 adduct (**8**) (Figure 2b).[10]

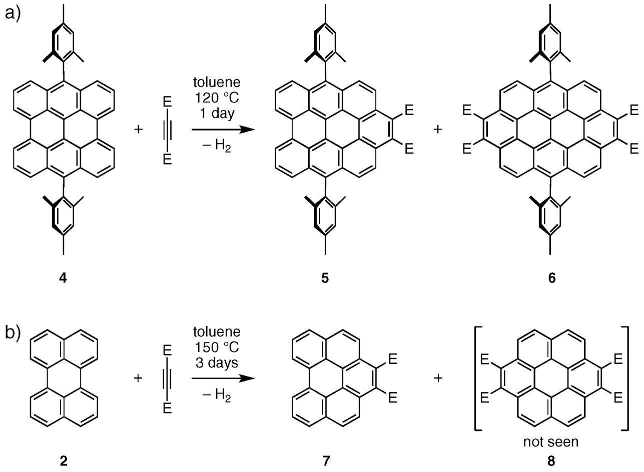

Figure 2. Diels−Alder additions of diethyl acetylenedicarboxylate to (a) 4,11-dimesitylbisanthene (**4**) and (b) perylene (**2**).

As a direct test of the prediction derived from the calculated activation energies in Figure 1, a competition experiment was conducted in which equal molar quantities of **2** and **4** were heated with diethyl acetylenedicarboxylate in toluene for 22 h at 100 °C. Under these conditions, only the longer periacene (**4**) is converted to its 1:1 Diels−Alder adduct (**5**), whereas the shorter one (**2**) survives totally unchanged (NMR spectra shown in the Supporting Information (SI)).

These results provide unambiguous experimental confirmation for our hypothesis that Diels−Alder cycloadditions should become progressively easier in bay regions at the ends of PAHs that represent progressively longer strips of armchair nanotube sidewalls.

Our findings have implications for the proposed metal-free growth of single-chirality CNTs by the strategy illustrated in Scheme 1. First, it should be noted that this strategy can be applied not only to nanotube end-cap templates but also to aromatic belts that represent short sections of nanotubes, open at both ends. For hydrogen-terminated armchair CNTs, Diels−Alder cycloadditions will be very difficult if the template is short (e.g., an [*N*]cycloparaphenylene[11] or an [*N*]cyclophenacene) but should become easier with longer templates[12] and as the tube grows (see SI). Whether or not acetylene itself can be coaxed to serve as the dienophile remains to be determined.

For small diameter nanotubes (e.g., [5,5]nanotubes), the addition of each new six-membered ring will require the introduction of further molecular strain. For larger diameter tubes, on the other hand (e.g., [10,10]nanotubes), that impediment will be significantly reduced. Our laboratory is currently working on synthetic approaches to nanotube end-caps of several different diameters.[1b,13]

Finally, we note that the Diels−Alder cycloaddition strategy for growing CNTs is not limited to armchair nanotubes. It will not work on [*N*,0]nanotubes ("zig-zag"), which have no bay regions where a dienophile could add, but it should work on chiral nanotubes that have at least one zig-zag edge that is interrupted by one or more bay region steps. In such nanotubes, transformation of a bay region into a new six-membered ring creates a new bay region, and the process can be repeated indefinitely (see SI). Nanotube edges that contain three quaternary carbon atoms in a row (so-called "cove regions"), however, are not amenable to growth solely by Diels−Alder cycloaddition chemistry.

The ultimate test of this strategy for metal-free growth of single-chirality CNTs must await the availability of suitable small hydrocarbon templates, many of which are being vigorously sought by synthetic organic chemists worldwide. "Masked acetylenes" that perform better as dienophiles than molecular acetylene would also be useful.

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Supporting Information Available: Experimental procedures for the synthesis of **4**, Diels−Alder cycloadditions of **2** and **4**, and competition experiment. Spectroscopic data for all new compounds and the competition experiment. Calculation details for the first and second Diels−Alder cycloadditions to the hydrocarbons in Figure 1 and *XYZ* coordinates of all species. Figures for a [*N*]cycloparaphenylene, [*N*]cyclophenacene, longer armchair template, and chiral template. This material is available free of charge via the Internet at http://pubs.acs.org.

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