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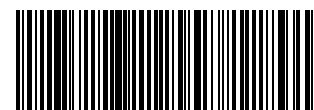
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COMMUNICATION

Facile air-oxidation of large aromatic hydrocarbon bay regions to bay region quinones: predicted oxygen-sensitivity of hydrogen-terminated carbon nanotubes†‡

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Dimesitylbisanthene (**1**) oxidizes to the corresponding bay region quinone (**2**) on standing in solutions exposed to air and ambient light. It is anticipated that hydrogen-terminated carbon nanotubes with bay regions on the rim are likely to exhibit even greater sensitivity toward air oxidation.

A Diels–Alder cycloaddition/rearomatization strategy has been proposed as one potential method for elongating short, hydrocarbon templates, such as hemispherical polyarenes and aromatic belts, into full length, single-wall, single-index (n , m) carbon nanotubes (n and $m \neq 0$, Fig. 1).^{1–4} The feasibility of transforming aromatic hydrocarbon bay regions into new, unsubstituted benzene rings in a single operation, as required by this strategy, has also been demonstrated recently, using the bay regions of dimesitylbisanthene (**1**) as models for those on the rims of carbon nanotubes and nitroethylene as a “masked acetylene” (Fig. 2).⁵ Herein we report the inordinately high reactivity of dimesitylbisanthene (**1**) toward bay region air oxidation, which leads to bay region quinone **2** (Fig. 2).⁶ This finding signals a warning about the potential oxygen-sensitivity of hydrogen-terminated carbon nanotubes; a single oxidation of this sort on the cylindrical rim of a growing carbon nanotube would preclude further elongation of the tube by the Diels–Alder cycloaddition/rearomatization protocol and would thereby terminate the growth. Only hydrogen-terminated nanotubes of the (n , 0) family (*i.e.*, “zig-zag” nanotubes), which have no bay regions on the rim, should be immune to such air oxidations; their lack of bay regions, however, also renders them unsuitable for elongation by the Diels–Alder cycloaddition/rearomatization strategy.

Quinone **2** was first discovered as a by-product from the synthesis of **1**, the last step of which involves an oxidative

photocyclization.¹ Intentional irradiation of an oxygen-saturated solution of purified **1** in a quartz vessel with UV light cleanly converts **1** to **2** in less than 30 minutes (Fig. 3). In Pyrex vessels, which filter out most light of wavelengths shorter than 300 nm, oxygen-saturated solutions of **1** still give **2** when irradiated with UV light, though on a time scale of hours, rather than minutes. Similarly, oxygen-saturated solutions of **1** in borosilicate NMR tubes also yield **2** slowly upon irradiation with a 250 W reflector incandescent bulb. In the solid state, dimesitylbisanthene (**1**) can be exposed to air in ambient light for many weeks without any significant oxidation, but solutions of **1** need to be protected from oxygen and/or light. Derivatives of **1** that still have one exposed bay region exhibit similar sensitivity to air and ambient light.⁶

Bisanthenes that lack mesityl groups on the *meso*-positions are highly susceptible to spontaneous oxidations that add endoperoxide bridges across the central rings of the anthracene units.^{7–9} As anticipated, the methyl groups at the 2- and 6-positions of our mesityl substituents successfully block access to the *meso*-carbon atoms and divert all Diels–Alder chemistry to the bay regions.^{1,5}

Both oxygen and UV light ($\lambda < 300$ nm) are required for the rapid bay region oxidation of dimesitylbisanthene (**1**). Quite possibly, hydrocarbon **1** serves as a good photosensitizer to

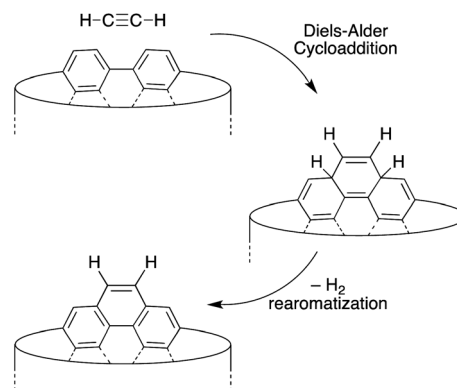


Fig. 1 Basic steps of the proposed Diels–Alder cycloaddition/rearomatization nanotube growth process, shown formally with acetylene.

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‡ Electronic supplementary information (ESI) available: Experimental details, spectra for quinone **2**, and CIF file for the X-ray crystal structure of quinone **2**. CCDC 865170. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25208b

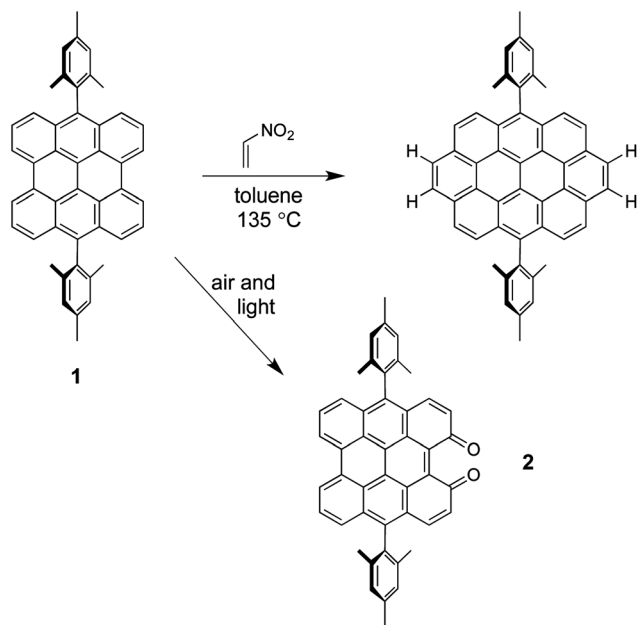


Fig. 2 Dimesitylbisanthene (**1**), a model for the bay regions on the rims of carbon nanotubes. Upper: One-step conversion of bay regions into new, unsubstituted benzene rings. Lower: Sensitivity toward oxidation.

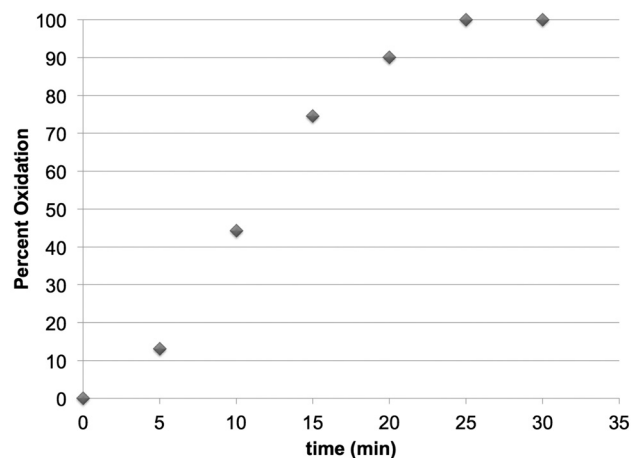


Fig. 3 Conversion of bisanthene **1** to quinone **2** by exposure to UV light. Percent oxidation = $1/(1 + 2)$. See ESI† for details.

generate singlet oxygen, which then adds in a Diels–Alder fashion to the bay region of a ground state **1** (Fig. 4). In the presence of excess oxygen, the initial cycloadduct (**3**) would be expected to oxidize quickly to the rearomatized cyclic peroxide (**4**), which could then open exothermically to the observed quinone (**2**). Alternatively, the excited state of **1** might react with triplet oxygen by electron transfer, followed by collapse of the radical ion pair to diradical intermediate (**5**). Radical coupling to form the second C–O bond would then generate the same cyclic peroxide **3**.

The oxidation of polycyclic aromatic hydrocarbons to bay region quinones by air and light is not unprecedented. Other examples are rare, however, and they have required much longer

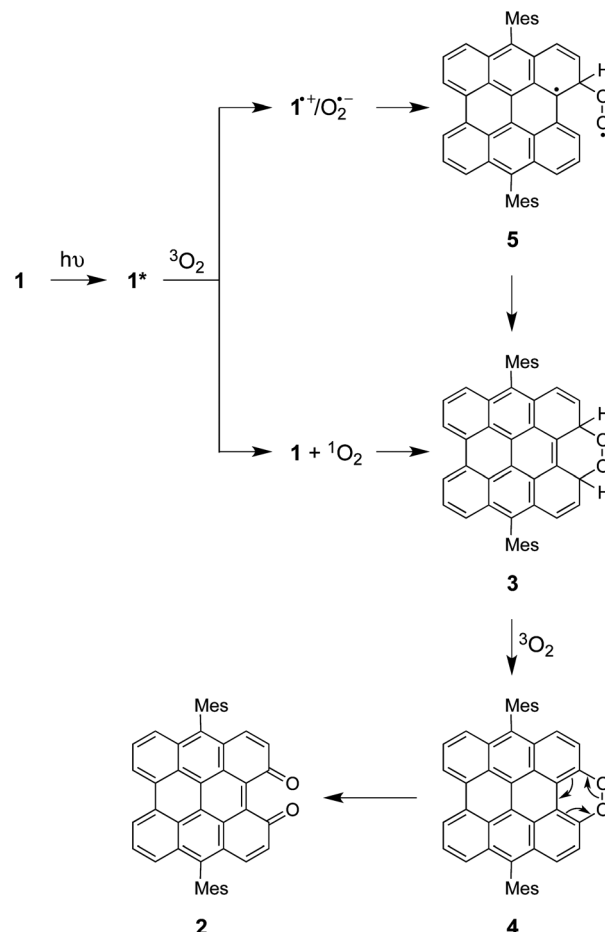


Fig. 4 Possible mechanisms for oxidation of dimesitylbisanthene (**1**) to the bay region quinone (**2**). Mes = mesityl.

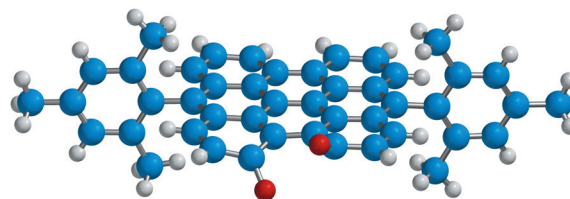


Fig. 5 X-ray crystal structure of the bay region quinone (**2**).

irradiation times¹⁰ or light sources of much higher intensity.¹¹ The complete conversion of **1** to **2** in less than 30 minutes when irradiated in the presence of oxygen is striking.

We see no evidence for formation of the bis-quinone. The remaining bay region in quinone **2** no longer belongs to an electron rich bisanthene but finds itself instead in an electron deficient benzo[*ghi*]perylene ring system, which is much less susceptible to bay region oxidation.

An X-ray crystal structure of **2** (Fig. 5) reveals a strongly twisted structure with a dihedral angle of 78.7° between the two carbonyl groups. The ¹³C NMR signal from the carbonyl carbon atoms at 186.5 ppm (in C₂D₂Cl₄) was our first clue that compound **2** is a quinone and not a normal endoperoxide. The equivalence of the *ortho*-methyl groups on the mesityl substituents (12H singlet at δ 1.94 ppm in the ¹H NMR spectrum, 400 MHz

in C₂D₂Cl₄) indicates that the barrier for racemization of this C₂-symmetric quinone must be low enough to allow rapid equilibration at room temperature. Calculations at the B3LYP/6-31G(d) level of theory predict a barrier of 8.6 kcal mol⁻¹, but we have made no attempt to measure the barrier experimentally.

As we have reported previously,³ hemispherical hydrocarbon precursors to (10,10) carbon nanotubes are predicted to show the same level of reactivity as **1** toward Diels–Alder cycloadditions. Smaller diameter (more acutely curved) cylindrical aromatic hydrocarbons are predicted to be less reactive, but those of larger diameter are predicted to display even higher reactivity. These predictions apply to both single-walled and multi-walled carbon nanotubes.

Conclusions

The oxidation of aromatic hydrocarbon bay regions by air and light to the corresponding bay region quinones occurs more readily in the extended bisanthene ring system than in the shorter perylene ring system. It is anticipated that hydrogen-terminated carbon nanotubes with bay regions on the rim, especially those of large diameter that are not strongly curved, are likely to exhibit even greater sensitivity toward air oxidation.

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