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Revisiting the Stability of Hexacenes

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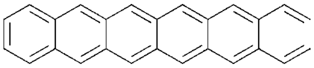
ABSTRACT



Hexacene (**1**)

The Strating–Zwanenberg photodecarbonylation was used to prepare hexacene (1). Compound 1 was found to be extremely unstable in solution, undergoing dimerization and oxidation. However, when generated in a polymer matrix, 1 survived for more than 12 h under ambient conditions. Hexacenes substituted at the 6 and 15 positions with the phenyl, *p-tert*-butylphenyl, and mesityl groups were synthesized using the quinone reduction method, but these compounds were also shown to be unstable in solution.

Poly(acene)s are an important class of polyaromatic hydrocarbons and consist of an aromatic linear array.[2] They are the basic building units of graphite[3] and carbon nanotubes[4] and are considered to be efficient organic electronic materials.[5] Pentacenes, for example, are a current choice in superconductors, organic thin-film transistors (OTFTs),[6] and organic light-emitting diodes.[7] Field effect mobility greater than 1 cm^2 V^{-1} s^{-1} has been reported using pentacene as the active layer in OTFT devices.[8] Higher poly(acene)s such as hexacene and heptacene show lower band-gaps (ΔE) than pentacene and are predicted to exhibit superior electronic properties.[9] However, the insolubility and instability of the higher poly(acene)s has limited their isolation and proper study for applications.[10]

Lower molecular weight poly(acene)s (up to pentacene) are usually synthesized by reduction of the corresponding quinones. A similar approach used for higher poly(acene)s proved to be unsuccessful since the quinones were overreduced to hydrogenated acenes.[2,11,12] Other methods of synthesis also failed for higher poly(acene)s, presumably because of their higher reactivity toward Diels−Alder additions which ultimately results in formation of either dimers or oxygen adducts (endoperoxides).[13] Recently, we used the Strating−Zwanenberg photodecarbonylation to achieve the first unequivocal synthesis of heptacene.[14] This reaction, first discovered in 1969, was employed by the Strating group in seeking the dimer of carbon monoxide.[15] Pentacene was also synthesized using the Strating−Zwanenberg photochemical route.[16] An impressive attribute of this reaction is that it is clean, producing a poly(acene) following the expulsion of carbon monoxide, either in a molecular form or a dimeric form, from a precursor α-diketone.

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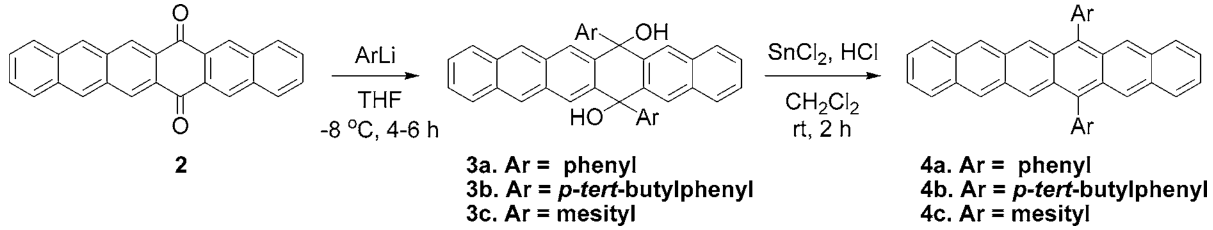
Scheme 1. Synthesis of Hexacene Derivatives



Although hexacene (**1**) is a known compound,[10b,11,17] it is still elusive in that its reported synthetic schemes are difficult to repeat. An extensive study of this compound is not available in the literature because of the synthetic difficulty. We recently revisited the question of the stability of hexacenes and ultimately succeeded in synthesizing **1** by the Strating–Zwanenberg method, employing the photodecarbonylation of 6,15-dihydro-6,15-ethanohexacene-17,18-dione (the precursor α-diketone of **1**). Although this method does not allow one to isolate **1**, it does provide a facile pathway to synthesize and study it. Since the photoprecursor is highly soluble in common organic solvents this assures flexibility and **1** can be routinely synthesized and studied using this method. We also discuss the attempted syntheses of **1** and its derivatives using the quinone method.

Nucleophilic addition of suitable aryllithiums to 6,15-hexacenequinone (**2**) produced diols (**3a**–**c**), which were further reduced by tin(II) chloride dihydrate/HCl to 6,15 disubstituted hexacenes (**4a**–**c**, Scheme 1). Matrix assisted laser desorption ionization (MALDI) mass spectra of the reaction mixture showed the appropriate molecular peaks, indicating formation of the hexacenes. A solution of crude **4a** showed the anticipated absorption in the visible region with the maximum at 684 nm. Further characterization was not possible, because **4a**–**c** could not be purified or isolated.

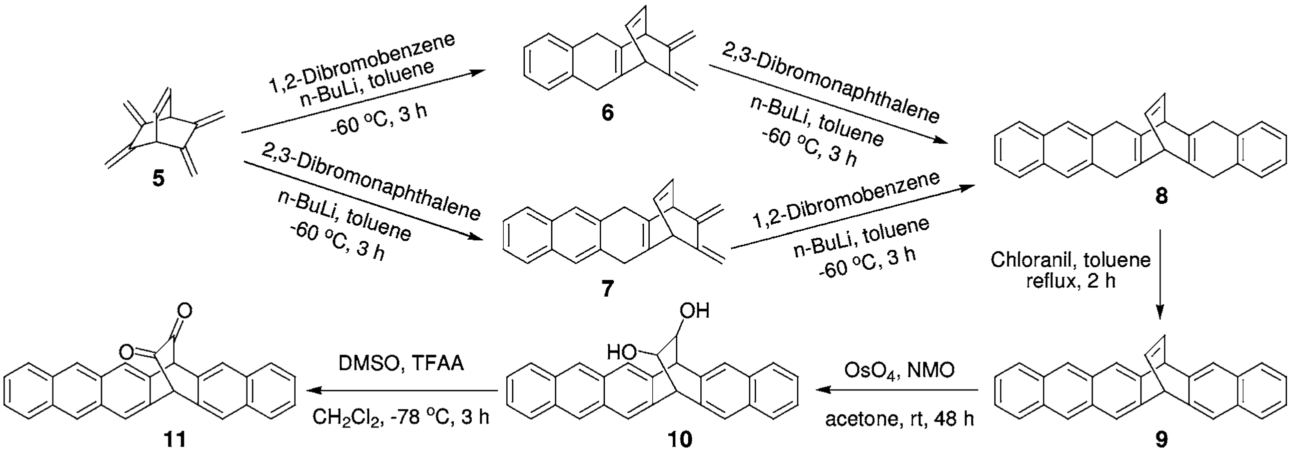
The failure to isolate **4a**–**c** indicates that not only **1** but also its derivatives are extremely reactive. Substitution of the central rings by aryl groups such as the *p*-*tert*-butylphenyl or mesityl groups could not prevent rapid oxidation or dimerization. Only a very bulky group stabilizes hexacene.[18]

Bicyclo[2,2,2]oct-2,3,5,6,7-pentaene (**5**) was coupled either with 1,2-dibromobenzene or with 2,3-dibromonaphthalene, and the product was subsequently subjected to aromatization and oxidation to prepare 6,15-dihydro-6,15-ethanohexacene-17,18-dione (**11**) (Scheme 2, see Supporting Information for synthetic details).

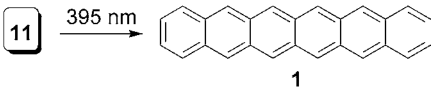
Photodecarbonylation of **11** was carried out both in solution and in a polymer matrix (Scheme 3). A solution of **11** in toluene showed an n–π^* band at 465 nm ($\epsilon = 850$), with additional π–π^* transitions at 327 (5000), 345 (5500), and 367 (4200) nm (Figure 1). This is similar to the absorption of **11** in the poly(methyl methacrylate), PMMA, matrix. A weak fluorescence ($\lambda_{\mathrm{em}} = 525$ nm, $\Phi_{\mathrm{F}} = 0.003$) was observed when the solution of **11** in toluene was excited at 460 nm. It also showed phosphorescence ($\lambda_{\mathrm{em}} = 570$ nm) at 77 K in a frozen matrix of methanol/ethanol (1:4). An array of UV-LEDs (395 ± 25 nm) was used to selectively excite the n–π^* transition and to prevent any subsequent photochemical side reactions.

A solution of **11** in toluene (4.0×10^{-4} M) was degassed using freeze–pump–thaw. Photolysis of this solution produced initially a new structured absorption band in the 550–700 nm region with maxima at 574, 612, and 672 nm (Figure 2). The new structured bands can be assigned to the π–π^* transition of **1** and are in good agreement with the absorption spectrum of **1** recorded in 1,2,4-trichlorobenzene.[10b] How-

Scheme 2. Synthesis of the α-Diketone of Hexacene



Scheme 3. Synthesis of Hexacene (**1**)



ever, the growth of this absorption continued only for a few minutes, after which its intensity diminished with subsequent irradiation. MALDI-MS analysis of the over-irradiated (40 min) solution indicated the formation of dimer of **1** as well as oxygen adducts. The latter formed through the reaction of **1** with residual oxygen in solution. Thus, after **1** is generated in solution, it rapidly undergoes dimerization and oxidation indicating it to be extremely reactive in solution. Compound **1** undergoes dimerization even when it is generated at a very low concentration ($<10^{-4}$ M). These results are surprising given that **1** is reported to have been sold commercially in the past!

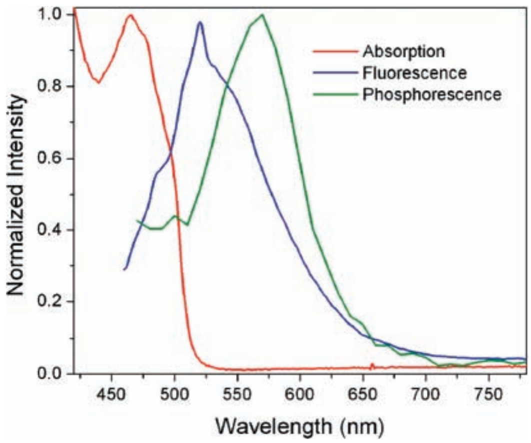


Figure 1. Normalized absorption (red), fluorescence (blue), and phosphorescene (green) spectra of **11** (absorption and fluorescence speactra recorded in toluene at room temperature and phosphorescence spectrum recorded in methanol/ethanol (1:4) matrix at 77 K).

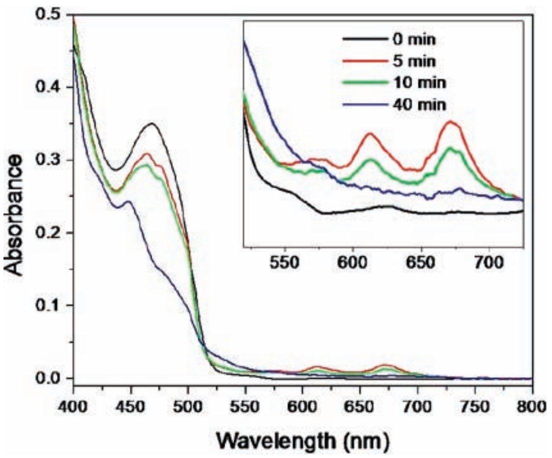
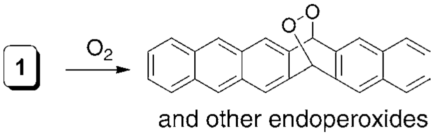


Figure 2. Absorption spectra recorded during and after irradiation of **11** in degassed toluene (inset: enlarged portion from 525 to 725 nm).

When similar experiments were carried out with solutions saturated with oxygen, immediate formation of endoperoxides of **1** was observed (Scheme 4). This was indicated by MALDI-MS as well as by ^{1}H NMR spectra.

Scheme 4. Oxidation of **1**



These results imply that when **1** is formed in solution, it immediately reacts with oxygen.[19] MALDI-MS analysis indicated the addition of one as well as two molecules of oxygen. The protons of the bridge C atoms of **11** appear at 5.36 ppm in the ^{1}H NMR spectrum. Two additional peaks appeared between 6 and 6.1 ppm in the ^{1}H NMR of an irradiated solution of **11** in $CDCl_3$ purged with oxygen. The intensity of these peaks increased with the time of irradiation (Figure 3). These are assigned to the protons at the carbon atoms attached to the oxygen bridge in the endoperoxides. The many peaks in the 6−6.1 region also indicate that

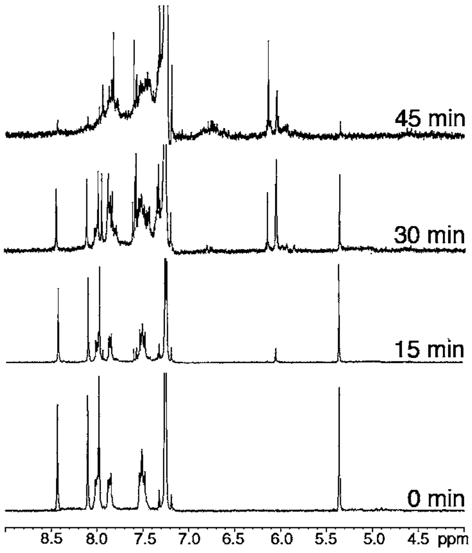


Figure 3. ^{1}H NMR spectra recorded at different times of irradiation of a $CDCl_3$ solution of **11** purged with oxygen (light source: a 395 nm UV-LED array).

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oxygen bridges form at different positions of **1** (for example, the 6−15 and/or 8−13 positions).

As we have previously shown with heptacene, photodecarbonylation can be conveniently used to generate **1** in the PMMA matrix. A semirigid polymer matrix enables retention of reactive **1** by preventing its dimerization. This also enables minimal contact of **1** with environmental oxygen reducing the rate of oxidation. Thus, when a PMMA film (thickness $\approx$ 0.5 mm) containing **11** (3.5×10^{-3} M) was irradiated using the UV-LED array, this produced **1** as the film turned green and showed structured absorption in the region of 550−700 nm (565, 614, and 672 nm) similar to that observed in solution (Figure 4). Quick dissolution of the irradiated film in dichloromethane and subsequent analysis by MALDI mass spectra confirmed formation of **1**.

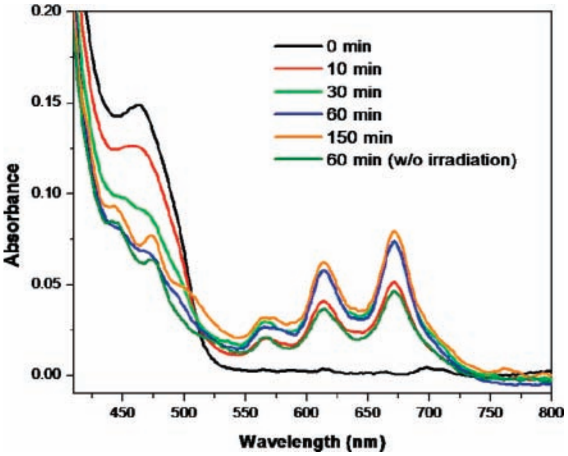

Figure 4. Absorption spectra recorded during and after irradiation of **11** in a PMMA film.

The intensity of the 672 nm absorption band of **1** gradually increased through the first 60 min of irradiation. But further irradiation resulted in no additional growth. In fact, the intensity of the 672 nm band started decreasing, irrespective of irradiation, indicating slow decomposition of **1** even in PMMA. Compound **1** could be retained in the matrix overnight under ambient conditions. Thus, in the PMMA matrix, **1** was found to be more stable than heptacene, which survives for about 4 h under the similar conditions.[14] These results attest to the unstable nature of **1** even under conditions manipulated so as to maintain its isolation; that is, in the solid PMMA matrix. Compound **1** seems to be consumed by oxidation with a small amount of molecular oxygen that diffuses into the matrix.

In summary, hexacene was synthesized using the Strating−Zwanenberg photodecarbonylation. It rapidly undergoes dimerization in solution even when generated at very low concentrations ($<10^{-4}$ M). Its generation in oxygen saturated solution exclusively leads to the formation of endoperoxides. Nevertheless, **1** was observed to be stable for more than 12 h when produced in a PMMA matrix. Substituents such as the phenyl, *p-tert*-butylphenyl, and mesityl groups at the 6 and 15 positions did not provide stability to the hexacenes.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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