J|A|C|S
COMMUNICATIONS

Photogeneration of Heptacene in a Polymer Matrix

Rajib Mondal, Bipin K. Shah, and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

Received May 31, 2006; E-mail: neckers@photo.bgsu.edu

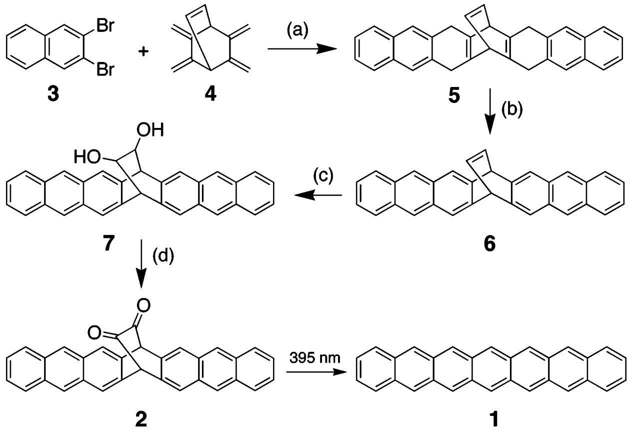
Polyacenes consist of an aromatic linear array. The largest whose synthesis has been authenticated is hexacene, $C_{26}H_{16}$. The synthetic history of the higher homologues is checkered. Heptacene (**1**) and octacene were both reported in 1942 by Clar, who claimed **1** formed from reducing heptacenequinone,[2] only later to withdraw this.[3] Marschalk also failed to reproduce the Clar synthesis.[4] Compound **1** was subsequently reported by Bailey, and, though the elemental analysis was correct, this report was also shown later to be wrong.[5] Compound **1** has been elusive by the attempted classical synthetic routes because such procedures instantly yield an array of dimers. The last report of the synthesis **1**, of which we are aware of in a Ph.D. dissertation[6] where the NMR spectra of the dimers is first presented.

Our attention to the polyacene problem was tweaked by the importance of linear poly(benzenoid) hydrocarbons in electronic applications.[7] Pentacenes, for example, are a current choice in superconductors,[8] organic thin-film transistors,[9] and organic light emitting diodes.[10] An obscure Chapman publication also had predicted that **1**, octacene, nonacene, and the poly(acenes) should be linear conductors.[11] Subsequent publications have been replete with theories about the stability of **1** or the lack thereof.[12] Other matters such as whether **1** might exist as an open shell diradical have also been discussed. Prevention of dimerization at the 7, 16 positions is a crucial factor in orchestrating stability, and Anthony et al. recently reported 7,16-bis(tris(trimethylsilyl)silylethynyl)-heptacene.[13]

Predictions aside,[12] the greater instability and poorer solubility resulting from an increased number of linearly fused rings has prevented the synthesis of **1** and higher polyacenes to this time. We now report the first synthesis of **1**. We used photochemical routes.

α-Diketones of ethanoanthracene and ethanopentacene are known to undergo photoelimination of two molecules of carbon monoxide.[14,15] The dione precursor of **1**, 7,16-dihydro-7,16-ethanoheptacene-19,20-dione (**2**), was prepared in 18% overall yield from 2,3-dibromonaphthalene[16] (**3**) and bicyclo[2,2,2]oct-2,3,5,6,7-pentaene[17] (**4**; Scheme 1). Treatment of two equiv of **3** with *n*-BuLi at −60 °C {naphthyne}, in the presence of **4** produces **5** (53%). Aromatization by refluxing **5** with chloranil for 2 h gives **6** (81%), which was converted to **7** (83%) using a catalytic amount of OsO_4 in the presence of 4-methylmorpholin-*N*-oxide (NMO). Modified Swern oxidation of **7** produced **2** (51%).[15] The target polyacene is obtained using a Strating-Zwanenburg photodecarbonylation of **2**,[18] carried out in a poly(methyl methacrylate) (PMMA) matrix enabling retention of highly reactive **1** through the prevention of thermal dimerization and oxidation (Scheme 1). An array of UV-LEDs (395 nm ± 25 nm) was used as the light source to prevent subsequent photochemical side reactions.

Scheme 1 [a]



[a] Reagents and conditions: (a) *n*-BuLi, toluene, −60 °C, 3 h.; (b) chloranil, toluene, 2 h.; (c) OsO_4, NMO, acetone, rt, 48 h.; (d) dimethyl sulfoxide, trifluoroacetic acid, CH_2Cl_2, −78 °C, 3 h.

A thin PMMA film containing **2** ($\sim 3.0 \times 10^{-3}$ M L^{-1}) was prepared (thickness ~0.5 mm, o.d. = 0.5 at 395 nm). When irradiated using the UV-LED array, a new structured absorption band extending from 600 to 825 nm and having a maximum at ~760 nm appeared in the film. This is assigned to the $\pi-\pi^*$ transition of **1** (Figure 1). The absorption of **1** recorded in the solid matrix is blue-shifted relative to that of 7,16-bis(tris(trimethylsilyl)-silylethynyl)heptacene ($\lambda_{max} = 810$ nm)[13] recorded in hexane. Quick dissolution of the irradiated film in CH_2Cl_2 and subsequent analysis by matrix assisted laser desorption ionization mass spectra (MALDI-MS) confirmed formation of **1**.

The intensity of the 760 nm absorption band of **1** gradually increased through the first 60 min of irradiation. But further irradiation achieved no additional enhancement. In fact, the intensity of the 760 nm band started decreasing after 60 min, irrespective of irradiation, and the band completely vanished in about 4 h. This attests to the unstable nature of **1** even under conditions manipulated so as to maintain its isolation, that is, in the solid PMMA matrix. Changes in the intensities of the bands at 420 and 450 nm are concomitant with that of the 760 nm band and assigned to **1** (Figure 1). The weak bands in the 500−600 nm region kept increasing with time and are likely due to pentacene derivatives that result when **1** dimerizes or reacts with oxygen at the 5 and 18 positions. The possibility of formation of similar tetracene and anthracene derivatives cannot be ruled out.

The S_0-S_1 energy gap of **1** (1.50 eV), calculated from the edge (825 nm) of the absorption band, correlates well with the calculated values (Table 1).[12a,19] In fact, it is closer to the theoretical value calculated for an open shell (OS) ground state. The S_0-S_1 energy gap of **1** also compares well with those for pentacene and hexacene obtained experimentally.[12a,19] For example, there is a difference of 0.35 eV between the S_0-S_1 energy gaps of pentacene and hexacene. Similarly, the difference between the S_0-S_1 energy gaps of hexacene and **1** is 0.29 eV.

A solution of **2** in toluene showed an $n-\pi^*$ band at 466 nm ($\epsilon = 1430$), with an additional $\pi-\pi^*$ transition at 368 nm ($\epsilon = 6640$) and 347 nm ($\epsilon = 8850$). This is similar to the observations in the

10.1021/ja063823i CCC: $33.50 © 2006 American Chemical Society

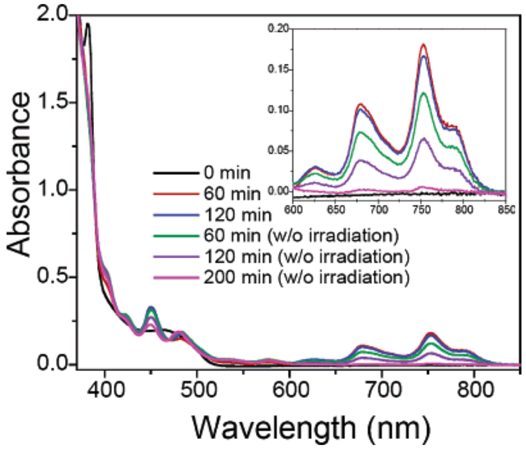


Figure 1. Absorption spectra recorded during and after irradiation of **2** in a PMMA film (inset: enlarged portion from 600 to 850 nm).

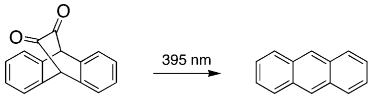
Table 1. Theoretical and Experimental S_0-S_1 Values of Acenes

	experimental S_0–S_1		TDDFT/6-31G* S_0–S_1	S_0(OS)–S_1[a]
compound	nm	eV	eV	eV
pentacene	582	2.14	1.95	
hexacene	695	1.79	1.54	1.57
heptacene	825	1.50	1.24	1.36

[a] S_0(OS)−S_1 values were calculated considering an open shell (OS) ground state, using the stabilization energy from ref 19b.

PMMA matrix. A weak fluorescence (λ_{em} − 530 nm) was observed when the solution of **2** was excited at 460 nm. It also showed phosphorescence (λ_{em} − 570 nm, triplet energy = 54.5 kcal/mol) at 77 K in a frozen matrix of methanol/ethanol (1:5).

9,10-Dihydro-9,10-ethanoanthracene-11,12-dione[14b] (**8**), the Strating−Zwanenburg photoprecursor of anthracene (similar to **2**), was also studied for comparison. A solution of **8** in toluene showed an $n-\pi^*$ transition at 461 nm ($\epsilon = 310$). Photolysis of **8** in toluene produced anthracene with a quantum efficiency of 0.02 (ferrioxalate actinometry). Photolysis of **8** in the PMMA film was equally facile, producing anthracene.

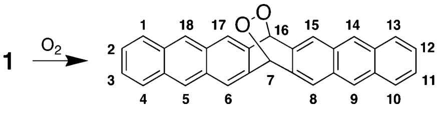


8

anthracene

The only difference between **2** and **8** is that the former did not produce **1** when irradiated in solution. Nevertheless, irradiation of an oxygen-saturated toluene solution of **2** produced oxygen adducts of **1** as observed by the MALDI-MS analyses. This indicates that as soon as **1** forms in the solution, it is trapped by oxygen as a result of its extremely high reactivity as a Diels−Alder diene.[20]

Formation of oxygen adducts of **1** in solution was further verified by ^{1}H NMR. The protons of the bridged C atoms of **2** appear at 5.4 ppm. Three additional peaks appeared between 6 and 6.3 ppm in the ^{1}H NMR of an irradiated solution of **2** in $CDCl_3$ purged with oxygen. These peaks can be assigned to the protons at the carbon atoms attached to the oxygen bridge. The reason for many proton peaks in the 6−6.3 region is that oxygen bridges can form at different positions of **1** (for example, the 5−18, 6−17, or 7−16 positions).



and other oxygen adducts

In summary, irradiation of **2** in the PMMA matrix at 395 nm produced **1**, which showed a long wavelength absorption band (600−825 nm), having a maximum at 760 nm. Compound **1** was found to be stable up to 4 h in the PMMA matrix. However, it was not stable in solution and immediately produces oxygen adducts in the presence of air.

Acknowledgment. We thank Dr. T. H. Kinstle and Dr. J. R. Cable for helpful discussions. R.M. is thankful to the McMaster Endowment for providing a fellowship. Support from Navy Office of Research (Grant No. N00014-05-1-0372) is greatly acknowledged.

Supporting Information Available: Synthesis and characterization of **2** and **8**, results of photolysis of **2** and **8** in solution and in the thin films of PMMA, MALDI-MS of **1**, and ^{1}H NMR of oxygen adducts of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Contribution No. 581 from the Center for Photochemical Sciences.
(2) Clar, E. *Ber. Dtsch. Chem. Ges.* **1942**, *75B*, 1330.
(3) Boggiano, B.; Clar, E. *J. Chem. Soc.* **1957**, 2681.
(4) Marschalk, C. *Bull. Soc. Chim.* **1943**, *10*, 511.
(5) Bailey, W. J.; Liao, C. *J. Am. Chem. Soc.* **1955**, *77*, 992.
(6) Fang, T. Heptacene, Octacene, Nonacene, Supercene and Related Polymers. Ph.D. Thesis, University of California, Los Angeles, CA, 1986.
(7) (a) Clar, E. Polycyclic Hydrocarbons; Academic Press: London and New York, 1964; Vols. 1 and 2. (b) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1997.
(8) Schön, J. H.; Kloc, C.; Batlogg, B. *Nature* **2000**, *406*, 702.
(9) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
(10) Wolak, M. A.; Jang, B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492.
(11) Kivelson, S.; Chapman, O. L. *Phys. Rev. B* **1983**, *28*, 7236.
(12) (a) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. *J. Am. Chem. Soc.* **2004**, *126*, 7416. (b) Raghu, C.; Pati, Y. A.; Ramasesha, S. *Phys. Rev. B* **2002**, *65*, 155204. (c) Pomerantz, M.; Cardona, R.; Rooney, P. *Macromolecules* **1989**, *22*, 304. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.
(13) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028.
(14) (a) Strating, J.; Zwanenburg, B.; Wagenaar, A.; Udding, A. C. *Tetrahedron Lett.* **1969**, *10*, 125. (b) Udding, A. C. Doctoral thesis, University of Groningen, Groningen, Netherlands, 1963.
(15) (a) Uno, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Yamada, H.; Okujima, T.; Ogawa, T.; Ono, N. *Tetrahedron Lett.* **2005**, *46*, 1981. (b) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Ogawa, T.; Ohara, K.; Ono, N. *Chem.*−*Eur. J.* **2005**, *11*, 6212.
(16) Bowles, D. M.; Anthony, J. E. *Org. Lett.* **2000**, *2*, 85.
(17) Gabioud, R.; Vogel, P. *Tetrahedron* **1980**, *36*, 149.
(18) Photodecarbonylation of diones are unusual reactions. In most instances, dione excited states become electron-transfer acceptors, as in the case of the well-known photoinitiator, camphor quinone. The Strating−Zwanenburg reaction is driven by the stability of the aromatic hydrocarbon. Compelling questions such as the nature of the excited-state involved in photodecarbonylation and the structure of the *carbon monoxide* fragment(s) (whether monomer or dimer) are under investigation.
(19) (a) Houk, K. N.; Lee, P. S.; Nendel, M. *J. Org. Chem.* **2001**, *66*, 5517. (b) Poater, J.; Bofill, J. M.; Alemany, P.; Solà, M. *J. Phys. Chem. A* **2005**, *109*, 10629.
(20) Schleyer, P. v. R.; Manoharan, M.; Jiao, H.; Stahl, F. *Org. Lett.* **2001**, *3*, 3643.

JA063823I