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Phenacenes from Diels–Alder Trapping of Photogenerated *o*-Xylylenols: Phenanthrenes and Benzo[*e*]pyrene Bisimide

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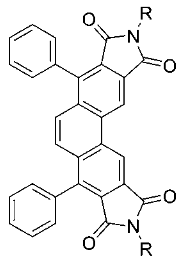
ABSTRACT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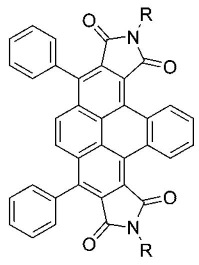
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The synthesis of phenanthrene and benzo[*e*]pyrene bisimides, 1 and 2, was accomplished via the Diels–Alder trapping of sterically congested *o*-xylylenols photochemically generated from 3,6-dibenzoyl-*o*-xylene and 1,4-dibenzoyl-9,10-dihydroanthracene, respectively. Absorption and emission from 2 are red-shifted from 1 and unsubstituted benzo[*e*]pyrene. The fluorescence quantum yield for 2 is an order of magnitude lower than that of 1 and comparable to that of the parent benzo[*e*]pyrene.

The synthesis of functionalized polycyclic aromatic hydrocarbons (PAHs), in particular naphthalene and perylene bisimides,[1−5] has received a significant amount of attention due to their potential application in liquid crystals,[2] electron-transfer systems,[3] fluorescent sensors,[4] and photovoltaics.[5] While the preparation of perylene and naphthalene bisimides from commercially available dianhydrides is well established, literature reports on the synthesis of bisimides from other PAHs are virtually nonexistent. Development of synthetic routes to these compounds is of interest because of their potentially unique photophysical and electrochemical properties and the applications that might arise from them.

The Diels−Alder trapping of *o*-xylylenols generated by the photoenolization of *o*-methylphenyl ketones is a well-known, high-yield synthetic route to fused six-membered ring

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(1) (a)Wu, J.; Watson, M. D.; Zhang, L.; Wang, Z.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 177, (b) Wang, Z.; Tomović, Ž.; Kastler, M.; Pretsch, R.; Negri, F.; Enkelmann, V.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 7794, (c) Müller, G. R.; Meiners, C.; Enkelmann, V.; Geerts, Y.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 61, (d) Quante, H.; Geerts, Y.; Müllen, K. *Chem. Mater.* **1997**, *9*, 495.

(2) (a) Liu, S.-G.; Sui, G.; Cormier, R. A.; Leblanc, R. M.; Gregg, B. A. *J. Phys. Chem. B* **2002**, *106*, 1307, (b) Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem. Eur. J.* **2001**, *7*, 2245, (c) Rohr, U.; Schilichting, P.; Bohm, A.; Gross, M.; Meerholz, K.; Brauchle, C.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434.

(3) (a) Rybtchinski, B.; Sinks, L. E.; Wasielewski, M. R. *J. Phys. Chem. A* **2004**, *108*, 7497, (b) Weiss, E. A.; Sinks, L. E.; Lukas, A. S.; Chernick, E. T.; Ratner, M. A.; Wasielewski, M. R. *J. Phys. Chem. B* **2004**, *108*, 10309, (c) Sinks, L. E.; Wasielewski, M. R. *J. Phys. Chem. A* **2003**, *107*, 611, (d) Giaimo, J. M.; Gusev, A. V.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 8530.

(4) (a) Zang, L.; Liu, R.; Holman, M. W.; Nguyen, K. T.; Adams, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 10640, (b) Mohr, G. J.; Spichiger, U. E.; Jona, W.; Langhals, H. *Anal. Chem.* **2000**, *72*, 1084.

(5) (a) Ferrere, S.; Zaban, A.; Gregg, B. A. *J. Phys. Chem.* **1997**, *101*, 4490, (b) Tsuzuki, T.; Hirota, N.; Noma, N.; Shirota, Y. *Thin Solid Films* **1996**, *273*, 177.

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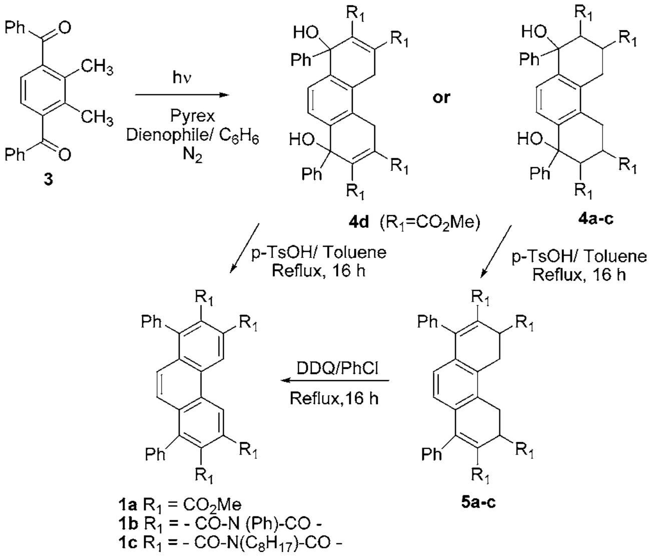
systems.[6] We have successfully extended this classic photochemical reaction to the preparation of anthracene bisimides and anthracene-based polyimides and polyesters.[7] Our approach employs bis(*o*-methylbenzophenone) derivatives, such as 2,5-diaroyl-*p*-xylenes, to create the framework for the polycyclic aromatic backbone via two tandem enolization and trapping sequences. The structure of these diketones is critical since it dictates the geometry of the resulting oligoacene backbone. Once these diketones are obtained, a library of molecules with a specific aromatic backbone can be readily accessed by varying the structure of the dienophile.

Our prior efforts have focused on diketones which afford *linear* aromatic systems. Recently, we have extended this chemistry to the synthesis of *angular* arenes, including sterically congested phenanthrenes, **1**, and the first example of a benzo[*e*]pyrene bisimide, **2**.[8] Steric crowding within the *o*-xylylenol can inhibit Diels−Alder trapping by hindering its access to dienophile. In addition, sterically congested *o*-xylylenols are well-known to undergo cyclization to the corresponding benzocyclobutanols.[9] Herein, we report the results of this study.

The synthesis of phenanthrenes, **1**, is outlined in Scheme 1. 3,6-Dibenzoyl-*o*-xylene, **3**, was prepared in 80% overall yield from the reaction of phenylmagnesium bromide with 3,6-dicyano-*o*-xylene.[10]

Scheme 1

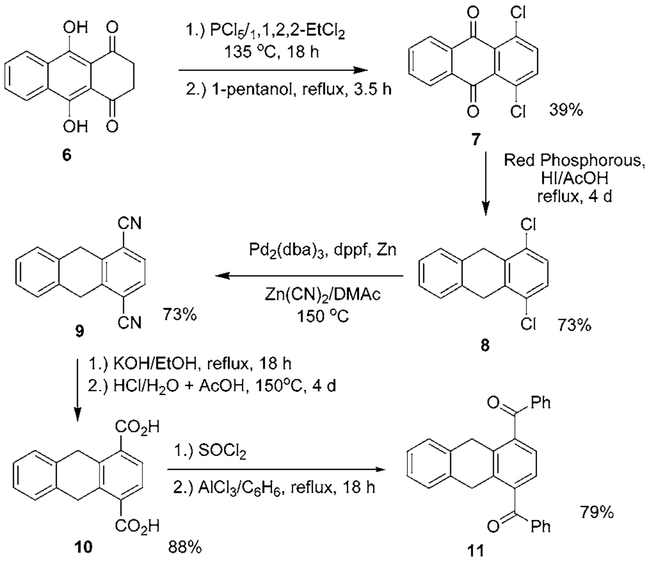


Photolysis of an N_2-degassed benzene solution of **3** and a slight stoichiometric excess (2.2 equiv) of either dimethyl fumarate, *N*-phenyl- or *N*-octylmaleimide produced the corresponding bisadducts **4a−c** in good to moderate yields. Attempts to use methylacrylate as the dienophile proved unsuccessful due to a competing polymerization of the acrylate.[11] Trapping with dimethyl acetylenedicarboxylate required a large excess of dienophile (10 equiv) and only produced bisadduct **4d** in 30% yield. This is due to the fact that **4d** is itself a good dienophile and can be consumed by reaction with *o*-xylylenols. Serendipitously, the highest yield, 86%, was obtained with *N*-octylmaleimide. Conversion of bisadducts into the corresponding phenanthrenes, **1a−c**, was achieved in good overall yield using standard acid-catalyzed dehydration followed by aromatization with DDQ.

While *o*-xylylenols produced from **3** are sterically crowded, the reasonable yields obtained by cycloaddition with *N*-phenylmaleimide and *N*-octylmaleimide suggested that trapping of sterically congested *o*-xylylenols is possible with compact, reactive dienophiles. To explore this, we turned our attention to the trapping of *o*-xylylenols produced from 1,4-dibenzoyl-9,10-dihydroanthracene, **11**. Successful trapping of these *o*-xylylenols would afford access into a new class of more complex aromatic bisimides based upon benzo[*e*]pyrene.

Diketone **11** was prepared from commercially available leucoquinazarin **6** as outlined in Scheme 2. Treatment of **6** with excess PCl_5, followed by refluxing the resulting chlorinated intermediate in 1-pentanol, produced 1,4-dichlo-

Scheme 2



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[6] (a) Yang, N. C.; Rivas, C. J, *J. Am. Chem. Soc.* **1961**, *83*, 2213, For an excellent review of this subject, see: (b) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.

[7] (a) Ilhan, F.; Tyson, D. S.; Meador, M. A. *Chem. Mater.* **2004**, *16*, 2978, (b) Meador, M. A. B.; Meador, M. A.; Williams, L. L.; Scheiman, D. A. *Macromolecules* **1996**, *29*, 8983.

[8] Typical benzo[*e*]pyrene derivatives do not include bisimide functionality. For examples, see: (a) Pothuluri, J. V.; Evans, F. E.; Heinze, T. M.; Cerniglia, C. E. *Appl. Microbiol. Biotechnol.* **1996**, *45*, 677, (b) Lee, H.; Shyamasundar, N.; Harvey, R. G. *J. Org. Chem.* **1981**, *46*, 2889, (c) Lehr, R. E.; Tayler, C. W.; Kumar, S.; Mah, H. D.; Jerina, D. M. *J. Org. Chem.* **1978**, *43*, 3462, (d) Wood, A. W.; Levin, W.; Thakker, D. R.; Yagi, H.; Chang, R. L.; Ryan, D. E.; Thomas, P. E.; Dansette, P. M.; Whittaker, N.; Turujman, S.; Lehr, R. E.; Kumar, S.; Jerina, D. M.; Conney, A. H. *J. Biol. Chem.* **1979**, *254*, 4408.

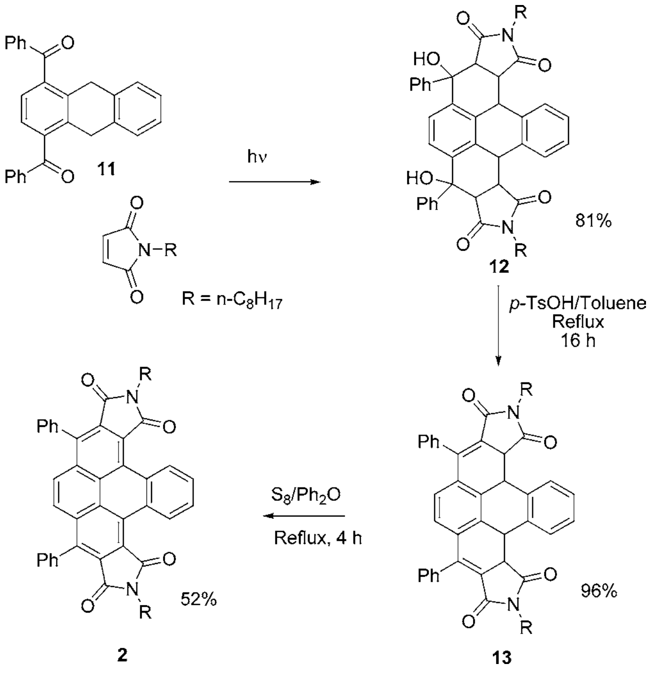
[9] (a) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405, (b) Itoh, Y.; Kano, G.; Nakamura, M. *J. Org. Chem.* **1998**, *63*, 5643.

[10] Obtained from the Spectrum Group, Ltd., and prepared following a modification of the methods previously reported by: (a) Lai, Y.; Hui-Tin Yap, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1373. and (b) Doyle, M. P.; Siegfried, B.; Dellaria, J. F. *J. Org. Chem.* **1977**, *42*, 2426.

roanthraquinone **7**. Reduction of **7** with red phosphorus and HI affforded 1,4-dichloro-9,10-dihydroanthracene **8**. Conventional nucleophilic aromatic subsitutions with NaCN or CuCN were not successful in converting **8** into the corresponding dinitrile **9**. Instead, a modification of an approach by Jin et al.[12] which utilizes $Zn(CN)_2$ as the source of NC- and tris(dibenzylidineacetone)dipalladium(0) ($Pd_2(dba)_3$), 1,1′-bis(diphenylphosphino)ferrocene (dppf), and zinc as catalysts provided **9** in 73% yield. Conversion of dinitrile **9** into the corresponding bisamide followed by acid-catalyzed hydrolysis provided diacid **10**, which was then converted to its diacid dichloride and used to prepare the target diketone **11** via a standard Friedel−Crafts reaction. The overall yield of **11** from leucoquinazarin **6** was 12%.

Photolysis of diketone **11** and trapping of the resulting *o*-xylylenols with *N*-octylmaleimide produced bisadduct **12** in 81% yield (Scheme 3). Dehydration of **12** with *p*-toluenesulfonic acid followed by aromatization with sulfur in refluxing diphenyl ether afforded the desired compound, *N*,*N*′-bis(octyl)-3,6-bis(phenyl)-benzo[*e*]pyrene-1,2,7,8-tetracarboxylbisimide **2**.

Scheme 3



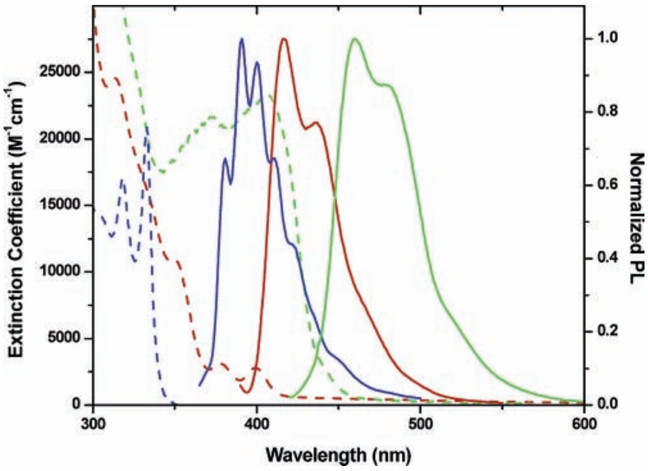


Figure 1. Absorption (dashed) and normalized emission spectra (solid) for benzo[*e*]pyrene (blue), benzo[*e*]pyrene bisimide **2** (green), and *N*-octyl phenanthrene bisimide **1c** (red) in CH_2Cl_2. Emission spectra were recorded using excitation at 375 or 332 nm.

A comparison of the absorption and emission spectra of benzo[*e*]pyrene, benzo[*e*]pyrene bisimide **2**, and a comparable phenanthrene bisimide **1c** in CH_2Cl_2 is shown in Figure 1. Both the absorption and emission spectra of benz[*e*]pyrene bisimide **2** are red-shifted from those of benzo[*e*]pyrene and phenanthrene bisimide **1c**. Benzo[*e*]pyrene bisimide **2** has a broad absorption spectrum ($\lambda_{max} = 373$ and 408 nm, $\epsilon = 21600$ and 23200 M^{-1} cm^{-1}, respectively) compared to the parent benzo[*e*]pyrene which has a structured absorption spectrum consisting of several bands between 250 and 340 nm. Phenanthrene bisimide **1c** is slightly blue-shifted from that of **2** with two bands at 399 and 378 nm ($\epsilon = 2800$ and 3100 M^{-1} cm^{-1}, respectively). Emission from benzo[*e*]pyrene bisimide **2** ($\lambda_{max} = 460$ nm) is red shifted from that of unsubstituted benzo[*e*]pyrene ($\lambda_{max} = 391$ nm) by 69 nm and from that of phenanthrene bisimide **1c** by about 44 nm ($\lambda_{max} = 416$ nm). Emission from both **2** and **1c** does not exhibit any solvatochromic behavior.

While both **1c** and **2** absorb in the near-visible region, **1c** has a considerably lower extinction coefficient and a smaller Stokes shift (17 nm for **1c** compared to 52 nm for **2**). The smaller Stokes shift is likely due to the more rigid nature of **1c**, limiting energy loss caused by excited-state structural relaxation. Molecular modeling predicts a slight bend in the backbone of **1c** (<5°). However, these calculations show a significantly greater distortion of **2** (>10° on two axes), Figure 2.[13] The preparation and properties of highly distorted aromatic systems have been studied extensively by Pascal[14] and, more recently, Wudl.[15] The observed red-shift in the absorption and emission spectra of **2** relative to that of the parent benzo[*e*]pyrene is consistent with that reported by Wudl[15] for so-called "twistacenes" and is likely due to a combination of the two phenyl substituents and the deformation of the benzo[*e*]pyrene nucleus.

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[11] This unwanted polymerization has been previously reported by Nicolau (Nicolaou, K. C.; Gray, D. L. F.; Tae, J. *J. Am. Chem. Soc.* **2004**, *126*, 613) and by us for diketone derived *o*-xylyenols with bisacrylates (Tyson, D. S.; Ilhan, F.; Meador, M. A. B.; Smith, D. D.; Scheimann, D. S.; Meador, M. A. *Macromlecules* **2005**, *38*, 3638).

[12] Jin, F.; Confalone, P. N. *Tetrahedron. Lett.* **2000**, *41*, 3271.

[13] X-ray crystallography on **1a** shows similar distortion of the phenanthrene nucleus. Attempts to grow single crystals from **2** proved unsuccessful.

[14] (a) Pascal, R. A., Jr.; McMillan, W. D.; Engen, V. D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4600, (b) Schuster, I. I.; Cracium, L.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron* **2002**, *58*, 8875, (c) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 1168.

[15] Xu, Q.; Duong, H. M.; Wudl, F.; Yang, Y. *Appl. Phys. Lett.* **2004**, *85*, 3357

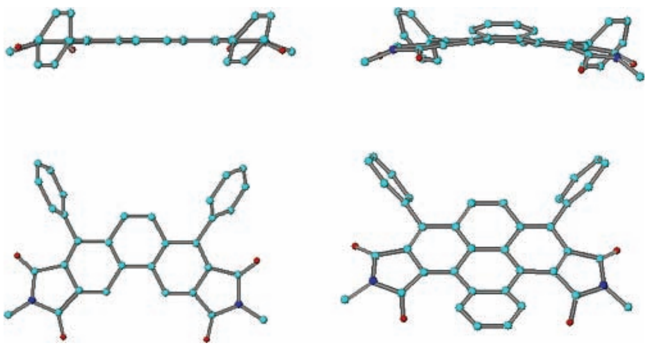

Figure 2. Molecular modeling generated representations of phenanthene bisimide **1c** (left) and benzo[*e*]pyrene bisimide **2** (right). Octyl chains have been replaced by methyls for visual clarity.

The fluorescence quantum yield, Φ_f, for **2** (0.054) is slightly higher than that of unsubstituted benzo[*e*]pyrene (0.037) and considerably lower than that of **1c** (0.24). Fluorescence lifetimes, τ_f , of **2** and **1c**, measured in CH_2Cl_2 by time-correlated single photon counting, were 2.17 and 4.48 ns, respectively. Since

$$\Phi_f = k_f/(k_f + k_d)$$

and

$$\tau_f = 1/(k_f + k_d)$$

then rate constants for fluorescence, k_f, and radiationless decay, k_d, can be readily calculated from measured Φ_f and τ_f . Accordingly, **2** has a k_f of 2.5×10^7 s^{-1} and a k_d of 4.4×10^8 s^{-1} . By comparison, **1c** has a k_f of 4.5×10^7 s^{-1} and a k_d of $7.4 \times 10^7 s^{-1}$. The higher k_d value for **2** is also likely due to steric induced distortion of the benzo[*e*]pyrene nucleus.

In conclusion, we have demonstrated that sterically crowded *o*-xylylenols can be successfully trapped with reactive dienophiles, such as *N*-subsituted maleimides in high yield. The resulting bisadducts can be readily converted into phenacenes including phenanthrene bisimide **1c** and the heretofore unknown benzo[*e*]pyrene bisimide **2**. Molecular mechanics suggest that the benzo[*e*]pyrene nucleus in **2** is twisted, similar to that observed in other sterically crowded arenes.[14,15] This crowding does not adversely affect the absorption and emission characteristics relative to that of the parent benzo[*e*]pyrene. We are currently investigating the use of this versatile chemistry in the preparation of functionalized benzo[*e*]pyrenes for potential use in luminescent polymers and liquid crystals.

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Supporting Information Available: Experimental details for the synthesis and characterization of **1a−c** and **2** including characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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