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Phenacenes: A Family of Graphite Ribbons. 1. Syntheses of Some [7]Phenacenes by Stilbene-like Photocyclizations[1]

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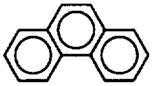
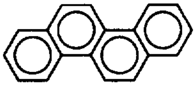
Abstract: The largest previously reported phenacene, the name we propose for the family of polycyclic aromatic compounds having fused benzene rings in an extended phenanthrene-like structural motif, contains only six rings ([6]phenacene). We have employed stilbene-like photocyclizations to synthesize the unsubstituted [7]phenacene, an extremely insoluble compound, as well as 2,13-di-*n*-pentyl[7]phenacene and 2,13-di-*tert*-butyl[7]phenacene, two alkyl-substituted derivatives with greatly improved solubilities.

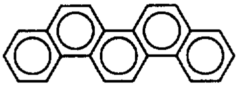
Phenanthrene, chrysene, picene, and fulminene are the first four members of a family of polycyclic aromatic compounds that we propose to designate as [n]phenacenes, where n is an integer that indicates the number of fused benzene rings. There appear to be no previous reports of any simple phenacene systems with seven or more rings. This can be ascribed to solubility problems, which increase severely with n as a consequence of the highly favorable crystal packing interactions that are expected for molecules of this shape.



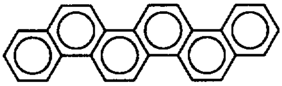
phenanthrene
([3]phenacene)
mp 101 °C



chrysene
([4]phenacene)
mp 256 °C



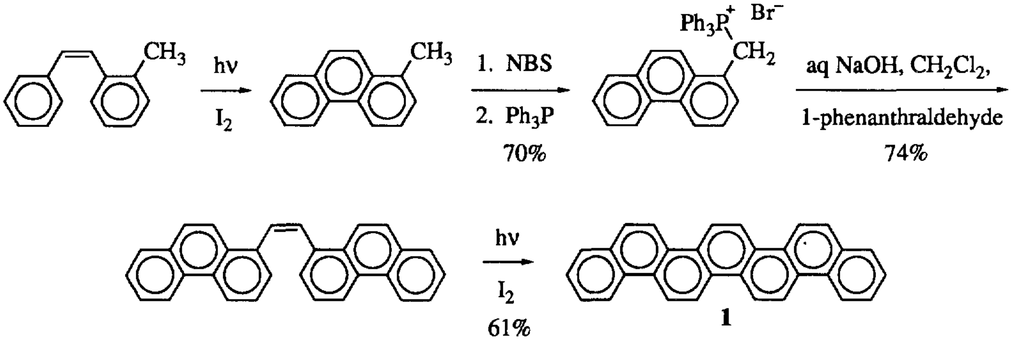
picene
([5]phenacene)
mp 364 °C



fulminene
([6]phenacene)
mp 467 °C

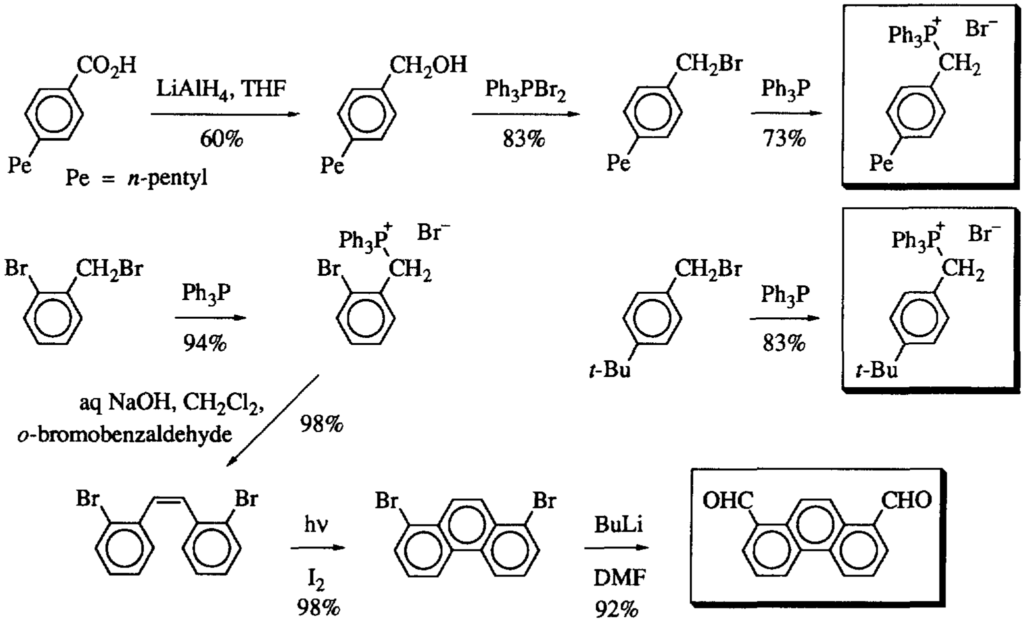
The members of the phenacene family of compounds can be viewed as graphite ribbons of varying lengths. In the expectation that phenacenes with large values of n might show interesting and useful properties as materials, we have begun to develop syntheses of these systems based on stilbene-like photocyclizations.[2] We report here our first experimental results, which involve the [7]phenacene system; in our continuing studies we are focusing our efforts on the synthesis of much longer phenacene systems.

We have synthesized the unsubstituted [7]phenacene (**1**)[3] by the route shown in Scheme 1[4] starting from 1-methylphenanthrene, a compound readily available from the photocyclization of *o*-methylstilbene.[2] As expected, (**1**) is an extremely insoluble material; it melts with decomposition at 565 °C.[5]

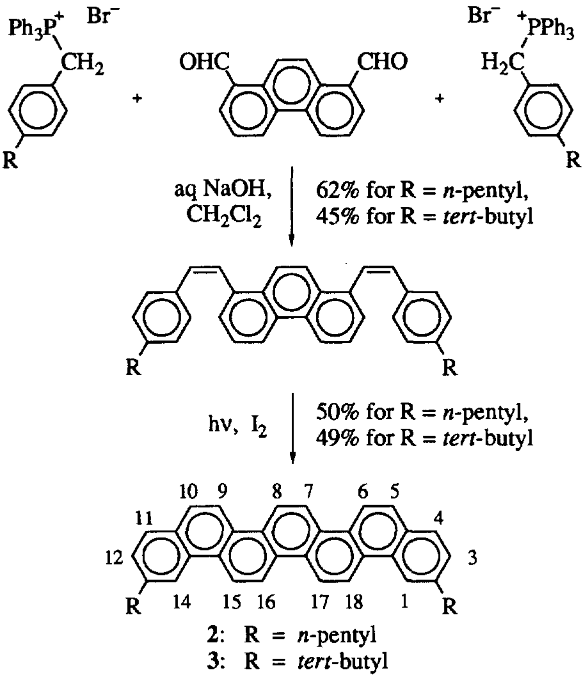


Scheme 1.[4] Synthesis of [7]phenacene (**1**)

Our strategy to overcome the prohibitive insolubility encountered with the parent [7]phenacene (**1**) involves incorporating alkyl substituents along the polycyclic framework in the hope that the resulting structural irregularity will lead to a significant decrease in the magnitude of the normal crystal packing interactions. To test the effectiveness of this strategy we have synthesized 2,13-di-*n*-pentyl[7]phenacene (**2**)[6] and 2,13-di-*tert*-butyl[7]phenacene (**3**)[7]. The key intermediates for these syntheses were constructed as shown in Scheme 2[4] and subsequently assembled as shown in Scheme 3.[4] As we had hoped, both the dialkyl derivatives **2** and **3** turn out to be moderately soluble compounds with melting points of 325 °C and 290 °C, respectively; these values are gratifyingly lower than the melting point of 565 °C found for the unsubstituted [7]phenacene (**1**).



Scheme 2.[4] Syntheses of some key intermediates



Scheme 3.[4] Syntheses of 2,13-di-*n*-pentyl[7]phenacene (**2**) and 2,13-di-*tert*-butyl[7]phenacene (**3**)

REFERENCES AND NOTES

1. (a) Presented in part at the 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, December 17-22, 1995, paper #3294, and at the 31st Middle Atlantic Regional Meeting of the American Chemical Society, Villanova, Pennsylvania, May 22, 1996, paper #145. (b) Taken in part from the M.A. Thesis of Kelly E. Butler, Bryn Mawr College, 1996.
2. Mallory, F. B.; Mallory, C. W. *Organic Reactions* **1984**, 30, 1-456.
3. (*E*)-1,2-Di-(1-phenanthryl)ethylene was obtained as a yellow solid with mp 345-348 °C: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.76 (br d, *J* = 8.3 Hz, 4 H; H-4, H-4', H-5, H-5'), 8.23 (d, *J* = 9.2 Hz, 2 H; H-10, H-10'), 8.01 (br d, *J* = 7.3 Hz, 2 H; H-2, H-2'), 8.00 (s, 2 H; H-α, H-α'), 7.93 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 2 H; H-8, H-8'), 7.83 (d, *J* = 9.2 Hz, 2 H; H-9, H-9'), 7.74 (dd, *J* = 8.3 Hz, *J* = 7.5 Hz, 2 H; H-3, H-3'), 7.73 - 7.61 (m, 4 H; H-6, H-6', H-7, H-7'). Anal.[8] Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.66; H, 5.42. A magnetically stirred solution of 138 mg (0.36 mmol) of this stilbene analog and 66 mg (0.26 mmol) of I_2 in 500 mL of benzene was irradiated with a 450-W Hanovia Hg lamp for 12.5 h. Filtration gave 84 mg (61%) of [7]phenacene (**1**) as a white solid that melted with decomposition at 565 °C.[5] Anal.[8] Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.21; H, 4.75.
4. For convenience the stilbene analogs in Schemes 1-3 are depicted as *Z* isomers. Actually, the Wittig reactions shown in these Schemes produce mixtures of *E* and *Z* isomers. For purposes of purification and

characterization of the Wittig product we routinely isomerize these mixtures entirely to the *E* isomer by treatment with iodine and visible light. The ultraviolet light that photocyclizes the *Z* isomer of a stilbene analog also interconverts its *E* and *Z* isomers, so either isomer can serve as the starting material for a photocyclization; it is often convenient to use the *E,Z* mixture obtained from the Wittig reaction.

5. We are grateful to Dr. Andrew R. McGhie of the University of Pennsylvania for determining the melting behavior of [7]phenacene (**1**) by differential scanning calorimetry.
6. (*E,E*)-1,8-Bis-(4-*n*-pentylstyryl)phenanthrene was obtained as a pale yellow solid, mp 138-139 °C: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.68 (d, *J* = 8.5 Hz, 2 H; H-4, H-5), 8.19 (s, 2 H; H-9, H-10), 7.90 (d, *J* = 16 Hz, 2 H; H-α', H-α"), 7.85 (d, *J* = 7 Hz, 2 H; H-2, H-7), 7.66 (t, *J* = 8 Hz, 2 H; H-3, H-6), 7.55 (d, *J* = 8 Hz, 4 H; H-2', H-2", H-6', H-6"), 7.23 (d, *J* = 8 Hz, 4 H; H-3', H-3", H-5', H-5"), 7.15 (d, *J* = 16 Hz, 2 H; H-β', H-β"), 2.64 (t, *J* = 8 Hz, 4 H; $\mathrm{C\underline{H}_2CH_2CH_2CH_2CH_3}$), 1.65 (m, 4 H; $\mathrm{CH_2C\underline{H}_2CH_2CH_2CH_3}$), 1.36 (m, 8 H; $\mathrm{CH_2CH_2C\underline{H}_2C\underline{H}_2CH_3}$), 0.91 (t, *J* = 7 Hz, 6 H; CH_3). Anal.[8] Calcd for $C_{40}H_{42}$: C, 91.95; H, 8.05. Found: C, 91.79; H, 7.85. A stirred solution of 100 mg (0.19 mmol) of this stilbene analog and 130 mg (0.51 mmol) of I_2 in 360 mL of cyclohexane was irradiated with a 450-W Hanovia Hg lamp for 12 h. Filtration gave 50 mg (50%) of 2,13-di-*n*-pentyl[7]phenacene (**2**). Recrystallization from toluene gave a pale yellow solid, mp 324-325 °C: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.10 (d, *J* = 9.3 Hz, 2 H; H-15, H-18 or H-16, H-17), 9.04 (s, 2 H; H-7, H-8), 9.03 (d, *J* = 9.3 Hz, 2 H; H-16, H-17 or H-15, H-18), 8.82 (d, *J* = 9.1 Hz, 2 H; H-6, H-9), 8.67 (s, 2 H; H-1, H-14), 8.05 (d, *J* = 9.1 Hz, 2 H; H-5, H-10), 7.97 (d, *J* = 8.1 Hz, 2 H; H-4, H-11), 7.55 (d, *J* = 8.0 Hz, 2 H; H-3, H-12), 2.97 (t, *J* = 8 Hz, 4 H; $\mathrm{C\underline{H}_2CH_2CH_2CH_2CH_3}$), 1.87-1.72 (m, 8 H; $\mathrm{CH_2C\underline{H}_2C\underline{H}_2CH_2CH_3}$), 1.44 (m, 4 H; $\mathrm{CH_2CH_2CH_2C\underline{H}_2CH_3}$), 0.96 (t, *J* = 7 Hz, 6 H; CH_3); UV (benzene, nm [rel inten]) 348 [1.0], 322 [2.4], 307 [3.8], 294 [2.9]. Anal.[8] Calcd for $C_{40}H_{38}$: C, 92.62; H, 7.38. Found: C, 92.62; H, 7.07.
7. (*E,E*)-1,8-Bis-(4-*tert*-butylstyryl)phenanthrene was obtained as a pale yellow solid, mp 232-233 °C: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.69 (d, *J* = 8.2 Hz, 2 H; H-4, H-5), 8.20 (s, 2 H; H-9, H-10), 7.92 (d, *J* = 16.0 Hz, 2 H; H-α, H-α'), 7.86 (d, *J* = 7.3 Hz, 2 H; H-2, H-7), 7.67 (t, *J* = 7.9 Hz, 2 H; H-3, H-6), 7.58 (d, *J* = 8.4 Hz, 4 H; H-2, H-2', H-6, H-6'), 7.45 (d, *J* = 8.4 Hz, 4 H; H-3, H-3', H-5, H-5'), 7.16 (d, *J* = 16.0 Hz, 2 H; H-β, H-β'), 1.37 (s, 18 H; CH_3). Anal.[8] Calcd for $C_{38}H_{38}$: C, 92.31; H, 7.69. Found: C, 92.31; H, 7.57. A magnetically stirred solution of 330 mg (0.67 mmol) of this stilbene analog, 170 mg (0.67 mmol) of I_2, and 9.4 mL (134 mmol) of propylene oxide[9] in 400 mL of benzene was irradiated with 300-nm lamps in a Rayonet reactor for 7 days. The solvent was evaporated and the crude product purified via chromatography on silica gel with hexane as eluent to give, after evaporation of the hexane, 160 mg (49%) of 2,13-di-*tert*-butyl[7]phenacene (**3**) as a pale yellow solid. Recrystallization from ethanol/toluene gave white needles, mp 288-290 °C: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.10 (d, *J* = 8.5 Hz, 2 H; H-16, H-17 or H-15, H-18), 9.06 (d, *J* = 8.5 Hz, 2 H; H-15, H-18 or H-16, H-17), 9.03 (s, 2 H; H-7, H-8), 8.88 (br s, 2 H; H-1, H-14), 8.82 (d, *J* = 9.1 Hz, 2 H; H-6, H-9), 8.04 (d, *J* = 9.1 Hz, 2 H; H-5, H-10), 7.99 (d, *J* = 8.4 Hz, 2 H; H-4, H-11), 7.78 (dd, *J* = 8.4 Hz, *J* = 1.7 Hz, 2 H; H-3, H-12), 1.57 (s, 18 H; CH_3); UV (benzene, nm [rel inten]) 348 [1.0], 322 [2.4], 306 [3.7], 294 [3.0]. Anal.[8] Calcd for $C_{38}H_{34}$: C, 93.02; H, 6.98. Found: C, 92.62; H, 7.20.
8. Elemental analyses were performed by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85018.
9. Liu, L.; Yang, B.; Katz, T. J.; Poindexter, M. K. *J. Org. Chem.* **1991**, 56, 3769-3775.

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