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Phenacenes: a family of graphite ribbons. Part 3: Iterative strategies for the synthesis of large phenacenes

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Abstract—Iterative strategies are reported for the synthesis of some large monodisperse [*n*]phenacenes, which are polycyclic aromatic hydrocarbon derivatives having *n* benzene rings fused in an extended phenanthrene-like structural motif. The key carbon–carbon bond-forming steps involve either Wittig or McMurry coupling reactions to give diarylethylenes, and oxidative photocyclizations of those diarylethylenes. *tert*-Butyl substituents on the phenacene framework serve as solubilizing groups. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

A few years ago we became interested in the synthesis and properties of some unprecedentedly large polycyclic aromatic compounds having many fused benzene rings in an extended zigzag or phenanthrene-like structural motif.[1,2] We have chosen to designate these systems as [*n*]phenacenes, where *n* is the number of fused benzene rings. Fig. 1 illustrates the concept that [*n*]phenacenes are related structurally to a single layer of graphite in the way that ribbons are related to sheets. Each layer of graphite (i.e. each graphene sheet) can be regarded as a psuedo two-dimensional molecule, since two of its dimensions (in-plane width and length) are each much longer than its third dimension (out-of-plane thickness). [*n*]Phenacenes with sufficiently large values of *n* might be regarded as psuedo one-dimensional analogs of a single layer of graphite.

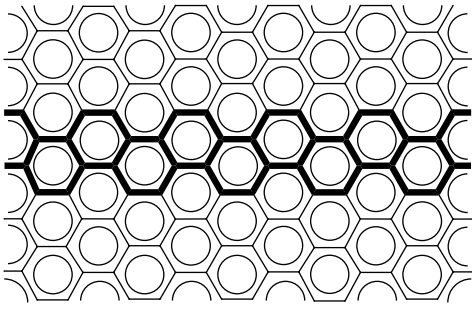

Figure 1. Representation of a portion of a single layer of graphite (a graphene sheet) illustrating the concept that [*n*]phenacene molecules can be regarded as graphite ribbons.

2. Results and discussion

At the time we began our work, [6]phenacene was the largest member of this family that had been reported; we quickly added [7]phenacene to this category.[1,2] The downward trend in the solubilities of the parent [*n*]phenacenes with increasing values of *n* becomes precipitous around *n*=6. It was clear that we would need to incorporate solubilizing groups as ring substituents to make it feasible to explore the synthesis of larger [*n*]phenacene systems. We have investigated several different groups for this purpose; at present we have settled on using *tert*-butyl substituents.

From the outset, our general strategy for the construction of [*n*]phenacenes has been based on the involvement of stilbene-like photocyclizations of 1,2-diarylethylene derivatives, a valuable method of wide scope for the synthesis of phenanthrene-like polycyclic aromatic systems.[3] This photochemical approach is illustrated for the parent stilbene system in Scheme 1. Upon irradiation with ultraviolet light in solution, *E*-stilbene and *Z*-stilbene interconvert photochemically. In addition, *Z*-stilbene photocyclizes under these conditions to give 4a,4b-dihydrophenanthrene as a transient intermediate. In the absence of a trapping agent, this intermediate reverts to *cis*-stilbene by both photochemical and thermal ring-opening reactions, but in the presence of iodine or oxygen it can be trapped oxidatively to give phenanthrene.

Keywords: stilbene-like photocyclizations; polycyclic aromatic hydrocarbon systems; divergent–convergent syntheses; phenacenes.

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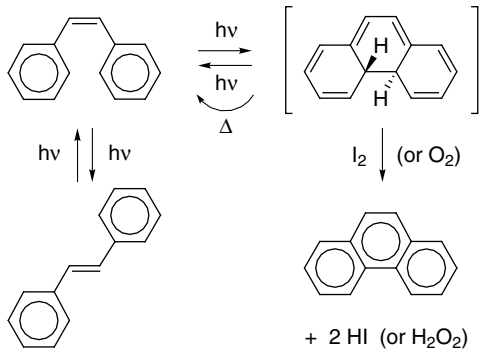


Scheme 1.

We are pursuing three different approaches to the synthesis of large [*n*]phenacenes, each involving iterative elongation of smaller [*n*]phenacenes. These different approaches employ similar strategies in the assembly process for the construction of the new carbon–carbon bonds. First the double bond of a diarylethylene is formed, either by Wittig coupling of an aryl aldehyde with an ylid derived from a benzylic triphenylphosphonium salt, or by McMurry coupling of an aryl aldehyde, and then the diarylethylene is photocyclized to form another carbon–carbon bond. In this chemistry we employ either bromo or methyl groups as latent aldehydes, and methyl groups as latent ylids.

2.1. Synthesis of unsymmetrical phenacenes

One of our iterative approaches involves a divergent–convergent[4] strategy, as illustrated in Scheme 2. This approach leads to the synthesis of unsymmetrically substituted phenacenes having bromo functionality on one terminal ring and methyl functionality on the other terminal ring. We refer to this as the $2n+1$ method, because each iteration converts a system with n benzene rings into a new system with $2n+1$ benzene rings. The starting material for the first iteration is 2-bromo-4-*tert*-butyltoluene (**1**), a compound that is readily prepared on a large scale by the reaction of commercially available 4-*tert*-butyltoluene with bromine in acetic acid.[5] Treatment of **1** with *N*-bromosuccinimide in carbon tetrachloride gave benzylic bromide **2**, and subsequent treatment of **2** with triphenylphosphine in acetone gave the corresponding benzylic phosphonium salt **3**. In a parallel reaction, lithium–bromine exchange of **1** using *n*-butyllithium in a mixture of hexane and THF, followed by treatment of the resulting aryllithium derivative with *N*,*N*-dimethylformamide, gave aldehyde **4**. A phase-transfer Wittig reaction in which 50% aqueous sodium hydroxide was added to a solution of phosphonium salt **3** and aldehyde **4** in CH_2Cl_2 produced stilbene derivative **5**.[†] To complete the first iteration, oxidative photocyclization of **5** by ultraviolet irradiation in hexane solution containing iodine as the trapping agent for the intermediate dihydrophenanthrene derivative gave the substituted phenanthrene **6**. The overall yield of the five-step synthesis of **6** from **1** was 54%.[‡] The methyl and bromo functionality that was present in starting material **1** is once again present in the product of the first iteration, **6**, which allows a second iteration to be carried out in an analogous way. As outlined in Scheme 2, phenanthrene **6** was transformed by way of bromomethyl compound **7**, phosphonium salt **8**, aldehyde **9**, and stilbene analog **10** to produce the [7]phenacene derivative **11** in an overall yield[‡] of 47% for the second iteration.

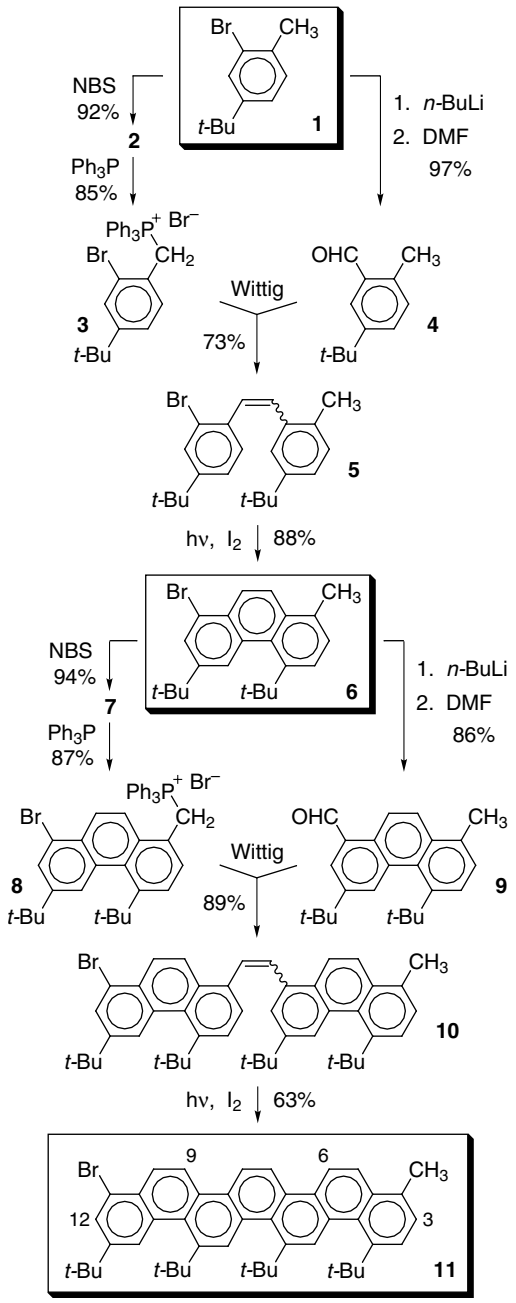
Our divergent–convergent iterative strategy seems especially well suited, in principle, for the synthesis of *very* large [*n*]phenacenes because the number of fused rings formed, n, is related *exponentially* to the number of iterations carried out, I; the actual relationship is $n=2^{(I+1)}-1$. Looking ahead optimistically beyond the two completed iterations outlined in Scheme 2, one can see that two additional iterations, if successful, would transform the [7]phenacene derivative **11** into the corresponding [15]phenacene and [31]phenacene derivatives, respectively.

2.2. Synthesis of symmetrical phenacenes by double photocyclizations

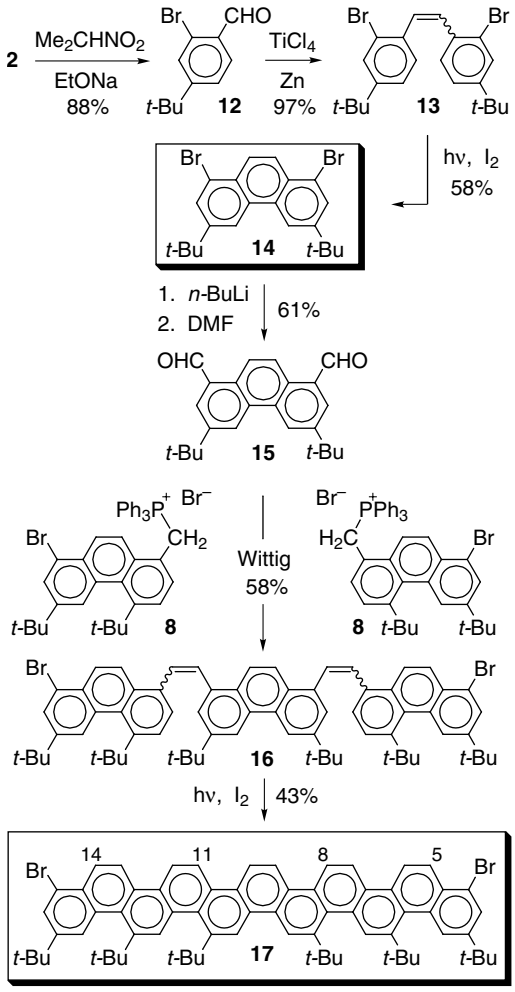
The other iterative approach we are investigating for the synthesis of large [*n*]phenacenes is a versatile method involving the double photocyclizations of the bis-stilbene derivatives that are produced by Wittig reactions of benzylic phosphonium salts with an appropriate centerpiece aromatic dialdehyde. This bis-stilbene approach necessarily produces symmetrically substituted phenacenes, in contrast with the $2n+1$ approach, which produces unsymmetrically substituted phenacenes as noted above. Scheme 3 illustrates one example of this bis-stilbene approach. We refer to this particular example as the $n+8$ method, because each interation transforms a phenacene system having n fused benzene rings into a new phenacene system having $n+8$ fused benzene rings. Treatment of bromomethyl compound **2** (Scheme 2) with the anion derived by deprotonation of 2-nitropropane gave aldehyde **12**. The coupling reaction of **12** using titanium tetrachloride and zinc gave stilbene derivative **13**, and the photocyclization of **13** gave the symmetrical dibromophenanthrene **14**, which can be

[†] The Wittig reactions reported herein produced the diarylethylenes as mixtures of *E* and *Z* isomers. For purposes of purification and characterization, solutions of these isomer mixtures containing small amounts of I_2 were irradiated with visible light from a 100 W tungsten bulb to generate iodine atoms by the photolysis of I_2. The resulting iodine atoms catalyzed the thermal *Z*-to-*E* isomerizations of the diarylethylenes to produce the thermodynamically favored *E*isomers. These (*E*)-diarylethylenes served as the starting materials for the subsequent ultraviolet photocyclizations (see Scheme 1).

[‡] To calculate the overall percentage yield for the conversion of **1** to **6** in the first iteration of this divergent–convergent method, one can imagine that 1.00 equiv. of **1** is divided into two portions of 0.55 and 0.45 equiv., respectively. Hypothetically, the 0.55 equiv. portion of **1** could be used to produce (in two steps with yields of 92 and 85%) 0.43 equiv. of phosphonium salt **3**, and the 0.45 equiv. portion could be used to produce (in one step with a yield of 97%) 0.43 equiv. of aldehyde **4**. Hypothetically, the subsequent Wittig reaction (73% yield) of 0.43 equiv. of **3** and 0.43 equiv. of **4** would give 0.31 equiv. of stilbene **5**, which would undergo photocyclization (88% yield) to give 0.27 equiv. of phenanthrene **6**. Note that if each step in this five-step first iteration took place in 100% yield, the overall theoretical yield from 1.00 equiv. of **1** would be only 0.50 equiv. of **6**. Therefore our overall experimental percentage yield of **6** is 0.27/0.50=54%. The overall experimental percentage yield for the conversion of **6** to **11** in the second five-step iteration can be calculated analogously to be 47% by imagining that 0.51 equiv. of **6** is used to synthesize phosphonium salt **8** and 0.49 equiv. of **6** is used to synthesize aldehyde **9**. The overall yields of 54 and 47%, respectively, for the first two iterations give a combined overall yield for the two iterations of 25%.



Scheme 2.

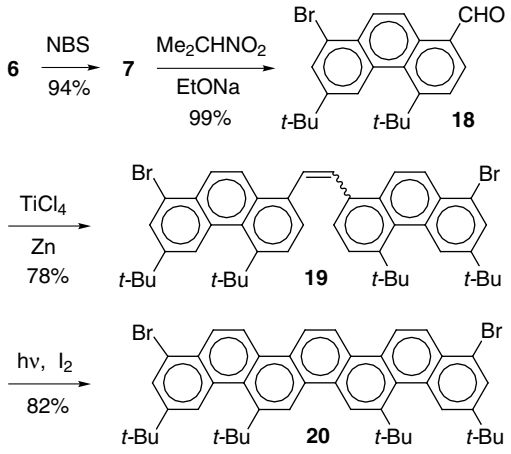


Scheme 3.

regarded as the starting material for the first iteration of this $n+8$ method. Treatment of **14** with *n*-butyllithium followed by *N*,*N*-dimethylformamide gave the dialdehyde centerpiece **15**, which was then subjected to a Wittig reaction with 2 equiv. of the phosphonium salt **8** (Scheme 2) to give bis-stilbene **16**. To complete the first iteration, bis-stilbene **16** was doubly photocyclized to give the dibromo[11]phenacene derivative **17**. The strategic concept of this $n+8$ method is that the dibromophenacene product of each iteration should be capable, in principle, of reacting with *n*-butyllithium and *N*,*N*-dimethylformamide to give a new dialdehyde that might serve as the centerpiece for a subsequent iteration involving phosphonium salt **8** (Scheme 2). For example, two additional iterations of this $n+8$ method, if successful, would transform the [11]phenacene derivative **17** sequentially into the corresponding [19]phenacene and [27]phenacene derivatives, respectively. Although the number of fused rings produced in the $n+8$ approach depends only *linearly* on the number of iterations accomplished, this approach nevertheless is quite efficient as a method for the synthesis of *moderately* large phenacenes.

2.3. Synthesis of symmetrical phenacenes by single photocyclizations

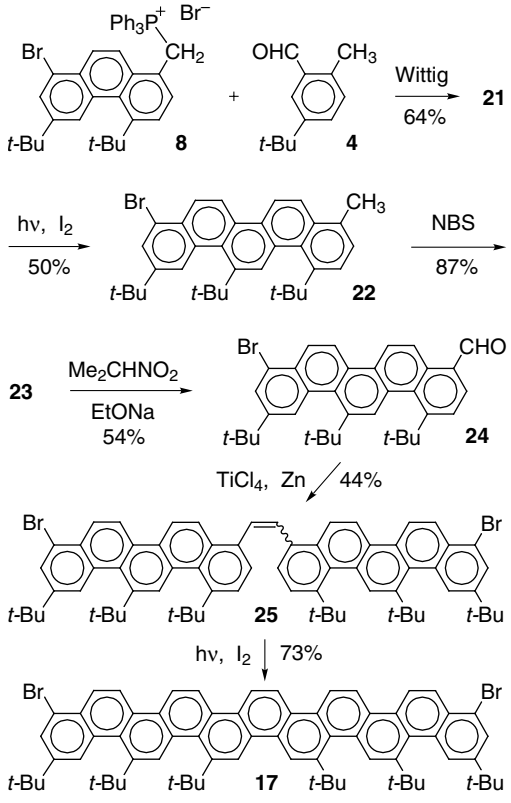
As an alternative to the centerpiece method for the synthesis of symmetrically substituted phenacenes by double photocyclizations of bis-stilbenes, we have developed a method that involves single photocyclizations of mono-stilbenes. This alternative method starts with an unsymmetrically substituted phenacene with *n* fused benzene rings and methyl and bromo substituents, respectively, on the two terminal rings, and transforms it into a symmetrically substituted phenacene with $2n+1$ fused rings and bromo substituents on each of the terminal rings. As shown in Scheme 4, for example, the [3]phenacene derivative **6** (Scheme 2) was subjected to benzylic bromination to give **7** (Scheme 2), and treatment of **7** with 2-nitropropane and sodium ethoxide gave aldehyde **18**. Coupling of **18** using titanium tetrachloride and zinc gave the symmetrical diarylethylene



Scheme 4.

19, which in turn was photocyclized to give the symmetrically substituted dibromo[7]phenacene derivative **20**.

Another example of this strategy is shown in Scheme 5. This particular example also illustrates how phosphonium salts and aldehydes of different sizes can be used to construct a diverse set of building blocks for the synthesis of large phenacenes. Wittig coupling of phosphonium salt **8** and aldehyde **4** (both from Scheme 2) gave diarylethylene **21**, and the photocyclization of **21** gave the [5]phenacene derivative **22**. Functionalization of the ring methyl group in **22** by benzylic bromination gave **23**, which was then transformed to aldehyde **24**. Coupling of **24** gave the symmetrical diarylethylene **25**, and photocyclization of **25** gave the dibromo[11]phenacene derivative **17**. This material was shown to be identical with the sample of **17** that had been synthesized by the centerpiece strategy outlined in Scheme 3, which provides additional support for our assignment of the structure of this compound.



Scheme 5.

2.4. Deviations from planarity of the polycyclic carbon frameworks of phenacenes

Our decision to use *tert*-butyl groups as solubilizing substituents was made in part because the reactions we are employing to assemble larger phenacenes from smaller ones are not compatible with the presence of any benzylic hydrogens other than those on the single methyl substituent whose chemical manipulation we are relying upon in our synthetic strategies. Because these *tert*-butyl groups are attached in the bay regions of our phenacenes, they experience significant intramolecular crowding with the hydrogen atoms at the opposite bay positions. As a consequence of these destabilizing steric interactions, each *tert*-butyl group would be expected to be forced up (or down) out of the rough local plane of the carbon framework of the polycyclic aromatic system in its immediate vicinity. One might consider a priori two limiting cases of cooperativity for the way in which the relief of this local steric crowding might manifest itself in the shape of the framework of the aromatic ring carbons for an extended phenacene derivative. First, if a given *tert*-butyl group is forced out of the rough plane of the ring carbon atoms in its immediate vicinity in one direction (e.g. 'up'), it might be that the adjacent *tert*-butyl group would experience this distortion in the *opposite* direction (e.g. 'down') as shown in Fig. 2(a). Alternatively, each of the *tert*-butyl groups might distort in *same* direction (all up or all down) as shown in Fig. 2(b). In the first case, the polycyclic framework of carbon atoms would be twisted out of its average plane alternatively in a clockwise sense and then in a counterbalancing counterclockwise sense along the path from one end of the phenacene to the other, with the end result that the two terminal rings might lie approximately in the same plane. In the second case, it would be expected that the 'plane' of the polycyclic framework of ring carbon atoms would twist continuously around the long dimension of the framework in a helical sense (either right-handed or left-handed) from one end of the phenacene to the other. We have succeeded in growing a crystal of the unsymmetrical [7]phenacene derivative **11** that was suitable for single-crystal X-ray analysis. As shown in Fig. 3, the results of that analysis show that at

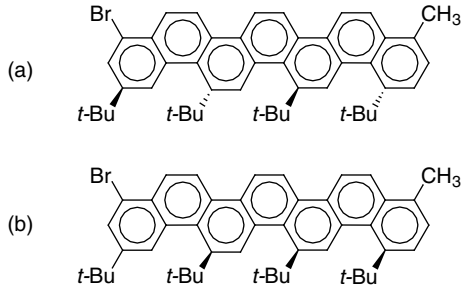


Figure 2. Structures of two hypothetical limiting possibilities for the stereochemical disposition of the *tert*-butyl substituents in the [7]phenacene derivative **11**: (a) with the *tert*-butyl groups arrayed in a syndiotactic sense, and (b) with the *tert*-butyl groups arrayed in an isotactic sense.

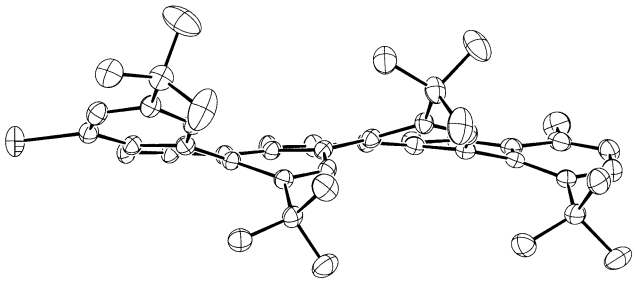


Figure 3. An ORTEP representation of the molecular structure of the [7]phenacene derivative **11** as determined by single crystal X-ray analysis. This edge-on view, with the rough plane of the polycyclic aromatic framework approximately perpendicular to the page, illustrates the syndiotactic disposition of the *tert*-butyl substituents.

least for this particular phenacene the *tert*-butyl substituents alternate up and down.

3. Conclusions

A long-term objective of our work is to synthesize [*n*]phenacenes with dramatically large values of *n* in the hope that these compounds might possess properties that could make them potentially interesting and useful as materials. In the shorter term, our objective is to produce a family of well-characterized monodisperse [*n*]phenacenes with different values of *n* to permit the systematic determination of trends in various properties of these compounds as a function of *n*. In this way, we hope to gain some fundamental insights about the structural and electronic properties of long conjugated π systems.

4. Experimental

4.1. General

Melting points were determined with an oil-bath apparatus and are uncorrected. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra were measured at 75 MHz in $CDCl_3$ solution at ambient temperature unless otherwise specified. All chemical shifts (δ) have been referenced to tetramethylsilane as an internal standard. For some compounds of relatively low solubility, ^{1}H NMR spectra were measured in 1,4-dichlorobenzene-d_4 solution at temperatures $\geq$55°C; the singlet signal from the incompletely deuteriated solvent molecules at 7.03 ppm relative to internal TMS was used as a secondary reference standard in the spectra obtained at these elevated temperatures. Photocyclizations were carried out in magnetically stirred hydrocarbon solutions in quartz vessels in a Rayonet reactor equipped with a set of 16 300 nm lamps. Elemental analyses were performed by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85018.

4.1.1. 2-Bromo-4-*tert*-butyltoluene (1). A previously reported method was used.[5] Following the slow addition of 21 mL (406 mmol) of bromine to a solution of 50 g (338 mmol) of 4-*tert*-butyltoluene in 150 mL of glacial acetic acid at room temperature, the solution was heated at 50°C for 5 d. The reaction mixture was allowed to cool to room temperature, water and aqueous sodium bisulfite were added, and the product was extracted with ether. The combined extracts were washed with water, dried with sodium sulfate, and filtered. Rotary evaporation of the filtrate gave a yellow liquid that was distilled (78–82°C, 0.03 mm Hg) to give 67.4 g (88%) of **1** as a pale yellow liquid: ^{1}H NMR δ 7.56 (d, J=1.8 Hz, 1H; H-3), 7.25 (dd, J=8.0, 1.8 Hz, 1H; H-5), 7.18 (d, J=8.0 Hz, 1H; H-6), 2.39 (s, 3H; ring CH_3), 1.32 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 150.94, 134.86, 130.60, 129.51, 125.02, 124.51, 34.59, 31.45, 22.53. Anal. Calcd for $C_{11}H_{15}Br$: C, 58.17; H, 6.66. Found: C, 58.30; H, 6.69.

4.1.2. 2-Bromo-4-*tert*-butylbenzyl bromide (2). A magnetically stirred mixture of 18.7 g (105 mmol) of *N*-bromosuccinimide, 23.8 g (105 mmol) of **1**, a pinch of benzoyl peroxide, and 150 mL of carbon tetrachloride was heated under reflux overnight. The reaction mixture was allowed to cool and then the succinimide was removed by filtration. The filtrate was rotary evaporated and the residue was distilled (104–122°C, 0.04 mm Hg) to give 29.6 g (92%) of **2** as a clear, colorless liquid: ^{1}H NMR δ 7.57 (d, J=1.9 Hz, 1H; H-3), 7.38 (d, J=8.1 Hz, 1H; H-6), 7.30 (dd, J=8.1, 1.9 Hz, 1H; H-5), 4.59 (s, 2H; CH_2Br), 1.29 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 153.83, 133.84, 130.81, 130.32, 125.05, 124.31, 34.67, 33.34, 31.03. Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61. Found: C, 42.91; H, 4.89.

4.1.3. 2-Methyl-5-*tert*-butylbenzaldehyde (4). A magnetically stirred solution of 15.6 g (69 mmol) of **1** in 400 mL of anhydrous ether was cooled in an ice bath under nitrogen. After the dropwise addition of 55 mL (138 mmol) of a 2.5 M solution of *n*-BuLi in hexanes, the reaction mixture was stirred for an additional 30 min, and then 14 mL (180 mmol) of DMF was added dropwise. The reaction mixture was allowed to warm to room temperature, and then was poured into dilute aqueous phosphoric acid. The product was extracted with ether, and the combined extracts were washed with sodium bicarbonate and water, dried with sodium sulfate, and filtered. The filtrate was rotary evaporated and the yellow liquid residue was chromatographed on silica gel with 5% ethyl acetate in hexanes as eluent to give 11.8 g (97%) of **4** as a pale yellow liquid: bp 70–85°C (0.03 mm Hg); ^{1}H NMR δ 10.28 (s, 1H; CHO), 7.82 (d, J=2.2 Hz, 1H; H-6), 7.52 (dd, J=8.0, 2.2 Hz, 1H; H-4), 7.20 (d, J=7.7 Hz, 1H; H-3), 2.63 (s, 3H; ring CH_3), 1.34 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 193.03, 149.42, 137.76, 133.83, 131.71, 130.95, 128.65, 34.52, 31.26, 18.99. Anal. Calcd for $C_{12}H_{16}O$: C, 81.88; H, 9.10. Found: C, 81.75; H, 8.92.

4.1.4. (*E*)-2-Bromo-4,5′-di-*tert*-butyl-2′-methylstilbene (5). A magnetically stirred solution of 7.7 g (25 mmol) of benzylic bromide **2** and 7.9 g (30 mmol) of triphenylphosphine in 100 mL of xylenes was heated under reflux overnight. The reaction mixture was cooled to room temperature. A beige solid was collected by vacuum filtration, washed with toluene, and dried in an oven at 75°C to give 12.2 g (85%) of the benzylic phosphonium salt **3**.

Phosphonium salt **3** (12.2 g, 21.5 mmol) was placed in 30 mL of methylene chloride along with 4.54 g (25.8 mmol) of aldehyde **4**. Then 10 mL of 50% aqueous sodium hydroxide was

added slowly and the vigorously stirred mixture was heated under reflux for 1 h. The layers were separated and the aqueous layer was washed with ether. The combined organic extracts were washed with water, dried with sodium sulfate, and filtered. The filtrate was rotary evaporated and 300 mL of cyclohexane was added to the residue. The insoluble triphenylphosphine oxide was removed by filtration. The filtrate was washed with 70% aqueous ethanol to remove residual triphenylphosphine oxide, dried over sodium sulfate, and filtered. A crystal of iodine was added to the filtrate, and the magnetically stirred solution was irradiated with visible light for 3 days to effect *Z*-to-*E* isomerization. The solution was washed with aqueous sodium bisulfite and the organic layer was rotary evaporated. The yellow liquid residue was purified by column chromatography on silica gel with hexanes as eluent to give 6.0 g (73%) of **5** as a clear, colorless liquid that spontaneously crystallized and subsequently was recrystallized to constant mp from hexanes: mp 81.5–82.5°C; ^{1}H NMR (assignments established by homonuclear decoupling) δ 7.62 (d, J=2.0 Hz, 1H; H-6′), 7.60 (d, J=8.8 Hz, 1H; H-6), 7.59 (d, J=1.8 Hz, 1H; H-3), 7.34 (dd, J=8.0, 2.1 Hz, 1H; H-5), 7.29 (A of AB q, J=15.9 Hz, 1H; H-α or H-α′). 7.22 (B of AB q, J=15.9 Hz, 1H; H-α′ or H-α), 7.25 (dd, J=7.9, 2.1 Hz, 1H; H-4′), 7.13 (d, J=8.0 Hz, 1H; H-3′), 2.39 (s, 3H; ring CH_3), 1.36 (s, 9H; 5′-$(CH_3)_3C$), 1.32 (s, 9H; 4-$(CH_3)_3C$); ^{13}C NMR δ 152.37, 149.02, 135.77, 134.74, 133.01, 130.20, 129.95, 129.33, 128.47, 126.48, 124.99, 124.78, 124.02, 122.74, 34.64, 34.43, 31.39, 31.13, 19.44. Anal. Calcd for $C_{23}H_{29}Br$: C, 71.87; H, 7.34. Found: C, 71.63; H, 7.60.

4.1.5. 1-Bromo-3,5-di-*tert*-butyl-8-methylphenanthrene (6). A solution of 2.5 g (6.5 mmol) of stilbene **5** and 0.8 g (3.1 mmol) of iodine in 1.0 L of hexanes was irradiated (Rayonet) for 3 d at 10–20°C. After the reaction mixture was concentrated to about 100 mL by rotary evaporation, it was washed with aqueous sodium bisulfite. The organic layer was dried over sodium sulfate and filtered. The filtrate was passed through a short pad of silica gel and then was rotary evaporated. The oily residue was triturated with acetonitrile to yield 2.2 g (88%) of **6** as colorless crystals: mp 140.6–141.0°C; ^{1}H NMR δ 8.24 (d, J=1.4 Hz, 1H; H-4), 8.03 (d, J=9.2 Hz, 1H; H-10), 7.83 (d, J=9.2 Hz, 1H; H-9), 7.83 (d, J=1.8 Hz, 1H; H-2), 7.77 (d, J=7.8 Hz, 1H; H-6), 7.34 (d, J=7.8 Hz, 1H; H-7), 2.65 (s, 3H; ring CH_3), 1.53 (s, 9H; $(CH_3)_3C$), 1.42 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 147.12, 146.54, 133.62, 132.88, 132.44, 132.28, 129.67, 129.27, 129.14, 129.07, 127.72, 124.72, 124.48, 122.43, 38.20, 35.46, 34.44, 31.62, 19.26; UV (benzene, nm [ϵ]) 324 [13,000], 314 [14,000], 286 [27,000]. Anal. Calcd for $C_{23}H_{27}Br$: C, 72.06; H, 7.05. Found: C, 71.98; H, 7.27.

4.1.6. 1-Bromo-3,5-di-*tert*-butyl-8-bromomethylphenanthrene (7). A procedure similar to that described above for benzylic bromide **2** was followed. A mixture of 5.11 g (28.7 mmol) of *N*-bromosuccinimide, 11.0 g (28.7 mmol) of methylphenanthrene **6**, a pinch of benzoyl peroxide, and 90 mL of carbon tetrachloride was heated under reflux for 48 h. Recrystallization of the crude product from hexanes yielded 12.5 g (94%) of **7** as a beige solid: mp 142.5–143.5°C; ^{1}H NMR δ 8.20 (d, J=1.2 Hz, 1H; H-4), 8.14 (d, J=9.3 Hz, 1H; H-10), 7.97 (d, J=9.3 Hz, 1H; H-9), 7.85 (d, J=1.8 Hz, 1H; H-2), 7.81 (d, J=7.9 Hz, 1H; H-6), 7.53 (d, J=7.9 Hz, 1H; H-7), 4.92 (s, 2H; CH_2Br), 1.52 (s, 9H; $(CH_3)_3C$), 1.42 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 150.20, 146.3, 132.62, 132.24, 131.29, 130.45, 129.96, 129.88, 129.61, 129.17, 127.27, 124.87, 122.90, 121.85, 39.46, 35.28, 34.09, 31.66, 31.38. Anal. Calcd for $C_{23}H_{26}Br_2$: C, 59.76; H, 5.67. Found: C, 59.90; H, 5.53.

4.1.7. 3,5-Di-*tert*-butyl-8-methylphenanthrene-1-carboxaldehyde (9). A procedure similar to that described above for aldehyde **4** was followed. Starting from 4.88 g (12.7 mmol) of bromophenanthrene **6**, 40 mL of anhydrous ether, 8.6 mL (19.1 mmol) of a 2.0 M solution of *n*-BuLi in pentane, and 2.0 mL (25.8 mmol) of DMF there was obtained, after recrystallization of the crude product from acetonitrile, 3.61 g (86%) of **9** as yellow crystals: mp 113.5–114.0°C; ^{1}H NMR δ 10.54 (s, 1H; CHO), 8.91 (d, J=9.3 Hz, 1H; H-10), 8.53 (d, J=1.9 Hz, 1H; H-4), 8.07 (d, J=2.1 Hz, 1H; H-2), 7.95 (d, J=9.3 Hz, 1H; H-9), 7.81 (d, J=7.8 Hz, 1H; H-6), 7.37 (d, J=7.9 Hz, 1H; H-7), 2.68 (s, 3H; ring CH_3), 1.53 (s, 9H; $(CH_3)_3C$), 1.48 (s, 9H; $(CH_3)_3C$); ^{13}C δ 193.92, 146.20. 134.93, 132.46, 132.01, 131.90, 131.48, 130.04, 129.20, 128.86, 127.17, 125.68, 120.75, 38.10, 35.29, 34.48, 31.55, 19.38. Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.89; H, 8.33.

4.1.8. (*E*)-1-(8-Bromo-4,6-di-*tert*-butyl-1-phenanthryl)-2-(8′-methyl-3′,5′-di-*tert*-butyl-1′-phenanthryl)ethene (10). A procedure similar to that described above for phosphonium salt **3** was followed to convert 22.9 g (49.4 mmol) of benzylic bromide **7** and 13.0 g (49.4 mmol) of triphenylphosphine in 150 mL of xylenes to 31.2 g (87%) of the corresponding phosphonium salt **8** as a beige solid.

A sample of 1.58 g (39.6 mmol) of sodium hydride (60% dispersion in mineral oil) was washed twice with hexanes and then was heated with 40 mL of DMSO at 60–80°C until the evolution of gas ceased. This solution was cooled to room temperature, and a slurry of 25.4 g (35.1 mmol) of phosphonium salt **8** in 100 mL of DMSO was added. The reaction mixture turned red, indicating the formation of the ylid. Then a slurry of 11.6 g (34.8 mmol) of aldehyde **9** in 100 mL of DMSO was added, and the mixture was heated to 80°C for 3.5 h until all of the red color disappeared. The cloudy yellow solution was cooled in an ice bath and filtered to give a yellow solid that was washed with methanol and dried under vacuum to yield 21.5 g (89%) of a mixture of diarylethylene **10** and its *Z* isomer. This material, along with a crystal of iodine, was dissolved in cyclohexane, and the magnetically stirred solution was irradiated with visible light for 2 d. The solution was washed with aqueous sodium bisulfite and the organic layer was dried with sodium sulfate and filtered. The filtrate was rotary evaporated and the residue was recrystallized from a mixture of toluene and 95% ethanol to give **10** as white crystals: mp 253.5–254.5°C; ^{1}H NMR δ 8.28 (d, J=1.5 Hz, 1H; H-5 or H-4′), 8.25 (d, J=1.4 Hz, 1H; H-4′ or H-5), 8.11 (A of AB q, J=9.4 Hz, 1H; H-9 or H-10), 8.04 (B of AB q, J=9.4 Hz, 1H; H-10 or H-9), 8.04 (d, J=9.5 Hz, 1H; H-10′), 7.95 (A of AB q, J=8.1 Hz, 1H; H-2 or H-3), 7.90 (B of AB q, J=8.1 Hz, 1H; H-3 or H-2), 7.89 (d, J=1.7 Hz, 1H; H-7 or H-2′), 7.88 (d, J=1.6 Hz, 1H; H-7 or H-2′), ca. 7.86 and 7.84

(presumably AB q with outer lines too weak to observe, 2H; H-α and H-α′), 7.78 (d, *J*=9.0 Hz, 1H; H-9′), 7.78 (d, *J*=ca. 8 Hz, 1H; H-6′), 7.34 (d, *J*=7.8 Hz, 1H; H-7′), 2.66 (s, 3H; ring CH_3), 1.58 (s, 18H; $(CH_3)_3C$), 1.50 (s, 9H; $(CH_3)_3C$), 1.45 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 148.30, 146.17, 145.92, 144.42, 133.46, 133.01, 132.67, 132.03, 131.96, 131.87, 131.37, 131.05, 130.62, 129.01, 128.94, 128.60, 128.45, 128.34, 128.27, 128.17, 126.45, 124.02, 123.91, 123.76, 122.60, 122.23, 121.68, 121.32, 38.28, 38.00, 35.24, 34.31, 34.18, 31.61, 31.43, 19.29. Anal. Calcd for $C_{47}H_{53}Br$: C, 80.89; H, 7.66. Found: C, 80.96; H, 7.58.

4.1.9. 11-Bromo-4-methyl-1,13,15,17-tetra-*tert*-butyl[7]phenacene (11). A suspension of 4.05 g (5.8 mmol) of stilbene **10** and 1.6 g (6.3 mmol) of iodine in 60 mL of toluene and 1 L of distilled hexanes was irradiated (Rayonet) for 60 h. Rotary evaporation of the reaction mixture and recrystallization of the residue from a mixture of toluene and 95% ethanol gave 2.54 g (63%) of **11** as a pale yellow powder: mp 378°C (dec); ^1H NMR ($CDCl_3$) δ 8.88 (A of AB q, *J*=9.3 Hz, 1H; H-7 or H-8), 8.74 (B of AB q, *J*=9.3 Hz, 1H; H-8 or H-7), 8.84 (s, 1H; H-16 or H-18), 8.79 (d, *J*=9.4 Hz, 1H; H-9), 8.75 (s, 1H; H-18 or H-16), 8.60 (d, *J*=9.3 Hz, 1H; H-6), 8.45 (d, *J*=1.3 Hz, 1H; H-14), 8.32 (d, *J*=9.2 Hz, 1H; H-10), 8.08 (d, *J*=9.2 Hz, 1H; H-5), 7.92 (d, *J*=1.7 Hz, 1H; H-12), 7.86 (d, *J*=7.8 Hz, 1H; H-2), 7.42 (d, *J*=8.1 Hz, 1H; H-3), 2.78 (s, 3H; ring CH_3), 1.65 (s, 9H; $(CH_3)_3C$), 1.57 (s, 18H; $(CH_3)_3C$), 1.51 (s, 9H; $(CH_3)_3C$); ^1H NMR (1,4-dichlorobenzene-d_4, 60°C) 8.94 (s, 1H; H-16 or H-18), 8.82 (s, 1H; H-18 or H-16), 8.77 (A of AB q, *J*=9.3 Hz, 1H; H-7 or H-8), 8.64 (B of AB q, *J*=9.3 Hz, 1H; H-8 or H-7), 8.69 (d, *J*=9.2 Hz, 1H; H-9), 8.51 (br s, 1H; H-14), 8.46 (d, *J*=9.2 Hz, 1H; H-6), 8.30 (d, *J*=9.2 Hz, 1H; H-10), 7.94 (d, *J*=9.2 Hz, 1H; H-5), 7.91 (d, *J*=1.7 Hz, 1H; H-12), 7.40 (d, *J*=7.7 Hz, 1H; H-2), 7.28 (d, *J*=7.8 Hz, 1H; H-3), 2.64 (s, 3H; ring CH_3), 1.66 (s, 9H; $(CH_3)_3C$), 1.62 (s, 9H; $(CH_3)_3C$), 1.59 (s, 9H; $(CH_3)_3C$), 1.44 (s, 9H; $(CH_3)_3C$); ^{13}C NMR ($CDCl_3$, 40°C) δ 146.53, 139.63, 138.93, 133.75, 132.14, 130.24, 129.57, 128.70, 128.58, 128.02, 127.44, 127.39, 126.90, 124.82, 123.85, 122.65, 122.44, 122.33, 120.41, 120.13, 38.39, 38.21, 35.66, 34.93, 34.56, 34.36, 32.82, 31.78, 19.60. Anal. Calcd for $C_{47}H_{51}Br$: C, 81.13; H, 7.39. Found: C, 81.12; H, 7.11.

A crystal of **11** suitable for single crystal X-ray analysis was grown from 1-methylnaphthalene solution by slow evaporation at 150°C under a stream of argon.

4.1.10. 2-Bromo-4-*tert*-butylbenzaldehyde (12). A solution was prepared from 22.1 mL of a 21% w/w solution of sodium ethoxide in absolute ethanol (68 mmol of NaOEt) and 225 mL of absolute ethanol. To this solution was added, under nitrogen, 6.1 mL (68 mmol) of 2-nitropropane followed by 19 g (62 mmol) of neat 2-bromo-4-*tert*-butylbenzyl bromide (**2**). The reaction mixture was stirred magnetically for 4 h at room temperature, and then it was filtered to remove sodium bromide. The filtrate was rotary evaporated and the residue was dissolved in ether and washed sequentially with water, 10% aqueous sodium hydroxide, and brine. Rotary evaporation of the ether layer and molecular distillation of the red residue under reduced pressure (0.01 mm Hg) gave 13.1 g (88%) of **12** as a light yellow oil: ^1H NMR δ 10.33 (s, 1H; CHO), 7.87 (d, *J*=8.2 Hz, 1H; H-6), 7.65 (d, *J*=1.6 Hz, 1H; H-3), 7.45 (dd, *J*=8.2, 1.4 Hz, 1H; H-5), 1.35 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 191.37, 159.78, 131.12, 130.88, 129.60, 127.28, 125.23, 35.40, 30.90. Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.60; H, 5.19.

4.1.11. (*E*)-2,2′-Dibromo-4,4′-di-*tert*-butylstilbene (13). To a magnetically stirred yellow slurry of 3.69 g (19.4 mmol) of titanium tetrachloride in 75 mL of THF that was cooled in an ice bath under nitrogen was added 2.32 g (35.3 mmol) of zinc dust. Then 4.26 g (17.7 mmol) of aldehyde **12** was added, and the mixture was heated under reflux for 4 h. The cooled reaction mixture was poured into dilute aqueous hydrochloric acid, and the product was extracted with hexanes. The combined extracts were washed with water and brine, dried with sodium sulfate, and filtered. The filtrate was rotary evaporated to give 3.86 g (97%) of **13** as a light-beige powder, which was recrystallized from a mixture of toluene and 95% ethanol to give **13** as white needles: mp 126–127°C; ^1H NMR δ 7.65 (d, *J*=8.3 Hz, 2H; H-6,6′), 7.58 (d, *J*=1.9 Hz, 2H; H-3,3′), 7.35 (dd, *J*=8.1, 2.0 Hz, 2H; H-5,5′), 7.34 (s, 2H; H-α,α′), 1.32 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 153.22, 134.48, 130.40, 129.62, 127.05, 125.32, 124.57, 35.13, 31.54. Anal. Calcd for $C_{22}H_{26}Br_2$: C, 58.69; H, 5.82. Found: C, 58.80; H, 5.70.

4.1.12. 1,8-Dibromo-3,6-di-*tert*-butylphenanthrene (14). A solution of 2.36 g (5.24 mmol) of stilbene 13 and 0.67 g (2.64 mmol) of iodine in 1 L of cyclohexane was irradiated (Rayonet) for 11 h. The reaction mixture was rotary evaporated and the dark solid residue was dissolved in a mixture of hexanes and toluene and filtered through alumina. The filtrate was rotary evaporated and the crystalline residue was recrystallized from a mixture of 95% ethanol and hexanes to give 1.36 g (58%) of **14** as a white needles: mp 131.5–132.5°C; ^1H NMR δ 8.63 (d, *J*=1.6 Hz, 2H; H-4,5), 8.19 (s, 2H; H-9,10), 7.98 (d, *J*=1.6 Hz, 2H; H-2,7), 1.49 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 150.75, 131.71, 130.12, 129.02, 126.30, 124.15, 118.47, 35.74, 31.75. Anal. Calcd for $C_{22}H_{24}Br_2$: C, 58.95; H, 5.40. Found: C, 59.12; H, 5.26.

4.1.13. 3,6-Di-*tert*-butylphenanthrene-1,8-dicarboxaldehyde (15). A procedure similar to that described above for aldehyde **4** was followed. Starting from 4.63 g (10.3 mmol) of dibromophenanthrene **14**, 50 mL of anhydrous ether, 19 mL (30 mmol) of a 1.6 M solution of *n*-BuLi in hexanes, and 2.92 g (40 mmol) of DMF there was obtained, after recrystallization of the crude product from a mixture of hexanes and toluene, 2.17 g (61%) of **15** as white crystals: mp 188.0–190.5°C; ^1H NMR δ 10.58 (s, 2H; CHO), 9.20 (s, 2H; H-9,10), 9.00 (d, *J*=1.9 Hz, 2H; H-4,5), 8.23 (d, *J*=1.9 Hz, 2H; H-2,7), 1.57 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 193.61, 149.14, 133.86, 131.69, 130.59, 128.56, 124.82, 124.42, 35.49, 31.49. Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.09; H, 7.46.

4.1.14. (*E*,*E*)-1,8-bis-(8-Bromo-4,6-di-*tert*-butyl-1-phenanthrylvinyl)-3,6-di-*tert*-butylphenanthrene (16). A Wittig procedure similar to that described above for stilbene **10** was carried out starting with 0.081 g (1.54 mmol, 60% dispersed in mineral oil) of NaH, 20 mL of DMSO, 0.92 g (1.28 mmol) of phosphonium salt **8**, and 0.21 g (0.61 mmol)

of dialdehyde **15**. The reaction was allowed to proceed overnight at 80°C. The crude Wittig product was dissolved in benzene containing a crystal of iodine, and the magnetically stirred solution was irradiated with visible light for 3 d to effect *Z*-to-*E* isomerization. The resulting product was recrystallized from a mixture of toluene and 95% ethanol to give 0.38 g (58%) of **16** as a white powder: mp 285–287°C; ^{1}H NMR δ 8.77 (br s, 2H; H-4,5), 8.25 (d, J=1.4 Hz, 2H; H-5′,5″), 8.14 (s, 2H; H-9,10), 8.10 (A of AB q, J=9.3 Hz, 2H; H-9′,9″ or H-10′,10″), 8.05 (B of AB q, J=9.3 Hz, 2H; H-10′,10″ or H-9′,9″), 8.00 (br s, 2H; H-2,7), 7.97 (A of AB q, J=15.7 Hz, 2H; alkenyl H), 7.84 (B of AB q, J=15.7 Hz, 2H; alkenyl H), 7.95 (A of AB q, J=8.0 Hz, 2H; H-2′,2″ or H-3′,3″), 7.88 (B of AB q, J=8.0 Hz, 2H; H-3′,3″ and H-2′,2″), 7.85 (d, J=1.8 Hz, 2H; H-7′,7″), 1.60 (s, 18H; $(CH_3)_3C$), 1.57 (s, 18H; $(CH_3)_3C$), 1.44 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 149.07, 148.64, 146.15, 135.75, 133.06, 132.87, 131.26, 130.60, 129.25, 129.16, 128.97, 128.84, 128.48, 128.44, 128.04, 125.51, 124.04, 122.22, 121.91, 38.51, 35.55, 35.49, 34.40, 31.81, 31.65. Anal. Calcd for $C_{70}H_{76}Br_2$: C, 78.05; H, 7.11. Found: C, 77.86; H, 7.18.

4.1.15. 4,15-Dibromo-2,17,19,21,24,26-hexa-*tert*-butyl[11]phenacene (17) from double photocyclization of 16. A solution of 1.14 g (1.1 mmol) of **16** and 0.80 g (3.1 mmol) of iodine in 1100 mL of cyclohexane was irradiated (Rayonet) for 73 h at ca. 20°C. The solution was concentrated to about 200 mL by rotary evaporation. The precipitated product was collected by filtration and rinsed with hexanes to give 0.49 g (43%) of **17** as a yellow solid. A small amount of this solid was recrystallized twice from *o*-dichlorobenzene to give an analytical sample of **17**: mp >335°C (dec); ^{1}H NMR (1,4-dichlorobenzene-d_4, 80°C) δ 9.31 (s, 2H; H-9,10 or H-22,23), 8.93 (s, 2H; H-22,23 or H-9,10), 8.86 (A of AB q, J=9.3 Hz, 2H; H-7,12 or H-8,11), 8.70 (B of AB q, J=9.3 Hz, 2H; H-8,11 or H-7,12), 8.78 (s, 2H; H-20,25), 8.71 (d, J=9.5 Hz, 2H; H-6,13), 8.54 (br s, 2H; H-1,18), 8.32 (d, J=9.7 Hz, 2H; H-5,14), 7.93 (d, J=1.8 Hz, 2H; H-3,16), 1.83 (s, 9H; $(CH_3)_3C$), 1.60 (s, 9H; $(CH_3)_3C$), 1.46 (s, 9H; $(CH_3)_3C$). Anal. Calcd for $C_{70}H_{72}Br_2$: C, 78.35; H, 6.76. Found: C, 78.41; H, 6.66.

4.1.16. 8-Bromo-4,6-di-*tert*-butylphenanthrene-1-carboxaldehyde (18). To a magnetically stirred solution prepared from 8.2 mL of a 21% w/w solution of sodium ethoxide in absolute ethanol (25 mmol of NaOEt) and 70 mL of absolute ethanol was added, under nitrogen, 2.3 mL (25 mmol) of 2-nitropropane followed by a solution of 10.6 g (22.9 mmol) of benzylic bromide **7** in 40 mL of benzene. The mixture was stirred for 24 h at room temperature, and then was filtered to remove sodium bromide. The filtrate was rotary evaporated, and the residue was dissolved in toluene and washed sequentially with water, 10% aqueous sodium hydroxide, and brine. The organic layer was dried over sodium sulfate and filtered. The filtrate was passed through a short pad of silica gel. Then the toluene was removed, initially using a rotary evaporator and then using a vacuum pump, to give 9.05 g (99%) of aldehyde **18** as a yellow solid: mp 119–122°C; ^{1}H NMR δ 10.43 (s, 1H; CHO), 9.02 (d, J=9.4 Hz, 1H; H-10), 8.19 (d, J=9.4 Hz, 1H; H-9), 8.15 (d, J=1.6 Hz, 1H; H-5), 8.03 (A of AB q, J=7.9 Hz, 1H; H-2 or H-3), 7.96 (B of AB q, J=7.9 Hz, 1H; H-3 or H-2), 7.89 (d, J=1.7 Hz, 1H; H-7); 1.53 (s, 9H; $(CH_3)_3C$), 1.43 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 192.90, 156.65, 146.86, 133.40, 132.27, 132.22, 129.74, 129.24, 128.80, 128.64, 128.41, 127.57, 123.14, 122.32, 122.25, 39.68, 35.71, 34.37, 31.76. Anal. Calcd for $C_{23}H_{25}BrO$: C, 69.52; H, 6.34. Found: C, 69.70; H, 6.25.

4.1.17. (*E*)-1,2-Di-(8-bromo-4,6-di-*tert*-butyl-1-phenanthryl)ethene (19). The addition by syringe of 2.8 mL (25 mmol) of titanium tetrachloride to 40 mL of magnetically stirred anhydrous THF maintained at 0°C under nitrogen gave an opaque yellow slurry. After 20 min, 3.14 g (48 mmol) of zinc dust was added, and the reaction mixture turned blue-gray. A solution of 9.25 g (24 mmol) of aldehyde **18** in 30 mL of anhydrous THF was added by cannula, and the reaction mixture was heated and maintained at reflux for 8 h. The reaction was quenched by the addition of dilute aqueous hydrochloric acid, and then was extracted three times with toluene. The toluene extract was washed with water, dried over sodium sulfate, and filtered. Rotary evaporation of the filtrate and recrystallization of the residue from a mixture of toluene and 95% ethanol gave 6.9 g (78%) of stilbene **19** as a bright yellow solid: mp 283–286°C; ^{1}H NMR δ 8.17 (d, J=1.4 Hz, 2H; H-5,5′), 7.99 (A of AB q, J=9.3 Hz, 2H; H-9,9′ or H-10,10′), 7.95 (B of AB q, J=9.3 Hz, 2H; H-10,10′ or H-9,9′), 7.85 (A of AB q, J=8.1 Hz, 2H; H-2,2′ or H-3,3′), 7.75 (B of AB q, J=8.1 Hz, 2H; H-3,3′ or H-2,2′), 7.77 (d, J=1.7 Hz, 2H; H-7,7′), 7.75 (s, 2H; H-α,α′), 1.49 (s, 18H; $(CH_3)_3C$), 1.36 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 148.90, 146.36, 133.11, 133.05, 132.31, 131.42, 129.34, 129.05, 128.67, 124.48, 124.13, 124.07, 122.10, 38.70, 35.68, 34.58, 31.83. Anal. Calcd for $C_{46}H_{50}Br_2$: C, 72.44; H, 6.61. Found: C, 72.53; H, 6.69.

4.1.18. 4,11-Dibromo-2,13,15,18-tetra-*tert*-butyl[7]phenacene (20). A solution of 1.20 g (1.6 mmol) of stilbene **19** and 0.4 g (1.6 mmol) of iodine in 50 mL of toluene and 500 mL of hexanes was irradiated (Rayonet) for 2.5 d. The precipitated product was collected by filtration and rinsed with hexanes to give 0.98 g (82%) of **20** as a yellow solid: mp 320°C (dec); ^{1}H NMR δ 8.99 (s, 2H; H-7,8 or H-16,17), 8.68 (s, 2H; H-16,17 or H-7,8), 8.66 (d, J=9.2 Hz, 2H; H-6,9), 8.31 (br s, 2H; H-1,14), 8.24 (d, J=9.2 Hz, 2H; H-5,10), 7.77 (d, J=1.7 Hz, 2H; H-3,12), 1.48 (s, 18H; $(CH_3)_3C$), 1.41 (s, 18H; $(CH_3)_3C$); ^{13}C NMR (45°C) δ 146.58, 146.35, 133.23, 130.67, 130.49, 129.39, 128.85, 128.71, 128.23, 127.33, 125.29, 125.07, 122.60, 122.37, 121.67, 39.08, 35.72, 35.11, 31.81. Anal. Calcd for $C_{46}H_{48}Br_2$: C, 72.63; H, 6.36. Found: C, 72.45; H, 6.50.

4.1.19. (*E*)-1-(8-bromo-4,6-di-*tert*-butyl-1-phenanthryl)-2-(5′-*tert*-butyl-2′-methylphenyl)ethene (21). The addition of 4.1 mL (8.2 mmol) of a 2.0 M solution of *n*-BuLi in pentane to a solution of 1.6 mL (11.0 mmol) of diisopropylamine in 25 mL of THF was followed by the addition of a solution of 5.92 g (8.2 mmol) of phosphonium salt **8** in 100 mL of THF. The reaction mixture turned red. A solution of 1.31 g (7.4 mmol) of aldehyde **4** in 20 mL of THF was added, and the mixture was heated under reflux overnight. The cooled reaction mixture was poured into aqueous ammonium chloride. The resulting mixture was extracted with toluene and the toluene extract was washed with brine and

rotary evaporated. The residue was dissolved in benzene, a crystal of iodine was added, and the magnetically stirred solution was irradiated with visible light for 5 d, after which it was washed with aqueous sodium thiosulfate. The organic layer was rotary evaporated and the residue was treated with hexanes. The insoluble material was removed by filtration and the filtrate was rotary evaporated. The residue was recrystallized from acetonitrile to give 2.86 g (64%) of **21** as white crystals. A small sample was recrystallized to constant mp from a mixture of toluene and 95% ethanol: mp 180–182°C; ^{1}H NMR δ 8.23 (d, J=1.8 Hz, 1H; H-5), 8.03 (s, 2H; H-9,10), 7.89 (A of AB q, J=8.1 Hz, 1H; H-2 or H-3), 7.73 (B of AB q, J=8.1 Hz, 1H; H-3 or H-2), 7.84 (d, J=1.8 Hz, 1H; H-7), 7.69 (d, J=2.2 Hz, 1H; H-6′), 7.65 (d, J=15.8 Hz, 1H; H-α), 7.35 (d, J=15.8 Hz, 1H; H-α′), 7.28 (dd, J=8.0, 2.0 Hz, 1H; H-4′), 7.16 (d, J=8.0 Hz, 1H; H-3′), 2.42 (s, 3H; ring CH_3), 1.55 (s, 9H; $(CH_3)_3C$), 1.43 (s, 9H; $(CH_3)_3C$), 1.39 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 149.32, 148.39, 146.10, 136.42, 133.29, 133.23, 131.00, 130.47, 129.14, 129.09, 128.80, 128.45, 127.01, 125.19, 124.18, 123.93, 122.72, 38.44, 35.47, 34.71, 34.37, 31.66, 31.64, 19.72. Anal. Calcd for $C_{35}H_{41}Br$: C, 77.62; H, 7.63. Found: C, 77.86; H, 7.48.

4.1.20. 9-Bromo-1,11,13-tri-*tert*-butyl-4-methyl[5]phenacene (22). A solution of 1.50 g (3.3 mmol) of stilbene **21** and 0.8 g (3.1 mmol) of iodine in 1 L of cyclohexane was irradiated (Rayonet) for 48 h. The reaction mixture was washed with aqueous sodium bisulfite and water, and the organic layer was rotary evaporated. The residue was recrystallized from a mixture of 95% ethanol and hexanes to give 0.89 g (50%) of **22** as a pale yellow solid: mp 246.5–248.0°C; ^{1}H NMR δ 8.70 (s, 1H; H-14), 8.68 (d, J=9.3 Hz, 1H; H-7), 8.48 (d, J=9.3 Hz, 2H; H-6), 8.42 (br s, 1H; H-12), 8.27 (d, J=9.2 Hz, 1H; H-8), 8.03 (d, J=9.2 Hz, 1H; H-5), 7.90 (d, J=1.6 Hz, 1H; H-10), 7.83 (d, J=7.8 Hz, 1H; H-2), 7.40 (d, J=7.7 Hz, 1H; H-3), 2.74 (s, 3H; ring CH_3), 1.59 (s, 9H; $(CH_3)_3C$), 1.51 (s, 9H; $(CH_3)_3C$), 1.49 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 146.41, 146.32, 138.65, 133.95, 132.49, 132.10, 130.16, 129.10, 128.64, 128.57, 128.00, 126.92, 124.52, 123.80, 122.59, 119.87, 38.27, 38.08, 35.58, 34.84, 34.17, 31.71, 19.71. Anal. Calcd for $C_{35}H_{39}Br$: C, 77.91; H, 7.28. Found: C, 78.16; H, 7.07.

4.1.21. 9-Bromo-4-bromomethyl-1,11,13-tri-*tert*-butyl[5]phenacene (23). A procedure similar to that described above for benzylic bromide **2** was followed. A mixture of 0.46 g (2.6 mmol) of *N*-bromosuccinimide, 1.40 g (2.6 mmol) of methyl[5]phenacene **22**, a pinch of benzoyl peroxide, and 25 mL of carbon tetrachloride was heated under reflux for 24 h. The reaction mixture was cooled and filtered to remove succinimide. A small amount of silica gel was added to the filtrate, the mixture was filtered, and the resulting filtrate was rotary evaporated. Recrystallization of the residue from acetonitrile yielded 1.41 g (87%) of benzylic bromide **23** as a yellow solid: mp 145–150°C; ^{1}H NMR δ 8.70 (d, J=9.4 Hz, 1H; H-7), 8.65 (s, 1H; H-14), 8.62 (d, J=9.2 Hz, 1H; H-6), 8.42 (d, J=1.1 Hz, 1H; H-12), 8.29 (d, J=9.2 Hz, 1H; H-8), 8.19 (d, J=9.2 Hz, 1H; H-5), 7.91 (d, J=1.7 Hz, 1H; H-10), 7.87 (d, J=7.9 Hz, 1H; H-2), 7.60 (d, J=7.9 Hz, 1H; H-3), 5.04 (s, 2H; CH_2Br), 1.58 (s, 9H; $(CH_3)_3C$), 1.52 (s, 9H; $(CH_3)_3C$), 1.49 (s, 9H; $(CH_3)_3C$); ^{13}C NMR (45°C) δ 150.45, 146.65, 139.29, 133.96, 133.02, 132.88, 131.68, 131.00, 130.22, 129.37, 129.02, 128.85, 128.17, 127.56, 127.36, 125.00, 122.98, 122.65, 122.48, 121.16, 38.75, 38.54, 35.79, 35.86, 34.34, 32.51, 31.89. Anal. Calcd for $C_{35}H_{38}Br_2$: C, 67.97; H, 6.19. Found: C, 68.06; H, 6.31.

4.1.22. 9-Bromo-1,11,13-tri-*tert*-butyl[5]phenacene-4-carboxaldehyde (24). A procedure similar to that described above for aldehyde **18** was followed. The crude product obtained from reaction of 0.49 mL of a 21% w/w solution of sodium ethoxide in anhydrous ethanol (1.5 mmol of NaOEt), 10 mL of anhydrous ethanol, 0.14 mL (1.5 mmol) of 2-nitropropane, and a solution of 0.87 g (1.4 mmol) of benzylic bromide **23** in 40 mL of benzene was dissolved in toluene and washed sequentially with water, 10% aqueous sodium hydroxide, and brine. The organic layer was dried over sodium sulfate and filtered. The filtrate was rotary evaporated, and the residue was recrystallized from a mixture of toluene and 95% ethanol to give 0.42 g (54%) of aldehyde **24** as a yellow solid: mp 224–227°C; ^{1}H NMR δ 10.49 (s, 1H; CHO), 9.27 (d, J=9.3 Hz, 1H; H-5), 8.71–8.68 (m, 2H; H-6 and H-7), 8.61 (s, 1H; H-14), 8.42 (br s, 1H; H-12), 8.32 (d, J=9.1 Hz, 1H; H-8), 8.09 (A of AB q, J=7.9 Hz, 1H; H-2 or H-3), 8.03 (B of AB q, J=7.9 Hz, 1H; H-3 or H-2), 7.92 (d, J=1.7 Hz, 1H; H-10), 1.59 (s, 9H; $(CH_3)_3C$), 1.52 (s, 9H; $(CH_3)_3C$), 1.49 (s, 9H; $(CH_3)_3C$); ^{13}C NMR δ 193.27, 156.57, 146.76, 139.64, 133.98, 133.74, 132.81, 132.59, 131.39, 129.52, 129.45, 129.19, 129.14, 129.06, 128.58, 128.12, 127.30, 125.28, 123.47, 123.02, 122.57, 39.51, 38.59, 35.80, 34.69, 34.34, 31.88. Anal. Calcd for $C_{35}H_{37}BrO$: C, 75.94; H 6.74. Found: C, 75.84; H, 6.63.

4.1.23. (*E*)-1,2-Di-4-(9-bromo-1,11,13-tri-*tert*-butyl[5]phenacenyl)ethene (25). A procedure similar to that described above for diarylethylene **19** was followed. The crude product obtained starting from 0.085 mL (0.77 mmol) of titanium tetrachloride, 0.095 g (1.46 mmol) of Zn dust, and 0.406 g (0.73 mmol) of aldehyde **24** was recrystallized from a mixture of toluene and 95% ethanol to give 0.17 g (44%) of diarylethylene **25** as a bright yellow solid that did not melt below 350°C: ^{1}H NMR δ 8.72 (s, 2H; H-14,14′), 8.70 (d, J=9.1 Hz, 2H; H-6,6′ or H-7,7′), 8.53 (d, J=9.3 Hz, 2H; H-7,7′ or H-6,6′), 8.44 (br s, 2H; H-12,12′), 8.32 (d, J=9.3 Hz, 2H; H-5,5′ or H-8,8′), 8.29 (d, J=9.1 Hz, 2H; H-8,8′ or H-5,5′), 8.03 (A of AB q, J=8.1 Hz, 2H; H-2,2′ or H-3,3′), 7.95 (B of AB q, J=8.1 Hz, 2H; H-3,3′ or H-2,2′), 8.01 (s, 2H; H-α,α′), 7.91 (d, J=1.3 Hz, 2H; H-10,10′), 1.64 (s, 18H; $(CH_3)_3C$), 1.55 (s, 18H; $(CH_3)_3C$), 1.50 (s, 18H; $(CH_3)_3C$); ^{13}C NMR δ 148.76, 146.69, 139.31, 133.62, 133.11, 132.66, 131.11, 130.34, 129.74, 129.43, 129.35, 129.06, 128.14, 127.37, 124.85, 123.79, 122.50, 120.45, 38.53, 38.47, 35.72, 34.94, 34.36, 31.84. Anal. Calcd for $C_{70}H_{74}Br_2$: C, 78.20; H, 6.94. Found: C, 78.41; H, 6.90.

4.1.24. 4,15-Dibromo-2,17,19,21,24,26-hexa-*tert*-butyl[11]phenacene (17) from photocyclization of diarylethylene 25. A solution of 150 mg (0.14 mmol) of **25** and 230 mg (0.91 mmol) of iodine in 50 mL of toluene and 300 mL of hexanes was irradiated (Rayonet) for 27 h. The solution was filtered and the precipitated product was collected by

filtration and rinsed with hexanes to give 87 mg of **17** as a yellow solid that did not melt below 350°C. Based on the recovery of 30 mg of starting material **25** from the filtrate, the 87 mg of product that was obtained represents a 73% yield of **17**: ^{1}H NMR (1,4-dichlorobenzene-d_4, 100°C) δ 9.31 (s, 2H; H-9,10 or H-22,23), 8.93 (s, 2H; H-22,23 or H-9,10), 8.86 (A of AB q, J=9.3 Hz, 2H; H-7,12 or H-8,11), 8.70 (B of AB q, J=9.3 Hz, 2H; H-8,11 or H-7,12), 8.78 (s, 2H; H-20,25), 8.71 (d, J=9.5 Hz, 2H; H-6,13), 8.54 (br s, 2H; H-1,18), 8.32 (d, J=9.1 Hz, 2H; H-5,14), 7.92 (br s, 2H; H-3,16), 1.82 (s, 18H; $(CH_3)_3C$), 1.59 (s, 18H; $(CH_3)_3C$), 1.46 (s, 18H; $(CH_3)_3C$).

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