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Phenyl Groups versus *tert*-Butyl Groups as Solubilizing Substituents for Some [5]Phenacenes and [7]Phenacenes

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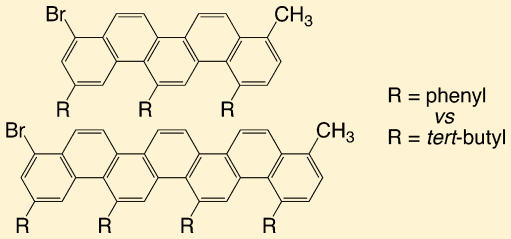
Supporting Information

ABSTRACT: In recent years, we have used the photocyclizations of diarylethylenes to synthesize a number of [*n*]phenacenes in the hope that they might be useful as the bridging groups for electron transfer processes in donor−bridge−acceptor molecules. Because [*n*]phenacenes with $n > 5$ are very insoluble, their synthesis and characterization has required the attachment of solubilizing substituents such as *tert*-butyl. The studies of Pascal and co-workers of some large polynuclear aromatic compounds having multiple phenyl substituents prompted us to explore the use of phenyls as alternative solubilizing groups for [*n*]phenacenes. Although phenyl groups turned out to provide significantly less solubilization than *tert*-butyl groups in these compounds, we found some interesting structural comparisons of the phenyl-substituted and *tert*-butyl-substituted [*n*]phenacenes.



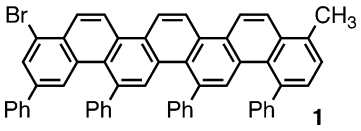
INTRODUCTION

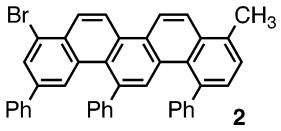
We have been investigating the family of large polycyclic aromatic compounds, for which we proposed the name [*n*]phenacenes[1−3] because they have *n* fused benzene rings in an extended zigzag phenanthrene-like structural motif. At the outset of our work, the largest known member of this family was the unsubstituted compound with $n = 6$, and our objective was to synthesize a series of [*n*]phenacenes with larger values of *n*. Much of our effort has been spent on finding suitable solubilizing groups that will allow the synthesis and characterization of these compounds. In our earliest work on [7]phenacene systems,[1,2] *n*-pentyl substituents were employed for this purpose, but after further exploration we switched to *tert*-butyl substituents because they lack reactive benzylic hydrogens and therefore allow a wider scope of synthetic pathways to be employed in the multistep construction of these compounds. Although we were successful in synthesizing several *tert*-butyl-substituted [7]phenacene and [11]phenacene systems,[1−3] we felt that the solubilizing capability of *tert*-butyl groups might be insufficient for our plans to synthesize a [15]phenacene. Inspired by Pascal's work[4] on the syntheses of large polynuclear aromatic molecules having multiple phenyl substituents, we explored whether phenyl groups might be more effective than *tert*-butyl groups in solubilizing [*n*]phenacenes.

RESULTS AND DISCUSSION

Syntheses. We report here the syntheses of two previously unknown compounds, the tetraphenyl-substituted [7]phenacene **1** (11-bromo-4-methyl-1,13,15,17-tetraphenyl[7]phenacene) and the triphenyl-substituted [5]phenacene **2** (9-bromo-4-methyl-1,11,13-triphenyl[5]phenacene).

All of our syntheses of [*n*]phenacenes over the years have employed the stilbene-to-phenanthrene type of oxidative photocyclization[5] for the sequential elongations of their aromatic backbones. As shown in Scheme 1, the syntheses of **1** and **2** each proceeded through the common intermediate 1-bromo-8-methyl-3,5-diphenylphenanthrene **3**. This compound was synthesized starting from the diazotization of 3-bromo-4-methylaniline **4** with nitrous acid followed by the addition of aqueous fluoroboric acid to give the tetrafluoroborate salt, and the subsequent treatment of the dry salt with potassium acetate in a benzene/acetonitrile solution under Gomberg−Bachmann[6,7] conditions to give biphenyl **5**. Treatment of **5** with *N*-bromosuccinimide gave benzylic bromide **6**, which was combined with triphenylphosphine to give phosphonium salt **7**. The treatment of **5** with *n*-BuLi followed by dimethylformamide gave aldehyde **8**, which was used in a Wittig reaction with phosphonium salt **7** to prepare a mixture of the *E* and *Z* isomers (as represented in Scheme 1 by a wavy bond) of stilbene **9**. This mixture of isomers was irradiated with visible light in a dilute cyclohexane solution containing a trace of iodine as a catalyst to give exclusively the pure *E* isomer for purification and characterization. Subsequent ultraviolet irradiation of the *E* isomer in hexanes with iodine as the oxidant caused a reversible *E*-to-*Z* isomerization accompanied by the oxidative photocyclization of the *Z* isomer to produce the





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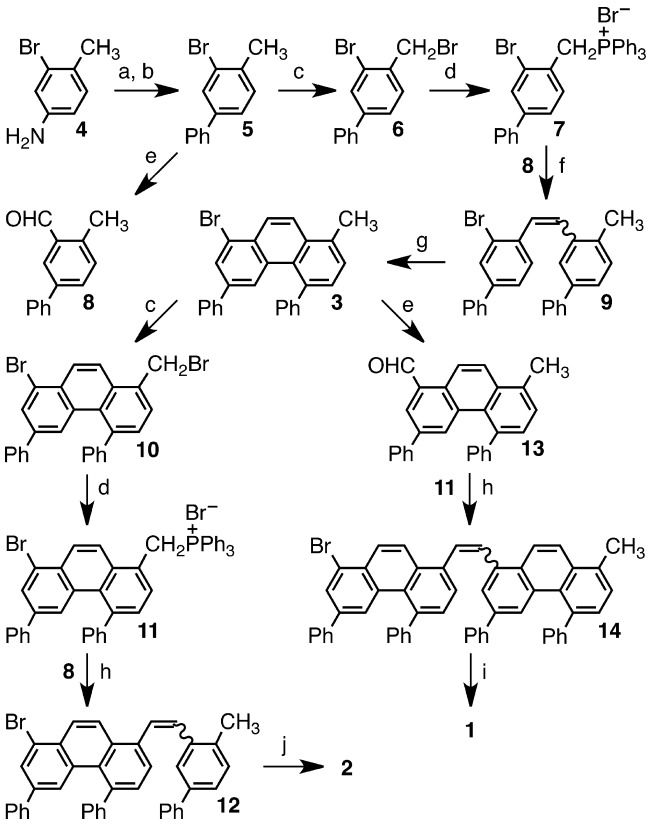
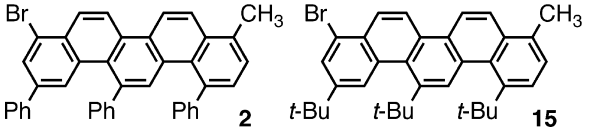
Scheme 1. Syntheses of [*n*]Phenacenes[a]



[a]Reagents and conditions: (a) HONO, aq HBF_4; (b) KOAc, benzene, CH_3CN; (c) NBS, CCl_4; (d) PPh_3; (e) *n*-BuLi, DMF; (f) 50% aq NaOH, CH_2Cl_2; (g) hν, I_2, hexanes; (h) *n*-BuLi, *i*-Pr_2NH; (i) hν, I_2, toluene; (j) hν, I_2, benzene.

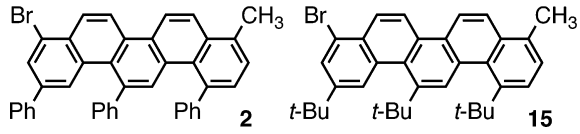
substituted phenanthrene **3**. Treatment of **3** with *N*-bromosuccinimide gave the benzylic bromide **10**, and the subsequent reaction of **10** with triphenylphosphine gave the phosphonium salt **11**. The Wittig reaction of **11** with aldehyde **8** gave a mixture of the *E* and Z isomers of diarylethylene **12**, from which the pure *E* isomer was obtained by the method described above for stilbene **9**. The ultraviolet photocyclization of the *E* isomer of **12** in benzene with iodine as the oxidant, following the method described above for the analogous preparation of **3**, produced the triphenyl-substituted [5]phenacene **2**. Treatment of the common intermediate **3** with *n*-BuLi followed by dimethylformamide gave aldehyde **13**, and a Wittig reaction of **13** with the phosphonium salt **11** gave diarylethylene **14**. The ultraviolet photocyclization of **14** in toluene with iodine as the oxidant produced the tetraphenyl-substituted [7]phenacene **1**.

Solubility Studies. In order to assess the effectiveness of phenyl substituents relative to *tert*-butyl substituents for the solubilization of phenacenes, the room-temperature solubility in benzene solution of triphenyl[5]phenacene **2** was compared directly with that of tri-*tert*-butyl[5]phenacene **15**.[3]



Two 4-mg samples of **2** and two 4-mg samples of **15** were each placed individually in one of four separate 10-mL round-bottom flasks containing small stir bars. The weight of each flask and its contents was recorded. Using a Pasteur pipet, benzene was added slowly with stirring to each flask at room temperature until only a small residue of solid remained, after which the four samples were allowed to stir for several hours. Additional benzene was then added dropwise very slowly to each of the stirred flasks until it appeared that the dissolution of the solids was complete. Each flask was then weighed, and the weight of benzene used to dissolve each sample was calculated by subtracting the initial weight of the flask, stir bar, and sample from the final weight that included the added benzene. The results of these measurements are given in Table 1. The phenyl

Table 1. Solubility Measurements in Benzene Solution

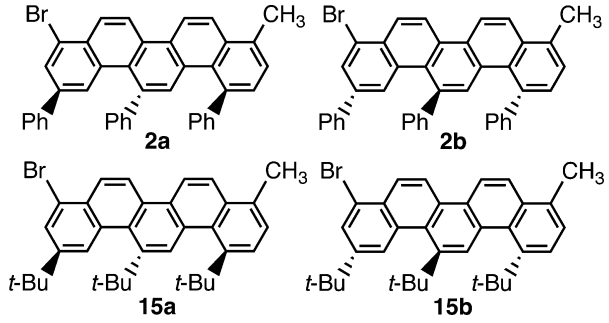


		sample amt		benzene[a,b] amt		solubility	
entry	cpd	mg	mmol	mg	mL	mol/L	ratio **15**/**2**
1a	**15**	4.0	0.0074	93.5	0.107	0.069	9.7
1b	**2**	4.0	0.0067	822.9	0.939	0.0071	9.7
2a	**15**	4.0	0.0074	92.6	0.106	0.070	10
2b	**2**	4.0	0.0067	836.6	0.954	0.0070	10

[a]Benzene density = 0.8765 g/mL. [b]Qualitatively, the solubility of **15** is also significantly larger than that of **2** in both hexanes and diethyl ether.

substituents in **2** proved to be about 10 times *less* effective than the *tert*-butyl substituents in **15** at solubilizing these two [5]phenacene systems in benzene. As discussed below, we believe this results from the crystal packing being more compact for **2** than for **15**. Qualitatively consistent with this, the melting point of **2** (290–291.5 °C) is higher than that of **15** (246.5–248.0 °C).

The intramolecularly adjacent pairs of phenyl substituents in **2** and *tert*-butyl substituents in **15** each undergo significant steric crowding against one another. As a consequence, these two compounds both exist as racemic mixtures as indicated below.



Our X-ray crystallographic determinations of the molecular structure and the crystal packing for the racemic mixture **2a** and **2b** are shown in Figure 1. The two phenyl groups that are attached in the two adjacent bay regions of the nearly planar [5]phenacene backbone each experience intramolecular steric crowding with the bay hydrogen on the other side of the same bay. As a consequence, these two phenyl groups are each twisted by about 60° around the single CC bonds that connect them to the [5]phenacene backbone, and they also are sterically forced by this crowding to bend in opposite directions above and below the approximate plane of the backbone. In contrast, the third phenyl group in the crystal of **2**,

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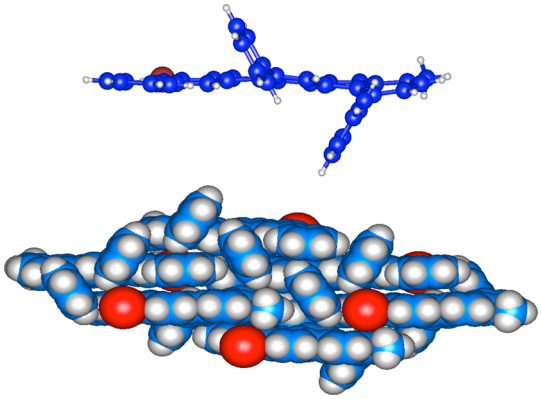


Figure 1. ORTEP representations of the X-ray crystallographic results for one molecule and also for a six-molecule cluster of the racemic phenyl-substituted [5]phenacene **2**.

which is attached to a nonbay carbon, is twisted out of the approximate plane of the backbone by only about 3°. This is reminiscent of the structure of biphenyl,[8] which in the gas phase has its two phenyl groups twisted by 44.4° around the bond linking them together, whereas in the crystal they are nearly coplanar because of the energetically favorable crystal packing between adjacent molecules.

For example, in the six-molecule cluster shown in Figure 1, the horizontal in-plane phenyl substituent on the molecule of **2** that is shown on the left half of the second layer from the top of the cluster experiences three intermolecular attractions: (a) a CH/π interaction between one of its ring hydrogens and the π system of the twisted phenyl ring that is bent slightly down from the phenacene molecule in the first layer of the cluster; (b) a CH/π interaction between its π system and an *ortho*-hydrogen from the twisted phenyl ring that is bent up from the molecule in the first layer; and (c) the π/π stacking of the horizontal in-plane extended π system of the phenyl group of interest in the second layer with the nearly planar phenacene backbone of the enantiomeric isomer of the molecule on the left half of the third layer of the cluster. Another example of a CH/π interaction involves the downward-pointing phenyl on the molecule of **2** on the right half of the second layer from the top and the phenacene backbone of the molecule of **2** in the fourth layer of the cluster. We suggest that this close packing accounts for the order-of-magnitude lower solubility reported in Table 1 for compound **2** relative to compound **15**.

Figure 2 shows the results of an RHF/6-31G calculation of an isolated single molecule of the analogous [7]phenacene system **16** using Gaussian 03, Revision B.05.[9] The nonbay phenyl substituent labeled A is calculated to be twisted by 43°, which suggests that a similar twist angle is likely for the nonbay phenyl group in the isolated single molecule of the related [5]phenacene **2**. This supports our conclusion that the twist angle of only 3° shown in Figure 1 for the analogous phenyl substituent in the crystal of **2** results from crystal packing effects.

We have been hampered in developing an explanation for the 10-fold greater solubility of the *tert*-butyl-substituted [5]-phenacene **15** as compared to that of the phenyl-substituted [5]phenacene **2** because we have been unable to grow an X-ray quality crystal of **15**. However, we previously determined the X-ray crystal structure[3] of the related *tert*-butyl-substituted [7]phenacene **17**, which we hoped would provide some insight into what would have been found from the analogous *tert*-butyl-substituted [5]phenacene **15**.

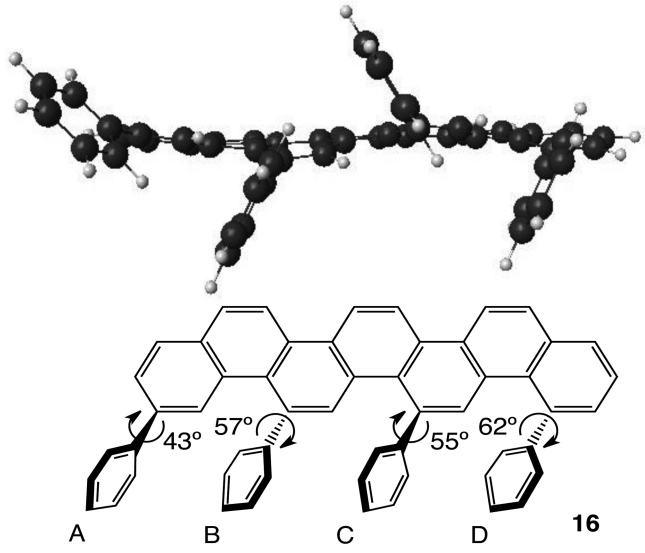
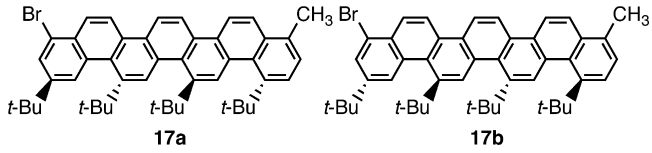


Figure 2. RHF/6-31G calculation[9] of the structure of a molecule of **16** and a visual representation of the magnitudes of the calculated twist angles between the phenyl substituents labeled A, B, C, and D and the [7]phenacene backbone.



Since *tert*-butyl groups are sterically more demanding than phenyl groups, they are forced to bend further above and further below the phenacene backbone in **17** than the analogous out-of-plane bending of the phenyl groups in **2** as shown in Figure 1. The phenacene backbone in **17** is somewhat more twisted than the phenacene backbone in **2**. The crystal packing pattern for the four-molecule cluster of **17** shown in Figure 3 is dramatically

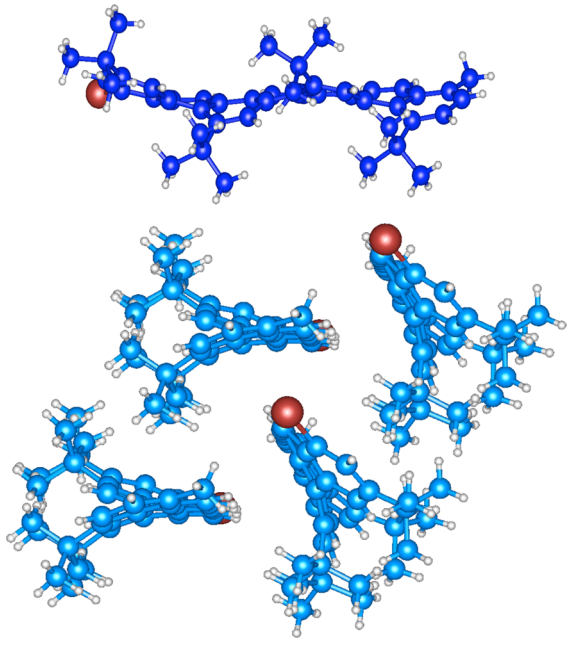


Figure 3. ORTEP representations of the previously reported[3] X-ray crystallographic results for the *tert*-butyl-substituted [7]phenacene **17**.

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different from the crystal packing pattern shown for the six-molecule cluster of **2** shown in Figure 1. The packing index for a crystal is defined as the percentage of the volume of the unit cell that is occupied by the atoms of the molecule. This is calculated by summing the volumes of all the individual atoms in the molecule using standard values of their van der Waals radii. We calculated these percentages for **2** and **17** using the PLATON program[10] and found that the packing index for the *tert*-butyl-substituted [7]phenacene **17** is only 64.8% whereas the packing index for the phenyl-substituted [5]phenacene **2** is 70.1%. On the assumption that the crystal packing index for the *tert*-butyl-substituted [5]phenacene **15** might be numerically similar to that for the *tert*-butyl-substituted [7]phenacene **17**, we suggest that this calculation may offer some support for our hypothesis that crystal packing is an important factor in accounting for the experimental finding given in Table 1 that the *tert*-butyl-substituted [5]phenacene **15** is 10-fold more soluble in benzene than the phenyl-substituted [5]phenacene **2**.

CONCLUSIONS

We have found that phenyl substituents are significantly less effective than *tert*-butyl substituents as solubilizing groups for [*n*]phenacenes such as **1** and **2**. We attribute this to the especially tight crystal packing that is illustrated in Figure 1 for the phenyl-substituted [5]phenacene **2** as contrasted with the crystal packing illustrated in Figure 3 for the *tert*-butyl-substituted [7]phenacene **17**. Phenyl substituents on [*n*]phenacenes can also be experimentally disadvantageous because the large number of phenyl hydrogens can sometimes obscure some of the ^{1}H NMR signals that are important for the verification of the molecular structures of those [*n*]phenacenes and their synthetic precursors. In our current work on the syntheses of large [*n*]phenacenes, we have solved the solubility problems by using modified *tert*-butyl groups in which one of the three methyl groups has been replaced by an *n*-octyl group.

EXPERIMENTAL SECTION

Photocyclizations were carried out in stirred solvents in Pyrex vessels surrounded by 16 300-nm lamps. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ solution at ambient temperature using TMS as an internal standard. Melting points were determined with an appropriate melting point apparatus and are uncorrected. Mass spectra were obtained using either GC–MS or HRMS instrumentation.

3-Bromo-4-methylbiphenyl (5). Concentrated HCl (50 mL) was added to a mixture of 30 g (0.16 mol) of 3-bromo-4-methylaniline **4** and 50 mL of water, and the mixture was cooled to −10 °C using an *i*-PrOH/dry ice bath. A solution of 15 g (0.22 mol) of $NaNO_2$ in 50 mL of water was added dropwise. After the addition was complete, 58.9 g (0.32 mol) of 48% HBF_4 was added slowly. The white precipitate that formed was collected by vacuum filtration, rinsed sparingly with cold water, cold methanol and cold diethyl ether, and then was dried overnight under a vacuum. A mixture of the dry fluoroborate salt, 1.44 L of benzene, 160 mL of acetonitrile, and 31.4 g (0.32 mol) of KOAc was then allowed to stir at room temperature for 6 h. The dark red mixture was filtered to remove insoluble impurities, and the solvent removed from the filtrate by rotary evaporation. The remaining oil was dissolved in 5% benzene in hexanes and poured though a plug of 1:1 silica/alumina. The solvent was removed, the oil redissolved in hexanes, and the solution poured though a short column of alumina. The oil remaining after rotary evaporation was vacuum distilled (bp 103–106 °C, 0.02 mmHg) to give 24.8 g (63%) of 3-bromo-4-methylbiphenyl **5** as a yellow oil (lit[11] mp 9 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (d, J = 1.8 Hz, 1H), 7.54–7.51 (m, 2H), 7.43–7.38 (m, 3H), 7.32 (tt, J = 7.2, 1.4 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 2.42 (s, 3H); GC–MS m/z 246/248 (M+). Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.49. Found: C, 63.26; H, 4.54.

(2-Bromo-4-phenylbenzyl)triphenylphosphonium bromide (7). A solution of 15.1 g (61 mmol) of 3-bromo-4-methylbiphenyl **5**, 10.9 g (61 mmol) of *N*-bromosuccinimide, and a small amount of benzoyl peroxide in 130 mL of CCl_4 was heated at reflux for 24 h. The reaction mixture was allowed to cool, and the succinimide was removed by vacuum filtration. The filtrate was rotary evaporated to give the benzyl bromide **6** as a yellow solid. Without further purification, **6** was dissolved in 91 mL of reagent grade acetone, and 16.1 g (62 mmol) of triphenylphosphine was added. The mixture was allowed to stir overnight at room temperature, after which the solid was collected by vacuum filtration, washed with toluene, and dried under a vacuum to give 26.2 g (71%) of phosphonium salt **7** as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83–7.72 (m, 9H), 7.68–7.61 (m, 8H), 7.50–7.34 (m, 6H), 5.75 (d, J = 14.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 30.6, 31.0, 117.0, 117.8, 126.2, 126.9, 127.6, 128.3, 129.0, 130.2, 131.1, 133.4, 134.3, 135.2, 138.4, 143.3. HRMS (ES+) Calcd for $C_{31}H_{25}BrP$ (M^+): 507.0877. Found: 507.0876.

2-Methyl-5-phenylbenzaldehyde (8). Biphenyl **5** (13.8 g, 56 mmol) was dissolved in 300 mL of anhydrous ether under N_2, and the solution was cooled in an ice bath while 55 mL (110 mmol) of 2 M *n*-BuLi in pentane was added dropwise, and the solution was then stirred in the ice bath for an additional 1 h. After 19 mL (245 mmol) of dimethylformamide was added dropwise, the mixture was allowed to warm to room temperature, after which it was quenched with 300 mL of 5% H_3PO_4. The aqueous layer was extracted twice with ether, and the ether extracts were washed 3 times with water and finally dried over Na_2SO_4. Removal of the solvent by rotary evaporation gave an orange oil that was vacuum distilled (bp 113–125 °C, 0.04 mmHg) to give a pale yellow oil that solidified on standing to give 10.0 g (92%) of **8** with mp 41.0–41.5 °C (lit.[12] mp 35.5–37.0 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.34 (s, 1H), 8.03 (d, J = 2.1 Hz, 1H), 7.71 (dd, J = 7.9, 2.1 Hz, 1H), 7.63–7.59 (m, 2H), 7.49–7.43 (m, 2H), 7.37 (tt, J = 7.3, 1.3 Hz, 1H), 7.34 (br d, J = 7.7 Hz, 1H), 2.71 (s, 3H); GC–MS m/z 196 (M+). Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.70; H, 6.23.

(*E*)-2-Bromo-2′-methyl-4,5′-diphenylstilbene (9). Phosphonium salt **7** (26.2 g, 44 mmol) was added to a solution of 9.8 g (50 mmol) of 2-methyl-5-phenylbenzaldehyde **8** in 60 mL of CH_2Cl_2. The resulting mixture was cooled in an ice bath, and 16 mL of 50% aqueous NaOH solution was added dropwise with vigorous stirring that was continued at room temperature for 6 h, after which the reaction mixture was poured into 100 mL of water. The aqueous layer was extracted 3 times with CH_2Cl_2, and the combined organic extracts were washed 3 times with water and then dried over Na_2SO_4. The solvent was removed by rotary evaporation, the orange residue was dissolved in hexanes, and the solution was filtered though a plug of silica to remove triphenylphosphine oxide. Rotary evaporation of the filtrate gave a mixture of *E* and *Z* isomers of alkene **9** as a yellow oil that was redissolved in 100 mL of cyclohexane, and a few crystals of iodine were added. The purple solution was stirred and irradiated with visible light from a 100-W tungsten bulb for 2 days to achieve *Z* to *E* isomerization. The solution was then washed with aqueous $NaHSO_3$ to remove the iodine, and the organic layer was dried over Na_2SO_4. The solvent was rotary evaporated to give a pale yellow solid that was recrystallized from 1:1 hexanes/toluene to give 14.7 g (79%) of **9** as a white crystalline solid with mp 115–117 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (d, J = 1.9 Hz, 1H), 7.85 (d, J = 1.9 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.64 (br d, J = 7.1 Hz, 2H), 7.59 (br d, J = 7.2 Hz, 2H), 7.56 (dd, J = 8.1, 1.8 Hz, 1H), 7.463 (t, J = 7.5 Hz, 2H), 7.456 (t, J = 7.3 Hz, 2H), 7.450 (A of AB q, J = 16.0 Hz, 1H), 7.447 (dd, J = 7.8, 2.0 Hz, 1H), 7.37 (br t, J = 7.2 Hz, 1H), 7.36 (br t, J = 7.3 Hz, 1H), 7.34 (B of AB q, J = 15.9 Hz, 1H), 7.27 (br d, J = 7.9 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 141.6, 140.8, 139.2, 139.0, 136.2, 136.0, 134.9, 131.2, 130.7, 129.1, 128.7, 128.53, 128.49, 127.6, 126,9, 126.8, 126.7, 126.5, 126.0, 124.4, 124.3, 19.4; GC–MS m/z 424/426 (M+). Anal. Calcd for $C_{27}H_{21}Br$: C, 76.24; H, 4.98. Found: C, 76.37; H, 5.16.

1-Bromo-8-methyl-3,5-diphenylphenanthrene (3). A solution of 2.63 g (6.18 mmol) of stilbene **9** and 0.80 g (3.2 mmol) of iodine in 1 L of silica-filtered hexanes was irradiated with 300-nm light for 42 h.

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When the reaction was complete as judged by GC−MS analysis, the hexanes were removed by rotary evaporation, and the resulting brown solid was dissolved in toluene. The red-purple toluene solution was washed with aqueous $NaHSO_3$ to remove the iodine. The toluene was removed by rotary evaporation to give a yellow solid that was recrystallized from 1:1 hexanes/toluene to give 2.38 g (91%) of beige crystals of phenanthrene **3** with mp 173.5−175.5 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.29 (br d, J = 9.4 Hz, 1H), 8.23 (dd, J = 1.5, 0.8 Hz, 1H), 8.07 (d, J = 9.4 Hz, 1H), 8.01 (d, J = 1.7 Hz, 1H), 7.56−7.49 (m, 3H), 7.51 (d, J = 7.4 Hz, 1H), 7.41 (br d, J = 7.4 Hz, 1H), 7.47−7.41 (m, 2H), 7.32−7.27 (m, 3H), 7.06−7.03 (m, 2H), 2.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 145.8, 139.2, 138.7, 136.9, 134.3, 132.19, 132.17, 130.7, 130.3, 129.3, 128.9, 128.7, 128.4, 127.7, 127.3, 127.2, 126.9, 126.5, 125.2, 124.4, 123.2, 20.0; GC−MS m/z 422/424 (M+). Anal. Calcd for $C_{27}H_{19}Br$: C, 76.60; H, 4.52. Found: C, 76.42; H, 4.40.

(8-Bromo-4,6-diphenyl-1-phenanthrylmethyl)triphenylphosphonium bromide (11). Phenanthrene **3** (0.90 g, 2.1 mmol) was dissolved in 15 mL of CCl_4, to which 0.37 g (2.1 mmol) of *N*-bromosuccinimde and a small amount of benzoyl peroxide were added. After the solution was heated at reflux for 24 h, the succinimide was removed by vacuum filtration, and the solvent was evaporated to give the bromomethyl compound **10** as a yellow solid. Without further purification, **10** and 0.63 g (2.4 mmol) of triphenylphosphine were dissolved in 10 mL of xylenes, and the solution was heated at gentle reflux overnight. After allowing the reaction mixture to cool to room temperature, vacuum filtration gave a pale yellow solid that was washed with cold xylenes and dried overnight under a vacuum to give 1.31 g, (82%) of the phosphonium salt **11**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (br s, 1H), 7.98 (d, J = 1.6 Hz, 1H), 7.83−7.71 (m, 12H), 7.60−7.46 (m, 10H), 7.35−7.26 (m, 5H), 7.03−7.00 (m, 2H), 6.14 (d, J = 14.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 144.9, 141.1, 138.9, 137.1, 134.9, 134.8, 134.6, 134.4, 132.8, 131.4, 131.0, 130.60, 130.56, 130.1, 130.0, 129.8, 129.5, 129.1, 128.7, 128.6, 127.6, 127.1, 127.0, 126.9, 125.5, 123.6, 123.5, 123.4, 123.1, 118.1, 117.3, 28.3, 27.8. HRMS (ES+) Calcd for $C_{45}H_{33}BrP$ (M^+): 683.1503. Found: 683.1503.

(*E*)-1-(8-Bromo-4,6-diphenyl-1-phenanthryl)-2-(2′-methyl-5′-phenyl)ethene (12). Phosphonium salt **11** (1.74 g, 2.3 mmol) was placed in 26 mL of THF under N_2, and to this white suspension was added a solution prepared from 6.5 mL of THF, 0.44 mL (2.5 mmol) of diisopropylamine, and 1.2 mL (2.4 mmol) of 2 M *n*-BuLi in pentane. This produced a bright red reaction mixture, indicating the formation of the ylid, to which was added a solution of 0.44 g (2.2 mmol) of 2-methyl-5-phenylbenzaldehyde **8** in 6.5 mL of THF. The resulting mixture was heated at reflux overnight, after which it was quenched with saturated aqueous NH_4Cl and then extracted three times with toluene. After the combined toluene extracts were washed with 70% EtOH to remove triphenylphosphine oxide, they were dried over Na_2SO_4. Evaporation of the solvent gave a mixture of the *E* and *Z* isomers of product **12**. This mixture was dissolved in hexanes, several crystals of iodine were added, and the purple solution was irradiated overnight with visible light from a 100-W tungsten bulb to achieve the *Z* to *E* isomerization. After the purple solution was washed with aqueous $NaHSO_3$ solution to remove the iodine, it was dried over Na_2SO_4. The solvent was removed by rotary evaporation to give a brown oil. A small amount of acetonitrile was added to the oil, and the mixture was sonicated for several hours to give 0.94 g (70%) of a yellow solid that was recrystallized from 1:1 hexanes/toluene to give **12** with mp 193−194 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.28 (br s, 2H), 8.24 (br d, J = 1.6 Hz, 1H), 8.02 (d, J = 1.6 Hz, 1H), 7.96 (br d, J = 1.7 Hz, 1H), 7.90 (br d, J = 15.7 Hz, 1H), 7.89 (d, J = 2.3 Hz, 1H), 7.71−7.68 (m, 2H), 7.56−7.27 (m, 15H), 7.07−7.04 (m, 2H), 2.53 (s, 3H). Anal. Calcd for $C_{41}H_{29}Br$: C, 81.86; H, 4.86. Found: C, 81.75; H, 4.64.

9-Bromo-1,11,13-triphenyl-4-methyl[5]phenacene (2). A solution of 100 mg (0.17 mmol) of alkene **12** and 110 mg (0.43 mmol) of iodine in 140 mL of benzene was irradiated with 300-nm light for 24 h, after which the reaction was judged complete by NMR analysis. The solvent was rotary evaporated, and the residue redissolved in toluene. Extraction with aqueous $NaHSO_3$ removed residual iodine, and the color of the solution faded to pale yellow. The toluene was removed by rotary evaporation, and the resulting 0.10 g (100%) of brown powder was recrystallized from 95% EtOH to give **2** as a white powder, mp 290−291.5 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.90 (d, J = 9.7 Hz, 1H), 8.83 (br d, J = 9.4 Hz, 1H), 8.69 (br d, J = 9.3 Hz, 1H), 8.29 (d, J = 9.4 Hz, 1H), 8.14 (v br s, 1H), 8.02 (d, J = 1.7 Hz, 1H), 7.96 (br s, 1H), 7.53−7.41 (m, 8H), 7.36−7.26 (m, 5H), 7.03−7.00 (m, 2H), 6.91−6.88 (m, 2H), 2.87 (s, 3H); UV peaks (cyclohexane) 279, 308, 340, and 355 nm (similar to the peaks of the *tert*-butyl analogue **15**[3] at 271, 305, 342, and 357 nm). Anal. Calcd for $C_{41}H_{27}Br$: C, 82.13; H, 4.54. Found: C, 82.37; H, 4.45.

8-Methyl-3,5-diphenylphenanthrene-1-carboxaldehyde (13). Phenanthrene **3** (2.2 g, 5.2 mmol) was dissolved in 190 mL of anhydrous diethyl ether. The solution was cooled to 0 °C under N_2, and 1.6 M *n*-BuLi in hexanes (8.3 mL, 13.3 mmol) was added dropwise. When the addition was complete, the reaction mixture was allowed to stir for 1 h, after which 2.0 mL (26 mmol) of dimethylformamide was added dropwise, the ice bath was removed, and the solution was allowed to stir for 2 h. The reaction was quenched with 5% H_3PO_4, and the layers were separated. The aqueous layer was extracted 3 times with toluene, and the combined organic layer was washed with aqueous $NaHCO_3$ and then with brine. After drying over Na_2SO_4, the solvent was rotary evaporated to give a solid that was recrystallized from toluene to give 0.66 g (34%) of **13** as a light yellow crystalline solid with a broad melting range (mp 117−145 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.57 (s, 1H), 9.19−9.16 (d, J = 9.5 Hz, 1H), 8.58 (d, J = 1.8 Hz, 1H), 8.21−8.18 (m, 2H), 7.56−7.43 (m, 7H), 7.33−7.32 (m, 1H), 7.31−7.30 (m, 2H), 7.10−7.09 (m, 2H), 2.83 (br s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 193.4, 145.9, 139.2, 138.7, 135.7, 134.5, 133.3, 133.2, 131.6, 131.0, 130.7, 129.6, 129.1, *ca.*128.71, 128.7, 127.9, 127.7, 127.0, 126.9, 126.1, 122.2, 20.1; GC−MS m/z 372 (M+). Anal. Calcd for $C_{28}H_{20}O$: C, 90.29; H, 5.41. Found: C, 90.55; H, 5.54.

(*E*)-1-(8-Bromo-4,6-diphenyl-1-phenanthryl)-2-(8′-methyl-3′,5′-diphenyl-1′-phenanthryl)ethene (14). Phosphonium salt **11** (1.03 g, 1.3 mmol) was combined with 30 mL of THF under N_2. A solution of 1.2 mL (1.9 mmol) of 1.6 M *n*-BuLi in hexanes, 0.4 mL (2.4 mmol) of diisopropylamine, and 7 mL of THF was added slowly though an addition funnel. The reaction solution turned red indicating the formation of the ylid. A solution of 0.50 g (1.3 mmol) of aldehyde **13** dissolved in 6 mL of THF was added with a syringe to the reaction flask, which was then heated slowly and allowed to stir overnight at gentle reflux. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution, and the aqueous layer was extracted twice with toluene. The combined organic layer was then washed with brine and finally dried over Na_2SO_4. The brown oil that remained after rotary evaporation was dissolved in hexanes and stirred overnight with an equal volume of 70% EtOH to remove triphenylphosphine oxide. A solid had formed, and the mixture was sonicated for 2 h before collecting 0.85 g (83%) of a yellow solid that was recrystallized from toluene to give **14** as a yellow powder, mp 237−248 °C (dec): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, J = 9.4 Hz, 1H), 8.29 (d, J = 9.4 Hz, 1H), 8.29 (br s, 1H), 8.27 (br s, 1H), 8.09−8.01 (m, 6H), 7.62−7.42 (m, 14H), 7.33−7.28 (m, 6H), 7.21−7.18 (m, 2H), 7.08−7.05 (m, 2H), 2.82 (s, 3H). Anal. Calcd for $C_{55}H_{37}Br$: C, 84.93; H, 4.80. Found: C, 84.76; H, 5.02.

11-Bromo-4-methyl-1,13,15,17-tetraphenyl[7]phenacene (1). A solution of 0.40 g (0.52 mmol) of alkene **14** and 0.24 g (0.95 mmol) of iodine in 300 mL of toluene was irradiated with 300-nm light for 6 h. The solid that formed during the irradiation was collected by vacuum filtration and washed with cold hexanes. Recrystallization of the solid from benzene gave 0.31 g (79%) of cream-colored phenacene **1**, mp >350 °C: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.10−8.89 (m, 4H), 8.51−8.49 (d, J = 8.86 Hz, 1H), 8.33−8.30 (d, J = 8.82 Hz, 1H), 8.13 (s, 1H), 8.02−7.99 (d, J = 6.7 Hz, 2H), 7.88 (s, 1H), 7.55−7.19 (m, 16H), 7.01 (m, 2H), 6.88−6.85 (d, J = 6.75 Hz, 4H), 2.36 (s, 3H). Anal. Calcd for $C_{55}H_{35}Br$: C, 85.15; H, 4.55. Found: C, 84.80; H, 4.80.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR spectra, ^{13}C NMR spectra, GC−MS data, HRMS data, and UV spectral data for key reaction products, X-ray crystallographic results (CIF) for compound **2**, and computational

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data for the structure of compound **16**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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