27, 104157-36-0; duroquinone, 527-17-3; 1,4-dihydroxy-2,3,5,6-tetramethylbenzene, 527-18-4; 1,4-dimethoxy-2,3,5,6-tetramethylbenzene, 13199-54-7; 1,4-diacetoxy-2,3,5,6-tetramethylbenzene, 5796-23-6; 2,3-dimethylbenzoquinone, 526-86-3; dimethyl 7-oxanorbornene-2,3-dicarboxylate, 4695-49-2; *all-exo*-2,3,5,6-tetrakis(hydroxymethyl)-7-oxanorbornane, 76196-51-5; benzoquinone, 106-51-4; naphthoquinone, 130-15-4; 6,7,12,13-tetrahydro-8,11-dihydroxy-6,13-epoxypentacene-1,4-dione, 104157-38-2.

Synthesis of a Soluble Nonacenetriquinone via a Bisisobenzofuran

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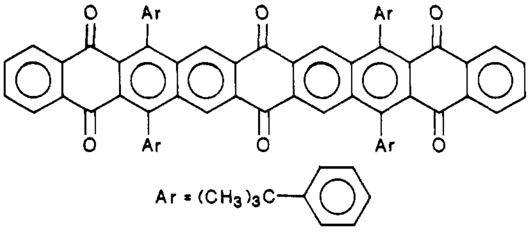
Received March 27, 1986

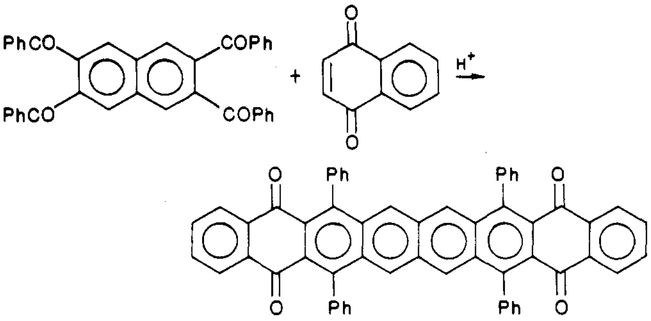
The known Diels–Alder reactions of 1,3-diarylisobenzofurans have been employed to develop a synthesis of a nonacenetriquinone (**1**). A 2:1 condensation of 2,5-bis(4-*tert*-butylphenyl)-3,4-diformylfuran (**17**) and cyclohexanedione gave the bisisobenzofuran **7**. This compound was treated with naphthoquinone and the resulting adduct was then aromatized to **1** by using trimethylsilyl triflate.

Organic chemists have a continuing interest in the synthesis and properties of large molecular frameworks. In this study we set out to develop a synthetic method for large, linear, polyquinoidal polyacenes and here report the preparation of the nonacenetriquinone (**1**). Considered in the context of polyacene hydrocarbons, like hexacene, quinoidal derivatives have interesting possibilities for variation of the electronic structure of the π-framework. It seems that by appropriately choosing quinone-, semiquinone- and hydroquinone-type groups the reactivity and the electrical, optical, and magnetic properties of these materials could be controlled.



1

Polyacenequinones have received sporadic attention. Although there are reports of such linearly annulated compounds with six to nine rings, the structure proofs are generally inadequate by modern standards. As with polyacene hydrocarbons, these long, flat molecules pack very well into crystals and are in general quite insoluble. This makes purification impossible and identification difficult. The synthetic methods previously employed include Friedel–Crafts reactions of phthalates,[1] aldol condensation[2] and Diels–Alder reactions.[3,4a] Compounds **2** and **3** are the largest compounds that have been well characterized. Compound **2** was isolated as red crystals and recrystallized from nitrobenzene,[2a] while **3** was a red-brown insoluble material.[2b]



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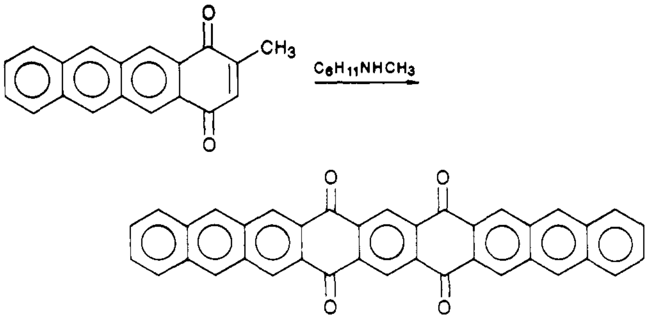

3

More recently a repetitive Diels–Alder approach to the synthesis of polyacenequinones has been devised and developed using tetramethylidene-7-oxanorbornane (**4**) as a reactant.[3] For example, benzoquinone and **4** were converted in several steps to the bis-diene **5**, which was then capped with naphthoquinone and converted to the eleven-ring quinone **6**.[3d,3e] Although **6** was totally insoluble

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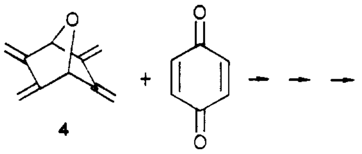

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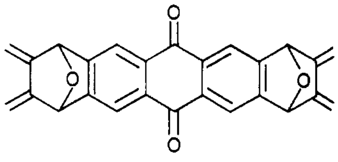

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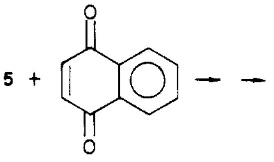
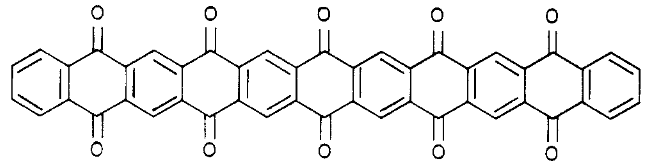
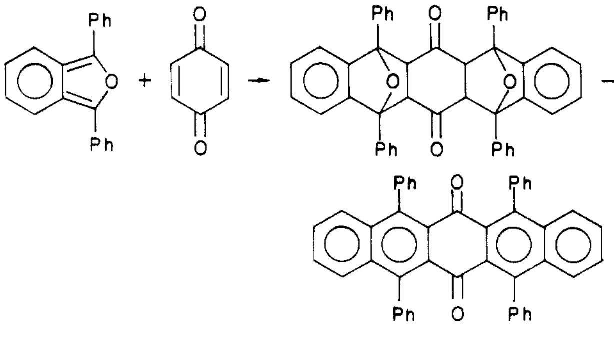




6

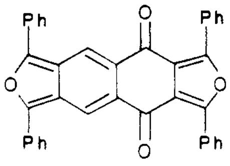
and, therefore, of doubtful purity, the repetitive Diels–Alder approach is still attractive.

The synthetic pathway to polyacenequinones investigated in this paper employs as its fundamental chemistry the Diels–Alder reaction of 1,3-diarylisobenzofurans with 1,4-quinones followed by the dehydrative aromatization of the Diels–Alder adduct (eq 1).[4a,5] This process has previously been reported for the synthesis of some relatively short polyacene derivatives.[4a] We speculated that



(1)

through the use of a bis(1,3-diarylisobenzofuran), this process could be adapted to grow large polyacenequinones of variable length. In principle, the use of solid support techniques would allow the controlled synthesis of these molecules. In addition, we conjectured that the aryl groups would improve the solubility of the polyacenequinones. Compound **7** was chosen as an appropriate bisisobenzofuran to investigate. It was expected that the electronic effects of the center quinone function of **7** would reduce the reactivity of this molecule as a diene in the Diels–Alder reaction. By analogy with the known 1,3-diphenyl-5,6-diformylisobenzofuran,[4b] however, compound **7** was anticipated to be sufficiently reactive. Although the isobenzofuran/furandione **8** is known,[2d] **7** appears to be the first bisisobenzofuran. To demonstrate the validity of the above concepts we report the synthesis of **7** and the reaction of **7** with naphthoquinone to give, after aromatization, the nonacenetriquinone **1**, *which is soluble.*



8

Results and Discussion

Prior to the preparation of **7** and **1**, the Diels–Alder/aromatization scheme was reinvestigated by using 1,3-diphenylisobenzofuran. The Diels–Alder reaction was found to proceed in high yield with both benzoquinone and naphthoquinone, but in our hands, the reported[4a] aromatization reaction was not observed with the bis adduct of benzoquinone. Instead extensive retro-Diels–Alder chemistry was observed. In the case of the Diels–Alder adduct with naphthoquinone it was found that the aromatization reaction could be induced with trifluoroacetic acid or boron trifluoride etherate in at least moderate yield and with trimethylsilyl triflate in 95% isolated yield. Upon the basis of the results of this reinvestigation and of previous considerations attention was turned to compound **7**. Its synthesis depended upon the development of a generalizable synthesis of 2,5-diaryl-3,4-diformylfurans. In this study *p*-*tert*-butylphenyl groups were chosen as the aryl groups. It was thought that the *tert*-butyls might improve solubility in the final product, and it turned out that they provided a convenient NMR marker in the synthesis.

The unsaturated 1,4-diketone **9** was prepared in 53% isolated yield by the Friedel–Crafts acylation of *tert*-butylbenzene with fumaryl chloride using aluminum chloride as catalyst. This diketone was reduced in essentially quantitative yield to the corresponding saturated diketone **10** with stannous chloride and hydrochloric acid in acetic acid.[6] Attempts were made to prepare compound **10** directly, by reacting (4-*tert*-butylphenyl)copper(I)[7–10] with succinyl chloride, but this approach did not succeed.[8–11]

Compound **10** was dehydratively cyclized to the 2,5-diarylfuran **11** in 94% yield with boron trifluoride etherate. This cyclization was, in our hands, effected in only moderate to low yields by using concentrated sulfuric acid[12] or polyphosphoric acid.[13] The corresponding 3,4-dibromofuran **12** was prepared in 95% yield by adding bromine to an ice-cooled solution of the furan **11** in chloroform.[14]

At this point in the synthesis the synthetic scheme temporarily diverged and proceeded by two different routes to the furandicarboxylic acid **15** (Scheme I). The route via the dilithiofuran **14** was short and convenient, but yields were very scale dependent. The route via the dicyanofuran **13** was scale independent and proceeded in high yields.

The dibromofuran **12** was converted in apparently almost quantitative yield to the dilithiofuran **14** by treatment with 5 equiv of *tert*-butyllithium at about −50 °C.[14–16]

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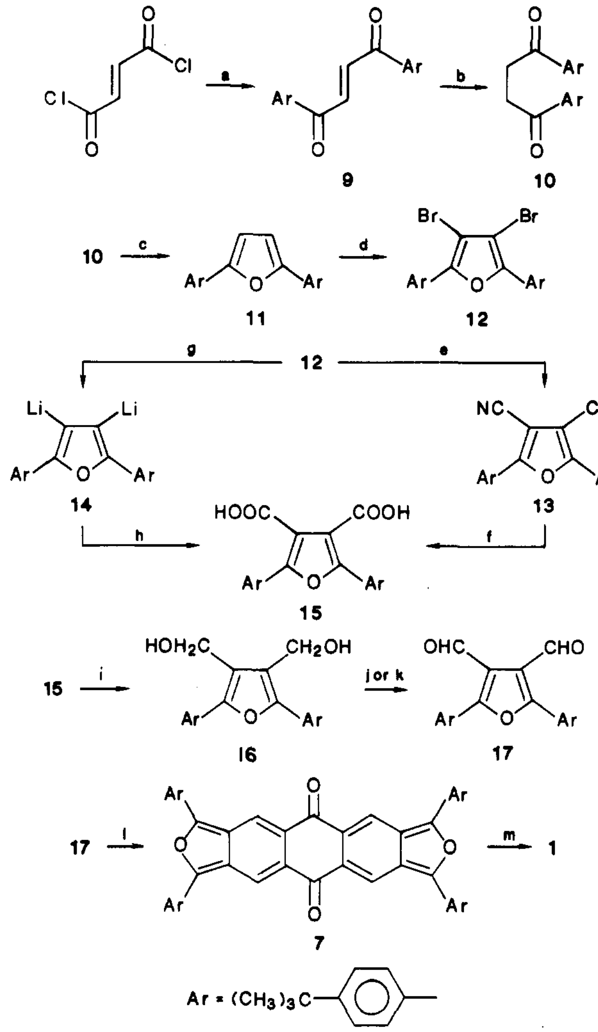
Scheme I[a]

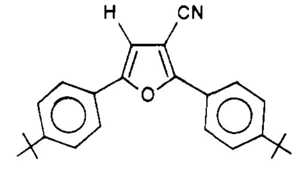


^{a}(a) $(CH_3)_3CPh$, $AlCl_3$, $CHCl_2CHCl_2$, room temperature, 2.5 h; (b) AcOH, $SnCl_2$, concentrated HCl, 50 °C, 5 min; (c) $BF_3{\cdot}OEt_2$, room temperature, 42 h; (d) Br_2, $CHCL_3$, 0 °C, 15 min; (e) CuCN, 1-methyl-2-pyrrolidinone, reflux, 5 h; (f) NaOH, $HOCH_2CH_2OH$, reflux, 126 h; (g) $(CH_3)_3CLi$, THF, −55 °C, 30 min; (h) CO_2, THF; (i) $BH_3{\cdot}THF$, THF, room temperature, 24 h; (j) Me_2SO, $(COCl)_2$, $(Et)_3N$, CH_2Cl_2, −55 °C, 15 min; (k) $BaMnO_4$, benzene, 75 °C, 4.25 h; (l) KOH, EtOH, 1,4-cyclohexanedione, room temperature, in the dark, 3 h; (m) naphthoquinone, $(CH_3)_3SiOSO_2CF_3$, $CHCl_3$, room temperature, in the dark, 24 h.

The yield of the dilithiofuran **14** was estimated by quenching the reaction mixture with water and then analyzing the reaction products by NMR and mass spectrometry. The results of such an experiment showed that the furan **11** was essentially the exclusive product, suggesting the efficient formation of its precursor, the dilithiofuran **14**. Neither *n*-butyllithium nor *sec*-butyllithium seemed to satisfactorily effect the transmetalation reaction, and less than 5 equiv of *tert*-butyllithium was also unsatisfactory.[15]

The dilithiofuran **14** was carboxylated to the furandicarboxylic acid **15** by using both gaseous and solid CO_2.[14-16] The yields were found to be quite variable, apparently depending on the reaction size. On a small scale (ca. 400 mg of **12**), using finely dispersed CO_2 gas, **15** was isolated in 61% yield. The same procedure on a large scale (1.26 g of **12**) gave **15** in only 11% yield. Using a very large excess of solid CO_2, **15** was obtained in 71% yield from about 200 mg of **12** and in 45% yield from 1.14 g of **12**.

The preparation of the furandicarboxylic acid **15** via the dicyanofuran **13** was clearly the better procedure for large-scale preparations. The dicyanofuran **13** was obtained from the dibromofuran **12** by treatment with anhydrous copper(I) cyanide (the Rosenmund–von Braun reaction) in refluxing 1-methyl-2-pyrrolidinone.[17] Dimethylformamide was investigated as a solvent for this reaction[18] but 1-methyl-2-pyrrolidinone was found to be preferable. The reaction product was found to be a mixture of the dicyanofuran **13** and the monocyanofuran **18** in an approximate ratio of 92:8. Attempts were made to prevent the formation of **18** by using carefully dried chemicals and glassware and by using pure copper(I) cyanide, but **18** was still formed. Pure dicyanofuran **13** was obtained by crystallization from heptane, leaving an approximately equal mixture of di- and monocyanofurans in the mother liquor. This mixture of **13** and **18** was not discarded but was used "as is" in the next reaction for the preparation of the furandicarboxylic acid **15** (vide infra).



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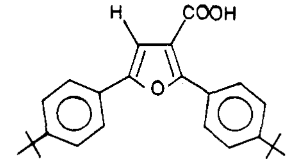
The pure dicyanofuran **13** was hydrolyzed by heating at reflux in a mixture of ethylene glycol and sodium hydroxide until the evolution of ammonia ceased.[19] The resulting furandicarboxylic acid **15** was obtained in 96% yield. The reaction time for this hydrolysis varied greatly depending upon (apparently) the reaction size, but this did not seem to affect the yield. When a mixture of the di- and monocyanofurans **13** and **18**, respectively, was hydrolyzed to the corresponding mixture of furan di- and monocarboxylic acids **15** and **19**, respectively, a satisfactory separation into the two components was accomplished simply by differential solubility in heptane. The combined yield of **15**, from pure **13** and from the mixture of **13** and **18**, as calculated from the dibromofuran **12**, was greater than 85%.



19

The furandicarboxylic acid **15** was reduced in essentially quantitative yield to the furan dialcohol **16** by treatment with borane in THF.[20] This furan dialcohol (**16**) was oxidized to the dialdehyde **17** in 75% yield with "activated Me_2SO" prepared from Me_2SO and oxalyl chloride.[21] This reaction was found to be clean, reproducible, and independent of the scale.

The oxidation of **16** to **17** was also accomplished (58% yield) with barium manganate in refluxing benzene.[22,23]

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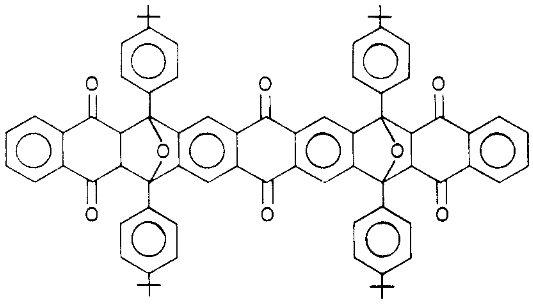
This reaction was heterogeneous and, in our hands, yields were not strictly reproducible. This barium manganate oxidation might, however, be the method of choice in some cases because of the much simpler procedure involved. Pyridinium dichromate (PDC)[24] was investigated as an oxidizing agent for **16**, but the yields of **17** were found to be quite low.

A number of attempts were made to prepare the furan dialdehyde **17** directly from either the dilithiofuran **14** or the dicyanofuran **13**. The dilithiofuran **14** was treated with an excess of an N,N-disubstituted formamide (both DMF and 1-formylpiperidine were employed), which after aqueous acid workup, did give the furan dialdehyde **17** but only in low yield.[25-27] The dicyano furan **13** was reduced with diisobutylaluminum hydride to give the furan dialdehyde **17** but again in only low yield.[28]

Compound **7**, a deep purple, light-sensitive solid, was prepared in apparently almost quantitative yield by the aldol condensation between 2 equiv of furan dialdehyde **17** and 1 equiv of 1,4-cyclohexanedione.[2] The ^{1}H NMR of the unpurified reaction product was consistent with the structure of compound **7** and essentially no other peaks were observed. Only one purple spot ($R_f \sim 0.9$ on silica gel developed with chloroform) was observed on TLC. Fast atom bombardment (FAB) mass spectrometry gave a parent ion (m/e 817 for the positive ion spectrum) which was the base peak. This bisisobenzofuran **7** was quite soluble in chloroform and toluene and seemed to be quite stable to heat and air in the absence of light. Upon exposure to light the purple solution became pale orange. Because of the sensitivity of this material to light, it was used, without further purification or characterization, directly in the next reaction.

The nonacene derivative **1** was prepared in 50% isolated yield by treating the purple solid **7** with 1,4-naphthoquinone and trimethylsilyl triflate in chloroform at room temperature. It is supposed that this reaction consists of a Lewis acid (Me_3Si^+) catalyzed Diels–Alder reaction[29,30] followed by a Lewis acid (Me_3Si^+) induced dehydrative aromatization to give the nonacene **1**. Compound **20** (the bis Diels–Alder adduct between the purple solid **7** and 1,4-naphthoquinone) is a possible intermediate in the reaction of **7** to **1**. However, if the dehydration reaction is faster than the Diels–Alder reaction, then the bis Diels–Alder adduct might not be formed, but rather cycloaddition followed by dehydration might occur on one side of **7** and then again on the other side.



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Aluminum chloride and boron trifluoride etherate were investigated as Lewis acids in this reaction.[29,30] When aluminum chloride was used the reaction mixture remained purple, indicating that the Diels–Alder reaction did not proceed. When boron trifluoride etherate was used, a low yield of **1** was obtained. In the absence of a catalyst the Diels–Alder reaction did not seem to proceed even at elevated temperatures. For example, when the purple solid **7** was heated at reflux in toluene with 1,4-naphthoquinone for 18.5 h, the reaction mixture was still a deep purple color. The use of high pressure, which is a thoroughly documented approach for inducing Diels–Alder chemistry, might facilitate the uncatalyzed Diels–Alder reaction.[31]

The nonacene derivative **1** is a bright yellow/gold solid which seems to be stable under normal conditions. It is quite soluble in chloroform and 1,1,2,2-tetrachloroethane and moderately soluble in dimethylformamide and toluene. The infrared spectrum of **1** showed the expected strong carbonyl absorbance at 1670 cm^{-1}, and the ^{1}H NMR spectrum was sharp and clean and showed six different kinds of protons. Downfield at δ 8.66 was a sharp four-proton singlet that was assigned to the aromatic hydrogens adjacent to the center quinone function. Two four-proton multiplets (δ 8.07–8.04 and 7.70–7.67) that closely resemble in both chemical shift values and in splitting pattern the aromatic protons of 1,4-naphthoquinone were assigned, by analogy, to the "α" and "β" hydrogens, respectively, of the terminal rings. Centered at δ 7.45 was the 16-proton AB doublet of the 4-*tert*-butylphenyls, and finally at δ 1.50 was the 36-proton singlet of the *tert*-butyl groups. Compound **1** was also characterized by ^{13}C APT NMR and fast atom bombardment (FAB) mass spectrometry. ^{13}C APT NMR uses a pulse sequence that produces a spectrum in which carbons with zero or two attached protons give a positive signal and carbons with one or three attached protons give a negative signal. The ^{13}C APT NMR results were consistent with the proposed structure **1**. The FAB mass spectrum gave a parent ion at m/e 1096 (negative ion spectrum), which was the base peak, and also gave high-resolution peak matching data which confirmed that the protonated parent ion (positive ion spectrum) had a molecular formula of $C_{78}H_{65}O_6$.

Conclusion. The original hypothesis that bulky *p*-*tert*-butylphenyl groups would solubilize such a large planar structure was validated. The synthetic approach that has been developed should be applicable to a variety of other aryl groups, and it seems that the bisisobenzofuran **7** should be useful for repetitive Diels–Alder processes with other quinones or diquinones.

Experimental Section

General Methods. Melting points were determined on a Mel-Temp capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Model 297, a Beckman AccuLab 1, or a Perkin-Elmer 1710 IRFT model infrared spectrophotometer and were calibrated with the 1601.8-cm^{-1} absorption of polystyrene. ^{1}H NMR spectra were measured at 79.5 MHz on a Varian CFT-20 instrument, at 200 MHz on an IBM-NR-200-AF instrument, and at 300 MHz on either a Nicholet NT-300-WB instrument or an IBM-NR-300-AF instrument. ^{13}C NMR were measured on an IBM-NR-300-AF instrument at 75.4 MHz. Chemical shifts were reported in δ units relative to internal Me_4Si. Electron-impact mass spectra were measured at 70 eV on an AEI MS-30 instrument. Fast atom bombardment (FAB) mass spectra were recorded at the University of Minnesota on a high-resolution VG-7070E-HF instrument using

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an ONPOE matrix and at the Midwest Center for Mass Spectrometry (MCMS), again with an ONPOE matrix. High-resolution FAB peak matching data were obtained at MCMS. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

(*E*)-1,4-Bis(4-*tert*-butylphenyl)but-2-ene-1,4-dione (9). A dry, nitrogen-purged 100-mL three-necked round-bottomed flask was fitted with a nitrogen bubbler, an overhead mechanical stirrer, a 30-mL pressure-equalizing dropping funnel, a thermometer, and a gas trap (for trapping the generated HCl gas). Aluminum chloride (13.4 g, 0.10 mol) and 1,1,2,2-tetrachloroethane (30 mL, freshly distilled) were added to the reaction flask, which was then cooled in an ice bath. Fumaryl chloride (4.53 mL, 0.042 mol, 98%) and *tert*-butylbenzene (19.44 mL, 0.126 mol) were added to the addition funnel and mixed to give a uniform solution. This solution was then added to the cooled reaction flask with vigorous stirring at a rate such that the reaction temperature remained below 10 °C (approximately 45 min). After the addition was completed, the reaction mixture was stirred with ice bath cooling for about 15 min, then the ice bath was removed, and the reaction mixture was allowed to warm to room temperature and was then stirred at room temperature for at least 2.5 h (letting the reaction continue overnight did not seem to affect the yield).

The reaction mixture was poured into a mixture of crushed ice and concentrated HCl. The aqueous phase was extracted with chloroform, and the combined organic phase was then washed with water, dried over sodium sulfate, and concentrated on a rotoevaporator to give an orange liquid. This liquid was concentrated further under high vacuum at a water bath temperature of about 55 °C. Almost 20 mL of colorless liquid distilled over, and the pot residue became a solid yellow paste.

The paste was dissolved in hot ethanol (50 mL) and crystallized at room temperature to give yellow crystalline plates (6.26 g, 43.8%). A second crop was obtained by concentrating the filtrate and cooling in the freezer for 3 days (small yellow plates, 0.74 g, 5.2%). A third crop was obtained from hexanes as solent (pale yellow crystals, 0.55 g, 3.8%). The combined yield of **9** was 52.8%. Physical data were collected on crop 1: mp 161.5–162.5 °C; ^{1}H NMR (acetone-d_6, 79.5 MHz) δ 8.10 (d, J = 7.2 Hz, 4 H), 8.01 (s, 2 H), 7.72 (d, J = 7.2 Hz, 4 H), 1.38 (s, 18 H); IR (KBr) 2955, 1644, 1601, 1566, 1461, 1404 cm^{-1}; mass spectrum, m/e 348 (parent ion); high-resolution mass spectrum calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2095. Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.70; H, 8.29.

1,4-Bis(4-*tert*-butylphenyl)butane-1,4-dione (10). A 250-mL three-necked round-bottomed flask was fitted with a nitrogen bubbler, a magnetic stirring bar, and a reflux condenser. To this flask were added acetic acid (40 mL), stannous chloride dihydrate (4.97 g, 22 mmol, handled under nitrogen), and concentrated HCl (6.2 mL). This mixture was heated in a water bath at 50 °C to give a clear colorless solution.

The diketone **9** (6.56 g, 18.82 mmol) was added to the reaction mixture in one portion with vigorous stirring, and any solid adhering to the side of the reaction vessel was washed into the reaction mixture with acetic acid (10 mL). After all of the solid dissolved to give a homogeneous solution (about 3–5 min at 50 °C bath temperature) the reaction mixture was heated for an additional 5 min. The reaction mixture was then poured into crushed ice immediately upon removal from the heating bath. The resulting white precipitate was collected by filtration and washed with water.

The white solid was crystallized from 95% ethanol (approximately 105 mL), collected by filtration, and washed with cold 95% ethanol to give white crystals (5.72 g, 86.7%). The mother liquor was concentrated under reduced pressure to give an off-white solid, which was crystallized from hexanes to give white crystals (0.369 g, 5.6%). The combined yield was 92.3%: mp 124–125 °C; ^{1}H NMR (acetone-d_6, 79.5 MHz) δ 8.04 (d, J = 8.7 Hz, 4 H), 7.63 (d, J = 8.7 Hz, 4 H), 3.45 (s, 4 H), 1.36 (s, 18 H); IR (KBr) 2951, 1670, 1605, 1616, 1463, 1399 cm^{-1}; mass spectrum, m/e 350 (parent ion); high-resolution mass spectrum calcd for $C_{24}H_{30}O_2$ 350.22457, found 350.2264. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.52; H, 8.67.

2,5-Bis(4-*tert*-butylphenyl)furan (11). A dry, nitrogen-purged, 250-mL, two-necked round-bottomed flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask were added the diketone **10** (6.0 g, 17.12 mmol) and then, via syringe at room temperature in one portion, boron trifluoride etherate (80 mL, freshly distilled from CaH as per Fieser and Fieser, *Reagents for Organic Synthesis*, Vol. I, pp 70). This reaction mixture, which quickly became a homogeneous clear orange-brown solution, was stirred at room temperature for 42 h at which time it had become a heterogeneous orange-brown mixture.

The reaction mixutre was then poured onto crushed ice (300–400 mL), and the precipitate was collected by filtration and washed with water to give a tan solid. This solid was crystallized from absolute ethanol (approximately 300 mL), collected by filtration, and washed with cold ethanol to give white crystalline needles (4.60 g, 80.8%). The mother liquor was concentrated to give a light brown solid, which was crystallized from 35 mL of ethanol to give tan crystalline needles (0.681 g, 11.97%). A third crop was obtained by concentrating the mother liquor from crop 2 to dryness and crystallizing the residue from nitromethane. The third crop was a pale tan powder, which appeared to be quite pure by TLC (0.078 g, 1.36%). The total combined yield was 94.2%. Physical data were collected on the white crystalline needles of crop 1: mp 165–166 °C; ^{1}H NMR (acetone-d_6, 79.5 MHz) δ 7.79 (d, J = 8.3 Hz, 4 H), 7.55 (d, J = 8.3 Hz, 4 H), 1.36 (s, 18 H); IR (KBr) 2961, 1486, 1460, 1359, 1255 cm^{-1}; mass spectrum, m/e 332 (parent ion); high-resolution mass spectrum calcd for $C_{24}H_{28}O$ 332.21401, found 332.2138. Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.86; H, 8.55.

3,4-Dibromo-2,5-bis(4-*tert*-butylphenyl)furan (12). The diarylfuran derivative **11** (2.12 g, 6.38 mmol) was added to a 200-mL uncovered round-bottomed flask containing a magnetic stirring bar. Chloroform (45 mL) was added to give a clear, homogeneous solution. The flask was cooled in an ice bath, and then bromine (2.04 g, 0.65 mL, 12.76 mmol) was added dropwise with stirring over about 15 min. (A possible procedural improvement might be to prepare a solution of bromine in $CHCl_3$ and add this solution rather than neat bromine.) After the addition of the bromine was complete the ice bath was removed, and the reaction mixture was stirred for approximately 15 min. The magnetic stirring bar was then removed, and the reaction mixture was concentrated under reduced pressure (on a rotoevaporator and then with a vacuum pump) to give a tan solid.

The tan solid was transferred, by using 20 mL of methanol, to a fritted glass funnel (medium porosity) without applied vacuum. The solid was ground to a fine powder under the methanol, and then the vacuum was applied to draw off the now orange liquid phase. This orange filtrate was discarded, but subsequent filtrates were not discarded. The vacuum was turned off, and 10 mL of methanol was added to the solid in the filter. The solid was again ground under the methanol, and then the vaccum was turned on. Then with the vacuum still on the solid was washed with 10 mL more of methanol. The solid was then a white powder (2.79 g, 89.25%), which was essentially pure by TLC (silica gel with hexanes, R_f 0.65).

The filtrates from the second and third washings were combined and concentrated under reduced pressure, and the residue was dissolved in dichloromethane and decolorized with activated carbon to give a near colorless solution. This solution was concentrated under reduced pressure and crystallized from ethanol to give white crystals (nuggets) (0.072 g). The total yield was 91.5%. Physical data were collected on material crystallized from ethanol: mp 151.5–152 °C; ^{1}H NMR (acetone-d_6, 79.5 MHz) δ 8.16 (d, J = 8.8 Hz, 4 H), 7.65 (d, J = 8.8 Hz, 4 H), 1.37 (s, 18 H); IR (KBr) 2970, 2905, 2890, 1503, 1490, 1457, 1362, 1265 cm^{-1}; mass spectrum, m/e 490 (parent ion, for the isomer containing one ^{79}Br and one ^{81}Br, the appropriate isotope pattern for two bromines was observed); high-resolution mass spectrum calcd for $C_{24}H_{26}{}^{79}Br^{81}BrO$ 490.03296, found 490.03296. Anal. Calcd for $C_{24}H_{26}Br_2O$: C, 58.80; H, 5.34. Found: C, 58.92; H, 5.49.

2,5-Bis(4-*tert*-butylphenyl)-3,4-dicyanofuran (13). A dry, nitrogen-purged, 100-mL three-necked, round-bottomed flask was fitted with a reflux condenser, a nitrogen bubbler, and a magnetic stirring bar. To this flask were added the dibromofuran **12** (5.07 g, 10.34 mmol, dried in a vacuum desiccator over P_2O_5), 1-methyl-2-pyrrolidinone (25 mL, dried over 4A molecular sieves), and copper(I) cyanide (3.7 g, 41.36 mmol). This mixture was heated at reflux for 5 h and then allowed to cool to about room temperature. The reaction mixture was poured into a 400-mL beaker, and then the reaction flask was rinsed into the beaker by using ~75 mL of an aqueous sodium cyanide solution (7.4 g of NaCN in 74 mL of H_2O). The contents of the beaker were stirred for approximately 5–10 min to allow the cyanide to completely complex with the copper species, then water (100 mL) was added, and the precipitate was collected by filtration, washed with water, and dried in a stream of air to give a grey solid.

The grey solid was given a preliminary purification by washing through a column of silica gel (50 g, 60–200 mesh) with chloroform using pressure as in flash chromatography.[32] Eight fractions of about 50 mL were collected. Most of the product came off as a tan band. Fractions two through seven were combined and concentrated to give a white solid (3.88 g), which gave two spots on TLC (silica gel with $CHCl_3$). This white solid was crystallized from heptane (320 mL) at room temperature to give beautiful white needles of **13** (3.12 g, 79%). The mother liquor was concentrated to give an off-white solid (730 mg, called MX(**13**,**18**) for future identification), which was shown to be a mixture of the dicyanofuran **13** (R_f ~0.6) and 2,5-bis(4-*tert*-butylphenyl)-3-cyanofuran (**18**, R_f ~0.7). This mixture was used without further purification in the next step. When the mixture was hydrolyzed to a mixture of mono- and dicarboxylic acids, "base line" purification was achieved by solubility differences (vide infra).

The white crystals of **13** were characterized: mp 245–247.5 °C; ^{1}H NMR ($CDCl_3$, 79.5 MHz) δ 8.01 (d, J = 8.8 Hz, 4 H), 7.58 (d, J = 8.8 Hz, 4 H), 1.36 (s, 18 H); IR (KBr) 2960, 2245, 1615, 1590 cm^{-1}; mass spectrum, m/e 382 (parent ion); high-resolution mass spectrum calcd for $C_{26}H_{26}N_2O$ 382.2045, found 382.2053. Anal. Calcd for $C_{26}H_{26}N_2O$: C, 81.64; H, 6.85. Found: C, 81.80; H, 6.86.

A small sample of **18** was obtained by preparative TLC (silica gel with $CHCl_3$) as an off-white solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.98 (d, 2 H), 7.67–7.44 (m, 6 H), 6.61 (s, 1 H), 1.36 (s, 9 H), 1.35 (s, 9 H); IR (KBr) 2997, 2257, 1622, 1517 cm^{-1}; mass spectrum, m/e 357 (parent ion).

2,5-Bis(4-*tert*-butylphenyl)-3,4-dicarboxyfuran (15). Method A. From 3,4-Dibromo-2,5-bis(4-*tert*-butylphenyl)furan (12). A dry, nitrogen-purged, 50 mL, two-necked, pear-shaped flask was fitted with a nitrogen bubbler and magnetic stirring bar. To this flask was added the dibromofuran derivative **12** (1.14 g, 2.33 mmol), then dry tetrahydrofuran (30 mL, freshly distilled from sodium and benzophenone) was added, and the flask was cooled in a 95% ethanol–dry ice bath (bath temperature −50 to −60 °C). To this cold solution was added dropwise with stirring over about 10 min a solution of *tert*-butyllithium (2.2 M in pentane, 5.3 mL, 11.67 mmol). After this addition was complete the resulting bright yellow solution was stirred with continued cooling for about 30 min.

This cold solution was transferred, via a double pointed needle, to a dry nitrogen-purged, 250-mL, three-necked, round-bottomed flask fitted with an overhead mechanical stirrer and containing a large excess of crushed solid CO_2. The transfer took about 10 min. This reaction mixture was stirred until it came to room temperature at which time it was concentrated on a rotoevaporator to remove the tetrahydrofuran. A white solid resulted. This solid was heated under high vacuum with a hot-air gun, and a clear colorless liquid distilled off (assumed to be pivalic acid), leaving a white powder. This powder was heated with about 30 mL of hexanes, allowed to cool to room temperature, collected by filtration, and washed with hexanes. This gave a white solid that, by NMR, was quite pure (0.445 mg, 45.4%, the yields were highly dependent upon the reaction scale, ranging from 11–71% and being inversely related to increasing reaction size). A microcrystalline material was obtained from carbn tetrachloride: mp, a change in physical appearance occurred between 130 and 135 °C; a second change in physical appearance occurred between 145 and 150 °C, and then the material melted to a clear liquid at about 246–250 °C; ^{1}H NMR ($CDCl_3$, 79.5 MHz) δ 7.81 (d, J = 8.3 Hz, 4 H), 7.51 (d, J = 8.3 Hz, 4 H), 1.36 (s, 18 H); IR (KBr) 2960, 1695, 1605, 1492 cm^{-1}; mass spectrum, m/e 420 (parent ion); high-resolution mass spectrum calcd for $C_{26}H_{28}O_5$ 420.19365, found 420.1941. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.27; H, 6.62.

Method B. From 2,5-Bis(4-*tert*-butylphenyl)-3,4-dicyanofuran (13). A mixture of dicyanofuran **13** (900 mg, 2.35 mmol), ethylene glycol (72 mL), and aqueous sodium hydroxide (3.0 M, 7.2 mL) was heated at reflux[33] with stirring until the evolution of ammonia ceased (as measured with a piece of wet pH paper held in the top of the condenser). The reaction mixture was heterogeneous at first but after about 1 h became a homogeneous bright yellow solution. The reaction mixture changed color during the course of the reaction from bright yellow to pale yellow to almost colorless, and this seemed to parallel the progress of the reaction. The total reflux time for this reaction was 126 h. The reflux time required was found to vary considerably with reaction scale, but this did not seem to affect the yield.

After the evolution of ammonia ceased the reaction mixture was let cool to room temperature and diluted with water (170 mL). This aqueous solution was acidified with 10% HCl (50 mL) and extracted with chloroform (4 × 55 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a viscous oil/semisolid. This material was thoroughly ground under H_2O (75 mL) to give a solid, which was collected by filtration, washed with water, and dried in a steam of air to give a white solid (949 mg, 96%), which was shown by ^{1}H NMR to be identical with compound **15** characterized in method A.

Method C. From a Mixture of 2,5-Bis(4-*tert*-butylphenyl)-3,4-dicyanofuran (13) and 2,5-Bis(4-*tert*-butylphenyl)-3-cyanofuran (18). In a 250-mL, round-bottomed flask were placed the off-white solid referred to as MX(**13**,**18**) in the procedure for the preparation of compound **13** (730 mg, this solid was a mixture of compounds **13** and **18**), ethylene glycol (60 mL), and aqueous sodium hydroxide (3.0 M, 6.0 mL). This reaction mixture was heated at reflux[33] with stirring until the evolution of ammonia ceased (as measured with a piece of moist pH paper, reaction time about 100 h). The workup procedure was similar to that of method B above and gave a slightly off-white solid (790 mg) that was a mixture of mono- and dicarboxylic acids **19** and **15**. This solid was heated at reflux in heptane (60 mL) for about 10 min, and then was allowed to cool to room temperature. The solid was collected by filtration and washed with heptane. A white solid was obtained (415 mg), which was shown by ^{1}H NMR to be essentially identical with compound **15** characterized in method A.

Upon concentration of the filtrate a pale tan solid (340 mg) was obtained which seemed to be almost pure **19**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.02 (d, 2 H), 7.67 (d, 2 H) 7.53–7.43 (m, 4 H), 7.09 (s, 1 H), 1.38 (s, 9 H), 1.35 (s, 9 H); IR (KBr) 2960, 1685 cm^{-1}: mass spectrum, m/e 376 (parent ion).

2,5-Bis(4-*tert*-butylphenyl)-3,4-bis(hydroxymethyl)furan (16). A dry, nitrogen-purged, 25-mL, two-necked, round-bottomed flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask was added the furandicarboxylic acid derivative **15** (440 mg, 1.048 mmol) and dry tetrahydrofuran (9 mL, freshly distilled from sodium and benzophenone). A rubber septum was inserted, and the flask was cooled in an ice bath. Borane–THF complex (1.0 M in THF, 2.72 mL, 2.72 mmol) was added dropwise with caution (delayed vigorous H_2 evolution may occur) to the stirred ice-cooled reaction mixture. The addition time was about 10 min. After the addition was complete the ice bath was removed, and the reaction mixture was allowed to stir at room temperatre for about 24 h.

The reaction mixture was then cautiously quenched with a 1:1 mixture of THF and water and then concentrated on a rotoevaporator to remove volatile organics. A little water was added to the concentrate, and this was then extracted with three portions of dichloromethane. The dichloromethane solution was filtered through Filter Aid and concentrated to dryness under reduced pressure to give a white solid (412.5 mg) in essentially quantitative yield. This solid was shown to be essentially pure by NMR. A microcrystalline material was obtained from carbon tetrachloride: mp 193–195 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (d, J = 8.3 Hz, 4 H), 7.47 (d, J = 8.3 Hz, 4 H), 4.82 (s, 4 H), 1.36 (s, 18 H);

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(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(33) A possible complication in this hydrolysis reaction arises from the conflicting requirements that while water is a necessary reagent the reflux temperature of ethylene glycol is 197 °C. No problems were encountered with this reaction in this laboratory, and we took no special precautions. To ensure the success of this hydrolysis, however, the reaction mixture must in some way be prevented from becoming dehydrated.

IR (KBr) 3350, 2978, 2915, 2879, 1509, 1499, 1360, 1264 cm^{-1}; mass spectrum, *m/e* 392 (parent ion); high-resolution mass spectrum calcd for $C_{26}H_{32}O_3$ 392.23513, found 392.2347.

2,5-Bis(4-*tert*-butylphenyl)-3,4-diformylfuran (17). Method A. A dry, nitrogen-purged, 100-mL, three-necked, round-bottomed flask was fitted with a nitrogen bubbler, a reflux condenser, and a magnetic stirring bar. To this flask were added the furan dialcohol derivative **16** (397.1 mg, 0.967 mmol) and dry benzene (24 mL, dried over 4A molecular sieves). After the mixture was stirred for several minutes, a clear, colorless, homogeneous solution resulted. Barium manganate (4.95 g, 19.34 mmol, crushed to a powder) was added in one portion, and the resulting heterogeneous reaction mixture was heated in an oil bath at 70–75 °C for 4.25 h (heating at reflux sometimes caused bumping and foaming).

The reaction mixture was then removed from the oil bath, cooled to room temperature, and filtered through Filter Aid. The dichloromethane solution was concentrated under reduced pressure, then redissolved in dichloromethane, and filtered again through Filter Aid. This dichloromethane solution was concentrated under reduced pressure to give a yellow solid, which crystallized from heptane to give pale yellow crystals (216 mg, 57.6%). Additional crystallization from heptane gave white needles upon which the physical data were collected: mp 145.5–146.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.44 (s, 2 H), 7.90 (d, J = 8.4 Hz, 4 H), 7.55 (d, J = 8.4 Hz, 4 H), 1.38 (s, 18 H); IR (KBr) 2961, 2901, 2865, 1680, 1653, 1601, 1559, 1533, 1485 cm^{-1}; mass spectrum, *m/e* 388 (parent ion); high-resolution mass spectrum calcd for $C_{26}H_{28}O_3$ 388.20383, found 388.2042. Anal. Calcd for $C_{26}H_{28}O_3$: C, 80.38; H, 7.26. Found: C, 80.21; H, 7.26.

Method B. A dry, nitrogen purged, 100-mL, three-necked, round-bottomed flask was fitted with two 10-mL pressure-equalizing dropping funnels, a nitrogen bubbler, a low-temperature thermometer, and a magnetic stirring bar. To this flask were added dichloromethane (17.5 mL, distilled from P_2O_5) and oxalyl chloride (0.772 mL, 8.85 mmol, freshly distilled), and then the flask contents were cooled in a dry ice–ethanol bath at −50 to −60 °C. To this reaction mixture was added, as quickly as possible while the reaction temperature was kept between −50 to −60 °C, a solution of Me_2SO (1.26 mL, 17.76 mmol, dried over 4A molecular sieves) in dry dichloromethane (3 mL). Addition time was about 4.5 min. After the addition was complete the reaction was stirred with cooling for about 2 min. Then a solution of the furan dialcohol **16** (1.13 g, 2.89 mmol) dissolved in dry dichloromethane (6 mL) and dry Me_2SO (0.35 mL, added to give a homogeneous solution) was added to the stirred reaction mixture as quickly as possible while the reaction temperature was maintained between −50 and −60 °C. The addition time was about 3.5 min. This mixture was stirred with cooling for approximately 25 min, and then triethylamine (6.2 mL, 44.5 mmol, dried over 4A molecular sieves) was added at such a rate that the reaction temperature remained between −50 and −60 °C (addition time about 3 min). This mixture was stirred with cooling for about 5 min, then the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature.

The reaction mixture was quenched with water and extracted with chloroform. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated on a rotoevaporator and then under high vacuum to give a yellow viscous oil that crystallized on standing. This material was dissolved in warm heptane, filtered, concentrated, and then crystallized from heptane (15 mL) to give very pale yellow crystals (613 mg, 54.6%). The mother liquor was concentrated to give a viscous orange-yellow oil, which was purified by flash chromatography[32] on silica gel (195 g, 230–400 mesh) with chloroform. Fractions containing pure **17** were combined and concentrated to give a tan solid (229 mg, 20.4%). Total yield was 75%.

Material prepared by method B was shown by ^{1}H NMR and TLC to be identical with compound **17** characterized in method A.

1,3,7,9-Tetrakis(4-*tert*-butylphenyl)anthra[2,3-*c*:6,7-*c*′]difuran-5,11-dione (7). A nitrogen-purged, 10-mL, two-necked, pear-shaped flask was fitted with a magnetic stirring bar and a nitrogen bubbler. To this flask were added the furan dialdehyde **17** (30 mg, 0.0772 mmol), 1,4-cyclohexanedione (4.33 mg, 0.0386 mmol), and ethanol (2.0 mL, nitrogen purged). This mixture was stirred for about 10 min to allow time for solubility (although the mixture remained heterogeneous), and then aqueous potassium hydroxide (0.76 M, 0.08 mL) was added, and the reaction mixture was quickly covered with aluminum foil and stirred in the dark for 3 h.

The reaction was worked up with minimum exposure to light and air. The reaction mixture was diluted with water and extracted with chloroform to give a deep purple chloroform phase. The chloroform extract was dried over Na_2SO_4 and concentrated under reduced pressure to give a deep purple solid (34 mg). This material was used without further purification, but TLC showed essentially just one purple spot and no starting material, and ^{1}H NMR indicated that it was quite pure: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.90 (s, 4 H), 7.92 (d, J = 8.43 Hz, 8 H), 7.55 (d, J = 8.46 Hz, 8 H), 1.41 (s, 36 H); FAB mass spectrum, *m/e* 816 (parent ion). This compound is very light sensitive and was not characterized further but was used directly in the next reaction.

6,10,17,21-Tetrakis(4-*tert*-butylphenyl)-5,8,11,16,19,22-nonacenehexone (1). A dry, nitrogen-purged, 10-mL, two-necked, round-bottomed flask was fitted with a nitrogen bubbler and a magnetic stirring bar. To this flask were added 1,4-naphthoquinone (30 mg, 0.190 mmol, sublimed), the purple compound **7** (34 mg, 0.0417 mmol) as a solution in chloroform (5 mL, dried over 4A molecular sieves), and then, in one portion via syringe, trimethylsilyl trifluoromethanesulfonate (0.5 mL, 2.59 mmol). This mixture was stirred in the dark (i.e., wrapped in aluminum foil) at room temperature for about 24 h.

The reaction was worked up by quenching with water, making basic with solid sodium carbonate, and extracting with chloroform. The combined organic extracts were washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to give a brown-yellow solid. This solid was triturated with acetone to leave a quite pure yellow solid (21 mg, 50% from compound **17**), which was essentially one spot on TLC (R_f ~0.5 on silica gel with $CHCl_3$). This material was purified further by flash chromatography[32] (silica gel with $CHCl_3$) to give a yellow/gold solid (19 mg, 45% from **17**). Crystals were obtained from 1,1,2,2-tetrachloroethane and chloroform: mp >360 °C (slowly darkens to a brown solid); ^{1}H NMR ($CDCl_3$, 300 mHz) δ 8.66 (s, 4 H), 8.06 (m, 4 H), 7.69 (m, 4 H), 7.61 (d, J = 8.16 Hz, 8 H) 7.23 (d, J = 8.31 Hz, 8 H), 1.50 (s, 36 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 183.95, 181.73, 150.62, 145.66, 137.87, 135.49, 134.80, 133.89, 131.43, 130.79, 130.61, 128.42, 127.06, 125.60, 34.83, 31.51; APT ^{13}C NMR ($CDCl_3$, 75.4 MHz) [carbons with 0 or 2 protons attached] δ 184.01, 181.60, 150.69, 145.73, 137.94, 135.56, 134.67, 131.50, 130.61, 34.90, [carbons with 1 or 3 protons attached] 133.96, 130.79, 128.50, 127.13, 125.67, 31.58; IR (KBr) 2989, 1649, 1579, 1408, 1325, 1249, 1101, 966 cm^{-1}; FAB mass spectrum, *m/e* 1096 (parent ion, negative ion spectrum); FAB high-resolution mass spectrum calcd for the protonated molecule $C_{78}H_{64}O_6$ 1097.4781, found (positive ion spectrum) 1097.4695.

Acknowledgment. This work was supported by the Office of Naval Research. The high-resolution FAB mass spectral determination was performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrument Faculty (Grant CHE 8211164). Acknowledgment of an NSF grant for the Minnesota mass spectrometer is also made.

Registry No. **1**, 103982-11-2; **7**, 103982-13-4; **9**, 103982-14-5; **10**, 103982-15-6; **11**, 103982-16-7; **12**, 103982-17-8; **13**, 103982-18-9; **14**, 103982-23-6; **15**, 103982-19-0; **16**, 103982-20-3; **17**, 103982-21-4; **18**, 103982-22-5; (*E*)-ClCOCH=CHCOCl, 627-63-4; $C_6H_5C(CH_3)_3$, 98-06-6; benzoquinone, 106-51-4; napthoquinone, 130-15-4; 5,5a,6,6a,7,12,12a,13,13a,14-decahydro-5,7,12,14-tetraphenyl-5,14:7,12-diepoxypentacene-6,13-dione, 104013-98-1; 1,3-diphenylisobenzofuran, 5471-63-6; 1,3-diphenylisobenzofuran, 5471-63-6; 5,12-diphenyl-5,5a,6,11,11a,12-hexahydro-5,12-epoxynaphthacene-6,11-dione, 103982-12-3.