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Repetitive Diels–Alder Reactions for the Growth of Linear Polyacenequinoid Derivatives

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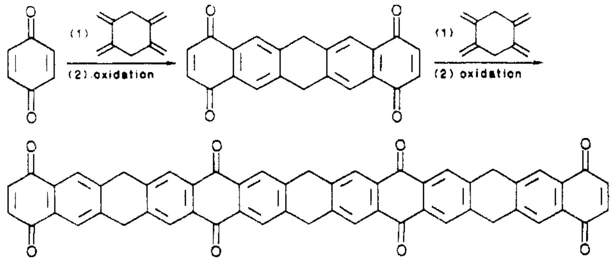
Starting from 2,3,5,6-tetramethylidene-7-oxanorbornane, repetitive quinone Diels–Alder/oxidation reactions produced a series of epoxypolyacenequinones with up to eleven linearly annulated rings. Epoxide ring opening–oxidation gave polyacenequinones with seven and eleven linearly annulated rings.

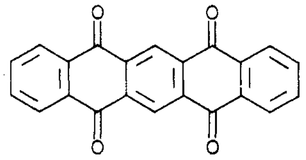
Our goal in this study was to develop a method for the synthesis of linear, multiring, polyquinoidal polyacenes. Such compounds are of theoretical and perhaps practical interest because of their electronic properties. Considered in the context of polyacene hydrocarbons, like hexacene, quinoidal derivatives have interesting possibilities for substantially varying the electronic structure of a large molecular framework, and by appropriately choosing quinone-, semiquinone-, and hydroquinone-type moieties the reactivity and the optical, magnetic, and electrical properties could be controlled. These functionalities might also be used to address the classic solubility problems that so restrict the study of linearly annulated polyacene hydrocarbons.[1] Lastly, these quinoidal groups also seemed to provide a synthetic advantage for the construction of such frameworks.

The synthetic route that has been explored here involves repetitive Diels–Alder reactions using appropriate bisdienes and quinones. Shown schematically in eq 1 is the conversion of monocyclic reactants to a quinoidal pentacyclic product and on in a second cycle to a tridecacyclic product. Continuation could in principle produce extraordinarily large, linearly annulated frameworks, and manipulation of the quinoidal or other groups could give desirable properties.



(1)

Previous polyacenepolyquinone syntheses fall primarily into three classes involving Friedel–Crafts,[2] aldol,[3] or Diels–Alder[4] condensations. For example, Mills has used Friedel–Crafts reactions of phthalates to prepare compound 1 in moderate yield.[2] In all this older work, the structure proof was based on elemental analysis and independent synthesis. Also prepared by this method were seven compounds with six to eight rings and varying numbers of quinones and hydroquinones. Only elemental analyses were obtained. No structural information was provided for a nine- or eleven-ring compound, each containing four hydroquinones and two quinones.



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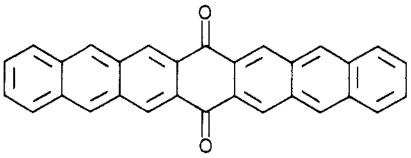

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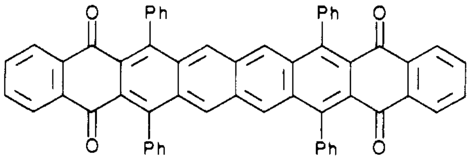

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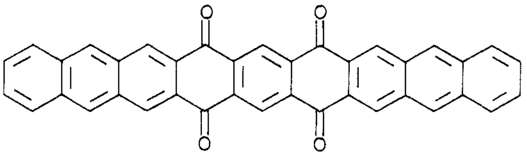

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Aldol condensations have been used to prepare six monoquinones with five, six, or seven rings, e.g., **2**.[3] Evidence has also been presented for the synthesis of the eight-ring compound, **3**.[4] The largest compound which has been reasonably characterized using spectroscopic techniques is **4**, prepared by base-catalyzed, oxidative dimerization of 2-methyl-1,4-tetracenedione.[5] In all cases these larger compounds are at best sparingly soluble. The single case where an NMR spectrum was reported used H_2SO_4 to protonate and solubilize the compound **1**. In a similar vein, mass spectra have seldom been reported, presumably because of the nonvolatility of these compounds.

Diels–Alder condensations of quinones and dienes have been reported to lead to one polyacenequinone with six rings[6] and several more thoroughly characterized products with five rings.[7] A variety of dienes and diene precursors have been treated with quinones to produce smaller products. Perhaps the most extensive studies have used *o*-xylylenes generated in situ from suitable precursors. Three of the most useful *o*-xylylene generating reactions are benzocyclobutene pyrolyses,[8] α,α'-dihalo-*o*-xylene re-

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(4) Lepage, L.; Lepage, V. *J. Heterocycl. Chem.* **1978**, *15*, 793.

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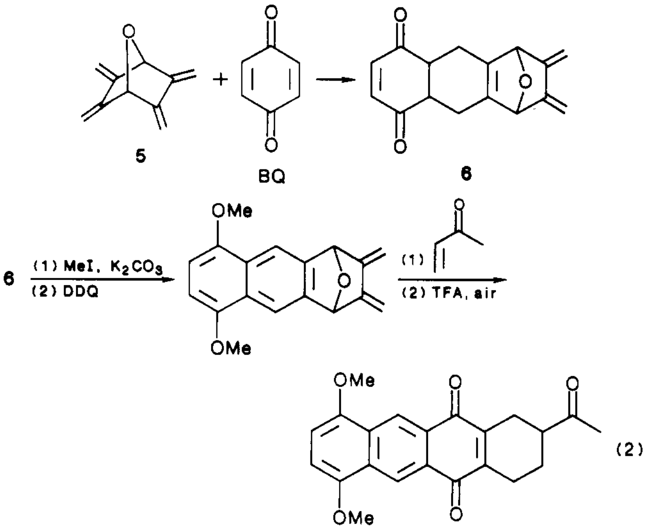
0022-3263/86/1951-4160$01.50/0

actions with iodide[9] and reactions of α-(trimethylammonio)-α′-(trimethylsilyl)-o-xylenes with fluoride.[10]

All of the above condensation methods and other relatives have been employed as tools in the recent drive to prepare anthracyclinone derivatives.[11] Of particular interest among these is the use of tetramethylidene-7-oxanorbonane **5** by Vogel and co-workers[12] as a bis-diene which could be sequentially condensed with two different Diels–Alder enes to build up the anthracyclinone skeleton. The epoxy bridge was opened with acid. The most pertinent reaction sequence is shown in eq 2. Compound **5** was attractive for repetitive Diels–Alder reactions because it was a selectively reactive bis-diene, because the epoxy bridge retained in intermediates was expected to help solubility and because there appeared an excellent prospect for versatility in the approach, depending on the structure of the two quinone enes and the type of epoxy ring opening–aromatization process employed.

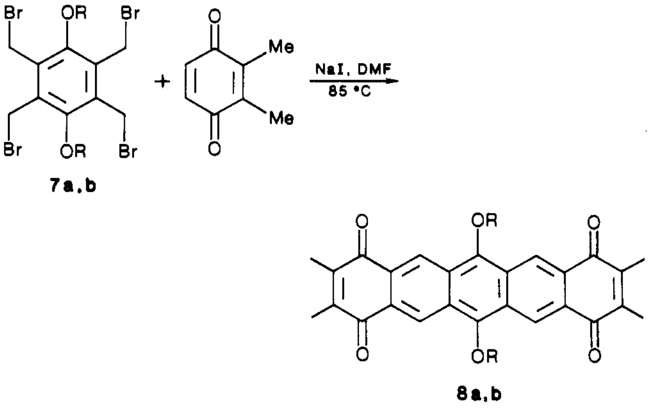


In the present study we have been able to begin with **5** and to demonstrate that the repetitive Diels–Alder, oxidation route could be used to construct molecular frameworks with up to eleven linearly annulated rings. We have also prepared two large polyacenequinones. As expected, solubility and volatility presented problems. Some of these problems were addressed synthetically, others were addressed by the use of two relatively new spectroscopic methods. Laser desorption Fourier transform mass spectrometer (LD-FTMS) was shown to be the mass spectroscopic method of choice for the analysis of these larger compounds.[13] For those polyacenequinones without solubility, ^{13}C cross-polarization, magic angle spinning (CP MAS) NMR spectroscopy was shown to give highly (1–2 ppm) resolved spectra on powder samples. Both techniques offer basic advantages for future studies and in principle could be employed to confirm the proposed structures from the literature, which were cited above.

Results

As indicated, some success has been achieved following the oxanorbornane **5** route. Our studies began, however, with an alternative pathway involving xylylene reactions. It may be instructive and it seems of some use to briefly summarize these results first. This will be followed by descriptions of the synthesis of epoxypolyacenequinones.

A Bisxylylene Route. Compounds that could be used to generate o-xylylene functionalities on both sides (1,2 and 4,5) of an aromatic ring were sought and, following the studies of LePage[9] and of Cava,[14] the reaction of iodide with a suitable tetra benzylic halide was explored. Two precursors (**7a,b**) proved to be accessible. Duroquinone was reduced with stannous chloride, methylated with methyl sulfate, and then brominated with N-bromosuccinimide, giving **7a**. In a similar way **7b** was prepared. These compounds were then reacted in DMF with iodide and 2,3-dimethylbenzoquinone. This quinone was chosen because it seemed likely that the product could be carried on by benzylic bromination to give a repetitive growth of larger acenes. The Diels–Alder reactions, including dehydrogenation, were successful, giving **8a** and **8b** in 18% and 21% yield, respectively. Compound **8a** was quite insoluble in all solvents, while **8b** was reasonably soluble in halogenated solvents and dissolved slightly in benzene or acetone. Structural identification was straightforward except for the mass spectra. These and all other large products generated in this study were very nonvolatile, and when high probe temperatures were used for electron-impact mass spectrometry (EI-MS) they underwent extensive decomposition. It was found that LD-FTMS[15] gave very useful, high-resolution, negative ion spectra for **8b** and for every other compound investigated. This technique uses the sample as a packed powder (neat or in KBr). Ionization and desorption comes from a CO$_2$-laser pulse. It seems an excellent analytical method for nonionic, nonvolatile, poorly soluble compounds.[13]



a, R = CH$_3$
b, R = CH$_3$CO

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[12] (a) Pilet, O.; Vogel, P. *Helv. Chim. Acta* **1981**, *64*, 2563. (b) Bessiere, Y.; Vogel, P. *Helv. Chim. Acta* **1980**, *63*, 232. (c) Carrupt, P.-A.; Vogel, P. *Tetrahedron Lett.* **1979**, 4533. (d) Tamariz, J.; Vogel, P. *Helv. Chim. Acta* **1981**, *64*, 188.

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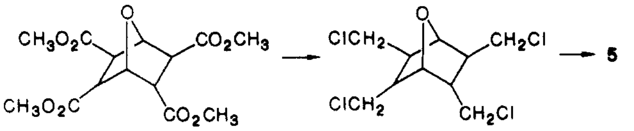
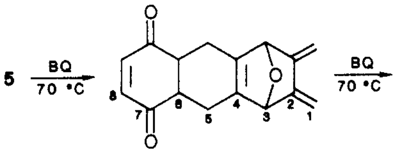
The Diels–Alder reactions were limited successes in that the yields were low and other similar reactions, e.g., **7a** with BQ, were even less successful. In all cases there were numerous byproducts. It seemed that *o*-xylylene intermediates were too reactive, and it was established that iodide reacted directly with quinones in DMF. Therefore, attention was turned to the more selective, direct reaction of **5** with quinones, in the absence of nucleophiles.

2,3,5,6-Tetramethylidene-7-oxanorbornane (5) Routes. Compound **5** was synthesized following the procedures of Vogel and co-workers[16] with minor modifications indicated in the Experimental Section. Following Diels–Alder addition of furan and maleic anhydride, a biscarbomethoxylation and esterification gave **9**. Reduction with lithium aluminum hydride and treatment with thionyl chloride gave tetrachloride **10**. Of particular utility was avoidance of isolation of **5**. This bis-diene is prone to polymerization and it is better to store quantities of **10**, generate **5** as needed, and react it without purification.



9 **10**

Reaction of **5** with BQ proceeded in refluxing CH_3CN to produce **6** in 91% yield, and using naphthoquinone (NQ) the adduct **11** formed in 83% yield. A complete double resonance study of the aliphatic protons in **11** revealed a proper assignment of the peaks to specific hydrogens as indicated in the Experimental Section. The stereochemistry of **6** which results from an endo-Diels–Alder addition was established by an X-ray structure on a derivative.[17] Similar stereochemistry presumably holds for **11**.



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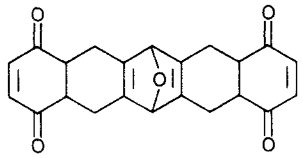

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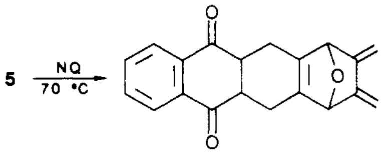

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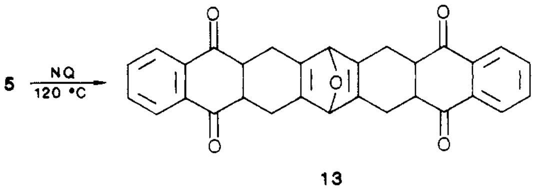
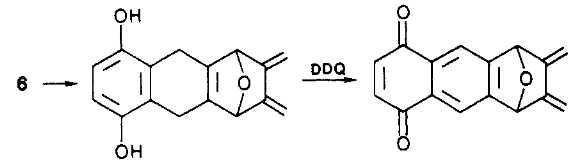
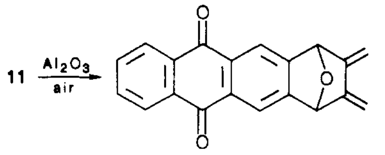


13

Synthesis of bis adducts **12** and **13** was possible by using either longer reaction times or higher temperatures. The products, which precipitated from the reaction mixtures were, however, extremely insoluble in all common solvents. This prevented purification and led to exploration of an alternative route to larger polyacenequinones. This route started with monoadduct **6**, which was tautomerized with K_2CO_3 in acetone to the hydroquinone **14** and then oxidized with DDQ to the key intermediate **15**. Even more simple was the oxidation of **11**, which was accomplished by stirring it in CH_2Cl_2 over alumina. It is presumed that alumina serves to tautomerize **11** to a naphthohydroquinone and that the oxidant is oxygen. This alumina air reaction did not take place with **6**, presumably because in comparison with **14**, a naphthohydroquinone from **11** should be more easily oxidized.



14 (80%) **15** (97%)



16 (96%)

It was great fortune to discover that the aromatized adducts **15** and **16** were reasonably soluble. This encouraged attempts to grow larger frameworks. In this regard **15** was a key intermediate since it could be converted to both a pentacyclic diquinone by using BQ and a pentacyclic bis-diene by using more tetraene **5**, and these could then be used repetitively for further growth. Indeed, reaction of **15** with BQ or NQ proceeded readily to give the adducts **17** and **18**. Similarly, **16** led to **19** and **20**. In all four cases the products could be mixtures of stereoisomers resulting from exo or endo addition. NMR gave no indication of isomers, however. Compounds **17**–**19** had reasonable or excellent solubility in halogenated solvents, while **20**, capped with NQ on both ends, was only weakly soluble in any common solvent.

The low solubility made it impossible to measure a solution-phase ^{13}C NMR spectrum for **20**. This problem was overcome, however, using solid-state NMR.[18] All the resonances in the ^{13}C CP-MAS spectrum, obtained on a powder, could be assigned to **20** on the basis of chemical shifts from model compounds run in solution. Assignments were confirmed by using interrupted decoupling to suppress ^{13}C lines from carbons with attached protons. EI-MS on **20** at 70 eV and 300 °C gave an appropriate high-resolution molecular ion, but the low spectrum intensity and visibly extensive pyrolysis indicated that the method was at its limit. Fast atom bombardment (FAB-MS) using several matrices including "magic bullet" (glycerol, tetraethanolamine, dithioerythritol, dithiothreitol) gave a molecular ion too weak for high-resolution measurements.[19] This probably resulted because **20** did not dissolve in the

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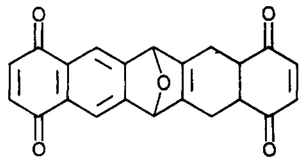
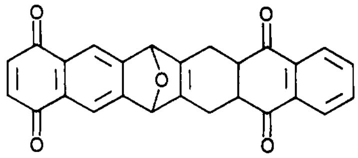
(18) Fyfe, C. A. *Solid-State NMR for Chemists*; CFC: Guelph, Ontario, 1983.

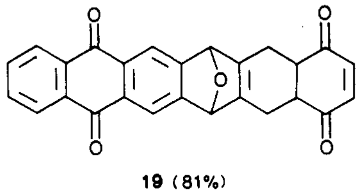
(19) This work was carried out under the direction of Dr. R. L. Cerny at the Midwest Center for Mass Spectrometry, University of Nebraska—Lincoln.



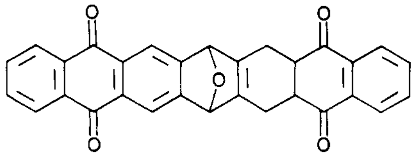
17 (56%)



18 (62%)



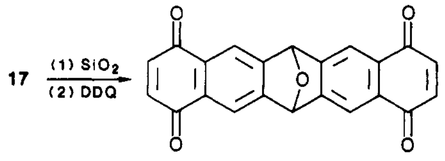
19 (81%)



20 (82%)

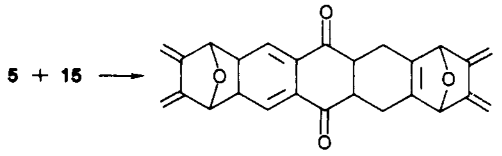
matrix. In contrast LD-FTMS with a solid sample gave an intense, high-resolution, negative ion spectrum with fragment ions from loss of H, H_2O, and $C_{10}H_6O_2$ (NQ).

The pentacyclic diquinone **17** was of special interest for the construction of larger frameworks. Therefore, it was tautomerized using silica (54% yield) and oxidized with DDQ to produce **21** (74%). Again, negative ion LD-FTMS proved useful. Retro-Diels–Alder cleavage being impossible, $(M-H)^-$ was the major ion. In contrast, EI-MS on **21** gave an inexplicable (M − 16) ion from loss of atomic oxygen and secondary ion mass spectrometry (SIMS) was unsuccessful.



21

The next goal was to prepare a pentacyclic bis-diene by using **15** and **5**. The Diels–Alder addition proceeded at 70 °C to give a 91% yield of an adduct **22**. Compound **22** could be composed of several stereoisomers. No attempt was made to separate these, and **22** was taken on by oxidation over alumina to the desired pentacyclic bis-diene **23** in 60% yield. Compound **23** was easily resolved into isomers with the oxygen bridges either syn or anti. The two isomers (R_f 0.2, 0.5; 1% acetone/CH_2Cl_2, alumina) had identical IR, MS, and ^1H and ^{13}C NMR spectra. The first component was assigned the syn structure because it had a lower R_f value. The anti structure has a center of symmetry and no dipole moment. The syn isomer is, therefore, more polar and can in principle more strongly bind to alumina by using both epoxy oxygens simultaneously.



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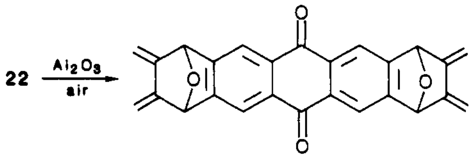
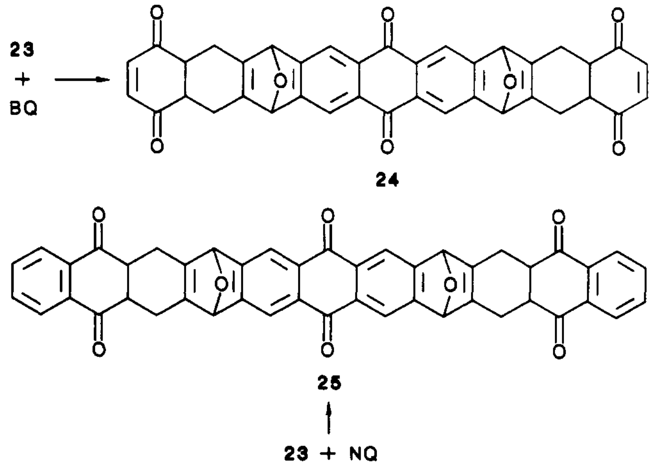


23

Studies intended to demonstrate the viability of the repetitive aspect of the approach have been undertaken using **23**. Since this bis-diene is relatively soluble, it seemed likely that the Diels–Alder addition would succeed, but it was unclear if the products would be soluble. Reaction of **23** in refluxing *o*-xylene with BQ gave **24** (62%), which was soluble in chloroform. Similarly, NQ gave **25** (59%), which had limited solubility. Both products gave high-resolution LD-FTMS spectra with major peaks from loss of H and retro-Diels–Alder cleavage. Again FAB-MS proved far less useful. Thus, the concept of repetitive Diels–Alder/oxidation reactions was demonstrated to be viable. Compound **24** is soluble, and it is an attractive candidate for further growth.



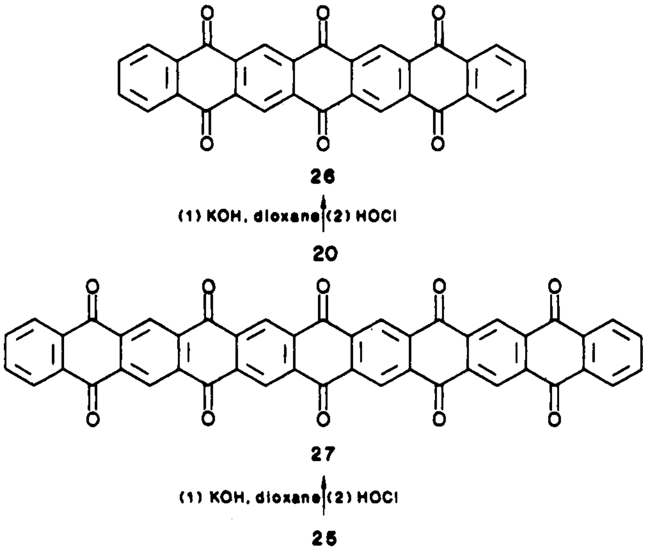
24

25

Next it was of interest to produce a fully oxidized and aromatized polyacenequinone product without epoxide bridges, and the conversion of **20** to **26** was selected as an appropriate goal. It was clear that without first attaching other solubilizing groups, products like **26** would be difficult to work with, but the potential of solid-state NMR and LD-FTMS made it worthwhile to try. Preliminary studies indicated that **20** would react with trifluoroacetic acid to a product tentatively identified as resulting from epoxide ring opening. Oxidation of this product with several reagents gave an insoluble product with IR and EI-MS data expected for **26**. Therefore, on a larger scale, **20** was dissolved in TFA and allowed to react in air for 27.5 h. An orange solid was collected, then suspended in dioxane, and treated with aqueous potassium hydroxide followed by hypochlorite. The IR spectrum of the product (74%) showed no indications of hydroxyl, ether, or aliphatic groups. In general, the spectrum was simple and similar to that of 9,10-anthraquinone as expected for structure **26**.

High-resolution EI-MS (positive ion) revealed the expected molecular ion for structure **26** with successive loss of CO molecules. The accurate mass LD-FTMS (negative ion) also indicated **26** was obtained. However, an unexpected peak of 904 amu was also observed in the LD-FTMS which was not observed by EI-MS. Recrystallization from boiling nitrobenzene produced a yellow microcrystalline material which did not show the 904 peak. Attempts to obtain satisfactory elemental analyses data on material which was repeatedly recrystallized (nitrobenzene) or extracted (chloroform, Soxhlet, 3 days) or sublimed (5 μm, 350 °C) were unsuccessful. It was not possible to acquire solution NMR data because this material was insoluble in all common solvents. However, the solid-state ^{13}C NMR spectrum further supported the structural assignment of **26**. One carbonyl signal was observed at 180 ppm. The interrupted decoupling spectrum was useful in assigning the four types of aromatic absorptions.

Work on removing the ether bridges of the bis adduct **25** was started, based on the method used for formation of **26**. The undecacene derivative **25** was stirred with TFA in the presence of air for 28 h. A dark red solid was collected and washed. A dioxane suspension of the red solid changed color to grayish blue on addition of aqueous potassium hydroxide. This suspension was then treated with hypochlorite. The color changed to a light yellow. Repeating the base and bleach treatment twice yielded a yellow suspension under alkaline conditions. The solid was separated and washed. The infrared spectrum indicated the absence of the ether bridges (840 cm^{-1}) and aliphatic functionality. The presence of a carbonyl and aromatic absorption were readily apparent. A spectrum of a Nujol mull weakly suggested the possibility of phenolic impurities. The LD-FTMS was acquired for this material. The molecular ion (728 amu, $C_{46}H_{16}O_{10}$) expected for undecacene-5,7,9,11,13,18,20,22,24,26-decone (**27**) was obtained. No ions of higher molecular weight were observed. An ion (714, $C_{46}H_{18}O_9$) not consistent with the expected fragmentation pattern was, however, apparent, and it is speculated that this material was not completely oxidized.



26

(1) KOH, dioxane (2) HOCl

20

27

(1) KOH, dioxane (2) HOCl

25

Discussion

The synthesis of large carbon frameworks has been pursued by several research groups interested in these compounds from a theoretical viewpoint.[20] Linearly annulated compounds of the type considered here have been primarily limited to polyacene hydrocarbons and quinones. It seemed important to approach the synthesis of such large frameworks in a systematic fashion and to develop a repetitive method that could be employed to grow larger and larger products. Repetitive Diels-Alder/oxidation pathways provide the first example of this systematic approach. Recognized at the outset was the problem of solubility. Any large, rigid molecule will have a tendency to precipitate. If the solubility is too low, structural identification will be difficult, and it will be nearly impossible to ascertain purity. Thus, any synthetic scheme should build in some measures to keep the intermediates and if possible the desired products soluble.

The results reported above provide a demonstration of the repetitive Diels-Alder/oxidation approach. Thus, the stepwise conversion of the monocyclic bis-diene **5** and BQ to the pentacyclic bis-diene **23** and on to the nonacyclic diquinone **24** shows the efficacy of the approach. Product **24** which is a candidate for further growth retains substantial solubility.

Frameworks that have been oxidized and aromatized to provide planar, polyacenequinone derivatives are of primary interest for study of their physical properties. Several routes, whereby the solubilizing oxygen bridge can be opened can be envisaged. In the present study we aimed at the simple polyquinones **26** and **27**. The structure proof for **26** is secure, but purity has not been unequivocally established. Compound **27** was clearly formed, but very limited data are available on this very insoluble material. The sequence employed which opened the oxygen bridge and then oxidized everything is of sufficiently high yield to be useful but may not be ideal. In other cases we have oxidized and then opened to form phenolic derivatives which have some solubility.[21] Clearly, the reductive conversion of quinone units to solubilizing ionic or bulky groups is an interesting possibility.

Finally, we note again the utility of LD-FTMS and ^{13}C NMR on insoluble solids. These techniques are indicated as being extremely important for the future. Our studies will continue, and information on the physical and electrochemical properties of these large, rigid frameworks is being collected.

Experimental Section

General Information. Preparative reactions were run with spectroscopic or HPLC grade solvents. Methanol was dried by treating with activated Linde-type 3A molecular sieves for 24 h. THF was freshly distilled from sodium and benzophenone (blue ketyl). Pyridine was dried over activated Linde-type 4A molecular sieves for 24 h. Acetonitrile was distilled from P_2O_5. Acetone was distilled from $CaSO_4$. Diglyme and *o*-xylene were distilled at reduced pressure from CaH_2.

Infrared spectra were obtained with a Beckman AccuLab 1 or 4250 instrument. ^1H NMR spectra were obtained with either a Varian FT-80 or a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were obtained from the same Nicolet instrument. Electron impact mass spectra were obtained on an AEI-MS30 instrument. The laser desorption mass spectra were obtained from the University of California—Riverside on a spectrometer that has been described.[15] Melting points were determined with a Mel-Temp apparatus and are uncorrected. Elemental analyses were obtained from M-H-W Laboratories.

1,4-Dihydroxy-2,3,5,6-tetramethylbenzene. To a suspension of duroquinone (1.03 g, 6.3 mmol) in ethanol (5 mL) was added a solution of stannous chloride (2.74 g, 12.2 mmol) in dilute hydrochloride acid (25 mL). The mixture was warmed on a hot plate with stirring until the yellow color disappeared. The product appeared on cooling and was vacuum filtered. Recrystallization from dilute ethanol containing a little stannous chloride and hydrochloric acid yielded white needles (1.05 g, 6.3 mmol, 100%),

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mp 231–232 °C (lit.[22] mp 233 °C).

1,4-Dimethoxy-2,3,5,6-tetramethylbenzene. In a three-necked, round-bottomed flask equipped with stirrer, condenser, and addition funnel was placed a mixture of durohydroquinone (4.04 g, 24.3 mmol), dimethyl sulfate (20 mL, 210 mmol), and MeOH (20 mL). Under a N_2 atmosphere, a saturated solution of potassium hydroxide in methanol was added dropwise until the mixture was alkaline (1.5 h). The mixture was gently warmed during this addition. The solution was acidified with sulfuric acid. After the methanol was concentrated, the mixture was added to water (100 mL) and extracted with diethyl ether (3 × 100 mL). The ether extracts were combined and washed with water (100 mL). The organic layer was dried with $MgSO_4$ and evaporated in vacuo. Recrystallization from methanol produced white needles (3.56 g, 18.4 mmol, 76% yield): mp 112–114 °C (lit.[23] mp 112–115 °C); IR (KBr) 3000 w, 2962 w, 2855 w, 1458 m, 1380 s, 1360 vs, 1320 vs, 1065 s, 1025 s, 760 s, 750 s. The NMR data were in excellent agreement with those of the literature.[24]

1,4-Dimethoxy-2,3,5,6-tetrakis(bromomethyl)benzene (7a). A solution of 1,4-dimethoxy-2,3,5,6-tetramethylbenzene (4.54 g, 23.4 mmol), NBS (32.9 g, 184.8 mmol), and a spatula tip of dibenzoyl peroxide in 300 mL of dry carbon tetrachloride was refluxed under a nitrogen atmosphere for 3 h. After cooling to room temperature, the white precipitate was collected by filtration. The product was recrystallized from acetone (first crop, 10.3 g, 20.2 mmol; second crop, 0.54 g, 1.1 mmol): mp 218–220 °C; TLC (silica gel dichloromethane) R_f 0.65; IR (KBr) 2930 w, 2830 vw, 1460 s, 1435 m, 1410 s, 1275 vs, 1210 m, 1195 m, 1140 m, 1020 vs, 925 m, 830 m, 630 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.75 (s, $ArCH_2Br$), 4.05 (s, $ArOCH_3$); EI-HRMS calcd for $C_{12}H_{14}{}^{79}Br_4O_2$ (M^+) 505.7726, found 505.7688; EI-MS, m/z (ion$^+$, relative intensity) 512 ($M^{81}Br_3$, 8.4), 510 ($M^{81}Br_2$, 14.1), 508 ($M^{81}Br$, 10.4), 506 (M, 2.2), 433 ($M^{81}Br_3 - Br$, 31.9), 431 ($M^{81}Br_2 - Br$, 97.8, 429 ($M^{81}Br - Br$, 100.0), 427 (M − Br, 32.5), 349 (M − 2Br, 2.2), 269 (M − 3Br, 50.4), 190 (M − 4Br, 64.9), 175 (M − 4Br − CH_3, 34.1). Anal. Calcd for $C_{12}H_{14}Br_4O_2$: C, 28.27; H, 2.77; Br, 62.69. Found: C, 28.46; H, 2.94; Br, 62.51.

1,4-Diacetoxy-2,3,5,6-tetramethylbenzene. Duroquinone (10.48 g, 63.8 mmol) was dissolved in acetic acid (150 mL) and acetic anhydride (300 mL). Zinc dust (15.52 g) and sulfuric acid (3 mL) were added. Under a nitrogen atmosphere, the mixture was refluxed until colorless (45 min). The zinc was collected by hot filtration and the filtrate concentrated in vacuo. Recrystallization from ethanol produced white needles (14.39 g, 57.6 mmol, 90.1% yield): mp 206–208 °C (lit.[25] mp 202–203 °C, lit.[22] mp 207 °C); ^{1}H NMR ($CDCl_3$) δ 2.33 (s, ArO_2CCH_3), 2.04 (s, $ArCH_3$).

1,4-Diacetoxy-2,3,5,6-tetrakis(bromomethyl)benzene (7b). 1,4-Diacetoxy-2,3,5,6-tetramethylbenzene (6.15 g, 24.6 mmol), NBS (23.36 g, 131 mmol), and a spatula tip full of dibenzoyl peroxide were placed in a flask equipped with a reflux condenser. Under an atmosphere of nitrogen, 600 mL of dry carbon tetrachloride was added. The reaction mixture was refluxed for 19 h. After cooling to 0 °C, the crude product was filtered off. The crude product was washed with 350 mL of hot acetone. The white crystals of **7b** (11.53 g, 20.5 mmol, 83%) were collected by filtration: mp 249–251 °C dec (lit.[26] mp 256–257 °C); TLC (silica gel dichloromethane) R_f 0.50; IR (KBr) 1760 vs, 1470 m, 1430 m, 1365 s, 1270 m, 1220 s, 1180 vs, 1140 vs, 1010 s, 960 m, 880 m cm^{-1}; ^{1}H NMR ($CDCl_3$) 4.47 (s, $ArCH_2Br$), 2.48 (s, ArO_2CCH_3); EI-HRMS calcd for $C_{14}H_{14}{}^{79}Br_4O_4$ (M^+) 561.7624, found 561.7654; EI-MS m/z (ion$^+$, relative intensity) 566 ($M^{81}Br_2$, 0.4), 564 ($M^{81}Br$, 0.4), 562 (M, 0.2), 524 ($M^{81}Br_2 - Ac$, 2.6), 483 (M − Br, 2.5); 482 ($M^{81}Br_3 - 2Ac$, 8.4), 480 ($M^{81}Br_2 - 2Ac$, 5.7), 443 (M − Ac − Br, 1.1), 363 ($M^{81}Br - Ac - 2Br$, 3.3), 323 ($M^{81}Br - 2Ac - 2Br$, 7.7), 241 ($M^{81}Br - 2Ac - 3Br$, 7.5); 161 (M − 2Ac − 4Br, 26.6), 43 (Ac, 100.0).

6,13-Dimethoxy-2,3,9,10-tetramethylpentacene-1,4,8,11-tetrone (8a). A mixture of **7a** (1.00 g, 2.0 mmol), 2,3-dimethylbenzoquinone (0.86 g, 6.4 mmol), and dry sodium iodide (1.88 g, 12.7 mmol) in dry dimethylformamide (10 mL) was heated to 85 °C, in the presence of air. After 24 h TLC (silica gel, dichloromethane) indicated the absence of the dimethylquinone. The cooled reaction mixture was poured into water (10 mL). Aqueous sodium bisulfite was added. The crude product was collected by filtration and air-dried. The red brown product (0.92 g) was chromatographed on a silica gel column with dichloromethane eluting solvent. Elution of a red band and evaporation of solvent in vacuo to dryness produced a red amorphous powder (0.16 g, 0.35 mmol, 18% yield): mp 370 °C dec; TLC (silica gel, dichloromethane) R_f 0.17; UV (CH_2Cl_2) λ_{max} 262 (4.71), 324 (4.43), 339 (4.64), 429 (3.51), 459 (3.68), 485 (3.89), 524 (3.96) nm; IR (KBr) 2900 vw, 1670 vs, 1600 m, 1440 m, 1360 m, 1350 s, 1270 vs, 1055 w, 1020 w, 960 w, 870 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.13 (s, H-5,7,12,14), 4.26 (s, $ArOCH_3$), 2.29 (s, $ArCH_3$); EI-HRMS, calcd for $C_{28}H_{22}O_6$ (M^+) 454.1416, found 454.1424, EI-MS m/z (ion$^+$, relative intensity) 454 (M, 49.7), 439 (M − CH_3, 100.0), 424 (M − 2CH_3, 6.1), 396 (M − 2CH_3 − CO, 3.6).

6,13-Diacetoxy-2,3,9,10-tetramethylpentacene-1,4,8,11-tetrone (8b). **7b** (1.01 g, 1.8 mmol), 1.2-dimethylquinone (0.84 g, 6.2 mmol), and dry sodium iodide (3.80, 25.5 mmol) were placed in a flask attached to a condenser. In the presence of dry air, dry DMF (10 mL) was added and the mixture heated to 85 °C. After 6 h, TLC (silica gel, dichloromethane) indicated the absence of the dimethylquinone. The cooled reaction mixture was poured into water (40 mL). Iodine was reduced with aqueous sodium bisulfite (5 mL) and the crude product collected by filtration. The crude product was chromatographed on a silica gel column with dichloromethane eluting solvent. Elution of an orange band and removal of solvent in vacuo produced an orange amorphous powder (0.20 g, 0.38 mmol, 21% yield): mp 170 °C dec; TLC (silica gel, dichloromethane) R_f 0.13; UV (CH_2Cl_2) λ_{max} 256 (4.70), 300 (4.29), 321 (4.30), 335 (4.52), 411 (3.47), 434 (3.45), 463 (3.41), 493 (3.43) nm; IR (KBr) ν(relative intensity) 2965 vw, 1760 vs, 1660 vs, 1610 s, 1440 m, 1370 s, 1285 vs, 1180 vs, 1140 m, 1040 m, 1020 m, 900 w, 855 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.79 (s, H-5,7,12,14), 2.77 (s, ArO_2CCH_3), 2.27 (s, $ArCH_3$); LD-FTHRMS calcd for $C_{30}H_{22}O_8$ (M^-) 510.1315, found 510.1320; LD-FTMS m/z (ion$^-$, relative intensity) 510 (M· 9.5), 467 ($(M - Ac)^-$, 93.9), 424 ($(M - 2Ac)^-$, 100.0).

Tetramethyl *all-exo*-7-Oxanorbornane-2,3,5,6-tetracarboxylate (9).[16] A mixture of dimethyl 7-oxanorbornene-2,3-dicarboxylate[27] (22.2 g, 1.32 × 10^{-1} mol), anhydrous $CuCl_2$ (80.0 g, 6.0 × 10^{-1} mol), 10% Pd/C (1.33 g, 1.24 × 10^{-3} mol), and anhydrous methanol (160 mL) was shaken (Parr apparatus) for 3–4 h at room temperature with CO (3–4 atm). After workup the white powder (33.2 g, 1.01 × 10^{-1} mol, 76.2% yield) was collected, mp 157–158 °C (lit. mp 156–157 °C).

***all-exo*-2,3,5,6-Tetrakis(hydroxymethyl)-7-oxanorbornane.**[16] A suspension of **9** (1.0 g, 3.06 × 10^{-3} mol) in anhydrous THF (10 mL) was added portionwise to a stirred suspension of $LiAlH_4$ (freshly purified, 0.31 g, 7.86 × 10^{-3} mol) in anhydrous THF (10 mL) maintained at 0 °C under a nitrogen atmosphere. The mixture was refluxed for 1 h. After the mixture cooled to 0 °C, water (2 mL) was added dropwise under N_2 atmosphere. The quenched mixture was heated under reflux for 1 min and immediately filtered through silica gel (5 g). The silica gel was extracted with boiling methanol (3 × 20 mL). The combined filtrates were evaporated in vacuo. Recrystallization from ethanol (15 mL) produced a white crystalline product (0.33 g, 1.51 × 10^{-3}, 50%): mp = 207–208 °C (lit. 208–209 °C).

Following the literature,[16] **10** was produced in 85% yield (21.0 g), mp 149 °C (lit.[16] mp 149 °C).

2,3,5,6-Tetramethylidene-7-oxanorbornane (5).[16] Solid *t*-BuOK (35.1 g, 3.13 × 10^{-1} mol) was added portionwise to a stirred solution of **10** (7.94 g, 2.72 × 10^{-2} mol) in anhydrous THF (200 mL) cooled to 0 °C. The mixture was stirred at room temperature for 18 h. Water (100 mL) was added until complete dissolution of KCl. The brownish mixture was extracted with pentane (3 × 200 mL). The organic extracts were combined and washed with water (6 × 200 mL). All glassware used in workup was thoroughly

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rinsed with distilled water. After drying ($MgSO_4$ + activated charcoal), the solution was evaporated in vacuo to dryness in the dark (flask wrapped with aluminum foil). White crystalline flakes (3.6 g, 2.47×10^{-2} mol, 91%) were obtained, mp 35–36 °C (lit. mp 35–37 °C).

1,2,3,4,8a,9,10,10a-Octahydro-2,3-bis(methylene)-1,4-epoxyanthracene-5,8-dione (6).[12] Under a nitrogen atmosphere the tetraene **5** (7.5 g, 5.14×10^{-2} mol) and benzoquinone (6.6 g, 6.11×10^{-2} mol) were refluxed in dry acetonitrile (100 mL). TLC analysis (silica gel, 4% acetone/CH_2Cl_2) revealed the absence of **5** after 24 h. The solvent was removed using a rotary evaporator. Washing the crude product with ether yielded white flakes (11.9 g, 4.7×10^{-2} mol, 91%): mp 147 °C dec (lit. mp 147 °C dec); TLC (silica gel, 4% acetone/dichloromethane) R_f 0.54. The IR, ^{1}H NMR, and EI-MS data were in agreement with those in the literature.[12] ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number assignment[28]) 198.89 (0, 7), 143.59 (0, 4), 139.35 (1, 8), 139.13 (0, 2), 101.60 (2, 1), 84.58 (1, 3), 46.51 (1, 6), 21.37 (2, 5).

1,2,3,4,5,5a,11a,12-Octahydro-2,3-bis(methylene)-1,4-epoxynaphthacene-6,11-dione (11). Under a nitrogen atmosphere, a solution of **5** (3.4 g, 2.3×10^{-2} mol) and naphthoquinone (4.12 g, 2.6×10^{-2} mol) was refluxed in dry acetonitrile (75 mL). As the reaction progressed a white precipitate was observed. After 75 h, TLC (silica dichloromethane) indicated the absence of **5**. Diethyl ether (75 mL) was added to the cooled reaction mixture. The solid was collected by filtration. Evaporation of the filtrate to dryness produced additional product. The combined products were thoroughly washed with diethyl ether (100 mL), generating a white powder (5.76 g, 1.9×10^{-2} mol, 83%), which was elementally pure: mp 202 °C discolor, 206 °C melt; TLC (silica gel, 1% acetone/dichloromethane) R_f 0.32; UV (dioxane) λ_{max} 222 (4.71), 242 (4.28), 292 (3.34), 304 (3.32) nm. IR (KBr) 3080 vw, 3005 w, 2940 w, 2920 vw, 2900 vw, 2840 vw, 1700 vs, 1680 vs, 1590 s, 1430 w, 1420 w, 1370 w, 1330 w, 1280 s, 1250 vs, 1060 m, 965 m, 940 m, 910 m, 895 m, 880 m, 840 m, 780 m, 725 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.12 (d × d, H-7,10), 7.79 (d × d, H-8,9), 5.26 (s, H-1,4), 5.07 (s, $=CH\mathit{H}$ endo), 4.96 (s, $=CH\mathit{H}$ exo), 3.30 (t, CH), 2.82 (d × d, CH_2), 2.23 (d × d, $C\mathit{H}_2$); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number assignment[28]) 197.10 (0, 7), 143.76 (0, 4), 139.29 (0, 2), 134.41 (1, 10), 133.86 (0, 8), 126.93 (1, 9), 101.46 (2, 1), 84.92 (1, 3), 46.88 (1, 6), 21.60 (2, 5); EI-HRMS calcd for $C_{20}H_{16}O_3$ (M^+) 304.1097, found 304.1090; EI-MS *m/z* (ion$^+$, relative intensity) 304 (M^+, 31.6), 286 ($(M - H_2O)^+$, 75.6), 276 ($(M - CO)^+$, 100.0), 252 ($(M - C_4H_4)^+$, 54.0), 224 ($(M - CO - C_4H_4)^+$, 20.5). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.70; H, 5.40.

5a,6,7,8,8a,14a,15,16,17,17a-Decahydro-7,16-epoxyheptacene-5,9,14,18-tetrone (13). A solution (120 °C) of **5** (0.41 g, 2.8×10^{-3} mol), naphthoquinone (0.96 g, 6.1×10^{-3} mol), and dry diglyme (6 mL) was refluxed, under a N_2 atmosphere. Within 15 min a white precipitate started to form. After 28 h the solid was collected by filtration from the cooled reaction mixture and washed with diethyl ether (20 mL). The white powder (0.51 g, 1.1×10^{-3} mol, 39%), identified as **13**, was insoluble in all common organic solvents. The filtrate was vacuum distilled to near dryness. The residue was washed with dichloromethane (20 mL). A white solid (0.24 g, 1.5×10^{-3} mol) was collected by filtration. ^{1}H NMR, IR, and mass spectral analysis identified this material as naphthohydroquinone. The dichloromethane filtrate was evaporated in vacuo and washed with diethyl ether. This material (0.20 g, 6.6×10^{-4} mol, 24%) was identified as **12** by ^{1}H NMR and EI-MS. **13**: mp 235 °C discolor, 255 °C dec; IR (KBr) 3070 vw, 2930 w, 2880 w, 1670 vs, 1650 vs, 1580 s, 1430 w, 1360 w, 1320 m, 1290 s, 1275 s, 1245 vs, 1050 m, 1010 m, 935 m, 830 m, 760 m, 740 m cm^{-1}; EI-HRMS calcd for $C_{30}H_{22}O_5$ (M^+) 462.1467, found 462.1464; EI-MS, *m/z* (ion$^+$, relative intensity) 462 (M^+, 6.4), 460 ($(M - 2H)^+$, 1.1), 454 ($(M - 8H)^+$, 1.1), 446 ($(M - O)^+$, 2.4), 440 ($(M - O - 6H)^+$, 1.2).

4a,5,6,7,7a,11a,12,13,14,14a-Decahydro-6,13-epoxypentacene-1,4,8,11-tetrone (12). A solution of **6** (0.17 g, 6.7×10^{-4} mol) and benzoquinone (0.49 g, 4.5×10^{-3} mol) in dry acetonitrile (4 mL) was refluxed. After 2 h a white precipitate was observed. After 44 h the reaction was terminated. TLC (silica gel, 4% acetone/dichloromethane) indicated that **6** and benzoquinone were not consumed entirely. The hot reaction mixture was filtered. The white powder (0.0375 g, 1.0×10^{-4} mol, 15%) was insoluble in all common organic solvents: mp 235 °C discolor, 255 °C brown; IR (KBr) 3050 w, 2980 m, 2910 m, 2890 m, 2850 w, 2830 w, 1670 vs, 1600 m, 1430 m, 1375 m, 1330 w, 1260 vs, 1190 m, 1100 s, 1055, 950 m, 860 m, 830 s, 800 w, 740 w cm^{-1}: EI-HRMS calcd for $C_{22}H_{18}O_5$ (M^+) 362.1152, found 362.1152; EI-MS *m/z* (ion$^+$, relative intensity) 362 (M^+, 21.9), 360 ($(M - 2H)^+$, 14.3), 358 ($(M - 4H)^+$, 17.1), 344 ($(M - H_2O),^+$ 14.3), 342 ($(M - H_2O - 2H)^+$, 12.4).

1,2,3,4,9,10-Hexahydro-5,8-dihydroxy-2,3-bis(methylene)-1,4-epoxyanthracene (14). **6** (5.2 g, 2.1×10^{-2} mol) was dissolved in dry acetone (350 mL). A spatula tip full of potassium carbonate was added, and the mixture was stirred at room temperature under a nitrogen atmosphere for 18 h. TLC indicated the absence of **6**. The dark reaction mixture was filtered to remove the base. The filtrate was evaporated to dryness by using a rotary evaporator. Washing the crude product with dichloromethane produced off-white flakes (4.2 g, 1.7×10^{-2} mol, 81%): mp 191–194 °C dec; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.23; IR (KBr and Nujol) 3380 bs, 3010 w, 2880 w, 2825 w, 1580 w, 1480 s, 1450 vs, 1420 s, 1360 s, 1325 s, 1245 vs, 1150 m, 1080 m, 950 s, 885 s, 830 s, 810 m, 735 m cm^{-1}; ^{1}H NMR (acetone-d_6) 7.65 (s, ArO*H*), 6.61 (s, H-6,7), 5.24 (s, $=CH\mathit{H}$ endo), 5.14 (s, H-1,4 and $=CH\mathit{H}$ exo), 3.46–3.27 (m, CH_2); EI-HRMS calcd for $C_{16}H_{14}O_3$ (M^+) 254.0941, found 254.0937; EI-MS, *m/z* (ion$^+$, relative intensity) 254 (M^+, 64.0), 237 ($(M - OH)^+$, 4.4), 225 ($(M - CO - H)^+$, 100.0), 202 ($(M - C_4H_4)^+$, 37.3), 185 ($(M - C_4H_4 - OH)^+$, 31.9).

1,2,3,4-Tetrahydro-2,3-bis(methylene)-1,4-epoxyanthracene-5,8-dione (15). The hydroquinone **14** (47.7 mg, 1.88×10^{-4} mol) and DDQ (90.9 mg, 4.00×10^{-4} mol) were suspended in benzene (4 mL). The mixture was refluxed under a nitrogen atmosphere for 24 h. TLC (alumina, 4% acetone/methylene chloride) indicated the absence of DDQ and hydroquinone **14** and the appearance of a new spot at $R_f = 0.51$. After cooling, the DDQ–hydroquinone was separated by filtration. The filtrate was extracted with a saturated solution of $NaHSO_3$ (5 × 10 mL). The organic phase was separated, dried ($MgSO_4$), and evaporated in vacuo. The yellow product (45.5 mg, 1.82×10^{-4} mol, 97%) was spectroscopically pure and acceptable for further synthetic use. Further purity was obtained by chromatography (alumina, dichloromethane): mp 225 °C dec sealed tube; TLC (alumina, dichloromethane) R_f 0.16, (alumina, 1% acetone/dichloromethane) R_f 0.29, (alumina, 4% acetone/dichloromethane) $R_f = 0.51$; UV (dioxane) λ_{max} 256 (4.44), 337 (3.52) nm; IR (KBr) 3909 w, 3080 vw, 3040 vw, 3020 w, 1670 vs, 1610 vs, 1360 m, 1315 vs, 1270 m, 1245 m, 1190 m, 1125 s, 1040 s, 955 s, 910 s, 890 s, 855 m, 840 vs, 770 m, 715 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05 (s, H-9,10), 6.99 (s, H-6,7), 5.74 (s, H-1,4), 5.41 (s, $=CH\mathit{H}$ endo), 5.33 (s, $=CH\mathit{H}$ exo); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number[28]) 183.68 (0, 7), 148.74 (0, 4), 141.25 (0, 2), 137.39 (1, 8), 130.97 (0, 6), 116.46 (1, 5), 104.27 (2, 1), 82.37 (1, 3); EI-HRMS calcd for $C_{16}H_{10}O_3$ (M^+) 250.0630, found 250.0630; EI-MS, *m/z* (ion$^+$, relative intensity) 250 (M^+, 100.0), 221 ($(M - CO - H)^+$, 29.2), 198 ($(M - C_4H_4)^+$, 23.9), 193 ($M - 2CO - H)^+$, 14.2), 165 ($(M - 3CO - H)^+$, 37.8), 139 ($M - 3CO - C_2H_2 - H$, 30.5). Anal. Calcd for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.60; H, 4.04.

1,2,3,4-Tetrahydro-2,3-bis(methylene)-1,4-epoxynaphthacene-6,11-dione (16). The cycloadduct **11** (36.1 mg, 1.19×10^{-4} mol) was placed on an alumina column. The eluting solvent was dichloromethane with gradually increasing acetone concentration. A broad yellow band eluted off. Evaporation in vacuo of the solvent produced a light yellow powder (34.1 mg, 1.14×10^{-4} mol, 96%), analytically pure: mp 236–238 °C dec sealed tube; TLC (silica gel, dichloromethane) R_f 0.14, (alumina, 1% acetone/dichloromethane) R_f 0.61; UV (dioxane) λ_{max} 262 (4.59), 321 (3.72) nm; IR (KBr) 3080 w, 3040 vw, 3020 w, 1670 vs, 1610 m, 1590 s, 1420 w, 1330 m, 1320 vs, 1300 vs, 1240 s, 1150 m, 1120 m, 960 m, 940 s, 890 s, 840 s, 700 s cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.34 (d × d, H-7,10), 8.28 (s, H-5,12), 7.83 (d × d, H-8,9), 5.77 (s, H-1,4), 5.42 (s, $=CH\mathit{H}$ endo), 5.35 (s, $=CH\mathit{H}$ exo); ^{13}C NMR ($CDCl_3$)

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[28] The scheme for numbering carbon atoms of structural formulas to be used for ^{13}C NMR assignments always begins with carbon-1 as the carbon atom on the far right-hand side of the structural formula in the text and proceeds to the left giving each unique carbon atom a number. Atoms related by symmetry are not numbered. As an example see structure **6**. This system is less cumbersome than using the IUPAC numbering system.

δ (attached H, carbon number assignment[28]) 182.91 (0, 7), 150.07 (0, 4), 142.51 (0, 2), 134.17 (1, 10), 133.78 (0, 8), 133.36 (0, 6), 127.28 (1, 9), 118.29 (1, 5), 105.34 (2, 1), 83.56 (1, 3); EI-HRMS calcd for $C_{20}H_{12}O_3$ (M^+) 300.0787, found 300.0795; EI-MS, *m/z* (ion$^+$, relative intensity) 300 (M^+, 100.0), 271 ($(M - CO - H)^+$, 45.1), 243 ($(M - 2CO - H)^+$, 17.2), 215 ($(M - 3CO - H)^+$, 34.4). Anal. Calcd for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03. Found: C, 79.84; H, 4.16.

4a,5,6,13,14,14a-Hexahydro-6,13-epoxypentacene-1,4,8,11-tetrone (17). Under a nitrogen atmosphere, **15** (1.75 g, 7.0×10^{-3} mol) and benzoquinone (13.3 g, 1.23×10^{-1} mol) were refluxed in dry *o*-xylene (63 mL). After 1.5 h TLC (silica gel, dichloromethane) indicated the absence of **15**. Diethyl ether (200 mL) was added to the cooled reaction mixture. The precipitate was collected by filtration. The crude product was washed with additional diethyl ether (100 mL) to yield a yellow powder (1.41 g, 3.93×10^{-3} mol, 56%). Recrystallization from acetone/diethyl ether produced pure material: mp 220 °C dec seal tube; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.44; UV (dioxane) λ_{max} 257 (4.41), 330 (3.54) nm; IR (KBr) 3060 w, 3010 vw, 2920 w, 2880 vw, 1685 vs, 1665 vs, 1610 s, 1425 w, 1370 m, 1310 vs, 1265 m, 1090 m, 1040 m, 840 vs, 710 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89 (s, H-7,12), 6.94 (s, H-9,10), 6.71 (s, H-2,3), 5.60 (s, H-6,13), 3.03 (t, CH), 2.92 (d × d, CH_2), 2.09 (d × d, CH_2); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number[28]) 198.40 (0, 2), 185.10 (0, 10), 154.86 (0, 7), 145.90 (0, 5), 139.40 (1, 1), 138.27 (1, 11), 130.87 (0, 9), 116.44 (1, 8), 83.79 (1, 6), 46.45 (1, 3), 22.67 (2, 4); EI-HRMS calcd for $C_{22}H_{14}O_5$ (M^+) 358.0841, found 358.0826; EI-MS, *m/z* (ion$^+$, relative intensity) 358 (M^+, 23.8), 354 ($(M - 4H)^+$, 7.7), 338 (M $- H_2O -$ 2H, 15.4), 258 ($(M - 3CO - CH_2 - H_2)^+$, 62.2), 221 ($(M - C_8H_9O_2)^+$, 100.0). Anal. Calcd for $C_{22}H_{14}O_5$: C, 73.74; H, 3.94. Found: C, 73.70; H, 4.13.

6,7,7a,13a,14,15-Hexahydro-6,15-epoxyhexacene-1,4,8,13-tetrone (18). A suspension of **15** (0.84 g, 3.36×10^{-3} mol) and naphthoquinone (5.1 g, 3.2×10^{-2} mol) in *o*-xylene (20 mL) was refluxed for 5 h. TLC (silica gel, 1% acetone/dichloromethane) indicated the absence of **15**. Diethyl ether (100 mL) was added to the cooled reaction mixture. The precipitate was collected by filtration and washed with excessive amounts of ether (400 mL). A yellow powder (0.85, 2.08×10^{-3} mol, 62%) was obtained: mp 200 °C dec; TLC (silica gel, 4% acetone/dichloromethane) R_f = 0.50; IR (KBr) 3040 vw, 2900 w, 1670 vs, 1650 vs, 1585 s, 1415 m, 1360 m, 1295 vs, 1250 s, 1060 m, 1025 m, 830 s, 760 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.11 (d × d, H-9,12), 7.90 (s, H-5,16), 7.81 (d × d, H-10,11), 6.95 (s, H-2,3), 5.60 (s, H-6,15), 3.35–1.96 (m, CH and CH_2); EI-HRMS calcd for $C_{26}H_{16}O_5$ (M^+) 408.0996, found 408.1013; EI-MS *m/z* (ion$^+$, relative intensity) 408 (M^+, 40.8), 390 ($(M - H_2O)^+$, 76.3), 362 ($(M - H_2O - CO)^+$, 21.1).

4a,5,6,15,16,16a-Hexahydro-6,15-epoxyhexacene-1,4,8,13-tetrone (19). Under a nitrogen atmosphere, **16** (49.3 mg, 1.6×10^{-4} mol) and benzoquinone (0.20 g, 1.9×10^{-3} mol) were refluxed in *o*-xylene (1 mL). TLC indicated the absence of **16** after 2 h. Diethyl ether (5 mL) was added to the cooled reaction mixture. The precipitate was collected by filtration and washed with diethyl ether (10 mL). The light yellow powder (53.1 mg, 1.3×10^{-4} mol, 81%) was spectroscopically pure: mp 200 °C dec; TLC (silica gel, 1% acetone/dichloromethane) R_f 0.20; IR (KBr) 3060 vw, 2920 w, 2850 w, 1670 vs, 1590 s, 1450 w, 1370 w, 1320 s), 1300 vs, 950 w, 840 m, 710 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.18 (d × d, H-9,12), 8.16 (s, H-7,14), 7.89 (d × d, H-10,11), 6.76 (s, H-2,3), 5.66 (s, H-6,15), 3.05–1.95 (m, CH and CH_2); EI-HRMS calcd for $C_{26}H_{16}O_5$ (M^+) 408.0998, found 408.1005; EI-MS, *m/z* (ion$^+$, relative intensity) 408 (M^+, 8.1), 390 ($(M - H_2O)^+$, 25.8), 380 ($(M - CO)^+$, 9.0), 363 ($(M - CO - OH)^+$, 11.0), 352 ($(M - 2CO)^+$, 5.6).

5a,6,7,16,17,17a-Hexahydro-7,16-epoxyheptacene-5,9,14,18-tetrone (20). Under a nitrogen atmosphere, **16** (51.2 mg, 1.7×10^{-4} mol) and naphthoquinone (0.28 g, 1.8×10^{-3} mol) were refluxed in *o*-xylene (1 mL). TLC (silica gel, dichloromethane) indicated the absence of **16**. Diethyl ether (15 mL) was added to the cooled reaction mixture. The precipitate was collected by filtration and washed with additional diethyl ether (50 mL). The yellow powder weighed 62.1 mg (1.4×10^{-4} mol, 82%): mp 275 °C dec; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.0; UV (dioxane) λ_{max} 222 (4.30), 267 (4.27), 305 (3.41) nm; IR (KBr) 3060 vw, 3000 vw, 2880 vw, 1680 vs, 1670 vs, 1610 m, 1595 s, 1420 m, 1380 m, 1325 s, 1200 vs, 1155 s, 955 m, 935 m, 845 s, 795 m, 720 s, 710 s cm^{-1}; ^{13}C NMR (solid-state CP-MAS) δ (attached H, carbon number assignment[28]) 199.9 (0, 4), 183.5 (0, 12), 155,6 (0, 9), 147.0 (0, 7), 135.6 (1, 1, 15), 133.2 (0, 3,11,13), 129.1 (1, 14), 126.7 (1, 2), 119.0 (1, 10), 116.4 (1, 83.8 (1, 8), 45.2 (1, 5), 21.7 (2, 6); EI-HRMS calcd for $C_{30}H_{18}O_5$ (M^+) 458.1154, found 458.1124; EI-MS, *m/z* (ion$^+$, relative intensity) 458 (M^+, 55.2), 454 ($(M - 4H)^+$, 38.8), 440 ($(M - H_2O)^+$, 100.0), 429 ($(M - CO - H)^+$, 25.6), 412 ($(M - CO - H_2O)^+$, 28.7); LDFT-MS, *m/z* (ion$^-$, relative intensity) 458 (M^-, 19.0), 457 ($(M - H)^-$, 55.7), 453 ($(M - 5H)^-$, 5.5), 439 ($(M - H - H_2O)^-$), 299 ($(M - H - C_{10}H_6O_2)^-$, 63.9), 286 ($(M - C_{10}H_6O_2 - CH_2)^-$, 100.0). Anal. Calcd for $C_{30}H_{18}O_5$: C, 78.59; H, 3.96. Found: C, 78.45; H, 4.16.

6,7,12,13-Tetrahydro-8,11-dihydroxy-6,13-epoxypentacene-1,4-dione. The cycloadduct **17** (0.28 g, 7.8×10^{-4} mol) was chromatographed on a silica gel (30.2 g) column. Elution with dichloromethane and gradual increase of acetone concentration produced two yellow bands. The first band (10% acetone/dichloromethane) was collected and the solvent evaporated in vacuo. Spectral analysis (IR, ^1H NMR, EI-MS) indicated that this fraction was a mixture of **17** and **21** (0.11 g, ≈39% by weight). The second band was collected and the solvent evaporated in vacuo. A yellow powder (0.15 g, 4.2×10^{-4} mol, 54%) was obtained: TLC (silica gel, dichloromethane) R_f 0.12; IR (KBr and Nujol) 3360 bs, 1660 vs, 1600 s, 1480 m, 1305 vs, 1260 s, 1125 m, 835 s, 790 m cm^{-1}; ^1H NMR (acetone-d_6) δ 8.01 (s, H-5,14), 7.65 (s, ArOH), 6.99 (s, H-2,3), 6.55 (s, H-9,10), 5.90 (s, H-6,13); EI-MS, *m/z* (ion$^+$, relative intensity) 358 (M^+, 7.2), 354 ($(M - 4H)^+$, 13.8), 340 ($(M - H_2O)^+$, 12.3), 338 ($(M - H_2O - 2H)^+$, 14.5), 326 ($(M - CO - 4H)^+$, 7.2).

6,13-Dihydro-6,13-epoxypentacene-1,4,8,11-tetrone (21). The hydroquinone (0.15 g, 4.2×10^{-4} mol) and DDQ (0.20 g, 8.7×10^{-4} mol) were refluxed in dioxane under a nitrogen atmosphere. A precipitate formed after 4 h. TLC (silica gel, 4% acetone/dichloromethane) indicated the absence of DDQ after 20 h. After cooling, the precipitate (DDQ hydroquinone) was separated by filtration. Pentane was added to the filtrate until a yellow precipitate was formed. After the mixture was cooled to 0 °C, filtration produced a yellow powder (0.11 g, 3.1×10^{-4} mol, 74%): mp 200 °C discolor, 280 °C light brown, 310 °C brown; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.44; UV (dioxane) λ_{max} 250 (4.27), 262 (4.38), 270 (4.44), 334 (3.40) nm; IR (KBr) 3060 w, 3020 vw, 1670 vs, 1620 s, 1435 w, 1350 w, 1305 vs,1120 m, 1040 m, 840 s, 810 m, 700 m; ^1H NMR ($CDCl_3$) δ 8.11 (s, H-5,7,12,14), 6.97 (s, H-2,3,9,10), 6.38 (s, H-6,13); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number[28]) 184.49 (0, 2), 152.19 (0, 5), 138.39 (1, 1), 131.63 (0, 3), 118.59 (1, 4), 82.11 (1, 6); EI-HRMS calcd for $C_{22}H_{10}O_5$ (M^+) 354.0526, found 354.0517; EI-MS, *m/z* (ion$^+$, relative intensity) 354 (M^+, 3.6), 338 ($(M - O)^+$, 13.5), 326 ($(M - CO)^+$, 5.9), 298 ($(M - 2CO)^+$, 3.7), 270 ($(M - 3CO)^+$, 3.6), 242 ($(M - 4CO)^+$, 2.8); LDFT-MS, *m/z* (ion$^+$, relative intensity) 354 (M^+, 100), 326 ($(M - CO)^+$, 80), 298 ($(M - 2CO)^+$, 70), 270 ($(M - 3CO)^+$, 40); 242 ($(M - 4CO)^+$, 20), 226 ($(M - 4CO - O)^+$, 15), 212 ($(M - 4CO - HCO)^+$, 12); LDFT-MS, *m/z* (ion$^-$, relative intensity) 354 (M^-, 33), 353 ($(M - H)^-$ 100), 325 ($(M - H - CO)^-$, 10).

1,2,3,4,5,5a,8,9,10,11,13a,14-Dodecahydro-2,3,9,10-tetrakis(methylene)-1,4:8,11-diepoxypentacene-6,13-dione (22). Under a nitrogen atmosphere, **15** (1.5 g, 6.0×10^{-3} mol) and **5** (0.9 g, 6.2×10^{-3} mol) were refluxed in acetonitrile (35 mL). After 49 h additional acetonitrile (50 mL) was added to the cooled reaction mixture. An orange-brown, insoluble, unidentified solid was separated by filtration. The filtrate was dried ($MgSO_4$ and activated charcoal) and evaporated to dryness in vacuo. The white flakes (2.2 g, 5.6×10^{-3} mol, 93%) were sufficiently pure for spectroscopic analysis. This material slowly decomposes on exposure to air and/or light. Refrigerated storage under a nitrogen atmosphere in a container wrapped with aluminum foil is highly recommended: mp 236 °C dec; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.38; UV (dioxane) λ_{max} 242 (4.45), 262 (4.16) nm; IR (KBr) 3080 w, 2990 w, 2920 w, 2880 w, 1690 vs, 1660 s, 1610 s, 1425 m, 1360 w, 1300 m, 1280 vs, 1230 s, 1155 s, 1055 m, 960 s, 890 vs, 840 vs, 780 m, 760 m, 710 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (s, H-7,12), 5.72 (s, H-8,11), 5.41 (s, =CH*H* endo), 533 (s, =CH*H* exo), 5.25 (s, H-1,4), 5.07 (s, =CH*H* endo), 4.95 (s, =CH*H* exo), 3.28 (t, CH), 2.80 (d × d, CH_2), 2.20 (d × d, CH_2); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number) 196.87 (0, 7), 150.46 (0, 4), 143.78 (0, 10), 142.30 (0, 2), 139.33 (0, 12), 134.21 (0, 6), 117.99 (1, 5), 105.48 (2, 1), 101.60 (2, 13), 84.75 (1, 11), 83.47 (1, 3), 46.95

(1, 8), 21.73 (2, 9); EI-MS, *m/z* (ion$^+$, relative intensity) 396 (M$^+$, 10.6), 378 ((M − H_2O)$^+$, 22.5), 368 ((M − CO)$^+$, 21.2).

1,2,3,4,8,9,10,11-Octahydro-2,3,9,10-tetrakis(methylene)-1,4:8,11-diepoxypentacene-6,13-dione (23). The cycloadduct **22** (54.7 mg, 1.38 × 10^{-4} mol) was stirred in methylene chloride with alumina (0.57 g) in the presence of air for 23 h. The alumina was collected by filtration and washed with methylene chloride (20 mL). Evaporation of the solvent in vacuo produced a light yellow powder (32.4 g, 8.27 × 10^{-5} mol, 60%) which was mixture of **23** isomers. Column chromatography (alumina, methylene chloride/acetone) separated the isomers. These materials are spectroscopically identical: anti isomer TLC (alumina, 1% acetone/methylene chloride) R_f 0.52, mp 271 °C dec; syn isomer TLC (alumina, 1% acetone/methylene chloride) R_f 0.22, mp 240 °C dec; UV (dioxane) λ_{max} 271 (4.80), 332 (3.69) nm; IR (KBr) 3010 w, 1670 vs, 1605 s, 1305 vs, 1235 m, 950 m, 895 vs, 840 s, 720 w, 710 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.26 (s, H-5,7,12,14), 5.76 (s, H-1,4,8,11), 5.42 (s, =CH*H* endo), 5.34 s, =CH*H* exo); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number[28]) 182.68 (0, 7), 150.08 (0, 4), 142.44 (0, 2), 133.60 (0, 6), 118.33 (1, 5), 105.40 (2, 1), 83.56 (1, 3); EI-HRMS calcd for $C_{26}H_{16}O_4$ (M$^+$) 392.1048, found 392.1029; EI-MS, *m/z* (ion$^+$, relative intensity) 392 (M$^+$, 100.0), 363 ((M − CO − H)$^+$, 36.1), 335 ((M − 2CO − H)$^+$, 28.5), 307 ((M − 3CO − H)$^+$, 19.4). Anal. Calcd for $C_{26}H_{16}O_4$: C, 79.58; H, 4.11. Found: C, 79.46; H, 4.16.

4a,5,6,10,11,11a,15a,16,17,21,22,22a-Dodecahydro-6,21:10,17-diepoxynonacene-1,4,8,12,15,19-hexone (24). A suspension of **23** (anti isomer, 47.1 mg, 1.18 × 10^{-4}) mol) and benzoquinone (0.16 g, 1.5 × 10^{-3} mol) in *o*-xylene (1 mL) was refluxed. After 2 h, TLC (silica gel, dichloromethane) indicated the absence of **23**. Diethyl ether (10 mL) was added to the cooled reaction mixture. The light yellow precipitate was collected by filtration and washed with diethyl ether (10 mL) (44.6 mg, 7.26 × 10^{-5} mol, 62%): mp 200 °C dec; TLC (silica gel, 4% acetone/dichloromethane) R_f 0.12; UV (dioxane) λ_{max} 277 (4.63), 335 (3.63) nm; IR (KBr) 3060 vw, 2920 vw, 2880 vw, 1670 vs, 1610 vs, 1370 m, 1300 vs, 1160 m, 960 m, 845 s, 750 m cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.07 (s, H-7,9,18,20), 6.71 (s, H-2,3,13,14), 5.62 (s, H-6,10,14,21), 3.06–2.91 (m, CH and CH_2), 2.17–2.00 (m, CH_2); ^{13}C NMR ($CDCl_3$) δ (attached H, carbon number[28]) 198.44 (0, 2), 182 n0,10), 154.93 (0, 7), 145.86 (0, 5), 139.41 (1, 1), 132.32 (0, 9), 117.06 (1, 8), 83.82 (1, 6), 46.50 (1, 3), 22.71 (2, 4); LDFT-HRMS calcd for $C_{38}H_{24}O_8$ ((M − H)$^-$) 607.1398, found 607.1408, LDFT-MS, *m/z* (ion$^-$, relative intensity) 607 ((M − H)$^-$, 100), 579 ((M − H − CO)$^-$, 18), 523 ((M − H − $C_4H_4O_2$)$^-$, 20), 499 ((M − H − $C_6H_4O_2$)$^-$, 63), 486 ((M − $C_6H_4O_2$− CH_2)$^-$, 28), 391 ((M − H − 2$C_6H_4O_2$)$^-$, 14).

5a,6,7,11,12,12a,18a,19,20,24,25,25a-Dodecahydro-7,24:11,20-diepoxyundecacene-5,9,13,18,22,26-hexone (25). A suspension of **23** (anti isomer, 62.8 mg, 1.6 × 10^{-4} mol) and naphthoquinone (0.26 g, 1.7 × 10^{-3} mol) in *o*-xylene was refluxed. TLC (alumina, dichloromethane) indicated the absence of **23** after 6 h. Diethyl ether (10 mL) was added to the cooled reaction mixture. The light yellow precipitate was collected by filtration and washed with diethyl ether (10 mL) (66.3 mg, 9.4 × 10^{-5} mol, 59%): mp 155 °C discolor, 200 °C red; TLC (alumina, 1% acetone/dichloromethane) R_f 0.08; IR (KBr) 3080 vs, 3020 vs, 2930 vs, 2890 vw, 1680 vs, 1660 vs, 1610 s, 1600 s, 1370 m, 1300 vs, 1255 vs, 1155 m, 965 m, 940 m, 850 m, 750 m, 710 w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.09 (s, H-8,10,21,23), 8.07 (d × d, H-1,4,14,17), 7.77 (d × d, H-2,3,15,16), 5.63 (s, H-7,11,20,24), 3.49–2.96 (m, CH and CH_2), 2.23–2.16 (m), C*H*$_2$); LDFT-HRMS calcd for $C_{46}H_{28}O_8$ (M$^-$) 708.1784, found 708.1788; LDFT-MS, *m/z* (ion$^-$, relative intensity) 708 (M$^-$, 21), 707 ((M − H)$^-$, 38), 549 ((M − H − $C_{10}H_6O_2$)$^-$, 100), 536 ((M − $C_{10}H_6O_2$ − CH_2)$^-$, 92), 391 ((M − 2$C_{10}H_6O_2$ − CH_2)$^-$, 24), 378 ((M − 2$C_{10}H_6O_2$ − 2CH_2)$^-$, 33).

Heptacene-5,7,9,14,16,18-hexone (26). In a round-bottomed flask equipped with a reflux condenser, open to the air, **20** (126 mg, 2.75 × 10^{-4} mol) was stirred in TFA (12 mL) at room temperature. Within 10 min, the yellow solution changed to an orange color and a precipitate started to form. After 27.5 h, the reaction mixture was filtered through a medium frit, washed with water (2 × 2 mL) and methanol (3 × 2 mL). The orange powder (119 mg, 2.52 × 10^{-4} mL, 92%) was weakly soluble in dioxane (10^{-5} M) and methylene chloride: UV (dioxane) λ_{max} 222 (4.54), 258 (4.83), 307 (4.32), 430 (3.75) nm; IR (KBr) ν(relative intensity) 3060 w, 2930 vs, 2880 vw, 1690 vs, 1670 vs, 1620 m, 1600 s, 1585 s, 1460 m, 1440 m, 1320 vs, 1285 vs, 1260 vs, 1200 m, 970 s, 780 m, 710 s cm^{-1}. Anal. Calcd for $C_{30}H_{16}O_6$: C, 76.27; H, 3.41. Found: C, 76.35; H, 3.66.

To a suspension of the above product (0.20 g, 4.3 × 10^{-4} mol) in dioxane (200 mL) in an Erlenmeyer flask was added KOH (2 mL, 6.8 × 10^{-1} M). The dark blue suspension was stirred at room temperature open to the air for 16 h. On addition of household bleach (10 mL), HCl (4 mL, 1.1 M, acidic to litmus), and dioxane (10 mL) the suspension changed color to a bright light yellow. After being stirred for 30 min, the mixture was made basic to litmus (KOH, 7 mL, 6.8 × 10^{-1} M), and dioxane (7 mL) was added. A greenish yellow suspension was observed and stirred for 1 h. Again on addition of bleach (10 mL), HCl (9 mL, 1.1 M, acidic to litmus), and dioxane (30 mL) the suspension changed color to a bright yellow. The suspension remained this color even after addition of KOH (15 mL, 6.8 × 10^{-1} M, basic to litmus) and dioxane. The precipitate was collected by filtration, washed with water (2 × 30 mL), and methanol (2 × 20 mL). The ocher-yellow powder (0.16 g, 3.4 × 10^{-4} mol, 79%) was insoluble in common organic solvents: mp >360 °C (nitrobenzene); IR (KBr) ν(relative intensity) 3060 w, 3040 w, 1680 vs, 1590 m, 1470 m, 1325 m, 1250 vs, 1160 m, 1145, 990 s, 695 s cm^{-1}; ^{13}C NMR (solid-state CP-MAS) δ (attached H, carbon number[28]) 180.0 (0, 4,8), 135.9 (0, 5,7), 132.8 (0, 3), 129.7 (1, 1), 127.1 (1, 2,6); EI-HRMS calcd for $C_{30}H_{12}O_6$ (M$^+$) 468.0633, found 468.0648; EI-MS, *m/z* (ion$^+$ relative intensity) 468 (M$^+$, 100.0), 440 ((M − CO)$^+$, 59.5), 412 ((M − 2CO)$^+$, 32.2), 384 ((M − 3 CO)$^+$, 27.3), 356 ((M − 4CO)$^+$, 25.4); LDFT-MS, *m/z* (ion$^-$, relative intensity) 468 (M$^-$, 100.0).

Undecacene-5,7,9,11,13,18,20,22,24,26-decone (27). In a round-bottomed flask equipped with a reflux condenser, **25** (27.7 mg, 3.91 × 10^{-5} mol) in TFA (3 mL) was stirred in the presence of air. After 27 h, chloroform (3 mL) was added. The precipitate was collected by filtration and washed with chloroform (2 × 3 mL) and diethyl ether (2 × 2 mL). A brownish red powder (25.0 mg) was obtained. A suspension of this red powder (14.2 mL) in dioxane (15 mL) was treated with KOH (0.2 mL, 6.8 M, basic to litmus). A grayish blue suspension was immediately observed. This suspension was stirred at room temperature in the presence of air for 23 h. A yellow suspension was observed on addition of bleach (1 mL), HCl (1 mL, 1.1 M, acidic to litmus), and dioxane (2 mL). After the mixture was stirred for 40 min, KOH (2 mL, 6.8 × 10^{-1} M, basic to litmus) and dioxane (2 mL) was added. A green suspension was observed and stirred for 70 min. Addition of bleach (1 mL), HCl (1.5 mL, 1.1 M, acidic to litmus), and dioxane (3 mL) regenerated a yellow suspension. After 20 min, addition of KOH (3 mL, 6.8 × 10^{-1} M, basic to litmus) and dioxane (3 mL) generated a greenish yellow suspension which was stirred for 1 h. Again, addition of bleach (1 mL), HCl (2 mL, 1.1 M acidic to litmus) and dioxane (3 mL) generated a bright yellow suspension. No color change was observed when the mixture was made basic (KOH, 3 mL, 6.8 × 10^{-3} M). The precipitate was collected by filtration, washed with water (2 mL) and methanol (2 × 2 mL). After drying, the yellow powder acquired a greenish tint (8.9 mg): IR (KBr) ν(relative intensity) 1680 vs, 1590 m, 1470 m, 1320 m, 1250 vs, 1175 m, 1005 s, 700 s cm^{-1}; LDFT-HRMS calcd for $C_{46}H_{16}O_{10}$ (M$^-$) 728.0744, found 728.0749, calcd for $C_{46}H_{18}O_9$ ((M′)$^-$) 714.0951, found 714.0956; LDFT-MS, *m/z* (ion$^-$, relative intensity) 728 (M$^-$, 100), 714 ((M′)$^-$, 28), 713 ((M′ − H)$^-$, 25), 700 ((M − CO)$^-$, 11), 698 ((M′ − O)$^-$, 17), 686 ((M′ − CO)$^-$, 8), 685 ((M′ − H − CO)$^-$, 6).

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Registry No. **5**, 53011-99-7; **6**, 77341-10-7; **7a**, 104157-20-2; **7b**, 6618-65-1; **8a**, 104157-21-3; **8b**, 104157-37-1; **9**, 76196-55-9; **10**, 75814-03-8; **11**, 104157-22-4; **12**, 104157-23-5; **13**, 104157-24-6; **14**, 104157-25-7; **15**, 104157-26-8; **16**, 104157-27-9; **17**, 104157-27-9; **18**, 104157-29-1; **19**, 104172-29-4; **20**, 104157-30-4; **21**, 104157-31-5; **22**, 104157-32-6; **23** (isomer 1), 104264-04-2; **23** (isomer 2), 104157-39-3; **24**, 104157-33-7; **25**, 104157-34-8; **26**, 104157-35-9;

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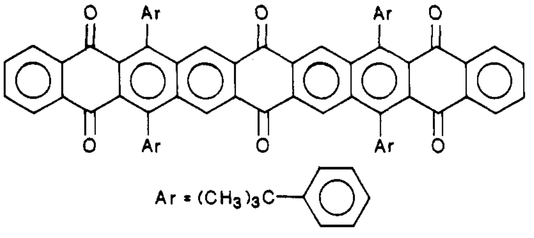
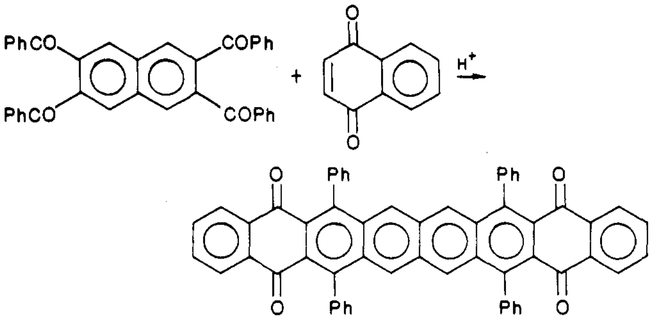
The known Diels–Alder reactions of 1,3-diarylisobenzofurans have been employed to develop a synthesis of a nonacenetriquinone (**1**). A 2:1 condensation of 2,5-bis(4-*tert*-butylphenyl)-3,4-diformylfuran (**17**) and cyclohexanedione gave the bisisobenzofuran **7**. This compound was treated with naphthoquinone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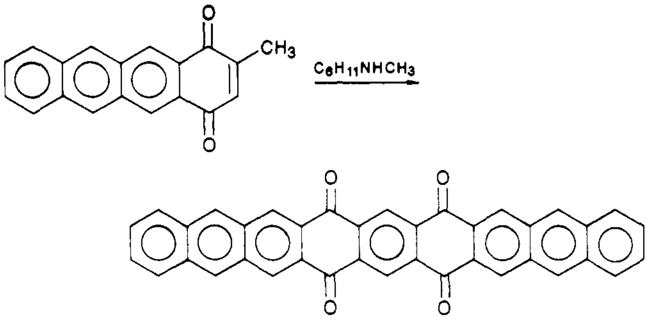

3

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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