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SYNTHESIS OF POLYACENEQUINONES VIA A BENZO[2,3-c]FURAN

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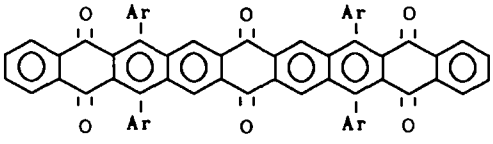
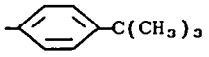
Abstract: 1,3-Bis(4-tert-butylphenyl)-4,7-diacetoxybenzo-(2,3-c)furan (3c) serves as a masked-dienophile/diene equivalent, which can elongate a 1,4-quinone by two rings. Elongation involves a three step sequence of Diels-Alder reaction, dehydrative-aromatization, and oxidative unmasking of the dienophile. This elongation strategy has been used to sequentially convert napthoquinone to a tetracenetetrone and a hexacenetetrone.

Polyacenequinones are of interest because they provide a rigid, linear molecular framework with an extended, delocalized π-system. Such compounds and their hydroquinone and semiquinone analogs can be expected to have unusual electrochemical, electrical and optical properties. Even so, the synthesis of polyacenequinones has received very limited study. In this laboratory we have investigated several approaches to the synthesis of such molecules.[1,2] Our basic strategy has been to develop a repetitive Diels-Alder method which allows incremental growth of linear polyacenequinones. In principle, there are two ways to accomplish this: 1) By employing solid support techniques to effect immobilization and site isolation. In this way a bis-diene and a bis-dienophile could be reacted repetitively in an alternating sequence to give long polyacenequinones of controlled length, without polymerization. 2) By using a single unsymmetrical molecular specie containing both diene and dieneophile equivalents, one of which is masked. With such a molecule, a sequence of a Diels-Alder reaction and unmasking of the new adduct could be done repetitively in solution to give polyacenequinones without polymerization.

We have previously reported on the use of symmetrical bisdienes in the synthesis of polyacenequinones.[1,2] It has been a particular goal of this work to produce soluble polyacenequinones. The solubility problem has been solved, as reported in reference 2, by the attachment of substituted aryl groups as in 1.



1

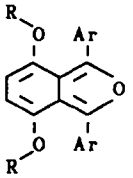
Ar = 

This compound is soluble in a variety of organic solvents, perhaps because the aryl groups prevent close packing of the molecules in the solid. This solubilization strategy is again employed successfully with the polyacenequinones prepared in this paper.

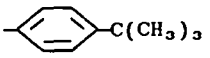
In this present study, we investigated the synthesis of polyacenequinones by the method 2) above, using an unsymmetrical molecule containing both a diene equivalent and a masked dienophile. We wanted a synthetic equivalent to structure 2 which would allow a quinone to be elongated by two rings.

2

Compound 3, a 4,7-dioxybenzo[2,3-c]furan, was chosen as an appropriate masked version of 2.



3

Ar = 

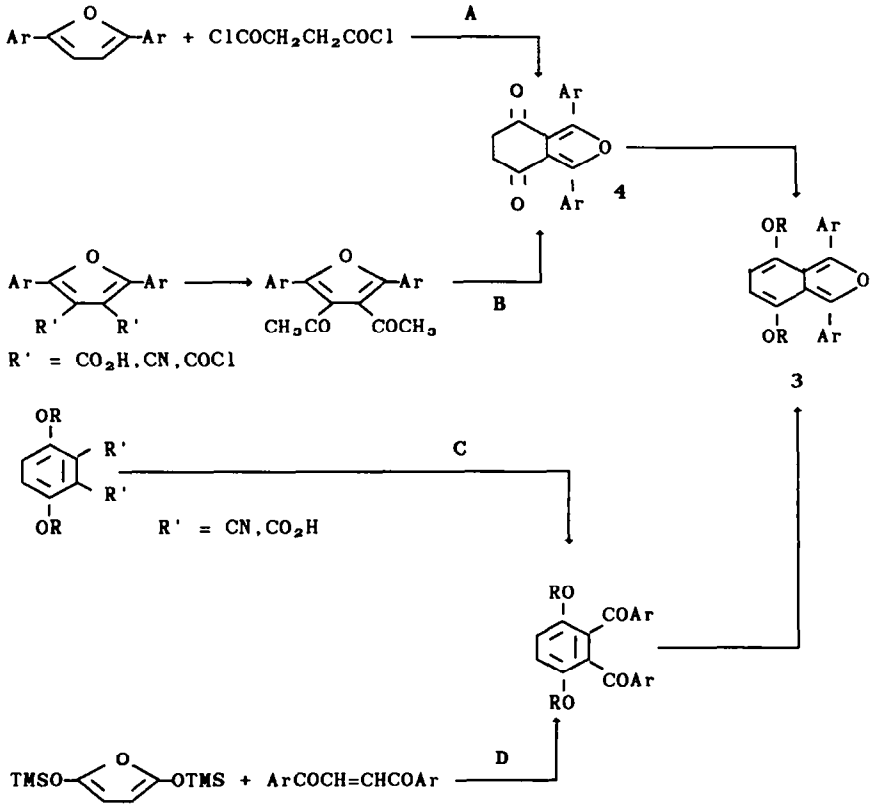
3a, R = $Si(CH_3)_3$
3b, R = CH_3
3c, R = $COCH_3$

Molecules of this type are known to be reactive as dienes in the Diels-Alder reaction, being essentially a stabilized ortho-xylylene.[3] The 1,3-diaryl substituents on 3 are appropriately positioned to convey solubility to the resulting polyacenequinones,[2] and the 4,7-dioxy functionality can be oxidized to a quinone.[4] Thus, a Diels-Alder, dehydration, oxidation sequence would produce an elongated quinone which could then be put through the cycle again, leading to further elongation.

Results and Discussion

Prior to an investigation of the chemistry described above, it was necessary to prepare the benzo[2,3-c]furan 3. Retro synthetic analysis generated several reasonable routes to compound 3 (Scheme 1), all of which were supported by some literature precedent.[5,6,7,8] In the course of this investigation, all of these routes were investigated to some extent. Within the limits of the reaction conditions explored, it turned out that only route A beginning with the 2,5-diarylfuran and succinyl chloride, proved successful.

Scheme 1. Routes to 3, Ar = p-C_6H_4-$C(CH_3)_3$



In the case of route B, attempts were made to prepare the 3,4-diacetyl-2,5-diarylfuran by: 1) reaction of the 2,5-diaryl-3,4-dicyanofuran[2] with methylmagnesium bromide followed by hydrolysis,[9] 2) reaction of the 2,5-diaryl-

3,4-furan dicarboxylic acid[2] with methyllithium,[10] and, 3) reaction of the corresponding diacid chloride with dimethylcopper(I) lithium.[11] At best, low yields of the bis-methylketone were obtained, and this route was not pursued further. Similarly for route C, attempts were made to prepare the bis-arylketone by: 1)the Friedel-Crafts reaction between 3,6-dimethoxy-1,2-benzenedicarboxylic acid[12] or the corresponding diacid chloride and tert-butylbenzene in the presence of a catalyst (CF_3SO_3H or $AlCl_3$),[13,14,15] 2) the reaction between 3,6-dimethoxy-1,2-benzenedicarboxylic acid and an aryllithium,[10] and, 3) the reaction between 3,6-dimethoxy-1,2-benzenedicarbonitrile[12] and an arylmagnesium bromide.[9] Again, little or no desired bis-arylketone was obtained and thus work on this route was discontinued. In the case of route D, the Diels-Alder reaction between the diene[8] and the dieneophile shown, followed by dehydration, gave the bis-arylketone in only low yield.

Following route A, the known 2,5-bis(4-tert-butylphenyl)furan[2] reacted at room temperature with succinyl chloride in the presence of 2.5 equivalents of aluminum chloride to give an approximately 35% yield of the cyclic diketone 4 resulting from a bis-Friedel-Crafts acylation.[5,13] A variety of catalysts were investigated (e.g. $SnCl_4$, $AgOSO_2CF_3$,[14,15] $TiCl_4$, CF_3SO_3H[14,15]), but aluminum chloride at 2.5 molar excess was found to give the best results. An attempt was made to prepare the mono-acylation product from succinic anhydride and 2,5-bis(4-tert-butylphenyl)furan[16] and then, in a separate step, effect the cyclization with polyphosphoric acid.[17] This, however, did not give as satisfactory a result as the aluminum chloride catalyzed bis-acylation.

The cyclic diketone 4 was readily converted into several benzo[2,3-c]furan derivatives (3a, 3b, 3c). Treatment of 4 with trimethylsilyl triflate and triethylamine in benzene gave an essentially quantitative yield of 3a,[18] while treatment of 4 with sodium hydride in DMF followed by dimethyl sulfate gave a good yield of 3b.[19] The diacetate derivative 3c was prepared both by treatment with acetic anhydride and pyridine at reflux (74-93%)[3] and with thallium(I)-ethoxide and acetyl chloride in benzene.[20] The method employing thallium(I)-ethoxide seemed to give an essentially quantitative yield of 3c, but because of the commercial unavailibility of the thallium(I)ethoxide, the pyridine/acetic anhydride method was used in this study for the preparation of larger quantities of 3c. It is possible that derivatives 3a,b could prove as satisfactory as the diacetate 3c (for example, the oxidation to the quinones might prove more facile), but 3c was employed here.

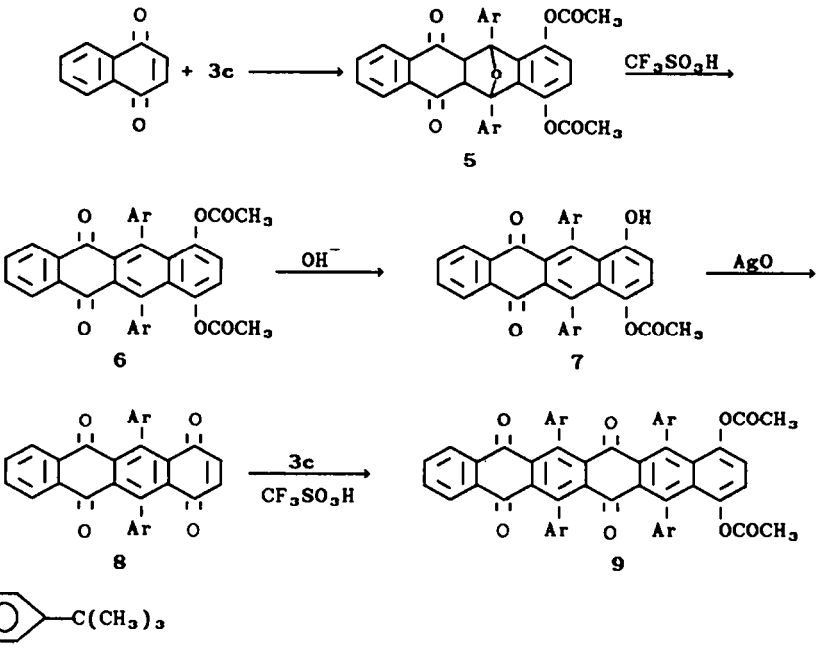
With the benzo[2,3-c]furan 3c now available, we proceeded to investigate the elongation chemistry. In order to facilitate the investigation, we chose 1,4-napthoquinone as the starting quinone. The specific compounds actually prepared in this study are shown in Scheme 2.

The benzo[2,3-c]furan 3c reacted at room temperature during about 18 hrs with 1,4-napthoquinone to give the Diels-Alder adduct 5 in from 54-97% yield after purification. This adduct was readily dehydratively aromatized by treatment with dilute trifluoromethane sulfonic acid in dichloromethane at 0 °C to give the tetracene 6 (67%). Attempts were made to oxidize 6 directly to the corresponding quinone 8 with both ceric ammonium nitrate[4e] and silver(II)-oxide,[4a,4b] but these attempts were unsuccessful. Therefore, 6 was hydrolyzed in high yield (87%) to the half acetate 7 by treatment with 3M sodium hydroxide in DMF. Compound 7 was then easily oxidized with silver(II)oxide to give the tetracene diquinone 8 in 45% yield.[4b]

Diquinone 8 did not react with another molecule of benzo[2,3-c]furan 3c in the absence of a catalyst; but in the presence of dilute trifluoromethane sulfonic acid,[21] both the Diels-Alder reaction and the subsequent dehydration

proceeded rapidly to give the hexacene derivative 9 (46% yield) as a chloroform soluble, red-orange solid.

Scheme 2. Synthesis of 9



These results demonstrate that the masked dienophile/diene, benzo[2,3-c]-furan scheme can be successful for 2-ring elongation of polyacene-1,4-quinones. In the present case, an unusual hexacene diquinone was produced. Since solubility can be a major concern when working with polyacenequinones, these particular derivatives are of considerable interest.

Experimental Section

General Methods. Melting points were determined on a Mel-Temp capillary melting point apparatus and were uncorrected. Infrared spectra were recorded on a Beckman spectrophotometer IR4250 and were calibrated with the 1601.8 cm^{-1} absorbtion of polystyrene. ^1H NMR spectra were measured at 200 MHz on an IBM-NR-200-AF instrument. Chemical shifts are reported in δ units relative to internal Me_4Si. Electron-impact mass spectra were measured on an AEI MS-30 instrument and Fast Atom Bombardment (FAB) mass spectra were recorded on a VG-7070E-HF instrument. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

1,3-Bis(4-tert-butylphenyl)-5,6-dihydrobenzo(2,3-c)furan-4,7-dione(4).

In a dry, nitrogen purged 50 ml 2-necked round bottomed flask was prepared a solution of 2,5-bis(4-tert-butylphenyl)furan[2] (1.0 g, 3.13 mmol) and succinyl chloride (0.35 ml, 3.13 mmol, distilled) in 1,1,2,2-tetrachloroethane (18.8 ml, dried over 4A molecular sieves). To this vigorously stirred ice cooled solution was added, portion wise over about 15-20 min., powdered solid alumnium chloride (1.0 g, 7.82 mmol). The now deep purple reaction mixture was stirred with ice bath cooling for about 20 min., and was then stirred at room temperature for 18 hr.

The reaction was quenched with ice, diluted with water and 10% aqueous HCl, and extracted with chloroform. The combined organic extracts were dried over Na_2SO_4 and concentrated, first under an aspirator vacuum and then under high vacuum (to remove $C_2H_2Cl_4$), to give a brown/orange viscous oil. This

material was purified by flash chromatography[22] on silica gel (230-400 mesh, 73 g) eluting with toluene. The desired product (R_f ~ 0.5 on silica gel w/ chloroform) was eluted as a pale yellow solution which upon concentration gave a tan solid (427 mg, 34.4%). This material was quite pure, and suitable for use in subsequent reactions, but it could be crystallized to give tan needles from either ethanol or heptane. Physical data were collected on crystals from ethanol: mp 212-213.5 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.28 (d, J=8.6 Hz, 4H), 7.53 (d, J=8.6 Hz, 4H), 3.00 (s, 4H), 1.37 (s, 18H); IR (KBr) 2965, 2910, 2870, 1685, 1615, 1575, 1549, 1500 cm^{-1}; mass spectrum, m/e 414 (parent ion); high-resolution mass spectrum calcd for $C_{28}H_{30}O_3$ 414.21948, found 414.2184. Anal. calcd for $C_{28}H_{30}O_3$: C, 81.13; H, 7.29. Found: C, 80.99; H, 7.33.

1,3-Bis(4-tert-butylphenyl)-4,7-bis(trimethylsiloxy)benzo(2,3-c)furan (3a).

In a dry, nitrogen purged 2-necked flask a solution of the furan diketone (4, 34 mg, 0.082 mmol), benzene (2 ml, dried over 4A molecular sieves), and triethylamine (114 µl, 83 mg, 0.82 mmol) was prepared. To this vigorously stirred solution was added trimethylsilyl trifluromethanesulfonate (39.6 µl, 45.5 mg, 0.205 mmol) dropwise over about 1-2 min. This mixture was then stirred at room temperature for about 15 min.

The reaction mixture was then quenched with water, diluted with benzene and washed with water. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a bright yellow viscous oil in essentially quantitative yield (46 mg). This material was essentially pure, as shown by tlc which gave only one spot (R_f ~ 0.4 on silica gel with carbon tetrachloride). Physical data were collected without purification: ^{1}H NMR ($CDCl_3$, 200MHz) δ 7.85 (d, J=8.5 Hz, 4H), 7.43 (d, J=8.5 Hz, 4H), 6.09 (s, 2H), 1.37 (s, 18H), 0.12 (s, 18H); high-resolution mass spectrum calcd for $C_{34}H_{46}O_3Si_2$ 558.29854, found 558.3009.

1,3-Bis(4-tert-butylphenyl)-4,7-dimethoxybenzo(2,3-c)furan (3b)

In a dry, nitrogen purged 25 ml 2-necked flask was prepared a solution of the furan diketone (4, 85 mg, 0.205 mmol) in N,N-dimethylformamide (5ml, dried over 4A molecular sieves). To a vigorously stirred solution of the above was added, portion wise at room temperature over about 2 min, solid sodium hydride (23.6 mg of a 50% oil dispersion, 0.513 mmol). This reaction mixture, which almost immediately became a deep red, was stirred for about 30 min at room temperature. Then dimethyl sulfate (97 µl, 1.03 mmol) was added dropwise over about 1 min, and the reaction mixture was stirred for about 15 min.

The reaction mixture was then diluted with water and extracted with methylene chloride, and the methylene chloride extracts were concentrated on a rotovap and then under high vacuum to remove the N,N-dimethylformamide. The resulting orange semisolid was purified by flash chromatography[22] eluting with chloroform:carbon tetrachloride (approx. 80:20). All bright yellow fractions were combined and concentrated to give a bright yellow solid (69 mg, 76%). Physical data were collected on this material: ^{1}H NMR ($CDCl_3$ 200 MHz) δ 7.94 (d, J=8.3 Hz, 4H), 7.45 (d, J=8.6 Hz, 4H), 6.07 (s, 2H), 3.86 (s, 6H), 1.37 (s, 18 H); mass spectrum, m/e 442 (parent ion); high-resolution mass spectrum calcd for $C_{30}H_{34}O_5$ 442.25078, found 442.2504.

1,3-Bis(4-tert-butylphenyl)-4,7-diacetoxybenzo(2,3-c)furan (3c)

Method A In a dry, nitrogen purged 25 ml 2-necked flask, fitted for reflux under nitrogen, was prepared a solution of compound 4 (100 mg, 0.2415 mmol), acetic anhydride (0.23 ml, 2.415 mmol), and pyridine (6.0 ml, dried over 4A molecular sieves). This solution was heated at reflux in the dark for about 7 hr, and then it was concentrated under reduced pressure to give a dark brown-

yellow residue. This residue was purified by flash chromotography[22] on silica gel (73 g, 230-400 mesh) eluting with chloroform. Fractions containing compound 3c were a bright yellow with a faint bluish glow, which upon concentration gave a yellow solid (113 mg, 94%). This material was quite pure and used "as is" in subsequent reactions, but crystallization occured readily from heptane to give small yellow plates. Physical data were collected on the crystals from heptane: mp 195.5-196.5 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.67 (d, J=8.6 Hz, 4H), 7.47 (d, J=8.5 Hz, 4H), 6.61 (s, 2H), 2.00 (s, 6H), 1.36 (s, 18H); IR (KBr) 2967, 2909, 2872, 1769, 1372, 1181 cm^{-1}; mass spectrum, m/e 498 (parent ion); high-resolution mass spectrum calcd for $C_{32}H_{34}O_6$ 498.24060, found 498.2408. Anal. calcd for $C_{32}H_{34}O_6$: C, 77.08; H, 6.87. Found: C, 76.98; H, 7.00.

Method B In a dry, nitrogen purged 10 ml 2-necked flask was prepared a solution of the furan diketone (4, 18 mg, 0.043 mmol) in benzene (2 ml, dried over 4A molecular sieves). To this solution, at room temperature with stirring, was added thallium(I) ethoxide (30.79 µl, 0.43 mmol), dropwise over about 1 min, and the resulting mixture was stirred at room temperature for about 3.5 hr. Acetyl chloride (92 µl, 1.30 mmol) was then added in one portion, and the reaction mixture quickly changed from deep red to bright yellow. After stirring for about 10 min, the reaction mixture was diluted with water and extracted with benzene. The benzene extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a yellow-brown viscous oil in essentially quantitative yield which was shown by tlc (silica gel with chloroform, $R_f \sim 0.5$) to be quite pure and to be identical with 3c prepared in Method A above.

1,4-Diacetoxy-5,12-bis(4-tert-butylphenyl)-5,12-oxo-6,11-tetracenedione (5).

In a dry, 50 ml 2-necked flask was prepared under a nitrogen atmosphere, a solution of compound 3c (393 mg, 0.789 mmol) and 1,4-napthoquinone (124.8 mg, 0.789 mmol, sublimed) in benzene (16 ml, dried over 4A molecular sieves). This solution was stirred at room temperature in the dark for 20.5 hr and was then concentrated under reduced pressure. Purification was accomplished by preparative tlc on silica gel developed with chloroform. The material was eluted from the silica gel with chloroform:methanol (approx. 85:15) to give an off-white solid (500 mg, 97%). This material was of satisfactory purity for subsequent reactions. A sample for characterization was purified further by crystallization from carbon tetrachloride to give a white powder. Physical data was collected on this white solid: mp-gradually darkened between approximately 165-200 °C, changing from a dark brown solid to a dark brown liquid at approximately 220 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.90 (d, J=8.5 Hz, 4H), 7.66 (m, 2H), 7.48 (m, 6H), 6.50 (s, 2H), 4.49 (s, 2H), 1.47 (s, 6H), 1.34 (s, 18H); IR(KBr) 2972, 2913, 2878, 1783, 1686, 1605, 1492, 1375, 1288, 1201, 1173 cm^{-1}; mass spectrum, (FAB, positive ion spectrum) m/e (relative intensity) 657.3 ($(M+H)^+$, 8.3), 498.3 (100), 483.2 (8.6), 456.3 (20), 414.2(50.4); high-resolution mass spectrum (FAB, positive ion spectrum) calcd for $C_{42}H_{41}O_7$ 657.2852, found 657.2825.

1,4-Diacetoxy-5,12-bis(4-tert-butylphenyl)-6,11-tetracenedione (6).

In a dry, nitrogen purged 25 ml 2-necked flask was prepared a solution of the Diels-Alder adduct 5 (99 mg, 0.151 mmol) in dichloromethane (6 ml, dried over 4A molecular sieves), and this solution was cooled in an ice bath. To this cooled, vigorously stirred solution was added, dropwise over about 20 min, a dichloromethane solution (2.5 ml) saturated with trifluoromethane sulfonic acid (this was prepared by stirring a mixture of 10 ml of dry dichloromethane and 0.1 ml of triflic acid at room temperature for about 15 min and then

letting the phases separate). After the addition was complete, the reaction mixture was stirred with ice bath cooling for about 15 min; and then it was washed with water three times, dried over sodium sulfate, and concentrated under reduced pressure to give a yellow-green viscous oil. This material was purified by preparative tlc on silica gel with chloroform:ether (40:1) to give a yellow solid (65 mg, 67%). Crystallization from ethanol gave small gold plates: mp 260.5-263 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.89 (m, 2H), 7.62 (m, 2H), 7.50 (d, J=8.3 Hz, 4H), 7.25 (d, J=8.2 Hz, 4H), 7.17 (s, 2H), 1.48 (s, 6H), 1.44 (s, 18H); IR (KBr) 2963, 2902, 2866, 1767, 1678, 1612, 1595, 1363, 1254, 1171 cm^{-1}; mass spectrum, m/e (relative intensity) 638.3 (M^+, 18.1), 596.2 (20.9), 554.2 (100), 498.2 (12.8), 442.1 (18.8); high-resolution mass spectrum calcd for $C_{42}H_{38}O_6$ 638.26681, found 638.2651. Anal. calcd for $C_{42}H_{38}O_6$: C, 78.98; H, 6.00. Found: C, 78.92; H, 6.05.

1-Acetoxy-4-hydroxy-5,12-bis(4-tert-butylphenyl)-6,11-tetracenedione (7).

To a homogeneous yellow solution of the tetracene derivative 6 (245 mg, 0.385 mmol) in N,N-dimethylformamide (36 ml) was added dropwise, over about 1-2 min, 2.6 ml of 3M aqueous sodium hydroxide, resulting in the immediate formation of a deep blue solution. This solution was stirred at room temperature for about 30 min, and was then quenched with 72 ml of ice cold 2.5% aqueous hydrochloric acid. The deep blue color disappeared, and a yellow precipitate formed. This precipitate was collected by filtration, washed with water, and dried to give a yellow solid (200 mg, 87%). Purification was accomplished by prep. tlc (silica gel with chloroform, R_f ~ 0.15): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.95-7.86 (m, 2H), 7.68-7.60 (m, 4H), 7.51-7.44 (m, 4H), 7.23 (d, J=8.8 Hz, 2H), 7.09 (d, J=8.5 Hz, 1H), 6.97 (d, J=8.5 Hz, 1H), 5.72 (s, 1H), 1.46-1.44 (m, 21H). After D_2O exchange, the only change in the ^{1}H NMR was that the one proton singlet at δ 5.72 disappeared; IR (KBr) 3459, 2965, 2905, 2871, 1769, 1682, 1613, 1600, 1439, 1368, 1347, 1260, 1206, 1190, 1068 cm^{-1}; mass spectrum, m/e (relative intensity) 596.2 (M^+, 10.8), 554.1 (100), 498.1 (19.4), 442.1 (31.4); high resolution mass spectrum calcd for $C_{40}H_{36}O_6$ 596.25625, found 596.2565.

5,12-Bis(4-tert-butylphenyl)-1,4,6,11-tetracenetetrone (8).

To a solution of compound 7 (58 mg, 0.0976 mmol) in THF (10 ml, freshly distilled from sodium and benzophenone) was added AgO (72.6 mg, 0.586 mmol, recently prepared).[23] This mixture was briefly sonicated to give a uniform suspension of AgO, and then 6M HNO_3 (0.1 ml) was added and the reaction mixture was stirred vigorously at room temperature for about 45 min. The reaction mixture was then diluted with water, extracted with chloroform, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by preparative tlc on silica gel developed with chloroform to give a red-orange solid (24 mg, 45%). Brick red micro crystals (nuggets) were obtained from ethanol. Mp 308-309 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.96 (m, 2H), 7.68 (m, 2H), 7.49 (d, J=8.4 Hz, 4H), 7.12 (d, J=8.4 Hz, 4H), 6.79 (s, 2H), 1.45 (s, 18H); IR (KBr) 2967, 2906, 2875, 1680, 1625, 1596, 1520, 1467, 1363, 1286, 1224, 1119, 1069 cm^{-1}, mass spectrum, m/e 552 (parent ion); high-resolution mass spectrum calcd for $C_{38}H_{32}O_4$ 552.23004, found 552.2328. Anal. calcd for $C_{38}H_{32}O_4$: C, 82.58; H, 5.84. Found: C, 82.71; H, 5.96.

1,4-Diacetoxy-5,7,14,16-tetrakis(4-tert-butylphenyl)-6,8,13,15-hexacenetetrone (9).

In a dry, nitrogen purged 25 ml round bottomed flask was prepared a solution of the benzo[2,3-c]furan 3c (30.5 mg, 0.0611 mmol) and the quinone 8 (27 mg, 0.0489 mmol) in benzene (8 ml, dried over 4Å molecular sieves). To this

vigorously stirred solution was added dropwise over several min. a dichloromethane solution (1.25 ml) saturated with triflic acid (this was prepared by stirring a mixture of 4 ml of dry dichloromethane and 40 µl of triflic acid at room temperature for about 15 min. and then letting the phases separate). This mixture was stirred at room temperature for about 20 min and was then washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure to give a red-orange residue. This was purified by preparative tlc on silica gel with chloroform (appearing as a yellow-orange band at $R_f \sim 0.15$) to give a yellow-orange solid (23 mg, 46%) which crystalized from ethanol as orange nuggets: mp 296-309 °C; ^{1}H NMR ($CDCL_3$, 200 MHz) δ 7.84 (m, 2H), 7.64 (m, 2H), 7.38 (d, J=8.4 Hz, 4H), 7.28 (d, J=8.4 Hz, 4H), 7.10-7.00 (m, 10H), 1.46 (s, 18H), 1.44 (s, 6H), 1.40 (s, 18H); IR (KBr) 2950, 2851, 2830, 1773, 1705, 1680, 1362, 1273, 1177, 1073 cm^{-1}; mass spectrum, m/e (relative intensity) 1032.1 (M^+, 17.4), 990.2 (25.0), 948.1 (100); FAB high-resolution mass spectrum calcd for $C_{70}H_{84}O_8$ 1032.4600, found (positive ion spectrum, therefore, M+H) 1033.4623.

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References

1. Thomas, A.D.; Miller, L.L. *J. Org. Chem.* **1986**, *51*, 4160.
2. Christopfel, W.C.; Miller, L.L. *J. Org. Chem.* **1986**, *51*, 4169.
3. Verine, A.; Lepage, Y. *Bull. Soc. Chim. Fr.* **1973**, 1154.
4. (a) Snyder, C.D.; Rapoport, H. *J. Am. Chem. Soc.* **1972**, *94*, 227.
   (b) Escobar, C.; Farina, F.; Martinez-Utrilla, R.; Paredes, C. *J. Chem. Research (S)*, **1980**, 156.
   (c) Kraus, G.A.; Neuenschwander, K. *Synth. Commun.*, **1980**, *10*, 9.
   (d) Kloc, K.; Mlochowski, J.; Syper, L. *Chem. Lett.*, **1980**, 725.
   (e) Jacob, III, P.; Callery, P.S.; Shulgin, A.T.; Castagnoli, Jr., N. *J. Org. Chem.*, **1976**, *41*, 3627.
   (f) Musgrave, O.C. *Chem. Rev.*, **1969**, *69*, 499.
   (g) McKillop, A.; Swann, B.P.; Zelesko, M.J.; Taylor, E.C. *Angew. Chem. Internat. Edit.*, **1970**, *9*, 74.
5. Friedrichsen, W. *Adv. Heterocycl. Chem.*, **1980**, *26*, 234.
6. (a) Ghera, E.; Gaoni, Y.; Perry, D.H. *J. Chem. Soc., Chem. Comm.*, **1974**, 1034.
   (b) Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *J. Am. Chem. Soc.*, **1977**, *99*, 1487.
   (c) Kobayashi, Y.; Taguchi, T.; Tokuno, E. *Tetrahedron Lett.*, **1977**, 3741.
7. Potts, K.T.; Elliott, A.J. *Org. Prep. Proced. Int.*, **1972**, *4*, 269.
8. Brownbridge, P.: Chan, T.H. *Tetrahedron Lett.*, **1980**, *21*, 3423.
9. Callen, J.E.; Dornfeld, C.A.; Coleman, G.H. *Org. Syn.*, **1955**, Coll. Vol., 3, 26. Moffett, R.B.; Shriner, R.L. *Org. Syn.*, **1955**, Coll. Vol., 3, 562.
10. Jorgenson, M.J. *Org. React.*, **1970**, *18*, 1. Rubottom, G.M.; Kim, C.W. *J. Org. Chem.*, **1983**, *48*, 1550.
11. Posner, G.H. *Org. React.*, **1975**, *22*, 253. Normant, J.F. *Synthesis*, **1972** 63.
12. Perchonock, C.D.; Loev, B. *Prostaglandins*, **1978** *15*, 623.
13. Nightingale, D.V.; Sukornick, B. *J. Org. Chem.*, **1959**, *24*, 497.
14. Effenberger, F.; Sohn, E.; Epple, G. *Chem. Ber.*, **1983**, *116*, 1195.
15. Effenberger, F.; Epple, G. *Angew. Chem. Internat. Edit.*, **1972**, *11*, 299. Butler, I.R.; Morley, J.O. *J. Chem. Research (S)*, **1980**, 358.
16. Berliner, E. *Org. React.*, **1949**, *5*, 229.
17. Snyder, H.R.; Werber, F.X. *J. Am. Chem. Soc.*, **1950**, *72*, 2965. Mosby, W.L. *J. Org. Chem.*, **1954**, *19*, 294. Popp, F.D.; McEwen, W.E. *Chem. Rev.*, **1958**, *58*, 321.
18. Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Gotz, A.; Hergott, H.H.; Hofmann, K.; Kober, W.; Krageloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis*, **1982**, 1. Simchen, G.; Kober, W. *Synthesis*, **1976**, 259.
19. Heiszwolf, G.J.; Kloosterziel, H. *J. Chem. Soc., Chem. Comm.*, **1966**, 51.
20. Taylor, E.C.; Mclay, G.W.; McKillop, A. *J. Am. Chem. Soc.*, **1968**, *90*, 2422.
21. Olah, G.A.; Meidar, D.; Fung, A.P. *Synthesis*, **1979**, 270.
22. Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.*, **1978** *43*, 2923.
23. Hammer, R.N.; Kleinberg, J. *Inorg. Syn.*, **1953**, *4*, 12.