CH_3); IR (CCl_4) 1650 cm^{-1} (C=N). Samples of this compound were somewhat contaminated with **35**.[32] When a portion of the crude product was stirred with aqueous hydrochloric acid (5%) prior to GC analysis, **36** was not observed.

37: ^1H NMR (CCl_4) τ 2.87 (m, 5, Ph), 6.96 (m, 1, CH), 7.44 (bd, J = 6 Hz, 2, $CHCH_2CO$), 7.87 (bt, J = 6 Hz, 2, CH_2CH_2CO), 8.78 (m, 10, all other CH_2's), 9.15 (m, 6, CH_3); IR (CCl_4) 1704 cm^{-1} (C=O); mass spectrum, m/z (relative intensity) 246 (M^+, 4), 91 (100).

38: ^1H NMR (CCl_4) τ 2.82 (m, 5, Ph), 6.92 (m, 1, CH), 7.42 (bd, J = 7 Hz, 2, $CHCH_2CN$), 7.92 (m, 2, CH_2CH_2CN), 8.68 (m, 10, all other CH_2's), 9.08 (m, 6, CH_3); IR (CCl_4) 1640 cm^{-1} (C=N). Samples of this compound were somewhat contaminated with **37**.[32]

Reactions of 3-Phenyl-2-propyn-1-amine (3) and *n*-Butyllithium. GC analysis (column A, 150 °C) of the crude products gave the following relative retention times: **4** (1.0), **5** (2.0). Hexadecane was used as the internal standard for determining yields.

Reactions of Benzonitrile (40) with *n*-Butyllithium. GC analyses (column C, 150 °C) of the crude products had the following relative retention times: **5** (1.0), **22d** (6.0), and three unidentified components (2.0, 6.9, and 8.0). Tetradecane was used as the internal standard for determining yields. The peaks due to the unidentified components constituted 0%, 17%, and 50% of the total GC peak area of a 1:1 reaction and 4%, 18%, and 8% of a 1:3 reaction.

Reactions of 22a and 23a with 19a. GC analysis (column A, 120 °C initially, but raised at a rate of 10 °C/min to 185 °C after **23a** had eluted) gave the following retention times: **19a** (1.0), **22a** (5.0), **23a** (6.0), **24a** (13). GC analysis of a solution of a mixture of **22a** and **23a** (18 mg) in diethyl ether (0.5 mL) gave a peak area ratio **23a**:(**22a** + **23a**) of 0.31. This solution was mixed rapidly with a solution of **19a** (17 mg) in diethyl ether (0.5 mL). GC analysis of a sample injected after only 1 min showed the absence of **23a** and a substantial peak for **24a**; the peak area ratio **24a**:(**22a** + **24a**) was 0.53. In another reaction, a solution of **22a** (20 mg) in diethyl ether (0.5 mL) was mixed rapidly with a solution of **19a** (18 mg) in diethyl ether (0.5 mL). The peak area ratio **24a**:(**22a** + **24a**) was 0 after 1 min, 0.05 after 30 min, and 0.30 after 522 min.

Reactions of 22f and 23d with 19f. GC analysis (column A, 145 °C initially, but raised at a rate of 8 °C/min to 204 °C after **22f** had eluted) gave the following relative retention times: **19f** (1.0), **23d** (1.9), **22f** (2.3), **24c** (6.4). GC analysis of a solution of a mixture of **22f** and **23d** (41 mg) in diethyl ether (0.5 mL) gave a peak area ratio **23d**:(**22f** + **23d**) of 0.33. This solution was mixed rapidly with a solution of **19f** (29 mg) in diethyl ether (0.5 mL). GC analysis of a sample injected after only 1 min gave a peak area ratio **23d**:(**22f** + **23d**) of 0.22 and a peak area ratio **24c**:(**22f** + **23d** + **24c**) of 0.14. After 45 min, the same ratios were 0.16 and 0.25, respectively. A solution of **22f** (24 mg) in diethyl ether (0.5 mL) was mixed rapidly with a solution of **19f** (17 mg) in diethyl ether (0.5 mL). GC analysis showed no **24c**, even after 180 min.

Acknowledgment. We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the NMR spectrometers and the mass spectrometer. We thank Dr. Raymond C. McLane for performing some control experiments.

Registry No. **1**, 107-11-9; **2**, 33083-83-9; **3**, 78168-74-8; **4**, 536-74-3; **5**, 502-56-7; **19a**, 111-26-2; **19b**, 107-10-8; **19c**, 64-04-0; **19d**, 5813-64-9; **19e**, 107-15-3; **19f**, 100-46-9; **20**, 780-25-6; **21a**, 61501-03-9; **21b**, 91-00-9; **22a**, 820-29-1; **22b**, 106-35-4; **22c**, 25870-62-6; **22d**, 1009-14-9; **22d** 2,4-dinitrophenylhydrazone, 2121-88-2; **22e**, 98-86-2; **22f**, 938-16-9; **23a**, 37027-36-4; **23b**, 29097-52-7; **23c**, 16659-09-9; **23d**, 33611-54-0; **23e**, 1013-88-3; **24a**, 37027-39-7; **24b**, 86885-94-1; **24c**, 86885-95-2; **24d**, 14428-98-9; **25a**, 37027-40-0; **25b**, 86885-96-3; **25c**, 5350-59-4; **26**, 86885-97-4; **27**, 98-84-0; **28**, 33083-81-7; **29**, 36653-37-9; **30**, 108-91-8; **31**, 108-94-1; **32**, 2626-61-1; **33**, 765-30-0; **34**, 4360-51-4; **35**, 19969-04-1; **35** 2,4-dinitrophenylhydrazone, 19969-05-2; **36**, 86885-98-5; **37**, 30242-38-7; **38**, 86885-99-6; **40**, 100-47-0; *n*-BuLi, 109-72-8; phenyllithium, 591-51-5; methyllithium, 917-54-4.

Synthesis of Heptiptycenes with Face-to-Face Arene Rings via a 2,3:6,7-Anthradiyne Equivalent

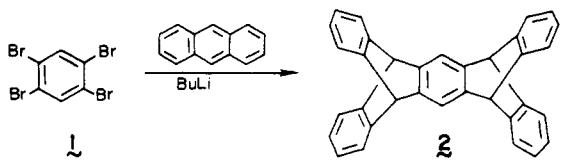
Harold Hart,* N. Raju, Mary Ann Meador, and Donald L. Ward†

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received April 20, 1983

1,2,4,5-Tetrabromobenzene reacts with 2 equiv of butyllithium and furan to give 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (**3**). Both double bonds in **3** are effective dienophiles. Thus **3** gives a bis(adduct) with anthracene which on dehydration gives the pentiptycene **6**. That is, **3** is a 2,3:6,7-anthradiyne equivalent. The central anthracene moiety in **6** adds benzyne to give the novel heptiptycene **12** with face-to-face arene rings. Analogous experiments with a dimethoxy analogue are also described. The crystal structure of *anti*-diepoxide **3** was determined.

Diaryne equivalents[1] have considerable potential for the rapid assembly of multiring systems. For example, the pentiptycene **2** was prepared in one step from anthracene and the diaryne equivalent 1,2,4,5-tetrabromobenzene (**1**).[2]



1 **2**

In this paper we use a different type of diaryne equivalent to synthesize analogues of **2** in which the "central" ring is an anthracene moiety. These analogues react with benzyne to give iptycenes with face-to-face arene rings.

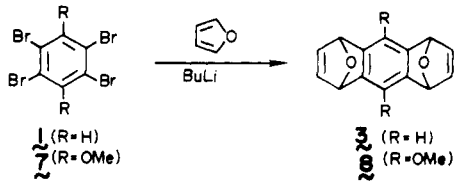
Results and Discussion

Treatment of **1** with *n*-butyllithium and excess furan gave the bis(adduct) **3**.[3] Both isomers (syn and anti) are

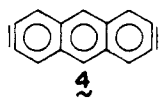
† To whom inquiries regarding the X-ray structure of **3** should be directed.

(1) Hart, H.; Lai, C-Y.; Nwokogu, G.; Shamoulian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6449.
(2) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.
(3) This adduct was first prepared by Dr. Yoshikazu Takehira, whom we thank.

0022-3263/83/1948-4357$01.50/0



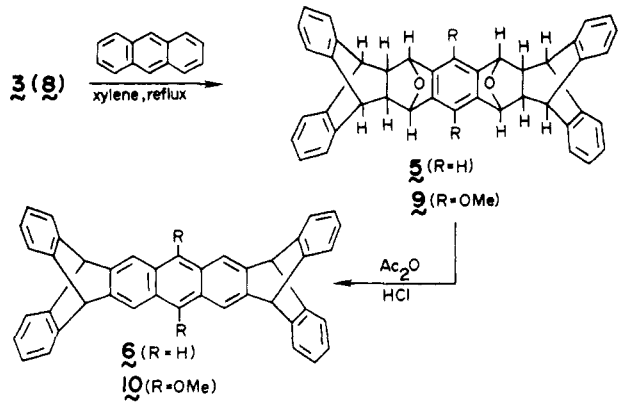
formed in nearly equal amounts and can be separated by differential solubility in methanol. An X-ray structure of the less soluble anti isomer is described at the end of this paper. Bis(adduct) 3 can be regarded as a synthetic equivalent of 2,3:6,7-anthradiyne 4, because it is well es-



4

tablished that analogous 1,4-epoxides (for example, 1,4-epoxy-1,4-dihydronaphthalene) are effective dienophiles[4] and that the oxygen bridge in the resulting cycloadducts can usually be removed to give an aromatic product.

As anticipated, reaction of 3 with 2 equiv of anthracene in refluxing xylene gave the bis(adduct) 5. *Anti*-3 gave

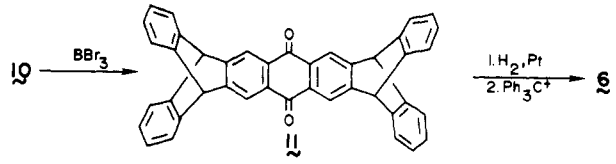


one isomer of 5, and *syn*-3 gave another stereoisomer of 5. The oxygen bridges were removed from either isomer of 5 with concentrated hydrochloric acid in acetic anhydride to give the pentiptycene 6.

Pentiptycene 6 is a white solid with a bluish tinge to the crystals. Its structure was apparent from its spectra and was confirmed by independent synthesis (vide infra). The proton NMR spectrum of 6 showed a four-proton singlet for the bridgehead hydrogens (δ 5.50) and two singlets, area ratio 4:2, for the uncoupled protons of the anthracene ring (δ 7.81, 8.06) as well as signals for the remaining 16 aryl protons. This proton spectrum contrasts with that of the precursor 5, which showed three four-proton singlets for the aliphatic protons[5] and a sharp two-proton singlet for the central aromatic protons.

The ^{13}C NMR spectrum of 6 showed only eight signals, as required by symmetry. The ultraviolet spectrum of 6 in acetonitrile contained numerous absorption bands as a consequence of the central anthracene moiety, the longest wavelength absorption appearing at 371 nm.

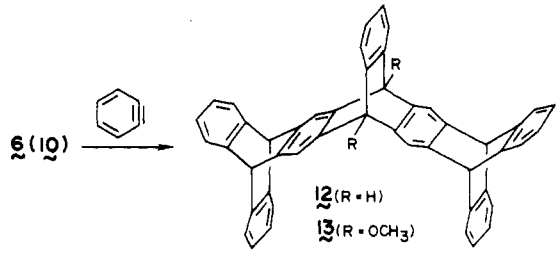
In a parallel series of experiments having as its goal an independent synthesis of 6, 1,4-dimethoxytetrabromobenzene (7)[6] was treated with butyllithium and excess furan to give bis(adduct) 8.[7] The crystalline product, mp 199–201 °C, is presumed to have the anti configuration.[8] Reaction of 8 with anthracene gave two stereoisomeric adducts **9a** (mp >415 °C) and **9b** (mp 359–361 °C) in nearly quantitative yield. The former precipitated from solution during the reaction. Each of these adducts separately or the mixture gave on dehydration with acetic anhydride and hydrochloric acid the dimethoxypentiptycene 10, mp 362–364 °C.



The ^1H NMR spectrum of 10 was similar to that of 6, with bridgehead protons at δ 5.54 and a singlet at δ 8.12 for the anthracene-type protons. The ^{13}C NMR spectrum of 10 showed nine peaks as required for its symmetry.

Conversion of 10 to 6 was accomplished as follows. Treatment with boron bromide gave the bright yellow quinone 11. With hydrogen over a platinum catalyst 11 gave the corresponding dihydroanthracene, which was oxidized by trityl cation to 6. The spectra of 6 obtained in this way were identical in all respects with those of 6 obtained directly from 3 via 5.

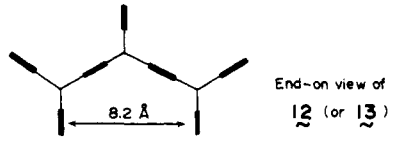
Reaction of either 6 or 10 with benzyne gave adducts 12 or 13, respectively. The structures of these adducts were



assigned from the method of synthesis and from the spectra. The ^1H NMR spectrum of 12 showed two sets of signals for the bridgehead protons, at δ 5.20 and 5.25 (area ratio 1:2), whereas in 13 there was only a single peak for the bridgehead protons, at δ 5.29. In addition, each spectrum showed a sharp singlet for the four unique, unsplit aryl protons (at δ 7.35 in 12, 7.69 in 13). The ^{13}C NMR spectra showed fewer peaks than theoretical, presumably due to accidental overlap of signals for the aryl carbons.

The ultraviolet spectra of 6 and 12 show striking differences. The spectrum of 12 is strictly benzenoid in character, the longest wavelength band appearing at 295 nm. The UV spectrum of 6, on the other hand, was rich with peaks, there being five maxima at wavelengths above 300 nm.

Heptiptycenes 12 and 13 have a geometry with several interesting structural features worthy of further exploration. Four of the aryl rings are arranged in a horseshoe shape which creates a nonpolar or lipophilic cavity with two parallel arene rings separated by approximately 8.2 Å. The possiblity that this cavity might trap nonpolar



(4) Wittig, G.; Härle, H.; Knauss, E.; Niethammer, K. *Chem. Ber* **1960**, *93*, 951. Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Kondo, A. *J. Org. Chem.* **1973**, *38*, 4100.

(5) The rigid framework of 5 results in dihedral angles close to 90° between adjacent sets of nonequivalent bridgehead protons, resulting in almost no coupling.

(6) Kohn, M.; Grün, S. *Monatsh.* **1925**, *45*, 663.

(7) Nwokogu, G. C., Ph.D. Thesis, Michigan State University, 1981.

(8) Absence of coupling between the bridgehead and vinyl protons supports this assignment.

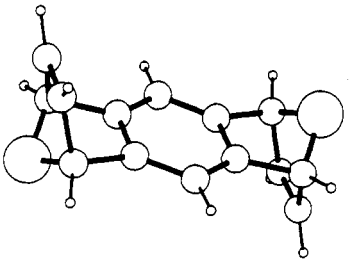


Figure 1. 1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene. Drawn by PLUTO (Motherwell, S. "Cambridge Crystallographic Data Files User Manual"; Crystallographic Data Centre: Cambridge, England, May, 1976) with atomic radii of 0.5 Å for O, 0.3 Å for C, and 0.1 Å for H.

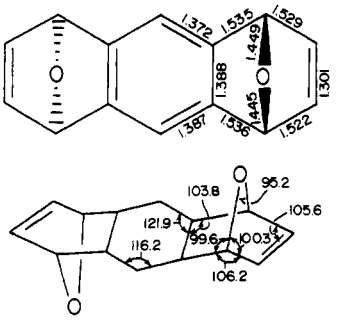
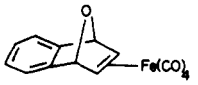


Figure 2. Selected bond distances and bond angles in 3.

small molecules (especially if the three remaining rings were to carry polar, hydrophilic substituents) is being explored. This cavity may also yield novel organometallic complexes. Finally, the possiblity that this cavity may, with two additional arene rings, be converted to a three-dimensional hexagonal array of benzenoid rings is under study.[9]

X-ray Structure of 3. A three-dimensional drawing of 3 is shown in Figure 1, and significant bond distances and angles are shown on the structures in Figure 2. The fusion of two oxabicyclo[2.2.1]heptene moieties on a single benzene ring does not bring about any dramatic structural changes when compared with a model compound containing one such moiety. For example, the crystal structure of the tetracarbonyl iron derivative 14 has been reported.[10]



14

The double bonds in 3 are, of course, shorter than the corresponding bond in 14 (1.30 vs. 1.39 Å), resulting in other predictable structural changes, such as contraction of the C(1)–O–C(4) angle (95° in 3, 96°–98° in 14). However all of the geometric changes are relatively minor, and 3 does not appear to be unduly strained compared with 1,4-epoxy-1,4-dihydronaphthalene.

Experimental Section

NMR spectra (^1H and ^{13}C) were recorded with a Bruker 250-MHz instrument with $CDCl_3$ as the solvent and tetramethylsilane (Me_4Si) as the internal reference. IR spectra were determined on a Perkin-Elmer Model 167 spectrometer. Mass spectra were measured at 70 eV with a Finnigan 4000 spectrometer with the INCOS data system. The instrument was operated by Ernest Oliver, whom we thank. Melting points were determined with a Mel-Temp apparatus, modified when necessary for high temperatures,[11] and are uncorrected. Anhydrous magnesium sulfate was the drying agent throughout, and the silica gel for chromatography was 230–400 mesh. Analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

1,4:5,8-Diepoxy-1,4,5,8-tetrahydroanthracene (3). To a stirred solution of 1,2,4,5-tetrabromobenzene[12] (3.94 g, 10 mmol) in dry toluene (200 mL) at −23 °C under argon was slowly added (4 h) *n*-butyllithium (7.7 mL, 12 mmol, of a 1.55 M solution in hexane diluted with 200 mL of dry hexane). After addition the mixture was slowly allowed to warm to room temperature. Methanol (1 mL) was added cautiously and the mixture was stirred for a few minutes. The organic layer was washed with water and dried. Solvent removal under reduced pressure gave a gummy yellow solid which partially dissolved on addition of methanol (10 mL). The off-white crystals which remained (0.7 g) were recrystallized from acetone to give small white plates of the anti isomer, mp 245 °C dec. The methanol solution was evaporated to dryness and the residue was recrystallized from ethyl acetate–hexane and then from methanol to give the pure syn isomer (0.8 g), mp 191–193 °C. The total yield of both isomers was 71%. ^1H NMR (anti) δ 5.62 (s, 4 H), 7.01 (s, 4 H), 7.18 (s, 2 H); ^{13}C NMR (anti) δ 82.23, 113.75, 143.30, 147.69; the NMR spectra of the syn isomer were virtually identical with those of the anti isomer (differences of δ 0.01 in the proton spectrum and 0.10 in the carbon spectrum). Mass spectrum, (anti) *m/e* 210 (43), 184 (26), 181 (13), 156 (34), 155 (63), 154 (31), 153 (100), 152 (73), 151 (18), 128 (22), 127 (13), 126 (10), 87 (12), 85 (29). Anal. Calcd for $C_{14}H_{10}O_2$ anti: C, 80.0; H, 4.76. Found C, 79.95; H, 4.87.

9,10-Dimethoxy-1,4:5,8-diepoxy-1,4,5,8-tetrahydroanthracene (8).[7] A procedure similar to that for 3 using 10 mmol of 1,2,4,5-tetrabromo-3,6-dimethoxybenzene,[6] 5 mL of furan, and 100 mL of toluene gave 8 (1.34 g, 50%) as colorless crystals from acetone–petroleum ether (30–60 °C): mp 199–201 °C; ^1H NMR δ 3.83 (s, 6 H), 5.83 (d, J = 0.5 Hz, 4 H), 7.0 (br s, 4 H); mass spectrum, *m/e* 270 (43), 215 (100), 199 (77), 183 (25), 139 (30), 63 (23), 43 (3).

The Adduct of 3 and Anthracene (5). A solution of diepoxide 3 (anti isomer) (2.1 g, 10 mmol) and anthracene (3.6 g, 20 mmol) in xylene (100 mL) was heated at reflux for 48 h. The reaction mixture was cooled to room temperature and the resulting white precipitate was collected (4.6 g, 80%) as a mixture of 5 and a trace of unreacted anthracene. The latter was removed by sublimation to give pure 5: mp >440 °C dec; ^1H NMR δ 2.13 (s, 4 H), 4.36 (s, 4 H), 4.82 (s, 4 H), 6.90 (s, 2 H), 6.98 (m, 4 H), 7.11 (m, 4 H), 7.19 (m, 4 H), 7.26 (m, 4 H); ^{13}C NMR δ 47.48, 48.80, 81.09, 110.08, 123.50, 123.68, 125.70, 125.97, 141.49, 144.25, 145.61; mass spectrum, *m/e* 566 (6), 530 (21), 375 (50), 370 (65), 362 (17), 339 (15), 203 (13), 191 (43), 178 (100), 44 (43).

The analogous reaction of *syn*-3 with anthracene gave a stereoisomer of 5 in 60% yield: mp 395 °C dec; ^1H NMR δ 2.13 (s, 4 H), 4.35 (s, 4 H), 4.80 (s, 4 H), 6.90 (s, 2 H), 6.98 (m, 4 H), 7.12 (m, 4 H), 7.18 (m, 4 H), 7.26 (m, 4 H); ^{13}C NMR δ 47.47, 49.07, 81.18, 110.04, 123.42, 123.70, 125.66, 126.0, 141.34, 144.19, 145.79.

Dehydration of 5. A suspension of 5 (800 mg, 1.4 mmol) in acetic anhydride (20 mL) and concentrated hydrochloric acid (4 mL) was heated at reflux for 8 h. The cooled reaction mixture was poured into 200 mL of ice–water and the resulting light yellow crystals were extracted with chloroform. The organic layer was washed successively with water and saturated sodium bicarbonate, and dried (Na_2SO_4). Removal of the solvent gave a light yellow residue which was recrystallized from methanol to give 300 mg (41%) of pentiptycene 6 as off-white crystals with a bluish tinge: mp >500 °C;[13] ^1H NMR δ 5.50 (s, 4 H, bridgehead protons), 7.02 (m, 8 H), 7.40 (m, 8 H), 7.81 (s, 4 H), 8.06 (s, 2 H); ^{13}C NMR δ 53.81, 121.34, 123.81, 125.11, 125.71, 130.58, 140.80, 144.40; UV (CH_3CN) λ_{max} 371 nm (ε 6540), 353 (8830), 336 (7150), 320 (4240), 306 (2030), 284 (212 000), 272 (81 270), 266 (60 500), 260 (61 600),

(9) Compounds approaching this type of cyclic array have recently been described: Lipczynska-Kochany, E.; Iwamura, H. *Chem. Lett.* **1982**, 1075.

(10) Raston, C. L.; Wege, D.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2153.

(11) To raise the temperature of the hot stage above the normal maximum, the voltage was increased once or twice from nominal 110 to 140 V with one or two Variacs.

(12) Scheufelen, A. *Justus Liebigs Ann. Chem.* **1885**, *231*, 152. Cox, B.; Kubler, D. G.; Wilson, C. A. *J. Chem. Educ.* **1977**, *54*, 379.

(13) The mother liquors yielded minor products whose structures have not yet been determined.

243 (23 200). Anal. Calcd for $C_{42}H_{26}$: C, 96.98, H, 4.90. Found: 96.46; H, 4.98.

The Adducts of 8 and Anthracene (9a, 9b). A solution of 8 (5.4 g, 20 mmol) and anthracene (7.12 g, 40 mmol) in xylene (250 mL) was heated at reflux until the anthracene was consumed (72 h, followed by TLC). The white solid which precipitated during the reaction was filtered and washed with benzene to give 6.2 g (9.90 mmol) of **9a**, mp 415 °C dec. The product was too insoluble and high melting to obtain spectra. Anal. Calcd for $C_{44}H_{34}O_4$: C, 84.35; H, 5.43. Found: C, 84.14; H, 5.30.

Concentration of the filtrate and recrystallization of the solid residue twice from chloroform–methanol gave 4.1 g (6.55 mmol) of **9b** as colorless needles: mp 359–361 °C; ^{1}H NMR δ 2.17 (s, 4 H, *ring juncture protons*), 3.96 (s, 6 H, *methoxyls*), 4.3 (s, 4 H, bridgehead protons adjacent to aromatic rings), 4.93 (s, 4 H, bridgehead protons adjacent to oxygen), 7.17 (m, 16 H, aromatic protons); mass spectrum, *m/e* 626 (0.5), 436 (4), 435 (39), 422 (60), 257 (5), 244 (5), 232 (13), 231 (100), 229 (9), 219 (4), 218 (32), 216 (14), 215 (12), 204 (7), 203 (45), 202 (5), 201 (10), 191 (24), 179 (5), 178 (29). Anal. Calcd for $C_{44}H_{34}O_4$: C, 84.35; H, 5.43. Found: C, 84.16; H, 5.35.

Dimethoxypentiptycene (10). A mixture of the insoluble adduct **9a** (400 mg, 0.64 mmol), acetic anhydride (10 mL), and concentrated hydrochloric acid (1 mL) was heated at reflux overnight. The reaction mixture was poured into ice-cold water and extracted with chloroform, and the chlorofom extracts were washed successively with water, saturated sodium bicarbonate solution, and water and dried. Evaporation of the solvent followed by chromatography of the crude product over silica gel with hexane as eluent gave anthracene (120 mg). Further elution with benzene gave 125 mg (0.21 mmol, 33%) of **10**, which was recrystallized from chloroform–hexane, mp 362–364 °C.

Under the same reaction conditions and workup, the soluble adduct **9b** gave **10** in 65% yield. In subsequent preparations, the mixture of crude adducts was dehydrated directly to give **10** in approximately 50% yield.

For **10**: ^{1}H NMR δ 4.0 (s, 6 H, methoxyl), 5.54 (s, 4 H, bridgehead protons), 7.07–7.46 (m, 16 H, aromatic), 8.12 (s, 4 H, aromatic); ^{13}C NMR δ 53.78, 53.88, 115.93, 123.62, 123.85, 125.71, 140.82, 144.20, 147.97; mass spectrum, *m/e* 590 (77), 576 (40), 575 (86), 295 (21), 280 (100), 272 (43), 257 (23), 252 (31), 251 (34), 250 (41), 44 (68). Anal. Calcd for $C_{44}H_{30}O_2$: C, 89.49; H, 5.08. Found: C, 89.16; H, 5.17.

Quinone 11. To a cooled (−78 °C) and stirred solution of boron *tribromide* (425 mg, 1.7 mmol) in dry methylene chloride (10 mL) was added, under argon, a solution of **10** (500 mg, 0.85 mmol) in dry methylene chloride (5 mL). The mixture was stirred at −78 °C for 1 h, then allowed to warm slowly to room temperature. Water (2 mL) was carefully added with cooling. The mixture was stirred for a few minutes, diluted with methylene chloride (50 mL), washed with water, and dried. Removal of the solvent gave a yellow solid (470 mg) which was fairly pure **11**. Recrystallization from chloroform–methanol gave 400 mg (84%) of pure **11** as bright yellow crystals, mp >350 °C dec. In this preparation, excess boron bromide drastically reduces the yield and increases the difficulty of product purification. IR (KBr) 1650 cm^{-1}; ^{1}H NMR δ 5.53 (s, 4 H, bridgehead protons), 6.85–7.25 (m, 16 H, aromatic), 8.13 (s, 4 H, aromatic); ^{13}C NMR δ 54.34, 121.86, 124.11, 125.90, 131.69, 143.68, 151.41, 171.15; mass spectrum, *m/e* 560 (64), 250 (10), 167 (18), 129 (22), 82 (19), 80 (16), 55 (16), 44 (100), 43 (27), 41 (15). Anal. Calcd for $C_{42}H_{24}O_2$: C, 90.00; H, 4.29. Found: C, 89.95; H, 4.33.

***Pentiptycene* 6 *from* Quinone 11.** A solution of quinone **11** (200 mg) in 15 mL of chloroform was reduced with hydrogen (60 psi) over 5% platinum on charcoal (20 mg) in the presence of one drop of concentrated hydrochloric acid. After 8–10 h the catalyst was filtered and the solvent was evaporated to give 180 mg of a pale yellow solid. The infrared spectrum showed no carbonyl or hydroxyl bands. The crude product was used directly in the next step.

A mixture of the crude reduction product (180 mg), triphenylmethanol (122 mg), and trifluoroacetic acid (3 mL) in 10 mL of benzene was heated at reflux under nitrogen for 6 h. Removal of the volatile material followed by trituration of the resulting black mass with ether left a colorless solid. This solid was washed with ether and recrystallized from chloroform to give 140–160 mg (74–85%) of **6**, identical in all respects with **6** obtained directly from **5**.

Heptiptycene 12. A mixture of pentiptycene (**6**) (200 mg, 0.377 mmol), benzenediazonium-2-carboxylate hydrochloride (210 mg, 1.12 mmol), and propylene oxide (2 mL) in 10 mL of 1,2-dichloroethane was heated at reflux for 6 h. Removal of the solvents and chromatography of the residue over silica gel with benzene as the eluent gave **13** (114 mg, 50%). On occasion, some starting material, which has the same R_f value as the product, was present, in which case the product was isolated by fractional crystallization. Recrystallization from chloroform gave pure **12** as colorless crystals: mp >525 °C; ^{1}H NMR δ 5.20 (s, 2 H), 5.25 (s, 4 H), 6.85 (m, 12 H), 7.21 (m, 8 H), 7.35 (s, 4 H); ^{13}C NMR δ 53.93, 54.11, 119.57, 123.22, 123.39, 124.98, 142.51, 142.68, 145.39, 145.51; UV (CH_3CN) λ_{max} 295 nm (ϵ 16,340), 282 (13,960), 272 (9,410). Anal. Calcd for $C_{48}H_{30}$: C, 95.04; H, 4.95. Found: C, 94.83; H, 5.07.

Dimethoxyheptiptycene (13). A mixture of dimethoxypentiptycene (**10**) (700 mg, 1.186 mmol), benzenediazonium-2-carboxylate hydrochloride (220 mg, 1.186 mmol), and propylene oxide (5 mL) in 20 mL of 1,2-dichloroethane was heated at reflux for 6 h. The solvents were evaporated under reduced pressure and the crude product was chromatographed over silica gel. Elution with benzene gave the heptiptycene **13** (530 mg, 76%) which was recrystallized from chloroform–methanol: mp >525 °C; ^{1}H NMR δ 4.30 (s, 6 H, methoxyls), 5.29 (s, 4 H, bridgehead), 6.9–7.4 (m, 20 H), 7.69 (s, 4 H); ^{13}C NMR δ 54.29, 57.64, 116.98, 120.81, 123.45, 124.81, 125.10, 142.16, 142.39, 144.63, 145.45. Anal. Calcd for $C_{50}H_{34}O_2$: C, 90.09; H, 5.10. Found: C, 89.99; H, 5.26.

Crystallographic Data and X-ray Structure Analysis of 3. Crystal data: Crystals of **3**, $C_{14}H_{10}O_2$, are orthorhombic; space group *Pbca*; a = 15.540 (6), b = 9.425 (5), c = 6.779 (3) Å; Z = 4; M_r = 210.23; ρ_c = 1.406 cm^{-3}. Lattice dimensions were determined with a Picker FACS-I diffractometer and Mo Kα_1 (λ = 0.70926 Å) radiation.

Intensity data were measured with Mo Kα radiation ($2\theta_{max}$ = 50°), yielding 876 total unique data and, based on $I > 2\sigma(I)$, 480 observed data. The data were reduced;[14] the structures were solved by direct methods[15] and the refinement was by full-matrix least-squares techniques.[16] The final R value was 0.052. The final difference Fourier map showed densities ranging from +0.37 to −0.35 with no indication of missing or incorrectly placed atoms.

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Registry No. 1, 636-28-2; *anti*-3, 87207-46-3; *syn*-3, 87248-22-4; 5, 87207-47-4; 6, 87207-48-5; 7, 19403-94-2; *anti*-8, 75686-28-1; 9, 87207-49-6; 10, 87207-50-9; 11, 87207-51-0; 12, 87207-52-1; 13, 87207-53-2; furan, 110-00-9; anthracene, 120-12-7; benzyne, 462-80-6.

Supplementary Material Available: Tables I–IV listing positional parameters, thermal parameters, bond lengths, and bond angles, and estimated standard deviations (4 pages). Ordering information is given on any current masthead page.

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