cooling to room temperature, 0.5 mL of concentrated HCl and 205 mg of 10% palladium on carbon were added. After shaking under 50 psi of hydrogen, the reaction mixture was filtered through Celite, and the filtrate was evaporated under vacuum. The residue was dissolved in 40 mL of 50:1 acetonitrile–methanol. To this solution was added 2 mL (27 mmol) of 37% aqueous formaldehyde and 120 mg (1.91 mmol) of sodium cyanoborohydride. After 15 min of being stirred, the solution was neutralized with glacial acetic acid. The resulting mixture was allowed to stir for 12 h. The sodium cyanoborohydride was quenched with aqueous methanol–ammonia. Chromatography (SiO_2, 10% ethanol–dichloromethane) afforded 166 mg (90% yield) of **3**: UV (H_2O) λ_{max} ~305 nm (ϵ ~7700), 260 (16600), λ_{min} 231 nm (ϵ 7400), (0.1 N HCl) λ_{max} 279 nm (ϵ 10700), λ_{min} 260 nm (ϵ 8300), (0.1 N NaOH) λ_{max} ~295 nm (ϵ ~9300), 263 (16400), λ_{min} 237 nm (ϵ 11200); ^1H NMR (Me_2SO) 11.31 (s, 1 H, N3-H), 8.00 (s, 1 H, C6-H), 7.40 (d, 2 H, J = 8.7 Hz, Ar), 6.71 (d, 2 H, J = 8.7 Hz, Ar), 6.24 (t, 1 H, J = 6.6 Hz, C1'-H), 2.90 ppm (s, 6 H, $N(CH_3)_2$); EIMS, m/e (relative intensity) 347 (M^+, 6.6), 231 (5-[*p*-(*N*,*N*-dimethylamino)-phenyl]uracil, 100), 188 (11), 160 (19), 117 (2'-deoxyribose, 4.0).

Anal. Calcd for $C_{21}H_{25}N_3O_7 \cdot H_2O$ (3',5'-di-*O*-acetyl derivative of **3**): C, 56.12; H, 6.06; N, 9.35. Found: C, 56.20; H, 5.99; N, 9.30.

5-(*p*-Aminophenyl)-2'-deoxyuridine (4). 5-(*p*-Nitrophenyl)-2'-deoxyuridine (**15**, 81 mg, 0.23 mmol) was dissolved in 50 mL of warm ethanol. Upon cooling to room temperature, 0.5 mL of concentrated HCl and 100 mg of 10% palladium on carbon were added. After shaking under 50 psi of hydrogen for 12 h, the mixture was filtered through Celite, and the filtrate was concentrated under vacuum. An aliquot of methanolic–ammonia solution was added to convert the amine salt to the free base. Chromatography (SiO_2, 10% ethanol–dichloromethane) afforded 80 mg (98% yield) of **4**: UV (H_2O) λ_{max} 295 nm (ϵ 8100), 252 (15600), λ_{min} 283 nm (ϵ 7700), 235 (7700), (0.1 N HCl) λ_{max} 280 nm (ϵ 10300), λ_{min} 261 nm (ϵ 7600), (0.1 N NaOH) λ_{max} ~286 nm (ϵ ~8800), 253 (15000), λ_{min} 234 nm (ϵ 13000); ^1H NMR (Me_2SO) 11.26 (s, 1 H, N3-H), 7.94 (s, 1 H, C6-H), 7.22 (d, 2 H, J = 8.4 Hz, Ar), 6.54 (d, 2 H, J = 8.4 Hz, Ar), 6.23 ppm (t, 1 H, J = 6.6 Hz, C1'-H); EIMS, m/e (relative intensity) 319 (M^+, 3.0), 203 (5-(*p*-aminophenyl)uracil, 100), 160 (21), 132 (28), 117 (2'-deoxyribose, 23).

Anal. Calcd for $C_{15}H_{17}N_3O_5 \cdot 0.5EtOH$: C, 56.13; H, 5.89; N, 12.27. Found: C, 55.90; H, 5.86; N, 12.05.

5-(*p*-Hydroxyphenyl)-2'-deoxyuridine (5). 5-[*p*-(Benzyloxy)phenyl]-2'-deoxyuridine (**7**, 53 mg, 0.13 mmol) was dissolved in 50 mL of warm ethanol. Upon cooling to room temperature, 120 mg of 10% palladium on carbon was added. After shaking under 45 psi of hydrogen for 18 h, the mixture was filtered through Celite. Chromatography (SiO_2, 10% ethanol–dichloromethane) of the filtrate afforded 40 mg (97% yield) of **5**: mp 189–191 °C (methanol); UV (H_2O) λ_{max} 287 nm (ϵ 7700), λ_{min} 267 nm (ϵ 6300), (0.1 N HCl) λ_{max} 287 nm (ϵ 8000), λ_{min} 267 nm (ϵ 6500), (0.1 N NaOH) λ_{max} 292 nm (ϵ 8000); ^1H NMR (Me_2SO) 8.03 (s, 1 H, C6-H), 7.36 (d, 2 H, J = 8.4 Hz, Ar), 6.75 (d, 2 H, J = 8.4 Hz, Ar), 6.23 ppm (t, 1 H, J = 6.6 Hz, C1'-H); CIMS (NH_3), m/e (relative intensity) 321 (M^+ + 1, 3.6), 204 (5-(*p*-hydroxyphenyl)uracil, 100), 160 (8.8), 117 (2'-deoxyuridine, 30).

Anal. Calcd for $C_{15}H_{16}N_2O_6 \cdot H_2O$: C, 53.25; N, 8.28; H, 5.36. Found: C, 53.60; N, 8.10; H, 5.10.

pK_a Determination. The ionization constants were determined by ultraviolet spectrophotometry.[10] Phosphate solutions from potassium phosphate monobasic and dibasic provided buffers in the pH range of 6.0–8.0. Borate solutions from sodium borate, provided the buffers in the pH range of 8.5–10.5. The ionic strength was 0.5.

Acknowledgment. This work was supported by a grant (Ca 7522) from the National Cancer Institute of the National Institutes of Health. We thank Professor Corwin Hansch for helpful discussion of these results.

Registry No. **1**, 951-78-0; **2**, 92510-77-5; **3**, 108664-86-4; **4**, 108664-87-5; **5**, 108664-88-6; **6**, 89647-11-0; **7**, 108664-89-7; **8**, 92510-80-0; **9**, 76756-28-0; **10**, 108664-90-0; **11**, 108664-91-1; **12**, 108664-92-2; **13**, 108664-93-3; **14**, 92524-53-3; **15**, 108664-94-4; PhI, 591-50-4; IC_6H_4-*p*-COOMe, 619-44-3.

New Iptycenes Using 2,3-Naphtho[*b*]triptycene[1] as a Synthon

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Received February 2, 1987

A new synthesis of the triptycene **1** (5,14-[1',2']benzeno-5,14-dihydropentacene) is described. Cycloaddition of endoxide **8** to diene **6** gave exo adduct **9**, which was successively dehydrated and dehydrogenated to give **1** in three steps and 47% overall yield. Cycloadducts **11–13** were obtained from **1** and tetracyanoethylene, dimethyl acetylenedicarboxylate, or maleic anhydride, respectively. Irradiation of **1** through Pyrex gave photodimer **26**. Pentiptycenes **16** and **18** were obtained in two steps using **1** as a synthon. Cycloaddition of 1,4-dichloro-2-butene to **1**, followed by dehydrohalogenation, gave diene **21**, which was then used as a synthon for functionalized pentiptycenes **22** and **25**. Finally, the new route to **1** was extended to the first synthesis of its naphthacene analogue **30**.

We recently summarized some of the ways in which the triptycene[2] framework can be elaborated to form iptycenes,[3] extended triptycenes that contain more than three aryl planes due to the presence of more than one bicyclo[2.2.2]octyl moiety.[4] The rigid framework, high thermal stability, and in the case of higher iptycenes, the cavities that lead to host–guest complexes[5] add interest to these structures.

In this paper we describe a new route to 2,3-naphthotriptycene **1** and make use of the anthracene moiety in **1** to construct several pentiptycenes. Certain products of these syntheses, or intermediates en route to them, are

(1) *Chemical Abstracts* nomenclature is 5,14-[1',2']benzeno-5,14-dihydropentacene.

(2) For a review of triptycene chemistry, see: Skvarchenko, V. R.; Shalaev, V. K.; Klabunovskii, E. I. *Russ. Chem. Rev. (Engl. Transl.)* **1974**, *43*, 951.

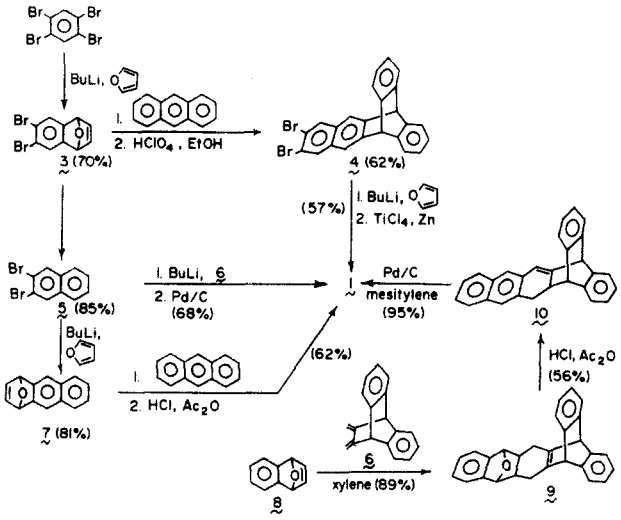
(3) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641.

(4) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.

(5) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675.

0022-3263/87/1952-3631$01.50/0

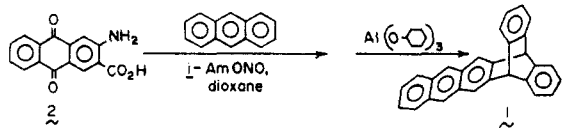
Scheme I



potential synthons for higher iptycenes.

Results and Discussion

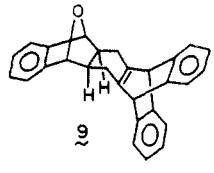
A New Synthesis of 2,3-Naphtho[*b*]triptycene (1). The original synthesis of 1[6] left something to be desired, in that the yield from aryne precursor **2** is only 8.4%; furthermore, the starting anthraquinone **2** is only available



in five steps from toluene[7] or in a low-yield multistep route from phthalic anhydride.[8] In view of the potential utility of **1** in iptycene synthesis, through cycloadditions to the anthracene moiety, we sought short, efficient syntheses of it that could be carried out in multigram quantities.

In a previous paper,[3] we described three routes to **1**, and we present here a fourth route. All of these routes are summarized in Scheme I.

Naphthalene 1,4-endoxide **8** is readily available from the reaction of benzyne with furan.[9] Heating **8** with diene **6**[3,10] in refluxing toluene for 72 h gave 89% of a single adduct **9** (mp 209–211 °C). Although not characterized fully, **9**



is thought to have the exo structure shown, because there is no coupling between the endoxide bridgehead protons and the adjacent methine protons.[11] Other features of the ^1H and ^{13}C NMR spectra are consistent with this assignment. Also, models show the endo isomer to be sterically crowded.

Dehydration of **9** (concentrated HCl, Ac_2O, 12-h reflux) afforded crystalline **10** (mp 217–219 °C) in 56% yield. Dehydration was accompanied by double-bond isomerization, as indicated by loss of the expected symmetry in the ^1H NMR spectrum. The spectrum showed one vinyl proton (δ 6.55, s) and two different bridgehead protons (δ 4.32, 4.87) as well as a triplet for the allylic proton (δ 2.32) and doublets of doublets for the two benzylic protons (δ 2.72, 2.96).

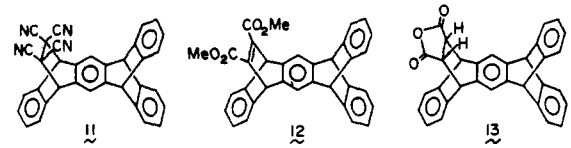
Dehydrogenation of **10** over palladium–charcoal (refluxing mesitylene, 3 days) gave **1** (mp 220–222 °C[3]) in 95% yield.

The four routes to **1** outlined in Scheme I are comparable in efficiency if all of the steps from commercially available starting materials are taken into account.[12] The route via **3** and **4** requires five steps and proceeds in 25% overall yield. The route via **3**, **5**, and **7** also requires five steps with a 30% overall yield. The route via **3** and **5** is shorter (four steps, 40% overall yield), but it requires diene **6**, which is not commercially available. Diene **6** can be synthesized in two steps and 85% overall yield from inexpensive precursors (1,4-dichloro-2-butene, anthracene)[3] and can be stockpiled.

The new route described here proceeds in three steps and 47% overall yield from **8**, which can either be purchased[14] or synthesized in one step and good yield[9] from inexpensive precursors (anthranilic acid, furan). This method suffers the same defect as the direct route from **5**, however, in that it does require the intermediate diene **6**.

In summary, all of the routes to **1** depicted in Scheme I require approximately the same number of steps and proceed in comparable overall yields, and all represent a vast improvement over the original route.[6] The particular choice among them will depend on which synthons are available. Also, the methods supplement one another if substituents are to be incorporated into **1**. For example, use of a 2,5-disubstituted furan in place of furan would allow one to place substituents at C6 and C13, or at C8 and C11, or at all four of these positions with the previously described methodology,[3] but at C7 and C12 with the new methodology described here.

Reactions of 1. Compound **1** gave cycloadducts **11–13** in essentially quantitative yield with tetracyanoethylene, dimethyl acetylenedicarboxylate, and maleic anhydride, respectively. The reactions required somewhat more

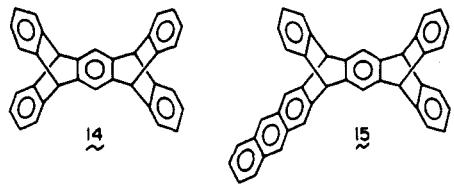


vigorous conditions than for anthracene, probably due to additional steric crowding by the 9,10-anthradiyl moiety present in **1**. Although two adducts are possible from maleic anhydride, only a single product (mp 320–322 °C) was obtained. Without evidence, we regard it to be most

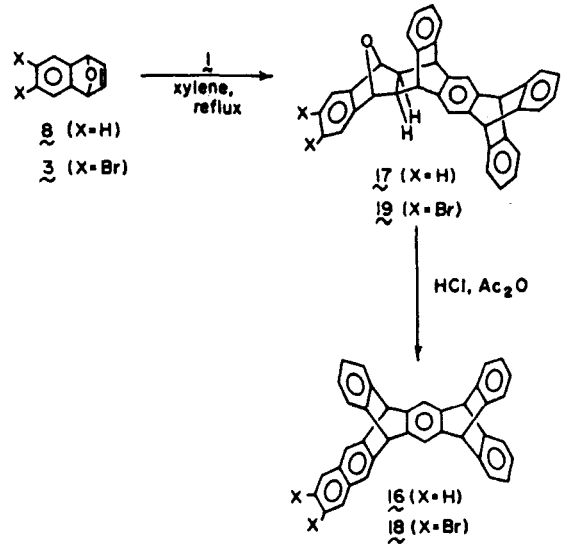
(6) Sugihashi, M.; Kawagita, R.; Otsubo, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2836.
(7) Hosoda, Y. *Senryo Kagaku (Gihodo, Tokyo)* **1957**, 556. This reference is unavailable to us.
(8) Zimmerman, H. E.; Amick, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3977. Hayes, P. C.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 1257.
(9) Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334. Wolthuis, E. *J. Org. Chem.* **1961**, *26*, 2215. Stiles, M.; Miller, R. G.; Burckhardt, U. *J. Am. Chem. Soc.* **1963**, *85*, 1792. Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.
(10) Meek, J. S.; Stacy, R. C. *J. Org. Chem.* **1961**, *26*, 300. Butler, D. N.; Snow, R. A. *Can. J. Chem.* **1972**, *50*, 795.
(11) Such couplings are usually 0–1 Hz for the exo isomer but 4–5 Hz for the endo isomer. Wittig, G.; Reuther, W. *Justus Liebigs Ann. Chem.* **1972**, *761*, 20. Takeshita, H.; Mori, A.; Sano, S.; Fujise, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1661.
(12) 1,2,4,5-Tetrabromobenzene is available from Aldrich Chemical Co., Milwaukee, WI.
(13) 2,3-Dibromonaphthalene (**5**), needed for the second and third routes, can also be prepared in two steps from the commercially available naphthalenebis(hexachlorocyclopentadiene) adduct (Aldrich). The overall yield is no better than that from 1,2,4,5-tetrabromobenzene, and on several occasions, we found the product to be contaminated with 1,3-dibromonaphthalene (unpublished results).
(14) Aldrich; it is quite expensive.
(15) For the nomenclature of iptycenes, see ref 4.

likely the less strained epimer shown.

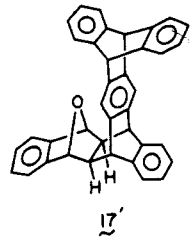
We have already described the synthesis of pentiptycenes **14** and **15** from **1** via the cycloaddition of benzyne or endoxide **7**, respectively.[3] We describe here the synthesis



of the skipped member in this series, i.e., **16**. Heating **8** with **1** in refluxing xylene gave a single adduct **17** in 91% yield. The aliphatic protons in the NMR spectrum of **17** appear as sharp two-proton singlets. The lack of coupling



between the methine protons and the two sets of adjacent bridgehead protons rules out endo addition (models show that both possible endo adducts are severely crowded)[11] but does not eliminate the alternate exo geometry **17′**.

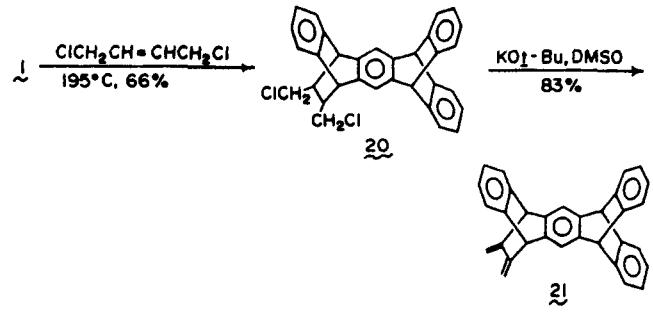


Indeed, the reaction of **7** with **1** described previously[3] gave both types of exo adducts in comparable yields. It is possible that isolation of a single adduct here is a reflection of the relative solubilities, since the cycloadditions are probably reversible.

Treatment of **17** with hydrochloric acid and acetic anhydride gave the desired pentiptycene **16**. The ^{1}H NMR spectrum of **16** showed two sets of bridgehead protons (δ 5.31, 5.41) and two sets of uncoupled aromatic protons (δ 7.48, 7.68) in addition to peaks for the remaining aryl protons. The ^{13}C NMR spectrum of **16** had the 19 peaks (2 aliphatic carbons at δ 53.59 and 53.96 and 17 aromatic carbons) as required by the symmetry.

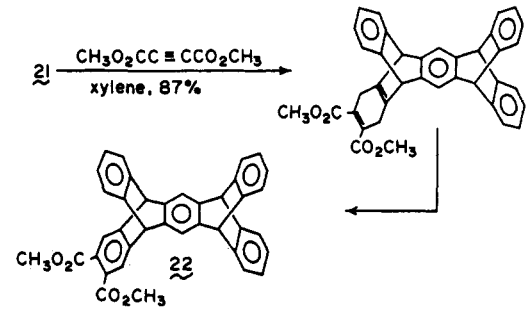
In an entirely analogous manner, the dibromo analogue **18** was prepared from the cycloaddition of **3** to **1** (see the Experimental Section).

The utility of diene **6** in iptycene synthesis prompted us to synthesize the analogous diene **21** from **1**. Cycloaddition of 1,4-dichloro-2-butene to **1** (sealed tube, 195 °C, 3 days) gave **20**, which was converted directly to **21** by



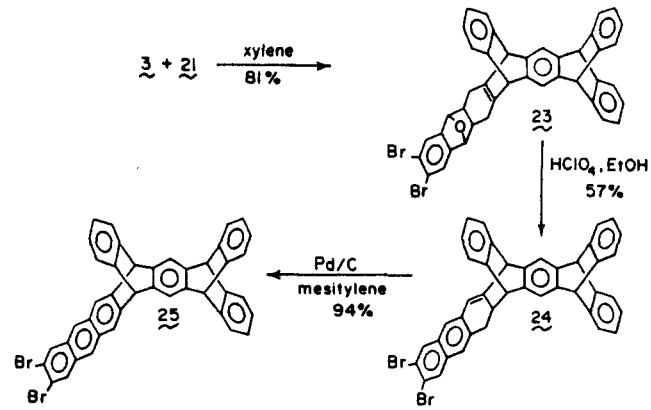
potassium *tert*-butoxide in Me_2SO. The structure of **21** was clear from its ^{1}H NMR spectrum, which showed two-proton singlets for the bridgehead (δ 5.20, 5.34), vinyl (δ 4.75, 5.05), and central aromatic protons (δ 7.36) as well as six sets of two-proton doublets of doublets for the remaining aryl protons. The ^{13}C NMR spectrum showed 16 peaks (4 aliphatic at δ 40.83, 54.99, 105.01, and 119.30 and 12 aromatic) as required by the symmetry of **21**.

The utility of **21** in iptycene synthesis was demonstrated with the preparation of functionalized pentiptycenes **22** and **25**. Heating diene **21** with dimethyl acetylenedi-



carboxylate in refluxing xylene for 56 h gave directly the pentiptycene diester **22** (mp 240–242 °C) in 87% yield. The expected dihydro-**22** was dehydrogenated (probably by air) under the reaction conditions. The mass spectrum of **22** showed an intense molecular ion peak at m/e 546. The ^{1}H NMR spectrum showed only three singlets in the aliphatic region, the bridghead protons (δ 5.29, 5.33) and the methyl protons (δ 3.80) and two-proton aromatic singlets (δ 7.40, 7.58), consistent with **22**, but not dihydro-**22**. Other features of the ^{1}H and ^{13}C NMR spectra were consistent with the structure.

Dibromopentiptycene **25** was prepared in three steps from diene **21** and endoxide **3** as shown. Endoxide **23** was obtained as a single stereoisomer (mp 327–328 °C dec),

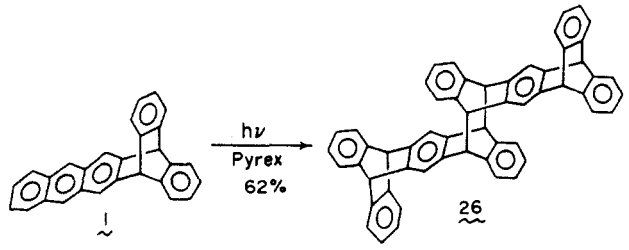


probably with the exo configuration (the endoxide bridgehead protons appeared as a singlet at δ 5.28).[11] Dehydration of **23** was accompanied by double-bond isomerization (vinyl singlet at δ 6.42 in **24**), as in the

dehydration of **9** (vide supra). Dehydrogenation of **24** was slow (4 days in refluxing mesitylene) but nearly quantitative, giving the high-melting **25** (mp >415 °C). The aromatic protons in **25** appeared as four two-proton singlets (δ 7.49 for the central benzenoid ring and δ 7.77, 8.06, and 8.20 for the anthracene moiety) and six additional sets of two-proton peaks; the bridgehead protons appeared as singlets at δ 5.32 and 5.42.

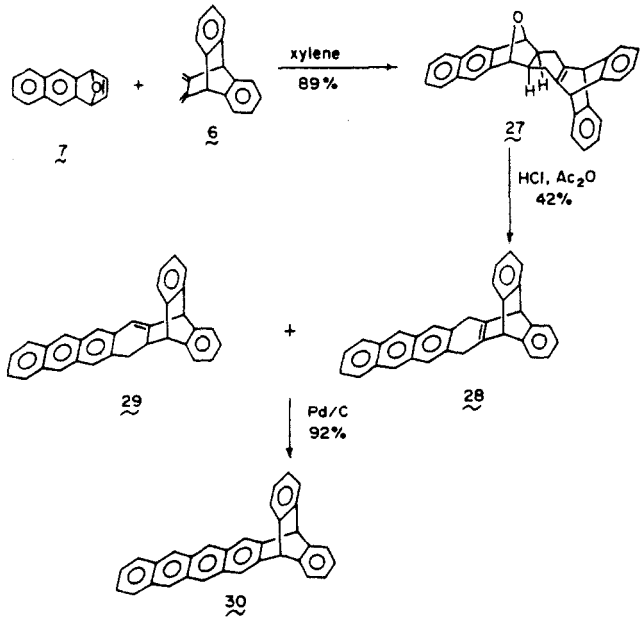
Table I presents a comparative summary of the proton NMR spectra of six pentiptycenes with a benzene, naphthalene, or anthracene moiety in one of the "outer" rings. The correlation of chemical shifts for protons in similar environments is evident.

Irradiation of 1. The anthracene moiety of 1 undergoes not only thermal [2 + 4] cycloadditions, as described above, but [4 + 4] photochemical cycloadditions, as illustrated by its photodimerization. Irradiation of a benzene solution of 1 through Pyrex was accompanied by crystallization from solution of a sparingly soluble dimer assigned the head-to-tail structure **26** on steric grounds. Its ^{1}H NMR



spectrum showed four-proton singlets at δ 4.27 and 5.12 for the bridgehead protons and a four-proton aromatic singlet at δ 6.84 for the uncoupled benzenoid ring protons, as well as six sets of four-proton doublets of doublets for the remaining aromatic protons. Upon heating to its melting point (281–283 °C), **26** reverted to the monomer 1.

Synthesis of 2,3-Anthraceno[*b*]triptycene (30). The new methodology introduced here for the synthesis of 1 was extended to the preparation of its previously unknown naphthacene analogue **30**. A xylene solution of diene **6**



and endoxide **7** was heated at reflux for 72 h to give adduct **27** in 89% yield. Once again, the endoxide bridgehead protons appeared as a singlet (δ 5.05), suggesting exo geometry. Dehydration with hydrochloric acid and acetic anhydride gave only a modest yield of the dehydration product, this time as a mixture of unrearranged (**28**) and rearranged (**29**) alkenes. Isomer **28** showed aliphatic proton singlets at δ 3.90 and 4.95 (ratio 4:2), whereas **29** showed two one-proton bridgehead singlets (δ 4.38, 4.92) and a vinyl singlet (δ 6.64). Dehydrogenation of the mixture gave the desired **30** (92%) as orange crystals (mp 362–364 °C). The ^{1}H NMR spectrum of **30** showed a singlet for the bridgehead protons (δ 5.53), two-proton singlets at δ 7.86, 8.46, and 8.56, and two-proton doublets of doublets at δ 7.35 and 7.45 for the naphthacene moiety, as well as two four-proton doublets of doublets for the benzenoid protons (δ 7.07, 7.46). Other spectral properties of **30** were consistent with its structure.

In summary, we have described here a new synthetic route to triptycene **1**, an extension of this methodology to the naphthacene analogue **30**, and a number of cycloaddition reactions of 1 that illustrate its utility as a synthon for higher iptycenes.

Experimental Section

General Procedures. NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker WM-250 spectrometer with $CDCl_3$ as the solvent and $(CH_3)_4Si$ as the internal reference. UV spectra were obtained with a Perkin-Elmer 200 spectrometer. Mass spectra were measured at 70 eV with a Finnigan 4000 spectrometer with the INCOS data system. Mass spectra of very high-melting compounds were measured either on a Hitachi M-80A spectrometer with a direct-inlet temperature of 300–400 °C at Ube Industries, Ube, Japan, or on a JEOL HX110 HF spectrometer using the field desorption (FD) technique at the Michigan State University Mass Spectrometry Facility. Melting points were determined with an electrothermal melting point apparatus (Fisher) and are uncorrected. Anhydrous $MgSO_4$ was the drying agent throughout. Silica gel for chromatography was either 70–200 or 230–400 mesh. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

5,14-[1′,2′-Benzeno]-7,12-epoxy-5,6,6a,7,12,12a,13,14-octahydropentacene (9). A solution of epoxide 8[9] (1.44 g, 10 mmol) and diene 6[3] (2.30 g, 10 mmol) in toluene (40 mL) was heated at reflux for 72 h. The solvent was removed (Rotavap), and the residue was triturated with hexane to give 3.33 g (89%) of adduct **9** (mp 209–211 °C) after recrystallization from toluene: ^{1}H NMR δ 1.87 (t, 2 H, J = 5–7 Hz), 2.20 (dd, 2 H, J = 7, 14 Hz), 2.82 (dd, 2 H, J = 5, 14 Hz), 4.78 (s, 2 H), 4.92 (s, 2 H), 6.85–6.91 (m, 4 H), 7.05–7.23 (m, 8 H); ^{13}C NMR δ 30.47, 42.01, 55.77, 84.98, 118.66, 122.39, 122.50, 124.09, 124.22, 126.40, 143.06, 145.46, 146.39; mass spectrum, m/e (relative intensity) 374 (M^+, 11), 356 (6), 256 (68), 215 (26), 202 (23), 178 (92), 118 (100), 90 (20).

5,14-[1′,2′-Benzeno]-5,5a,6,14-tetrahydropentacene (10). A solution of **9** (2.99 g, 8 mmol) in concentrated hydrochloric acid (15 mL) and acetic anhydride (60 mL) was heated at reflux for 12 h. The cooled mixture was poured into 300 mL of ice–water, and the resulting precipitate was filtered, washed with water, and dried. Column chromatography using CH_2Cl_2–hexane (1:4) as the eluent gave 1.59 g (56%) of **10** as colorless crystals: mp 217–219 °C; ^{1}H NMR δ 2.32 (t, 1 H, J = 5 Hz), 2.72 (dd, 1 H, J = 5.5, 14 Hz), 2.96 (dd, 1 H, J = 5, 14 Hz), 4.32 (s, 1 H), 4.87 (s, 1 H), 6.55 (s, 1 H), 7.11 (m, 4 H), 7.31 (m, 6 H), 7.32 (s, 1 H), 7.38 (s, 1 H), 7.64 (m, 2 H); mass spectrum, m/e (relative intensity) 356 (M^+, 29), 354 (7), 353 (5), 352 (4), 278 (2), 178 (100), 176 (13).

5,14-[1′,2′-Benzeno]-5,14-dihydropentacene (1). A solution of **10** (1.07 g, 3 mmol) in mesitylene (50 mL) containing 150 mg of 10% Pd–C was heated under argon at reflux for 72 h. The hot solution was filtered, and the catalyst was rinsed with methylene chloride (20 mL). The combined filtrate was concentrated under reduced pressure and recrystallized from cyclohexane to give 1.01g (95%) of 1 [mp 220–222 °C (lit.[3] mp 221–222 °C)].

TCNE Adduct of 1. A solution of 1 (254 mg, 1 mmol) and tetracyanoethylene (128 mg, 1 mmol) in benzene (50 mL) was heated at reflux for 3 h. The green solution gradually faded as a white precipitate formed. The cooled solution was filtered and washed with benzene to give 472 mg (98%) of adduct **11** as a colorless powder that was recrystallized from acetone–hexane: mp 288 °C dec; ^{1}H NMR δ 5.69 (s, 2 H), 5.75 (s, 2 H), 6.90, 7.00,

Table I. ^{1}H NMR Spectra (δ) of [n^b.1.1^b.1.1]Pentiptycenes[15]

		position[a]						
n	compd	5	7	6	8	9	10	remaining aryl protons
1	**14**	5.30	5.30	7.43	7.28[b]			6.92[b]
	22	5.29	5.33	7.40	7.58			6.87–6.92 (6 H),[c] 7.22–7.33 (6 H)[c,d]
2	**16**	5.31	5.41	7.48	7.68	7.63[b]		6.83–6.95 (6 H),[c] 7.25–7.34 (8 H)[c]
	18	5.34	5.40	7.49	7.50	7.88		6.86–6.99 (6 H),[c] 7.25–7.35 (6 H)[c]
3	**15**	5.33	5.44	7.51	7.80	8.18	7.89[b]	(6.86, 6.91, 6.98),[b] 7.27–7.38 (8 H)[c]
	25	5.32	5.42	7.49	7.77	8.20	8.06	(6.85, 6.91, 6.98, 7.25, 7.29, 7.35)[b]

[a] Numbers correspond to the *Chemical Abstracts* nomenclature as derivatives of dibenzenopentacenes (n = 1), -hexacenes (n = 2), or -heptacenes (n = 3). All peaks are two-proton singlets unless stated otherwise. [b] Two-proton doublets of doublets. [c] Multiplets. [d] The spectrum also shows a six-proton singlet at δ 3.80 for the methyl protons.

7.37, 7.39, 7.48, and 7.64 (aromatic dd, each 2 H),[16] 7.82 (s, 2 H); mass spectrum, m/e (relative intensity) 354 (98), 353 (67), 128 (53), 76 (52), 58 (28), 43 (100). Anal. Calcd for $C_{34}H_{18}N_4$: C, 84.63; H, 3.76. Found: C, 84.41; H, 3.90.

DMAD Adduct of 1. A solution of 1 (531 mg, 1.5 mmol) and dimethyl acetylenedicarboxylate (147 mg, 1.5 mmol) in benzene (20 mL) was heated at reflux for 5 h. The resulting precipitate was filtered and washed with hexane to give 707 mg (95%) of **12**: mp 304–306 °C; ^{1}H NMR δ 3.73 (s, 6 H), 5.31 (s, 2 H), 5.35 (s, 2 H), 6.89–6.98 (m, 6 H), 7.27–7.35 (m, 6 H), 7.42 (s, 2 H); mass spectrum, m/e (relative intensity) 496 (M^+, 11), 481 (5), 437 (13), 398 (17), 370 (21), 354 (94), 341 (22), 243 (32), 213 (39), 178 (51), 165 (43), 149 (67), 121 (59), 105 (94), 91 (87), 85 (82), 44 (100). Anal. Calcd for $C_{34}H_{24}O_4$: C, 82.24; H, 4.87. Found: C, 82.07; H, 4.95.

MA Adduct of 1. A solution of 1 (708 mg, 2 mmol) and maleic anhydride (196 mg, 2 mmol) in xylene (20 mL) was heated at reflux for 5 h. The resulting white precipitate was filtered and washed with hexane to give 868 mg (96%) of **13** as colorless crystals: mp 320–322 °C; ^{1}H NMR δ 3.38 (s, 2 H), 4.71 (s, 2 H), 5.40 (s, 2 H), 6.92, 7.02, 7.13, 7.25, 7.32, and 7.41 (aromatic dd, each 2 H),[16] 7.39 (s, 2 H); mass spectrum (CI), m/e (relative intensity) 453 (M + 1, 2), 384 (2), 355 (7), 251 (4), 99 (100), 85 (65). Anal. Calcd for $C_{32}H_{20}O_3$: C, 84.94; H, 4.45. Found: C, 84.70; H, 4.59.

5,16-[1′,2′]:7,14-[1″,2″]Dibenzeno-5,7,14,16-tetrahydrohexacene (16). A solution of 1 (708 mg, 2 mmol) and endoxide **8**[9] (317 mg, 2.2 mmol) in xylene (60 mL) was heated at reflux for 72 h. The solvent volume was reduced (Rotavap), and the resulting residue was triturated with hexane to give 906 mg (91%) of adduct **17** as a tan solid: mp ca. 367 °C dec; ^{1}H NMR δ 1.97 (s, 2 H), 4.22 (s, 2 H), 4.80 (s, 2 H), 5.30 (s, 2 H), 6.88, 6.92, 6.97, 7.06, 7.18, 7.24, 7.33 (aromatic dd, each 2 H except the signal at δ 7.06 which was 4 H),[16] 7.25 (s, 2 H); ^{13}C NMR δ 47.25, 48.85, 53.97, 81.13, 118.63, 119.62, 123.41, 123.53, 125.01, 125.89, 126.16, 141.17, 141.54, 142.94, 145.29, 145.58, 146.71 (two signals overlapped or absent); mass spectrum, m/e (relative intensity) 498 (M^+, 43), 480 (10), 472 (42), 457 (100), 380 (31), 367 (76), 354 (29), 353 (33), 352 (29), 265 (6), 252 (7), 239 (9), 178 (10), 131 (19), 118 (13).

To a solution of **17** (747 mg, 1.5 mmol) in acetic anhydride (30 mL) was added 4 mL of concentrated HCl, and the mixture was heated at reflux for 10 h. The cooled solution was poured into ice–water and extracted with CH_2Cl_2. The extract was washed with 10% Na_2CO_3 and water, dried, and concentrated. The residue was chromatographed over silica gel with CH_2Cl_2–hexane (1:4) as eluent to give 382 mg (53%) of **16** as colorless crystals: mp >335 °C dec; ^{1}H NMR (see Table I); ^{13}C NMR δ 53.59, 53.96, 119.80, 121.44, 123.38, 123.51, 124.06, 125.03, 125.41, 125.55, 125.85, 127.35, 131.66, 141.73, 142.07, 142.89, 144.65, 145.24, 145.33; mass spectrum, m/e (relative intensity) 480 (M^+, 8), 472 (8), 457 (16), 396 (6), 384 (14), 178 (100), 144 (56), 115 (26), 84 (27), 43 (58); UV (cyclohexane) λ_{max} 324 nm (ϵ 30 452), 310 (30 408), 289 (31 876), 279 (32 103), 272 (32 057), 251 (33 348), 227 (55 284). Anal. Calcd for $C_{38}H_{24}$: C, 94.97; H, 5.03. Found: C, 95.13; H, 4.85.

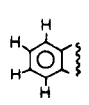
10,11-Dibromo-5,16-[1′,2′]:7,14-[1″,2″]dibenzeno-5,7,14,16-tetrahydrohexacene (18). A solution of 1 (1.062 g, 3 mmol) and endoxide **3** (997 mg, 3.3 mmol) in xylene (160 mL) was heated at reflux for 72 h. The precipitate that formed on cooling was collected and saved. The filtrate was concentrated (Rotavap), and the residue was triturated with acetone (15 mL). The resulting solid was filtered, washed with a little acetone, and combined with the original precipitate. Recrystallization from xylene gave adduct **19** (1.75 g, 89%) as colorless crystals: mp 410 °C dec; ^{1}H NMR δ 1.57 (s, 2 H), 4.08 (s, 2 H), 4.54 (s, 2 H), 5.36 (s, 2 H), 6.91, 6.99, 7.05, 7.14, 7.30, 7.41 (dd, 2 H each),[16] 7.27 (s, 2 H), 7.28 (s, 2 H); ^{13}C NMR δ 46.80, 48.25, 54.05, 80.47, 119.47, 121.83, 123.43, 123.51, 123.58, 124.16, 125.11, 125.23, 126.01, 140.78, 141.07, 143.16, 145.15, 145.68, 147.69.

A mixture of **19** (1.312 g, 2 mmol), acetic acid (300 mL), and concentrated H_2SO_4 (8 mL) was heated at reflux overnight. The cooled solution was poured into ice–water and extracted with CH_2Cl_2. The extract was washed with 20% Na_2CO_3 solution and water, dried, and concentrated. Flash column chromatography of the residue using CH_2Cl_2–hexane (1:3) as eluent gave 778 mg (61%) of **18** as a colorless solid: mp >430 °C dec; ^{1}H NMR see Table I; ^{13}C NMR δ 53.39, 53.90, 119.94, 120.28, 121.30, 121.54, 123.43, 123.65, 125.11, 125.67, 131.37, 131.56, 141.12, 143.13, 143.59, 144.08, 145.17 (two peaks missing or overlapped); mass spectrum (FD), m/e (relative intensity) 640 (47), 638 (100), 636 (35); UV (cyclohexane) λ_{max} 337 nm (ϵ 20 274), 323 (20 175), 293 (21 412), 282 (21 371), 273 (21 091), 249 (28 068), 228 (25 580), 221 (25 288). Anal. Calcd for $C_{38}H_{22}Br_2$: C, 71.49; H, 3.47. Found: C, 71.32; H, 3.40.

15,16-Dimethylene-5,14-ethano-7,12-[1′,2′]benzeno-5,7,12,14-tetrahydropentacene (21). A solution of **1** (7.08 g, 20 mmol) in 1,4-dichloro-2-butene (50 mL, cis–trans mixture) was heated in a sealed tube at 190–195 °C for 3 days. The solvent was distilled to leave a black residue, which was chromatographed over silica gel with CH_2Cl_2–hexane (1:3) as the eluent to give 6.31 g (66%) of **20** as a cis–trans mixture: mp ca. 265 °C dec; ^{1}H NMR (cis) δ 2.32 (dd, 2 H, J = 5, 10 Hz), 2.92 (dd, 2 H, J = 10, 11 Hz), 3.25 (dd, 2 H, J = 5, 11 Hz), 4.32 (s, 2 H), 5.35 (s, 2 H); ^{1}H NMR (trans) δ 2.31 (dd, 2 H, J = 3, 9 Hz), 2.75 (dd, 2 H, J = 9, 11 Hz), 3.36 (dd, 2 H, J = 3, 11 Hz), 4.43 (s, 2 H), 5.36 (s, 2 H), the aromatic peaks were too complex to assign to individual isomers but appeared at δ 6.89, 7.01, 7.06, 7.24, 7.29 and 7.39 (all dd),[16] 7.36 (s); mass spectrum, m/e (relative intensity) 480 (5), 478 (5), 379 (9), 365 (5), 354 (62), 334 (15), 297 (9), 178 (39), 121 (32), 106 (100), 105 (90).

To a solution of **20** (5.74 g, 12 mmol) in Me_2SO (80 mL) and THF (20 mL) was added 4.03 g (36 mmol) of potassium *tert*-butoxide. The solution was stirred at room temperature overnight, then poured into ice–water, and extracted with ether. The organic layer was washed with brine, dried, and evaporated (Rotavap), and the residue was column chromatographed with CH_2Cl_2–hexane (1:4) as the eluent to give 4.29 g (88%) of **21** as colorless crystals (EtOH): mp 282 °C dec; ^{1}H NMR δ 4.75 (s, 2 H), 5.05

(16) The aromatic protons of many of the iptycenes appear either in typical AA′BB′ patterns described here as doublets of doublets (dd) for benzenoid rings of the type



or as singlets for rings of the type

or as multiplets if these signals overlap. The coupling constants are ordinary for these systems and are not reported.

(s, 2 H), 5.20 (s, 2 H), 5.34 (s, 2 H), 6.89, 6.96, 7.03, 7.22, 7.28 and 7.32 (dd, 2 H each),[16] 7.36 (s, 2 H); ^{13}C NMR δ 40.83, 54.99, 105.02, 119.30, 123.07, 123.33, 123.44, 125.00, 125.07, 126.18, 138.64, 141.79, 143.54, 143.82, 145.28, 145.33; mass spectrum, *m/e* (relative intensity) 406 (M^+, 76), 391 (9), 354 (80), 228 (34), 203 (26), 195 (35), 178 (100), 163 (17), 151 (15), 91 (53), 43 (39). Anal. Calcd for $C_{32}H_{22}$: C, 94.55; H, 5.45. Found: C, 94.43; H, 5.37.

Dimethyl 5,14-[1′,2′]:7,12-[1″,2″]Dibenzeno-5,7,12,14-tetrahydropentacene-2,3-dicarboxylate (22). A solution of diene **21** (812 mg, 2 mmol) and dimethyl acetylenedicarboxylate (2 mL) in xylene (20 mL) was heated at reflux for 56 h. Solvent removal (Rotavap) gave a yellow oil, which was column chromatographed with ethyl acetate–hexane (1:3) as the eluent to yield 950 mg (87%) of **22** as colorless crystals: mp 240–242 °C; ^{1}H NMR see Table I; ^{13}C NMR δ 52.38, 53.53, 53.88, 119.93, 123.41, 123.63, 123.71, 125.07, 125.42, 129.04, 141.11, 143.03, 143.99, 145.18, 148.77, 167.86 (three peaks missing or overlapped); mass spectrum, *m/e* (relative intensity) 546 (M^+, 52), 487 (3), 428 (13), 427 (14), 263 (24), 258 (28), 252 (89), 213 (44), 206 (24), 178 (31), 59 (80), 44 (100). Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79. Found: C, 83.66; H, 4.58.

11,12-Dibromo-5,18-[1′,2′]:7,16-[1″,2″]dibenzeno-5,7,16,18-tetrahydroheptacene (25). A solution of diene **21** (1.218 g, 3 mmol) and endoxide **3** (0.997 g, 3.3 mmol) in xylene (60 mL) was heated at reflux for 60 h. The cooled solution was concentrated and triturated with hexane. The resulting precipitate was filtered and washed with hexane to give 1.72 g (81%) of **23** as a tan solid: mp 327–328 °C dec; ^{1}H NMR δ 1.78 (dd, 2 H, J = 5, 7 Hz), 2.13 (dd, 2 H, J = 7, 14 Hz), 2.72 (dd, 2 H, J = 5, 14 Hz), 4.67 (s, 2 H), 4.83 (s, 2 H), 5.28 (s, 2 H), 6.79, 6.89, 6.96, and 7.10 (dd, 2 H),[16] 7.34 (dd, 4 H),[16] 7.28 (s, 2 H), 7.37 (s, 2 H); mass spectrum, *m/e* (relative intensity) 710 (1), 708 (2), 706 (1), 432 (2), 354 (1), 276 (1), 252 (2), 178 (3), 105 (4), 91 (8), 44 (100).

To a solution of **23** (1.416 g, 2 mmol) in ethanol (300 mL) was added slowly 15 mL of 72% perchloric acid, and the mixture was heated at reflux for 16 h. The cooled mixture was poured into ice–water, extracted with CH_2Cl_2, and dried. Evaporation of the solvent and column chromatography of the crude product using CH_2Cl_2–hexane (1:3) as the eluent gave 787 mg (57%) of **24**: mp >360 °C dec; ^{1}H NMR δ 2.25 (dd, 1 H, J = 5, 6 Hz), 2.68 (dd, 1 H, J = 6, 13 Hz), 2.87 (dd, 1 H, J = 5, 13 Hz), 4.23 (s, 1 H), 4.77 (s, 1 H), 5.34 (s, 2 H), 6.43 (s, 1 H), 6.92 (m, 4 H), 7.08 (dd, 2 H),[16] 7.14 (s, 1 H), 7.19 (s, 1 H), 7.25 (m, 4 H), 7.32 (dd, 2 H),[16] 7.35 (s, 1 H), 7.36 (s, 1 H), 7.86 (s, 1 H), 7.89 (s, 1 H).

A solution of **24** (690 mg, 1 mmol) in mesitylene (20 mL) containing 100 mg of 10% Pd–C under argon was heated at reflux for 4 days. The hot solution was filtered, and the solvent was removed under reduced pressure to give 647 mg (94%) of **25**: mp >415 °C dec; ^{1}H NMR, see Table I; ^{13}C NMR δ 53.47, 54.03, 119.92, 120.93, 121.06, 123.43, 123.70, 123.99, 124.77, 125.11, 125.81, 130.86, 132.09, 141.00, 145.34, 147.50 (five peaks missing, possibly due to the low solubility of **25**); mass spectrum (FD), *m/e* (relative intensity) 690 (65), 688 (100), 686 (40). Anal. Calcd for $C_{42}H_{24}Br_2$: C, 73.27; H, 3.51. Found: C, 73.02; H, 3.69.

Irradiation of 1. A solution of **1** (354 mg, 1 mmol) in 15 mL of anhydrous benzene was irradiated through Pyrex by a Hanovia 450-W medium-pressure lamp. After 3 h, the resulting precipitate was filtered, washed with benzene, and dried to give 219 mg (62%) of dimer **26** as a colorless powder (mp 281–283 °C dec to **1**). The dimer was sparingly soluble in organic solvents: ^{1}H NMR (benzene-d_6) δ 4.27 (s, 4 H), 5.12 (s, 4 H), 6.17, 6.60, 6.85, 6.95, 6.98, and 7.21 (dd, 4 H each),[16] 6.84 (s, 4 H); mass spectrum (thermal reversal to **1**), *m/e* (relative intensity) 354 (100), 353 (70), 352 (57), 276 (3), 176 (45). Anal. Calcd for $C_{56}H_{36}$: C, 94.88; H, 5.12. Found: C, 94.69; H, 5.23.

5,16-[1′,2′]Benzeno-5,16-dihydrohexacene (30). A solution of endoxide **7**[17] (854 mg, 4.4 mmol) and diene **6** (920 mg, 4 mmol) in xylene (60 mL) was heated at reflux for 72 h. The solvent was removed (Rotavap) and the residue recrystallized from methanol to give 1.51 g (89%) of cycloadduct **27**: mp ca. 245 °C dec; ^{1}H NMR δ 1.98 (dd, 2 H, J = 5, 7 Hz), 2.27 (dd, 2 H, J = 7, 14 Hz), 2.86 (dd, 2 H, J = 5, 14 Hz), 4.80 (s, 2 H), 5.05 (s, 2 H), 6.84, 6.91, 7.18, 7.23, 7.40, and 7.73 (dd, 2 H each),[16] 7.52 (s, 2 H); ^{13}C NMR δ 30.37; 42.63, 55.79, 84.98, 116.86, 122.42, 122.52, 124.12, 124.26, 125.59, 128.07, 132.75, 142.84, 143.55, 146.41, 146.92; mass spectrum, *m/e* (relative intensity) 424 (M^+, 1), 406 (2), 350 (4), 253 (3), 228 (5), 215 (7), 202 (6), 178 (25), 168 (100), 152 (4), 139 (10).

To a solution of **27** (1.27 g, 3 mmol) in acetic anhydride (100 mL) was added 12 mL of concentrated HCl, and the mixture was heated at reflux for 10 h. The cooled solution was poured into ice–water and extracted with CH_2Cl_2. The extract was washed with 10% Na_2CO_3 and water, dried, and evaporated. The resulting residue was column chromatographed with CH_2Cl_2–hexane (1:3) as the eluent to give 511 mg (42%) of a mixture of **28** and **29**: mp >250 °C dec; ^{1}H NMR (for **28**) δ 3.90 (s, 4 H), 4.95 (s, 2 H), 6.97 and 7.37 (dd, 4 H each),[16] 7.46 and 7.92 (dd, 2 H each),[16] 7.76 and 8.27 (s, 2 H each), (for **29**) δ 2.35 (t, 1 H, J = 5–7 Hz), 2.79 (dd, 1 H, J = 7, 13 Hz), 3.07 (dd, 1 H, J = 5, 13 Hz), 4.38 (s, 2 H), 4.92 (s, 1 H), 6.64 (s, 1 H), 7.06, 7.12, 7.46, and 7.90 (dd, 2 H each),[16] 7.37 (dd, 4 H),[16] 7.50, 7.55, 8.18, and 8.21 (s, 1 H each);[16] mass spectrum (mixture), *m/e* (relative intensity) 406 (M^+, 2), 354 (4), 228 (9), 212 (28), 191 (12), 178 (46), 119 (20), 94 (99), 56 (63), 41 (100).

A solution of **28** and **29** (406 mg, 1 mmol) in 30 mL of mesitylene containing 50 mg of 10% Pd–C was heated at reflux for 48 h. The hot solution was filtered, and the catalyst was washed with 20 mL of toluene. The combined filtrates were concentrated under reduced pressure to give 372 mg (92%) of **30** as orange crystals: mp 362–364 °C dec; ^{1}H NMR δ 5.53 (s, 2 H), 7.07 and 7.46 (dd, 4 H each), 7.35 and 7.95 (dd, 2 H each), 7.86, 8.46, and 8.56 (s, 2 H each); ^{13}C NMR δ 53.52, 121.18, 123.81, 124.98, 125.58, 125.86, 126.04, 128.20, 130.58, 131.27, 140.60, 143.88 (one peak missing or overlapped); mass spectrum, *m/e* (relative intensity) 404 (M^+, 100), 403 (47), 402 (39), 202 (7), 201 (49), 200 (12); UV (cyclohexane) λ_{max} 469 nm (ϵ 16 363), 440 (16 283), 415 (15 129), 404 (14 992), 392 (14 685), 382 (14 517), 370 (14 425), 302 (81 787), 291 (72 602), 281 (69 551). Anal. Calcd for $C_{32}H_{20}$: C, 95.01; H, 4.99. Found: C, 94.62; H, 5.38.

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Registry No. **1**, 13929-87-8; **3**, 106750-88-3; **6**, 36439-82-4; **7**, 22187-13-9; **8**, 573-57-9; **9**, 108947-35-9; **10**, 108947-36-0; **11**, 108947-37-1; **12**, 108947-38-2; **13**, 108947-39-3; **16**, 108947-40-6; **17**, 108947-40-6; **18**, 108947-43-9; **19**, 108947-42-8; *cis*-**20**, 108947-44-0; *trans*-**20**, 109010-38-0; **21**, 108947-45-1; **22**, 108947-46-2; **23**, 108947-47-3; **24**, 108947-48-4; **25**, 108947-49-5; **26**, 108947-50-8; **27**, 108947-51-9; **28**, 108947-53-1; **29**, 108947-52-0; **30**, 108947-54-2; TCNE, 670-54-2; DMAD, 762-42-5; MA, 108-31-6; *cis*-$ClCH_2CH{=}CHCH_2Cl$, 1476-11-5; *trans*-$ClCH_2CH{=}CHCH_2Cl$, 110-57-6.

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