Molecular Ladders Constituted of Laterally-Fused 1,4-Cyclohexadiene Subunits. Open-Chain Models of the [n]Beltenes

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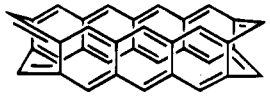
A practical synthesis of 2,3,6,7-tetramethylene-1,4,5,8-tetrahydronaphthalene (**11**) has opened up several avenues for the elaboration of molecules consisting largely or exclusively of 1,2:4,5-fused 1,4-cyclohexadiene subunits. Diels–Alder addition of dienophiles to both 1,3-diene segments of this reactive hydrocarbon leads directly to 1,4,5,6,7,10,11,12-octahydrotetracene and substituted derivatives of this polyolefin. A route to the hexacene homolog is available by twofold [4 + 2] cycloaddition of a benzyne followed by Birch reduction. For reasons of solubility, the benzyne should carry alkyl groups in its 4- and 5-positions. Finally, a two-step cyclohomologation scheme is described that allows for the systematic controlled extension of the structural features present in **11** to its tetra- and hexacyclic congeners. The insolubility of the latter hydrocarbon limits its further exploitation in synthesis.

More than a decade ago, Kivelson and Chapman described a theoretical study of infinite *linear* polyacenes and pointed out the many potential advantages offered by *cyclic* variants of these maximally unsaturated systems.[1] The concept of belting aromatic rings in this way was not only novel, but replete with synthetic pitfalls since the largest known linear acene is heptacene.[2] More recent theoretical work has focused on *cyclo*-anthracene,[3] but the obviously high strain in this system greatly reduces general interest in its preparative acquisition. The explosion of activity in fullerene chemistry has caused Diederich and Whetten to recognize that [9]-cyclacene (**1**) constitutes a key substructure of C_3-C_{78}.[4] Despite the efforts of several research groups,[5,6] however, no cyclic polyacene of any size has yet been prepared.



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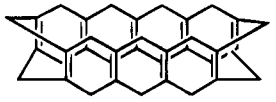

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In a companion development, Alder and Sessions proposed in 1985 on the basis of MM2 force field calculations that molecular belts constructed by lateral fusion of 1,4-cyclohexadiene subunits would be relatively unstrained for [8]beltene and higher analogues.[7] A series of such compounds ([9]beltene is illustrated in **2**) would be of interest as potential hosts for a wide range of guest molecules. Through-space $\pi-\pi$ interactions with resultant strong splitting of the π-levels ("columnar homoconjugation") has been proposed for [n]beltenes with n = 3–5.[8] Although significant advances have been made in this area by several investigators,[9–12] all of the end-products incorporate aryl and/or bridged spacers, thereby failing to correspond to the structural features uniquely characteristic of these systems.

Results and Discussion

In our view, the preparation of *cyclic* beltenes should be accompanied by efforts to produce their *linear* equivalents. In this way, direct spectroscopic comparison is made possible between the two series of structurally related skipped polyolefins. These undertakings need not be formally divorced if tactical advantage is taken of the common use of intermediates in both series. The strategy detailed herein for the synthesis of molecular ladders constituted of 1,4-cyclohexadiene rings is based on repetitive Diels–Alder cycloadditions to **11**. In principle, **11** should be capable of bilateral cyclohomologation to any desired chain length by [4 + 2] cycloaddition to 2 equiv of a butatriene equivalent. Once elongated, the chain could be capped by condensation with an acetylene synthon, benzyne, or similar dienophile to produce a closed ladder. Use of an appropriate acetylenic dienophile, particularly under high pressure conditions, might also lead to the formation of beltene systems.

The synthesis of **11** began with the bromination of 2,3-dimethylbutadiene[13] followed by twofold NBS bromination and reduction of **3** with zinc–copper couple to afford the labile 2,3-bis(bromomethyl)-1,3-butadiene (**4**)[14] (Scheme 1). Diels–Alder cycloaddition of diethyl acetylenedicarboxylate to **4** in refluxing toluene gave **5**, thereby setting the stage for a second reductive debromination and

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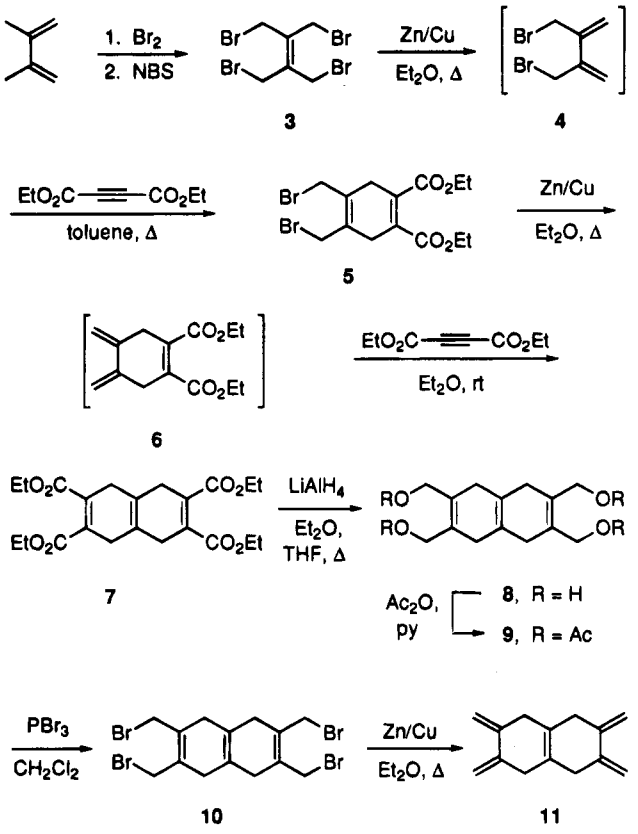
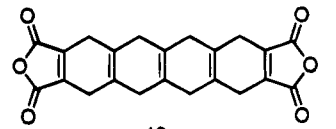
Scheme 1



formation of the highly reactive triene diester **6**. Immediate capture of **6** with another 1 equiv of diethyl acetylenedicarboxylate in ether at 20 °C afforded **7**. Recourse was made to the tetraethyl ester when we recognized that the solubility of **7** in organic solvents is vastly improved over that of the tetramethyl ester.

The methodology utilized for the production of **11** from **7** was adopted from an earlier report by Angus and Johnson.[15] The present work differs from this precedent in that four functional groups must be brought into reaction. Reduction with lithium aluminum hydride afforded the highly insoluble tetraol **8** in only 30% yield. The reduction of enedioic esters has long been recognized to be problematical because of competing C=C reduction.[16] Substitution of the "ate" complex from *n*-BuLi and DIBAL-H, as recommended by Anatanarayan and Hart,[17] instantly turned the reaction mixture black and gave no detectable **8**. Solubilization of **8** can be accomplished by conversion to the tetraacetate. This step is not a necessary prelude to brominative substitution since the acidic PBr_3 reagent dissolved the tetraol and delivered the sensitive tetrabromide **10** in 90% yield. For comparison, the pH neutral PBr_3·pyridine reagent fails to dissolve **8** or react with it. Heating **10** in ether with zinc–copper couple[18] afforded **11** in quantitative yield. This tetramethylene derivative was generally prepared immediately prior to use and kept in solution to retard polymerization.

Initial studies concerned with the response of **11** to treatment with dienophiles quickly revealed the limitations of the repetitive Diels–Alder approach. Condensation with excess di-*tert*-butyl acetylenedicarboxylate followed by acid-catalyzed loss of isobutylene and water gave the dianhydride **12**.[19] Tetracyano compound **13** was produced in 37% yield upon exposure of **11** to excess dicyanoacetylene,[20] while tetraketone **14** was isolated in



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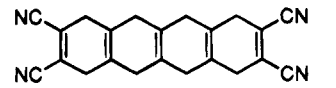

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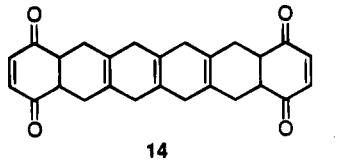

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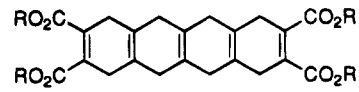


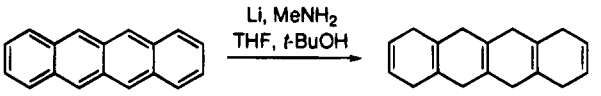
15a, R = Me **c**, R = *n*-Bu
b, R = Et **d**, R = *t*-Bu

37% yield from reaction with freshly sublimed *p*-benzoquinone. Relevantly, the characterization of **12**–**14** was severely hampered by their total insolubility in the common organic solvents. Solid state ^{13}C NMR analysis of **14** confirmed its symmetrical nature, although a distinction between C_{2v} or C_{2h} character was not possible.

In an effort to prepare soluble bis-adducts, **11** was subjected to Diels–Alder cycloaddition with a series of dialkyl acetylenedicarboxylates. By varying the alcohol component of the ester from methyl to ethyl to *n*-butyl as in **15a**–**c**, solubility could be dramatically improved.

The addition of only 1 equiv of dialkyl acetylenedicarboxylate to **11** produced the labile monoadducts **16a** and **16b** (Scheme 2). The further condensation of these intermediates with a second dienophile furnished **17**–**20**, of which only the last two were sufficiently soluble to be amenable to chromatographic purification.

Pentaene **22**, the longest known hydrocarbon chain of 1,4-cyclohexadiene rings, has been prepared by dissolving metal reduction of tetracene (**21**).[21] To prepare **22** from **11**, it becomes necessary to cap its conjugated diene units with an acetylene equivalent.[22] One of the more reliable



21 **22**

of such reagents is (*E*)-1,2-bis(phenylsulfonyl)ethylene,[23] which when added to **11** in a 2-fold molar excess afforded tetrasulfones **23** and **24** as two inseparable isomers in 64% yield (Scheme 3). Despite the quite low solubility

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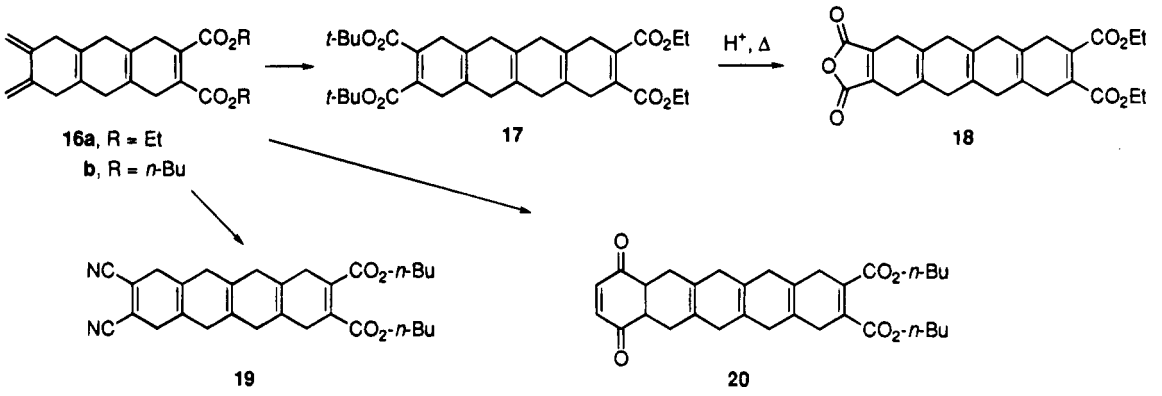
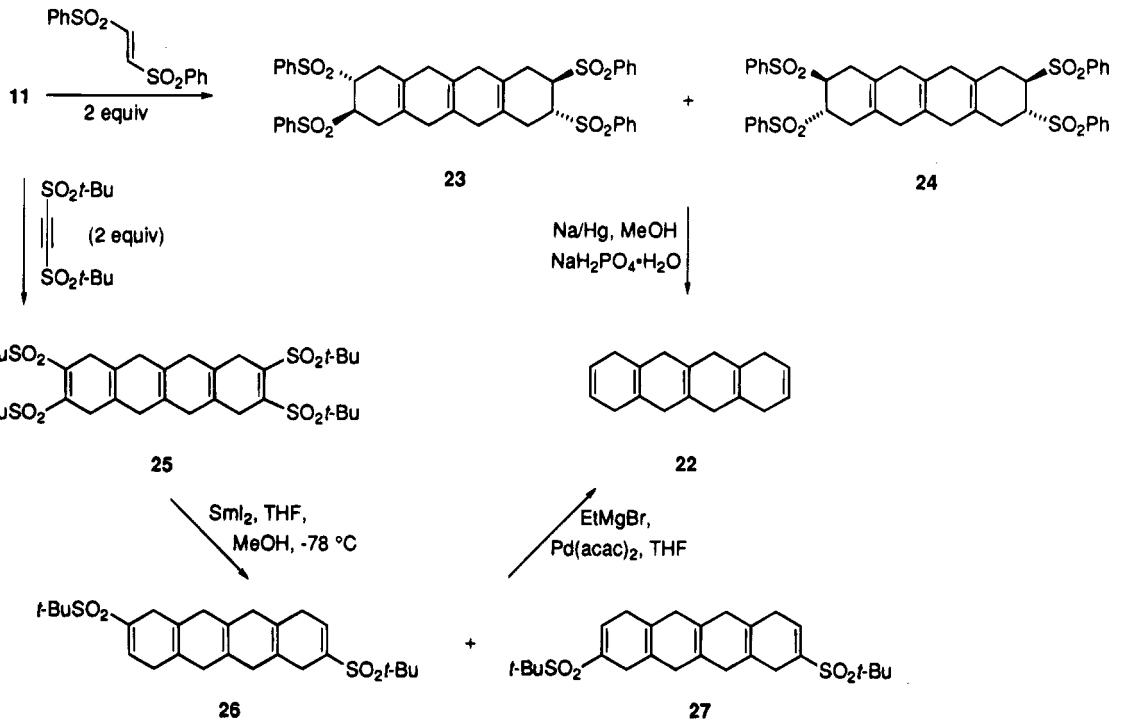
Scheme 2



Scheme 3



of these adducts, it proved possible to achieve their reductive desulfonylation to **22** (44%) with sodium amalgam.[24] In order to circumvent the insolubility problems associated with **23/24**, our attention was turned to bis(*tert*-butylsulfonyl)acetylene[25] as the dienophile. In this instance, the soluble isomerically pure tetrasulfone **25** was obtained in 50% yield and desulfonylation was accomplished in two-step fashion. Initial treatment with samarium iodide[26] produced **26** and **27**, both of which were converted into **22** by palladium-catalyzed reduction with ethylmagnesium bromide.[27]

On the strength of these results, the unknown hexacyclic linear array of 1,4-cyclohexadiene rings defined by **29a** was next targeted (Scheme 4). Treatment of **11** with excess benzyne, generated in situ from 1,2-dibromobenzene and *n*-butyllithium, afforded **28a** in 31% yield. The very limited solubility of this hydrocarbon precluded its projected Birch reduction to **29a**. Consequently, recourse was made to the introduction of solubilizing alkyl chains at specific sites in the molecular framework such that electronic characteristics would not be appreciably altered and the formation of isomeric mixtures would be precluded. To this end, 1,2-dibromo-4,5-di-*n*-hexylbenzene[28] was transformed into the derived benzyne by *n*-butyllithium as before in the presence of **11**. The resulting bis-adduct **28b** proved to be sufficiently soluble in warm solutions of THF containing *tert*-butyl alcohol to be added in this form to a cold (−7 °C) solution of lithium in methylamine. The heptaene **29b** so formed was sufficiently soluble to be examined by NMR.

Further extension of the capping strategy to encompass the octacyclic homolog was briefly examined in the context of naphthalyne synthetic equivalents of the 1,4-dehydronaphthalene 1,4-endoxide type (Scheme 5).[29] Conversion of **11** to **31a** and **31b** was achieved by heating the pentaene with either the known **30a**[29] or **30b** in toluene for 10−17 h. As regards the more soluble **31b**, a 2:1 mixture of diastereomers could be defined by ^{1}H

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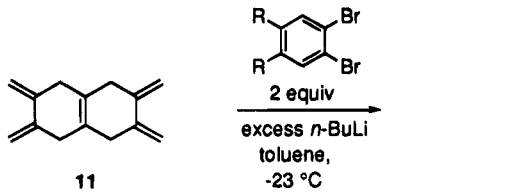
Scheme 4



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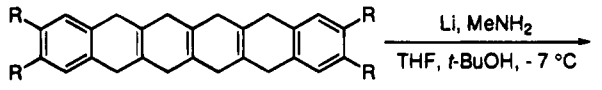
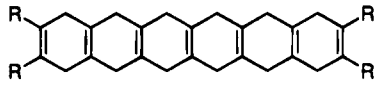
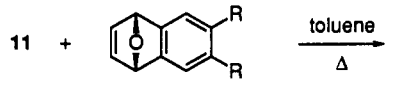


28a, R = H
b, R = *n*-hexyl

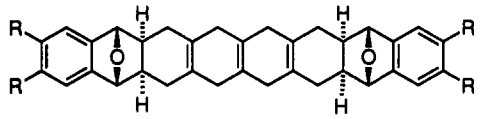


29a, R = H
b, R = *n*-hexyl

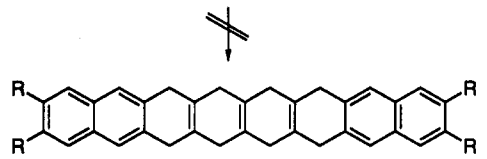
Scheme 5



30a, R = H
b, R = *n*-hexyl



31a, R = H
b, R = *n*-hexyl



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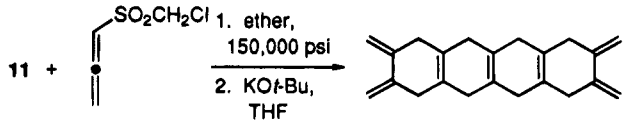
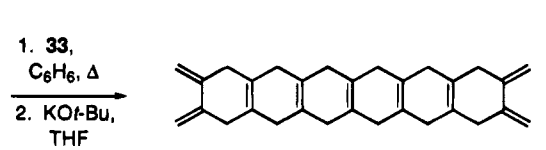
Scheme 6



33 **34**



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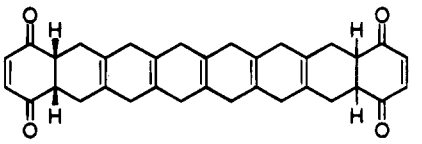
NMR analysis. Adhering to precedent, we first sought to dehydrate **31b** by warming in toluene containing a catalytic quantity of *p*-toluenesulfonic acid. These conditions were immediately recognized to cause double bond isomerization and formation of a myriad of inseparable bond shift isomers. Unfortunately, no dehydrating agent was found which did not also promote π-bond relocation. On this basis, it was concluded that the preparation of an octacyclic ladder would be more realistically realized by the capping of a homolog of **11** with an acetylene equivalent.

Of the several methods previously described for the elaboration of 1,2-dimethylene units,[30-34] that due to Block and Putman[34] was considered best suited to our purposes. These workers recognized that chloromethyl 1,2-propadienyl sulfone (**33**) is a reasonably reactive dienophile whose adducts can be transformed via the Ramberg-Bäcklund rearrangement to 1,3-dienes. This last step, which is carried out under alkaline conditions, was not expected to cause disruption of the existing π-bond arrangement. The short sequence constitutes a convenient two-step cyclohomologation.

As shown in Scheme 6, the 2-fold cycloaddition of **33** to **11** was best effected in ether solution under a pressure of 150 000 psi for 2 days. The pale yellow precipitate isolated from the reaction mixture was directly dissolved in THF and treated with 2 equiv of potassium *tert*-butoxide. Hydrocarbon **34** was isolated as a high melting white solid in 20% yield. Repetition of this process starting with **34** gave rise in turn to **35**, another substance of notably low solubility. As a consequence of this property, attempts to purify **35** proved to be counterproductive; it is best used directly in subsequent [4 + 2] cycloadditions.[35]

Reaction of **34** with 2 equiv of *p*-benzoquinone or maleic anhydride produced the insoluble diadducts **36** and **37**, respectively, as inseparable mixtures of syn and anti isomers. The more soluble tetraester **38** produced by comparable reaction with dimethyl fumarate was obtained pure by column chromatography. All attempts to recrystallize this substance resulted in its decomposition. Exposure of **34** to 10 equiv of benzyne (from 1,2-dibromobenzene and *n*-butyllithium) afforded the insoluble triadduct **39** in 56% yield. Its structure has been tentatively assigned on the basis of MS and solid state ^{13}C NMR (TOSS CPMAS) data.[36] The more symmetrical



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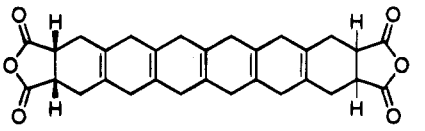

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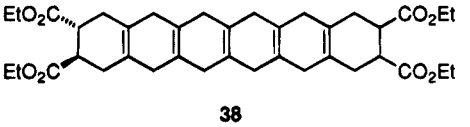

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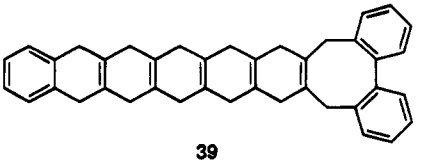

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benzyne diadduct was not isolated upon decreasing the level of benzyne significantly or by generating the benzyne alternatively from the diazonium salt of anthranilic acid.

Conclusions

The family of doubly-functionalized Diels–Alder dienes that we have succeeded in synthesizing hold utility as building blocks for the construction of molecular ladders in a highly controlled manner. Although the path now appears clear for the production of a myriad of multicyclic systems, the low solubility of many of these products is not conducive to their exploitation in more extended synthetic undertakings. Although this complication can be offset to some degree by the incorporation of alkyl chains, this tactic does little to allow access to the parent hydrocarbons which are the targets of most immediate interest. However, plausible alternatives may ultimately be arrived at and it is hoped that the early experiments described herein will facilitate and hasten the ultimate realization of these goals.

Experimental Section

General Procedure. All manipulations were performed under an inert (nitrogen unless otherwise noted) atmosphere. Solvents were dried over 4 Å molecular sieves before their distillation. Benzene, diethyl ether, tetrahydrofuran, and toluene were distilled from sodium–benzophenone ketyl. Dichloromethane, dimethyl sulfoxide, hexamethylphosphoric triamide, pyridine, and triethylamine were each distilled from calcium hydride. Carbon tetrachloride was distilled from phosphorus pentoxide. All reagents were reagent grade and purified where necessary. Organic extracts were dried over magnesium sulfate. Melting points were determined in open capillaries and are uncorrected. Solid state ^{13}C NMR spectra were recorded at 75 MHz using the total suppression of sidebands cross-polarization magic-angle spinning (TOSS CP-MAS) technique. High resolution mass spectra were recorded at The Ohio State University Chemical Instrumentation Center. Elemental analyses were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Tetraethyl 1,4,5,8-Tetrahydronaphthalene-2,3,6,7-tetracarboxylate (7). Prepared following the literature procedures (see text): mp 138 °C (from ethanol); IR (KBr, cm^{-1}) 1739, 1708, 1277, 1246, 1062; ^1H NMR (300 MHz, $CDCl_3$) δ 4.22 (q, J = 7.1 Hz, 8 H), 2.90 (s, 8 H), 1.28 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.5, 132.1, 120.5, 61.2, 31.7, 14.0; MS m/z (M^+) calcd 420.1784, obsd 420.1764.

2,3,6,7-Tetrakis(hydroxymethyl)-1,4,5,8-tetrahydronaphthalene (8). A solution of **7** (5.00 g, 11.9 mol) in THF (50 mL) was added dropwise to a suspension of lithium aluminum hydride (1.35 g, 35.7 mmol) in ether (250 mL) at 0 °C. The reaction mixture was brought to reflux for 10 h and cooled to 0 °C. Water (1.4 mL) followed by 15% NaOH solution (1.4 mL) and more water (4.2 mL) was added dropwise. The slushy mixture was filtered, and the filter cake was transferred to a 500 mL flask and extracted with boiling methanol (200 mL) for 15 min. The hot suspension was rapidly filtered, and the whole process was repeated two more times. The methanol extracts were combined and cooled to 0 °C. The white precipitate which formed was collected by filtration (0.928 g, 31%): mp 241 °C dec (methanol); IR (KBr, cm^{-1}) 3265, 2874, 1654, 1560, 1420, 1046, 1015, 988, 728; ^1H NMR (300 MHz, DMSO-d_6) δ 4.47 (t, J = 5.4 Hz, 4 H), 3.97 (d, J = 5.3 Hz, 8 H), 2.60 (s, 8 H); ^{13}C NMR (75 MHz, DMSO-d_6) ppm 130.2, 122.4, 59.6, 33.0; MS m/z (M^+) calcd 252.1361, obsd 252.1394.

2,3,6,7-Tetrakis(acetoxymethyl)-1,4,5,8-tetrahydronaphthalene (9). To a solution of acetic anhydride (5 mL) and dry pyridine (1.5 mL) was added **8** (38 mg, 0.15 mmol), and the suspension was stirred at rt overnight. The reaction mixture was cooled to 0 °C, and the product was precipitated by the addition of ice–water. The tetraacetate **8** was isolated by suction filtration (49 mg, 77%): mp 133.5–134.5 °C (from ethanol; IR (KBr, cm^{-1}) 1737, 1373, 1255, 1026, 961; ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 8 H), 2.68 (s, 8 H), 2.05 (s, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 170.8, 129.4, 122.0, 63.0, 33.6, 20.8; MS m/z ($M^+ - 2CH_3CO_2H$) calcd 300.1361, obsd 300.1378. Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.84; H, 6.71. Found: C, 62.48; H, 6.94.

2,3,6,7-Tetrakis(bromomethyl)-1,4,5,8-tetrahydronaphthalene (10). To a solution of **8** (562 mg, 2.23 mmol) in CH_2Cl_2 (25 mL) was added PBr_3 (0.42 mL, 4.46 mmol). The reaction mixture was stirred at rt overnight, diluted with CH_2Cl_2 (100 mL), washed sequentially with water, saturated $NaHCO_3$ solution, and brine, and then dried. The solvent was evaporated, and the residue was recrystallized from ethyl acetate to afford colorless crystals of **10** (1.01 g, 90%): mp 203 °C dec (ethyl acetate); IR (film, cm^{-1}) 1655, 1467, 1208, 1079; ^1H NMR (300 MHz, $CDCl_3$) δ 4.06 (s, 8 H), 2.77 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 131.2, 121.8, 34.0, 30.4; MS m/z (M^+) calcd 499.7984, obsd 499.7959. Anal. Calcd for $C_{14}H_{16}Br_4$: C, 33.37; H, 3.20. Found: C, 33.36; H, 3.19. This compound must be stored in the dark at 0 °C to prevent decomposition.

2,3,6,7-Tetramethylene-1,4,5,8-tetrahydronaphthalene (11). A solution of **10** (100 mg, 0.198 mmol) and Zn/Cu couple (194 mg) in dry ether (10 mL) was refluxed for 1 h, cooled, filtered through a short pad of Celite, washed with water and brine, and dried. The solvent was evaporated to afford **11** as a pale yellow oil in quantitative yield. The product polymerizes when not kept in solution: IR (film, cm^{-1}) 1637, 1425, 1302, 891; ^1H NMR (300 MHz, $CDCl_3$) δ 5.10 (d, J = 1.9 Hz, 4 H), 4.77 (d, J = 1.9 Hz, 4 H), 2.85 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 145.3, 125.2, 108.7, 37.7; MS m/z (M^+) calcd 184.1252, obsd 184.1249.

1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylic Dianhydride (12). A solution of di-*tert*-butyl acetylenedicarboxylate (181 mg, 0.80 mmol) and **11** [prepared from **10** (136 mg, 0.27 mmol)] in ether (5 mL) was stirred under reflux for 24 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/ethyl acetate, 10:1) to afford tetraester **15d** as a white solid (48 mg, 30%); mp >240 °C dec (from methylcyclohexane); IR (KBr, cm^{-1}) 1718, 1368, 1279, 1137; ^1H NMR (300 MHz, $CDCl_3$) δ 2.84 (s, 8 H), 2.45 (s, 8 H), 1.50 (s, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.2, 132.8, 123.0, 121.9, 81.3, 34.9, 32.3, 28.0; MS m/z (M^+) calcd 636.3662, obsd 636.3738. Anal. Calcd for $C_{38}H_{52}O_8$: C, 71.67; H, 8.23. Found: C, 71.53; H, 8.22.

A solution of **15d** (48 mg, 0.075 mmol) and *p*-toluenesulfonic acid (one crystal) in toluene (4 mL) was refluxed for 4 h and cooled to rt. The precipitate was collected and triturated with ether to afford **12** as an insoluble tan solid (24 mg, 85%); mp > 300 °C dec; IR (KBr, cm^{-1}) 1846, 1792, 1443, 1268, 1065, 907, 716; MS m/z (M^+) calcd 376.0947, obsd 376.0937.

2,3,8,9-Tetracyano-1,4,5,6,7,10,11,12-octahydrotetracene (13). A solution of **11** [(prepared from **10** (176 mg, 0.35 mmol)] and dicyanoacetylene (large excess) in ether (10 mL) was stirred at rt for 24 h. The precipitate was collected by filtration and triturated with ether to afford **13** as an insoluble tan solid (62 mg, 51%): mp >270 °C dec; IR (KBr, cm^{-1}) 2225, 1630, 1439, 1112; MS m/z (M^+) calcd 336.1375, obsd 336.1341.

Diels–Alder Cycloaddition between 30 and *p*-Benzoquinone. A solution of **11** [(prepared from **10** (150 mg, 0.30 mmol)] and freshly sublimed *p*-benzoquinone (71 mg, 0.66 mmol) in 1,2-dichloroethane (25 mL) was refluxed for 16 h. The precipitate was collected and triturated with 1,2-dichloroethane to leave **14** as an insoluble white solid (45 mg, 37%); mp > 275 °C dec; IR (film, cm^{-1}) 1675; ^{13}C NMR (75 MHz, solid state) ppm 201.1, 142.1, 136.7, 123.7, 45.4, 36.6, 30.0, 27.9; MS m/z (M^+) calcd 400.1674, obsd 400.1676.

Tetramethyl 1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylate (15a). A solution of **11** [(prepared

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from **10** (90 mg, 0.18 mmol)] and dimethyl acetylenedicarboxylate (254 mg, 1.79 mmol) in benzene (4 mL) was stirred at rt for 24 h. The precipitate was collected and triturated with ether to leave **15a** as a white solid (26 mg, 31%): mp 294 °C (from toluene); IR (KBr, cm^{-1}) 1719, 1658, 1434, 1277, 1139, 1063; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 12 H), 2.91 (s, 8 H), 2.48 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.3, 132.7, 122.9, 121.8, 52.2, 34.8, 32.0; MS m/z (M^+) calcd 468.1784, obsd 468.1786. Attempts to recrystallize **15a** from various solvents resulted in decomposition.

Tetraethyl 1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylate (15b). A solution of **11** [(prepared from **10** (1.41 g, 2.78 mmol)] and diethyl acetylenedicarboxylate (968 mg, 5.69 mmol) in ether (100 mL) was stirred at rt for 3 d. The precipitate was collected and triturated with ether to leave **15b** as a white solid (563 mg, 40%). The supernatant was concentrated and purified by chromatography on silica gel (elution with hexanes/ether, 3:1) to afford a small quantity of **16a** (see below for characterization).

For the diadduct **15b**: mp 226 °C (from ethyl acetate); IR (KBr, cm^{-1}) 1731, 1719, 1709, 1275, 1251, 1147, 1063; ^1H NMR (300 MHz, $CDCl_3$) δ 4.23 (q, J = 7.1 Hz, 8 H), 2.90 (s, 8 H), 2.47 (s, 8 H), 1.30 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.9, 132.5, 122.9, 121.8, 61.1, 34.8, 32.1, 14.0; MS m/z (M^+) calcd 524.2410, obsd 514.2375. Anal. Calcd for $C_{30}H_{36}O_8$: C, 68.68; H, 6.92. Found: C, 68.63; H, 6.91.

Tetra-*n*-butyl 1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylate (15c). A solution of di-*n*-butyl acetylenedicarboxylate (99 mg, 0.44 mmol) and **11** [(prepared from **10** (202 mg, 0.40 mmol)] in toluene (5 mL) was stirred at rt overnight and then warmed to 75 °C for 4 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/ ether, 10:1 gradient to 2:1) to afford diadduct **15c** (60 mg, 24%) and the monoadduct **16b** (31 mg, 19%).

For diadduct **15c**: mp 121–122 °C (from ether); IR (KBr, cm^{-1}) 1734, 1719, 1276, 1255, 1069; ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (t, J = 6.7 Hz, 8 H), 2.90 (s, 8 H), 2.47 (s, 8 H), 1.64 (m, 8 H), 1.39 (m, 8 H), 0.94 (t, J = 7.4 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.0, 132.5, 122.9, 121.8, 65.0, 34.8, 32.1, 30.5, 19.1, 13.7; MS m/z (M^+) calcd 636.3662, obsd 636.3681. Anal. Calcd for $C_{38}H_{52}O_8$: C, 71.67; H, 8.23. Found: C, 71.68; H, 8.24.

For monoadduct **16b**: IR (KBr, cm^{-1}) 1721, 1257; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (d, J = 1.5 Hz, 2 H), 4.76 (d, J = 1.4 Hz, 2 H), 4.17 (t, J = 6.7 Hz, 4 H), 2.89 (s, 4 H), 2.83 (s, 4 H), 2.48 (s, 4 H), 1.63 (m, 4 H), 1.39 (m, 4 H), 0.94 (t, J = 7.4 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 168.0, 145.3, 132.5, 124.1, 121.7, 108.7, 65.0, 37.3, 35.2, 32.1, 30.5, 19.1, 13.7; MS m/z (M^+) calcd 410.2457, obsd 410.2454.

Diethyl 6,7-Dimethylene-1,4,5,8,9,10-hexahydroanthracene-2,3-dicarboxylate (16a). A solution of diethyl acetylenedicarboxylate (51 mg, 0.30 mmol) and **11** [(prepared from **10** (136 mg, 0.27 mmol)] in ether (5 mL) was stirred at rt for 24 h. The precipitated tetraester **15b** was collected by centrifugation (15 mg, 11%). The supernatant was concentrated and the residue was purified by chromatography on silica gel (elution with hexanes/ether, 3:1) to afford **16a** as a white solid (46 mg, 48%). This compound aromatizes rapidly and should be used immediately.

For monoadduct **16a**: mp 89 °C; IR (KBr, cm^{-1}) 1738, 1724, 1709, 1283, 1257, 1071; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (d, J = 1.7 Hz, 2 H), 4.77 (d, J = 1.7 Hz, 2 H), 4.23 (q, J = 7.1 Hz, 4 H), 2.90 (s, 4 H), 2.83 (s, 4 H), 2.48 (s, 4 H), 1.30 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.9, 145.3, 132.5, 124.1, 121.7, 108.7, 61.1, 37.4, 35.2, 32.0, 14.0; MS m/z (M^+) calcd 354.1831, obsd 354.1852.

Di-*n*-butyl 6,7-Dimethylene-1,4,5,8,9,10-hexahydroanthracene-2,3-dicarboxylate (16b). A solution of di-*n*-butyl acetylenedicarboxylate (99 mg, 0.44 mmol) and **11** [(prepared from **10** (202 mg, 0.40 mmol)] in methylcyclohexane (5 mL) was stirred at rt for 2 d. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/ether, 4:1) to afford **16b** as a colorless oil (41 mg, 25%) identical to the material described above. This compound aromatizes rapidly and should be used immediately.

2,3-Di-*tert*-butyl 8,9-Diethyl 1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylate (17). A solution of di-*n*-butyl acetylenedicarboxylate (84 mg, 0.19 mmol) in ether (4 mL) was stirred under reflux for 1 d. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/ether, 2:1) to afford **17** as a white solid (51 mg, 46%): mp 151.5 °C (from hexanes); IR (KBr, cm^{-1}) 1719, 1367, 1269, 1139, 1065; ^1H NMR (300 MHz, $CDCl_3$) δ 4.23 (q, J = 7.1 Hz, 4 H), 2.90 (s, 4 H), 2.84 (s, 4 H), 2.46 (s, 8 H), 1.50 (s, 18 H), 1.30 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.9, 167.2, 132.7, 132.6, 123.0, 121.9, 121.8, 81.3, 61.1, 34.84, 34.79, 32.3, 32.1, 28.0, 14.0; MS m/z (M^+) calcd 580.3036, obsd 580.3034. Anal. Calcd for $C_{34}H_{44}O_8$: C, 70.32; H, 7.64. Found: C, 70.44; H, 7.60.

1,4,5,6,7,10,11,12-Octahydrotetracene-2,3,8,9-tetracarboxylic 2,3-Anhydride Diethyl Ester (18). A solution of **17** (51 mg, 0.088 mmol) and *p*-toluenesulfonic acid (one crystal) in toluene (4 mL) was refluxed for 6 h. The precipitate was collected and triturated with ether to afford **18** as a white solid (28 mg, 71%): mp 284 °C; IR (KBr, cm^{-1}) 1846, 1772, 1715, 1269, 1066; ^1H NMR (300 MHz, $CDCl_3$) δ 4.24 (q, J = 7.1 Hz, 4 H), 3.02 (s, 4 H), 2.92 (s, 4 H), 2.6 (s, 4 H), 2.5 (s, 4 H), 1.31 (t, J = 7.1 Hz, 16 H); MS m/z (M^+) calcd 450.1678, obsd 450.1677.

Di-*n*-butyl 2,3-Dicyano-1,4,5,6,7,10,11,12-octahydrotetracene-8,9-dicarboxylate (19). A solution of dicyanoacetylene (large excess) and **16b** (31 mg, 0.076 mmol) in ether (5 mL) was stirred at rt for 1 d. The precipitate was collected and triturated with ether to afford **19** as a white solid (32 mg, 88%): mp 238 °C (from toluene); IR (KBr, cm^{-1}) 2226, 1714, 1273; ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (t, J = 6.7 Hz, 4 H), 2.96 (s, 4 H), 2.89 (s, 4 H), 2.47 (s, 8 H), 1.65 (m, 4 H), 1.39 (m, 4 H), 0.94 (t, J = 7.4 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 167.9, 132.4, 123.6, 122.5, 121.7, 120.9, 115.3, 65.1, 34.6, 34.4, 32.8, 32.0, 30.5, 19.1, 13.7; MS m/z (M^+) calcd 486.2518, obsd 486.2514. Anal. Calcd for $C_{30}H_{34}O_4N_2$: C, 74.05; H, 7.04. Found: C, 73.76; H, 7.10.

Diels–Alder Cycloaddition between 16b and *p*-Benzoquinone. A solution of freshly sublimed *p*-benzoquinone (18 mg, 0.17 mmol) and **16b** (35 mg, 0.085 mmol) in ether (5 mL) was stirred at rt for 1 d. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/chloroform/ethyl acetate, 4:4:1) to afford **20** as a white solid (20 mg, 45%): mp 187 °C (from methylcyclohexane); IR (NaCl film, cm^{-1}) 1725, 1712, 1677, 1268; ^1H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 2 H), 4.17 (t, J = 6.7 Hz, 4 H), 3.26 (t, J = 4.7 Hz, 2 H), 2.89 (s, 4H), 2.44 (s, 8 H), 2.38 (dd, J = 4.5, 17.6 Hz, 2 H), 2.07 (dd, J = 4.5, 17.6 Hz, 2 H), 1.64 (m, 4 H), 1.39 (m, 4 H), 0.94 (t, J = 7.3 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 200.0, 168.0, 139.3, 132.5, 123.4, 122.9, 121.7, 65.0, 46.8, 35.6, 34.7, 32.1, 30.5, 28.3, 19.1, 13.7; MS m/z (M^+) calcd 518.2668, obsd 518.2674. Anal. Calcd for $C_{33}H_{38}O_6$: C, 74.10; H, 7.38. Found: C, 73.94; H, 7.25.

2,3,8,9-Tetrakis(phenylsulfonyl)-1,2,3,4,5,6,7,8,9,10,11,-12-dodecahydrotetracene (23 and 24). A solution of **11** [(prepared from **10** (190 mg, 0.38 mmol)] and (*E*)-1,2-bis-(phenylsulfonyl)ethylene (256 mg, 0.829 mmol) in $CHCl_3$ (100 mL) was stirred at rt for 5 d. The precipitate was collected by filtration and triturated with ether to leave **23/24** as an insoluble white solid (173 mg, 64%): mp > 300 °C dec (from 1,2-dichloroethane); IR (film, cm^{-1}) 1437, 1314, 1141, 730; ^1H NMR (300 MHz, DMSO-d_6) δ 7.81 (d, J = 7.4 Hz, 8 H), 7.75 (t, J = 7.5 Hz, 4 H), 7.59 (t, J = 7.7 Hz, 8 H), 3.84 (d, J = 5.8 Hz, 4 H), 2.35 (br s, 8 H), 2.13 (br s, 8 H); ^{13}C NMR (75 MHz, solid state, TOSS CPMAS) ppm 137.1, 136.0, 127.9, 126.2, 120.9, 118.8, 53.4, 34.3, 24.0; MS (FAB) m/z (M^+ + H) calcd 800.16, obsd 801.45. Anal. Calcd for $C_{42}H_{40}O_8S_4$: C, 62.97; H, 5.03. Found: C, 62.98; H, 4.95.

2,3,8,9-Tetrakis(*tert*-butylsulfonyl)-1,4,5,6,7,10,11,12-octahydrotetracene (25). A solution of **11** [(prepared from **10** (75 mg, 0.15 mmol)] and di-*tert*-butylsulfonylacetylene (75 mg, 0.28 mmol) in $CHCl_3$ (2 mL) was stirred at rt for 2 d. The solvent was evaporated, and the residue was chromatographed on silica gel (elution with $CHCl_3$/MeOH, 60:1) to afford **25** as a white solid (53 mg, 50%): mp > 300 °C (160 °C dec); IR (film, cm^{-1}) 1284, 1118; ^1H NMR (300 MHz, $CDCl_3$) δ 3.34 (s, 8 H),

2.56 (s, 8 H), 1.48 (s, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.9, 123.8, 122.9, 64.5, 38.9, 34.4, 25.0; MS (FAB) m/z ($M^+ + H$) calcd 716.25, obsd 717.51. Anal. Calcd for $C_{34}H_{52}O_8S_4$: C, 56.95; H, 7.31. Found: C, 56.96; H, 7.37.

2,8- and 2,9-Di-(*tert*-butylsulfonyl)-1,4,5,6,7,10,11,12-octahydrotetracene (26 and 27). A deoxygenated solution of **25** (46 mg, 0.064 mmol) in THF (12 mL) and MeOH (0.5 mL) was added portionwise via cannula to a freshly prepared solution of SmI_2 (20 mL, 0.1 M in THF) at −78 °C. The reaction mixture was stirred for a further 2 h at −78 °C, poured into a saturated K_2CO_3 solution, and extracted with CH_2Cl_2 (3 × 50 mL). The extracts were combined, dried, and concentrated. The residue was triturated with ether to leave **26/27** as a white solid (11 mg, 37%); mp > 300 °C (dec at 270 °C); IR (film, cm^{-1}) 1282, 1109; ^1H NMR (300 MHz, $CDCl_3$) δ 6.88 (m, 2 H), 2.98 (m, 4 H), 2.91 (m, 4 H), 2.50 (s, 4 H), 1.39 (s, 18 H); MS m/z (M^+) calcd 476.2055, obsd 476.2055. Anal. Calcd for $C_{26}H_{36}O_4S_2$: C, 65.51; H, 7.61. Found: C, 65.17; H, 7.55.

1,4,5,6,7,10,11,12-Octahydrotetracene (22). A. From **23/24**: A slurry of **23/24** (100 mg, 0.125 mmol) and $NaH_2PO_4 \cdot H_2O$ (760 mg, 5.5 mmol) in methanol (10 mL) was purged with N_2 for 15 min. With efficient stirring, 2% sodium amalgam (2.9 g) was added in portions. The reaction mixture was stirred overnight at rt and filtered. The filter cake was washed first with water to dissolve the inorganic salts and next with $CHCl_3$ to dissolve the remaining organic material. The organic extract was washed with water and dried. The solvent was evaporated, and the residue was chromatographed on alumina (elution with hexanes) to afford **22** as a white solid (13 mg, 44%): mp 240 °C (lit.[21] mp 241 °C from THF); IR (film, cm^{-1}) 1407, 993, 654; ^1H NMR (300 MHz, $CDCl_3$) δ 5.74 (s, 4 H), 2.57 (s, 8 H), 2.45 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 124.5, 123.43, 123.39, 35.6, 30.6; MS m/z (M^+) calcd 236.1565, obsd 236.1563.

From **26/27**: Ethylmagnesium bromide (0.1 mL, 1 M in THF) was added to a suspension of **26/27** (11 mg, 0.023 mmol) and $Pd(acac)_2$ (1 mg, 0.002 mmol) in dry THF (2 mL) at rt. The reaction mixture was stirred at rt for 2 h and then brought to reflux for a further 30 min before being filtered and quenched with saturated NH_4Cl solution. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined extracts were washed with saturated $NaHCO_3$ solution and brine prior to drying and solvent evaporation. The residue was purified by chromatography on neutral alumina (elution with hexanes/toluene, 2:1) to afford **22** as a white solid (3 mg, 55%): mp 239 °C.

5,6,7,8,13,14,15,16-Octahydrohexacene (28a). To a solution of **11** [(prepared from **10** (250 mg, 0.496 mmol)] and 1,2-dibromobenzene (1.17 g, 4.96 mmol) in dry toluene (10 mL) was added *n*-BuLi (3.16 mL, 1.6 M in hexanes, 5.06 mmol) dropwise at −23 °C. The reaction mixture was warmed to rt overnight and quenched with ice cold methanol. The precipitate was collected and washed with water, methanol, and ether to leave **28a** as an insoluble white solid (56 mg, 31%); mp > 300 °C (from toluene); IR (KBr, cm^{-1}) 1495, 1456, 1442, 1414, 745, 736; ^1H NMR (500 MHz, CD_2Cl_2) δ 7.141 (s, 4H), 7.139 (s, 4 H), 3.31 (s, 8 H), 2.65 (s, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2) ppm 128.3 (2 C not observed), 128.0, 126.1, 35.9, 34.7; MS m/z (M^+) calcd 336.1878, obsd 336.1871. Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.89; H, 7.21.

2,3,10,11-Tetra-*n*-hexyl-5,6,7,8,13,14,15,16-octahydrohexacene (28b). To a solution of **11** [(prepared from **10** (125 mg, 0.248 mmol)] and 1,2-dibromo-4,5-di-*n*-hexylbenzene (301 mg, 0.744 mmol) in dry toluene (9 mL) at −23 °C was added *n*-butyllithium (0.72 mL, 1.2 M in hexanes) dropwise. The reaction mixture was stirred at −23 °C for 1 h, allowed to warm gradually to rt overnight, quenched with MeOH (2 drops), and freed of solvent. Water was added and the product was extracted into CH_2Cl_2. The extracts were combined, washed with brine, and dried. The solvent was evaporated, and the residue was first triturated with pentane and then recrystallized from toluene to afford colorless crystals of **28b** (37 mg, 22%): mp 195 °C (toluene); IR (film, cm^{-1}) 2954, 2922, 2857, 2806, 1467, 902; ^1H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 4 H), 3.25 (s, 8 H), 2.62 (s, 8 H), 2.56 (t, J = 7.9 Hz, 8 H), 1.57 (m, 8 H), 1.42−1.30 (br m, 24 H), 0.91 (t, J = 6.8 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 138.1, 131.9, 128.5, 123.9, 123.6, 35.7, 34.0, 32.4, 31.8, 31.5, 29.5, 22.6, 14.1; MS m/z (M^+) calcd 672.5634, obsd 672.5609. Anal. Calcd for $C_{50}H_{72}$: C, 89.22; H, 10.78. Found: C, 89.18; H, 10.68.

2,3,10,11-Tetra-*n*-hexyl-1,4,5,6,7,8,12,13,14,15,16-dodecahydrohexacene (29b). A warm solution of **28b** (88 mg, 0.13 mmol) in THF (20 mL) and dry *t*-BuOH (3.1 mL, 33 mmol) was added dropwise to a solution of lithium (455 mg, 66 mmol) in $MeNH_2$ (30 mL) at −7 °C. The reaction mixture was stirred under reflux for 4 h. The $MeNH_2$ was allowed to evaporate slowly overnight. The residue was quenched with ice−water (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with water and brine and then dried. The solvent was evaporated to afford **29b** as a white solid (46 mg, 52%): mp 204 °C (THF); IR (film, cm^{-1}) 1468, 1422; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (s, 8 H), 2.48 (s, 8 H), 2.46 (s, 8 H), 2.04 (m, 8 H), 1.41−1.30 (br m, 32 H), 0.89 (m, 12); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 128.0 (one carbon not observed), 123.6, 123.5, 99.7, 35.4, 35.2, 32.4, 31.8, 29.5, 28.4, 22.6, 14.1; MS m/z (M^+) calcd 676.5947, obsd 676.5958. Anal. Calcd for $C_{50}H_{76}$: C, 88.69; H, 11.31. Found: C, 88.48; H, 11.26.

Diels−Alder Cycloaddition between 11 and 30a. A toluene (4 mL) solution of **11** [(prepared from **10** (250 mg, 0.50 mmol)] was added dropwise to a refluxing solution of **30a** (157 mg, 1.09 mmol) in toluene (10 mL). The reaction mixture was refluxed for 10 h and cooled to rt . The precipitate was collected and triturated with hexane to leave **31a** as a white solid (154 mg, 66%); mp > 275 °C (from 1,2-dichloroethane); IR (film, cm^{-1}) 1459, 995, 746; ^1H NMR (300 MHz, CD_2Cl_2) δ 7.23−7.19 (m, 4 H), 7.13−7.10 (m, 4H), 4.94 (s, 4 H), 2.54 (s, 8 H), 2.24 (dd, J = 6.5, 14.0 Hz, 4 H), 2.14−2.07 (m, 4 H), 1.93−1.87 (m, 4 H); MS m/z (M^+) calcd 472.2402, obsd 472.2380. Anal. Calcd for $C_{34}H_{32}O_2$: C, 86.40; H, 6.83. Found: C, 86.71; H, 6.81.

1,4-Epoxy-6,7-di-*n*-hexyl-1,4-dihydronaphthalene (30b). Furan (15 mL, 206 mmol) was slowly added to *n*-butyllithium (18.3 mL, 1.5 M in hexanes) at −78 °C over 15 min. A solution of 1,2-dibromo-4,5-di-*n*-hexylbenzene[28] (9.15 g, 22.6 mmol) in ether (10 mL) was slowly introduced at −78 °C over 30 min. The reaction mixture was stirred for 40 min at −78 °C, allowed to warm to 0 °C, and quenched with water (50 mL). The layers were separated, and the aqueous phase was extracted with ether (2 × 25 mL). The combined extracts were washed with brine and dried. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes/ethyl acetate, 20:1) to afford **30b** as a colorless oil (4.5 g, 69%); IR (film, cm^{-1}) 1456, 1281, 987, 850; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08 (s, 2 H), 7.01 (t, J = 1.0 Hz, 2 H), 5.68 (s, 2 H), 2.57 (m, 4 H), 1.56 (m, 4 H), 1.36 (br m, 12 H), 0.93 (t, J = 6.7 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 146.1, 142.8, 136.7, 121.4, 82.2, 32.8, 31.7, 31.4, 29.4, 22.6, 14.0; MS m/z (M^+) calcd 312.2453, obsd 312.2454. Anal. Calcd for $C_{22}H_{32}O$: C, 84.56; H, 10.32. Found: C, 84.43; H, 10.42.

Diels−Alder Cycloaddition between 11 and 30b. A solution of **11** [(prepared from **10** (987 mg, 1.96 mmol)] and **30b** (1.29 g, 4.12 mmol) in toluene (20 mL) was refluxed for 17 h. The solvent was evaporated, and the residue was recrystallized from ethyl acetate to afford **31b** as colorless crystals (554 mg, 35%): mp 199−201°C dec (from ethyl acetate); IR (film, cm^{-1}) 1466, 996, 917, 875, 857; ^1H NMR (300 MHz, CD_2Cl_2) δ 6.99 (s, 4 H), 4.87 (s, 4 H), 2.59 (m, 8 H), 2.54 (s, 8 H), 2.19 (m, 4 H), 2.09 (m, 4 H), 1.89 (m, 4 H), 1.55 (m, 8 H), 1.35 (br m, 24 H), 0.91 (m, 12 H); ^{13}C NMR (75 MHz, CD_2Cl_2) ppm 144.1, 138.9, 127.8, 124.8, 119.9, 85.3, 43.1, 36.3, 33.3, 32.5, 32.2, 32.0, 29.9, 23.1, 14.3; MS m/z (M^+) calcd 808.6158, obsd 808.6164. Anal. Calcd for $C_{58}H_{80}O_2$: C, 86.08; H, 9.97. Found: C, 86.08; H, 9.92.

2,3,8,9-Tetramethylene-1,4,5,6,7,10,11,12-octahydrotetracene (34). A solution of **11** [(prepared from **10** (500 mg, 0.99 mmol)] and chloromethyl 1,2-propadienyl sulfone (605 mg, 4.0 mmol) in ether (9 mL) was pressurized to 150 000 psi at rt for 2 d. The precipitate was collected, triturated with ether, redissolved in THF (20 mL), and treated with potassium *tert*-butoxide (180 mg, 1.6 mmol). The mixture was stirred for 1

h, the solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with hexanes) to afford **34** as a white solid (75 mg, 41%): mp > 300 °C (from THF); IR (film, cm^{-1}) 1733, 1631, 1462, 1431, 887; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (d, J = 1.8 Hz, 4 H), 4.77 (d, J = 1.7 Hz, 4 H), 2.84 (s, 8 H), 2.48 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 145.6 (one carbon not observed), 124.3, 108.5, 37.5, 35.6; MS m/z (M^+) calcd 288.1878, obsd 288.1870.

2,3,10,11-Tetramethylene-1,4,5,6,7,8,9,12,13,14,15,16-dodecahydrohexacene (35). A solution of **34** (66 mg, 0.23 mmol) and chloromethyl 1,2-propadienyl sulfone (140 mg, 0.92 mmol) in benzene (6 mL) was refluxed for 16 h. The reaction mixture was cooled to rt, and the precipitate was triturated with ether. The crude bis(chloromethyl) sulfone was dissolved in THF (10 mL) and treated with potassium *tert*-butoxide (0.18 mL, 1 M in *tert*-butyl alcohol). The reaction mixture was stirred for 1 h at rt, and the solvent was evaporated under reduced pressure. The residue was purified by chromatography on Florisil (elution with hexanes) to afford **35** as an insoluble, pale yellow solid (9 mg, 10%); mp > 300 °C; MS m/z (M^+) calcd 392.2504, obsd 392.2528.

Diels–Alder Cycloaddition between 34 and *p*-Benzoquinone. A solution of **34** (10 mg, 0.035 mmol) and freshly sublimed *p*-benzoquinone (11 mg, 0.11 mmol) in 1,2-dichloroethane (20 mL) was refluxed for 12 h. The precipitated product was collected and triturated with ether to leave **36** as a pale yellow solid (15 mg, 85%); mp > 300 °C dec; IR (film, cm^{-1}) 1676, 1443, 1267, 1089; ^{13}C NMR (75 MHz, solid state) ppm 201.0, 141.8, 136.7, 131.2, 123.2, 45.5, 36.3, 30.0, 28.1; MS m/z ($M^+ - H_2$) calcd 502.2144, obsd 502.2177.

1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16-Hexadecahydrohexacene-2,3,10,11-tetracarboxylic Dianhydride (37). A solution of freshly sublimed maleic anhydride (66 mg, 0.67 mmol) and **34** (97 mg, 0.34 mmol) in CH_2Cl_2 (50 mL) was stirred at rt for 1 d. The precipitate was collected and triturated with CH_2Cl_2 to afford **37** as an insoluble white solid (39 mg, 24%); mp > 300 °C dec; IR (film, cm^{-1}) 1844, 1770; MS m/z (M^+) calcd 484.1886, obsd 484.1880.

Tetraethyl 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16-Hexadecahydrohexacene-2,3,10,11-tetracarboxylate (38). A solution of diethyl fumarate (119 mg, 0.69 mmol) and **34** (80 mg, 0.28 mmol) in CH_2Cl_2 (5 mL) was refluxed for 2 d. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with CH_2Cl_2/MeOH, 100:1) to afford **38** as a white solid (115 mg, 66%): mp 220–226 °C; IR (film, cm^{-1}) 1733, 1442, 1375, 1307, 1252, 1178, 1029; ^1H NMR (300 MHz, $CDCl_3$) δ 4.22–4.07 (m, 8 H), 2.93–2.83 (br m, 4 H), 2.56–2.31 (br m, 16 H), 2.28–2.09 (br m, 8 H), 1.25 (t, J = 7.1 Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 174.8, 124.0, 123.3, 123.2, 60.5, 41.9, 35.6, 35.2, 32.1, 14.2; MS m/z (M^+) calcd 632.3349, obsd 632.3360. Anal. Calcd for $C_{38}H_{48}O_8$: C, 72.13; H, 7.65. Found: C, 72.11; H, 7.63.

Diels–Alder Cycloaddition between 34 and Excess Benzyne. A solution of **34** (58 mg, 0.20 mmol) and 1,2-dibromobenzene (472 mg, 2.0 mmol) in dry toluene (20 mL) was treated dropwise with *n*-butyllithium (1.54 mL, 1.3 M in hexanes) at ambient temperature. The reaction mixture was stirred for 14 h and quenched with MeOH (few drops). The precipitate was collected and washed with water, acetone, and ether to leave **39** as a pale yellow solid (58 mg, 56%), mp > 300 °C; ^{13}C NMR (75 MHz, solid state, mixed 1:1 with silica gel) ppm 141.5, 132.5, 127.9, 123.6, 35.0; MS m/z (M^+) calcd 512.2504, obsd 512.2487.

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Supporting Information Available: ^1H and/or ^{13}C NMR spectra of those compounds lacking combustion data (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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