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Synthesis of Supertriptycene[1] and Two Related Iptycenes

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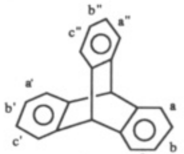
A 10-step 23–30% overall yield synthesis of supertriptycene (**2**) from vinyl chloride **5** is described. Anthracene **3** is the key intermediate, prepared from **5** in six steps and 41–53% yield (Scheme II). *trans*-1,2-Dichloroethene adds to **3** to give adduct **22** (94%), which is then converted to **2** in three steps and 70% yield (Scheme IV). A key step in the latter sequence is the remarkable cycloaddition of unactivated alkene **26** to hindered diene **4** in excellent yield. Supertriptycene (**2**), $C_{104}H_{62}$, shows only seven peaks in its ^{1}H NMR spectrum and 12 peaks in its ^{13}C NMR spectrum, consistent with its D_{3h} symmetry. The hydrocarbon is stable to well over 500 °C. Anthracene **3** was also converted to undecaiptycene **12** and to tridecaiptycene **16**; the latter was also independently synthesized in two steps from alkene **26** and diene **28**.

Twenty-four iptycenes[2] (excluding enantiomers) can be generated by fusing 9,10-anthradiyl moieties to the benzenoid bonds of triptycene **1**.[3] To the ultimate structure, with six 9,10-anthradiyls fused to **1** (at the a, c, a′, c′, a″ and c″ bonds) we assign the trivial name supertriptycene (**2**).[1] The beauty of this D_{3h} molecule is best appreciated by viewing molecular models (Figures 1 and 2).



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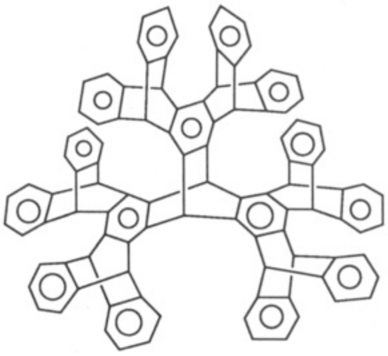

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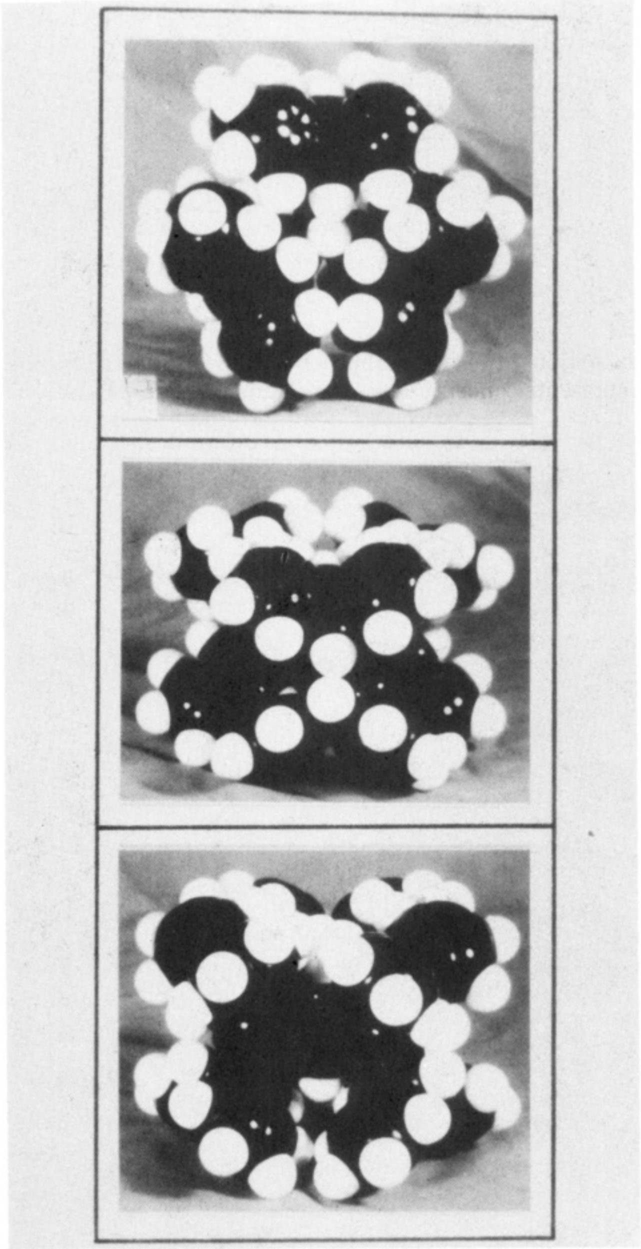

Figure 1. Three views of supertriptycene: top, down a C_3 axis; middle, down a C_2 axis; bottom, into one of three equivalent cavities.

Supertriptycene is interesting for several reasons. First, it has three large cavities that might act as selective hosts, each lined with six benzenoid rings. Second, it should show

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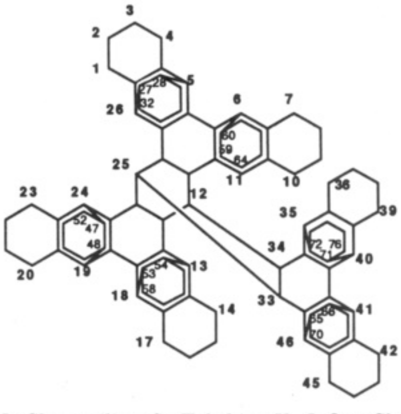
(1) The Chemical Abstracts name is 5,6,11,12,13,18,19,24,25,26,35,40,41,46-tetradecahydro-35,40[1′,2′]:41,46[1″,2″]-dibenzeno-5,26-[1′,2′]:6,11[1″,2″]:13,18[1‴,2‴]:19,24[1⁗,2⁗]-tetrabenzeno-12,26-[6′,7′]-*endo*-pentaphenodinaphtho[2,3-*a*:2′,3′-*c*]trinaphthylene. We thank Dr. Kurt Loening and Joy E. Merritt, Chemical Abstracts Service, for supplying this name. The numbering system is as shown on the following structure:



(2) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432.

(3) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641–1654.

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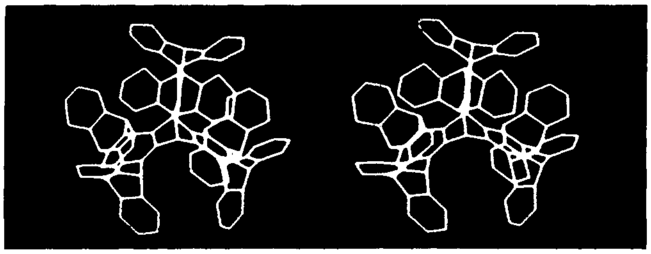
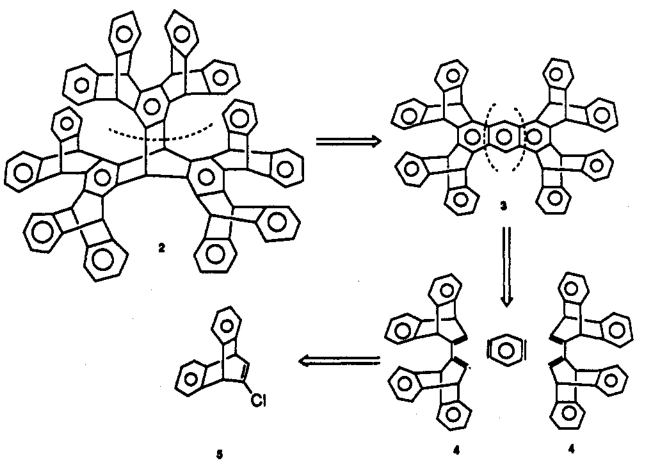


Figure 2. Computer-drawn stereomodel of 2.

Scheme I



exceptional thermal stability.[3,4] Third, supertriptycene represents conceptually a three-dimensional "expansion" of the triptycene core in a manner similar to that recently developed for starburst dendrimers.[5] Finally, there was the synthetic challenge that led to new methodology for assembling iptycenes.

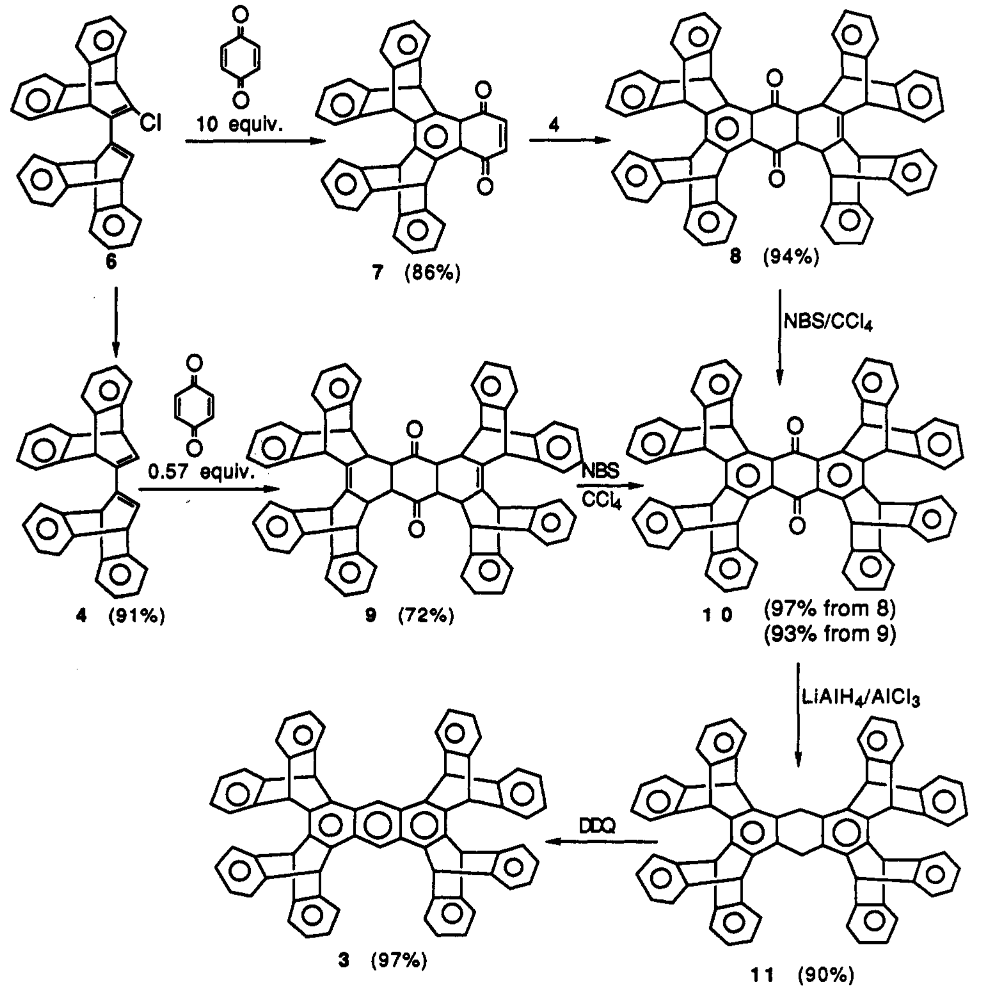
We describe here the details of a 10-step synthesis of 2 (overall yield 23–30%) from vinyl chloride 5.[6] The synthesis features a novel and remarkably high-yield Diels–Alder reaction between two unactivated hydrocarbons. A key intermediate in the synthesis is the anthracene 3, which we have employed to prepare two other new iptycenes, 12 and 16, with four and five 9,10-anthradiyl moieties, respectively, fused to the basic triptycene framework.

Results and Discussion

A retrosynthetic analysis of supertriptycene is depicted in Scheme I. Removal of one of the three equivalent branches leads to anthracene 3 from which one could presumably reconstruct the third branch through Diels–Alder chemistry on the central ring of the anthracene moiety. In turn, 3 might become available through the use of a 1,4-benzadiyne equivalent[7] and a diene such as 4. The latter would be available through coupling[8] of the known[2,9] vinyl chloride 5. One advantage of this route is the intermediacy of 3 which, as will be seen, can be used to construct other iptycenes.

Synthesis of Anthracene 3. Two successful routes to anthracene 3 are depicted in Scheme II. Chloro diene 6,[10] available in 78% yield[8] from the reaction of vinyl chloride 5 and *n*-BuLi, was treated with 1,4-benzoquinone (a benzadiyne equivalent) with the hope of obtaining anthra-

Scheme II

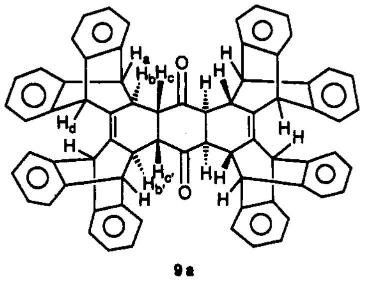


quinone **10** directly (through bis-cycloaddition, elimination of HCl, and aromatization of the resulting bis-diene with excess quinone). Numerous experiments using various ratios of **6** and benzoquinone led only to complex mixtures, but with a 10-fold excess of benzoquinone the naphthoquinone **7** was obtained as a bright yellow solid, mp 393 °C, in 86% yield. Thus, the desired HCl elimination and aromatization occurred, but only on the monocycloadduct. The ${}^{1}H$ NMR spectrum of **7** showed two singlets for the bridgehead protons (δ 6.13, 7.41), a singlet for the vinyl protons (δ 6.77), and two 8-proton multiplets for the aryl protons, and the ${}^{13}C$ spectrum confirmed the bridgehead carbons (δ 48.69, 50.27) and showed equivalent carbonyls at δ 188.55.

Attempts to construct anthraquinone **10** from chloro diene **6** and naphthoquinone **7** led only to inseparable mixtures. However, use of the unsubstituted diene **4**[11] instead of chloro diene **6** gave cycloadduct **8** as a white solid, mp 380–382 °C, in excellent yield. The ${}^{1}H$ NMR spectrum of **8** showed four 2-proton singlets for the bridgehead protons, two at δ 4.57 and 5.31 for the nonaromatic side of the molecule and two at δ 6.04 and 6.63 (nearly the same as in **7**) for the aromatic side. There was also a mutiplet at δ 1.85 for the cyclohexene ring protons, as well as expected peaks for the aryl protons. The ${}^{13}C$ spectrum supported the structure, important features being six peaks for the six pairs of sp^3 carbons and a single peak for the carbonyl carbons.

Adduct **8** was aromatized to the desired anthraquinone **10** (pale yellow, mp >450 °C) in nearly quantitative yield by bromination–dehydrobromination with *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride. Quinone **10**, with D_{2h} symmetry, has only two magnetically unique bridgehead protons (δ 6.08, 7.10) and four unique aryl protons. The ${}^{13}C$ spectrum shows two peaks for the bridgehead carbons (δ 50.01, 50.70), one peak for the carbonyl carbons (δ 188.63) and only nine peaks for the 60 sp^2 carbon atoms, as required.

In view of the successful cycloaddition of diene **4** to naphthoquinone **7**, we returned to the reaction with benzoquinone. In constrast to the results with chlorodiene **6**, reaction of **4** with 0.57 equiv of benzoquinone in refluxing xylenes gave bis-cycloadduct **9**, mp 405–407 °C, in good yield. The ${}^{1}H$ and ${}^{13}C$ NMR spectra were consistent with the formation of a single stereoisomer, most probably **9a**.



9a

Thus, the ${}^{13}C$ spectrum showed only one carbonyl carbon (δ 209.56) and only four sp^3 carbons (δ 43.67, 48.12, 48.51, and 52.92). Bridgehead proton H_d appeared as a 4-proton singlet at δ 5.32 whereas the other bridgehead proton H_a gave rise to a 4-proton doublet at δ 4.47, $J_{ab} = 2.2$ Hz. The signal for H_b was a four-proton doublet of doublet of doublets, coupled not only to H_a but to H_c ($J_{bc} = 7.3$ Hz) and to $H_{c'}$ ($J_{bc'} = 3.0$ Hz). Consistent with this assignment, H_c appeared as a doublet of doublets, coupled with H_b and $H_{b'}$. The four-bond coupling between H_b and $H_{c'}$ is consistent with a rigid structure with the geometry shown.

Diketone **9** was readily aromatized to anthraquinone **10** with NBS in refluxing CCl_4. The two routes to **10** depicted in Scheme II are nearly equal in efficiency. The "upper" route requires four steps (including the synthesis of **4** from **6**) but occurs in somewhat higher overall yield (71%) than the "lower" three-step route (61% overall).

Reduction of anthraquinone **10** to anthracene **3** proved difficult. Catalytic hydrogenation[12] or reduction with aluminum trialkoxides,[13] sodium borohydride–trifluoroacetic acid,[14] or zinc–sodium hydroxide[15] gave mixtures of products. Zinc–acetic acid–pyridine[16] gave mainly **3** but the product always contained substantial amounts of the dihydroanthracene and was difficult to purify. Success was finally achieved using lithium aluminum hydride–aluminum chloride, which gave dihydroanthracene **11** in 90% yield, contaminated with only traces of **3**. Pure **11** could be obtained by treatment with a small amount of tetracyanoethylene followed by chromatography. The ${}^{1}H$ NMR spectrum showed a singlet for the benzylic protons (δ 4.24) and the two sets of bridgehead protons (δ 5.90, 5.94), and the ${}^{13}C$ spectrum confirmed the presence of three sets of sp^3-hybridized carbons (δ 28.71, 50.58, 50.84).

Catalytic dehydrogenation of **11** with Pd/C in refluxing mesitylene failed, but oxidation with dichlorodicyanoquinone (DDQ) in refluxing benzene gave a nearly quantitative yield of the desired anthracene **3**. But since **3** forms complexes with any excess DDQ and with its reduced form DDQH, it was necessary to absorb the crude product on silica gel and heat at 250–300 °C under vacuum for a few minutes before chromatographic purification.

Anthracene **3** is a yellow solid, mp >500 °C. It showed a strong M^+ peak at m/e 882. The ${}^{1}H$ NMR spectrum showed two 4-proton singlets for the bridgehead protons (δ 6.31, 6.42), multiplets for the "outer" aromatic rings, and a singlet at δ 9.26 for the two anthracene protons. The ${}^{13}C$ spectrum had peaks for two aliphatic and nine (of 10) aromatic carbons as required for the D_{2h} symmetry of this C_{70} hydrocarbon.

Synthesis of Iptycenes 12 and 16. To test the ability of anthracene **3** to enter into cycloaddition reactions at the central ring we carried out several reactions with dienophiles as a prelude to conversion of **3** into supertriptycene.

Addition of benzyne to anthracene **3** gave undecaiptycene **12** in 58% yield. Compound **12** is the first iptycene to be synthesized (of five that are possible[3]) with four 9,10-anthradiyl groups fused to the triptycene framework. Consistent with its C_{2v} symmetry, **12** showed three bridgehead proton singlets in its ${}^{1}H$ NMR spectrum, with relative areas 2:2:1 at δ 5.83, 6.01 and 6.29, and three sp^3 carbon peaks in the ${}^{13}C$ spectrum (δ 45.78, 49.92 and 50.17).

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(4) Bashir-Hashemi, A.; Hart, H.; Ward, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 6675–6679.

(5) For a review, see: Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138–175 and especially pp 150–151.

(6) For a preliminary account, see: Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1990**, *112*, 3687–3688.

(7) Hart, H.; Lai, C-y.; Nwokogu, G. C.; Shamouilian, S. *Tetrahedron* **1987**, *43*, 5203–5224.

(8) Shahlai, K.; Hart, H. *J. Am. Chem. Soc.* **1988**, *110*, 7136–7140.

(9) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193–2197.

(10) Huebner, C. F.; Puckett, R. T.; Brezchfta, M.; Schwartz, S. L. *Tetrahedron Lett.* **1970**, 359–362.

(11) Shahlai, K.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2615–2620.

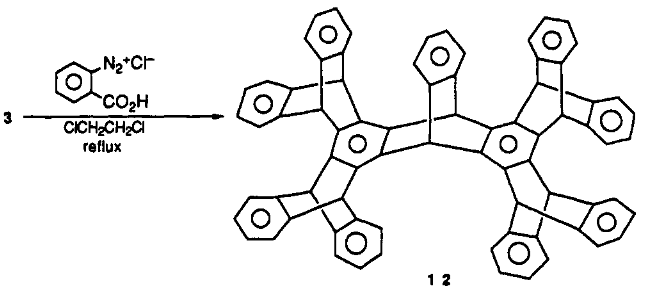
(12) Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357–4360.

(13) Coffey, S.; Boyd, V. *J. Chem. Soc.* **1954**, 2468–2470.

(14) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763–765.

(15) Martin, E. L. *J. Am. Chem. Soc.* **1936**, *58*, 1438–1442.

(16) Clar, E. *Chem. Ber.* **1948**, *81*, 68–71; *J. Chem. Soc.* **1949**, 2013–2016, 2440–2442.



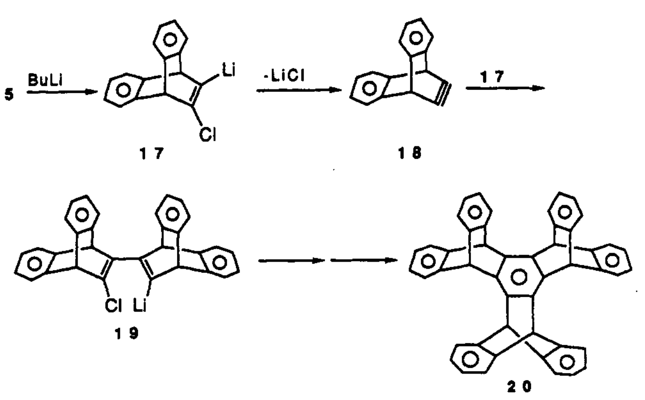
To assess the reactivity of **3** toward a less reactive and more sterically demanding dienophile, we attempted the synthesis of tridecaiptycene **16** as outlined in Scheme III. Addition of anthracene 1,4-endoxide **13** to the central ring of **3** proceeded in refluxing decalin to give an excellent yield of a single adduct, mp 460–462 °C. We assume that addition occurred to the exo face of the endoxide as shown, since endo addition would jam the naphthalene moiety into the nearby aryl rings. The ^{1}H NMR spectrum of **14** shows seven two-proton singlets for the aliphatic protons.

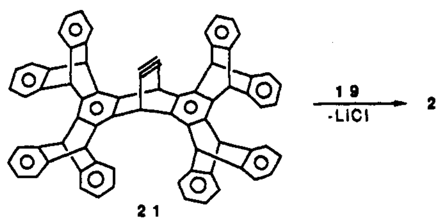
Endoxide **14** was dehydrated with acetic anhydride in the presence of hydrochloric acid. The ^{1}H NMR spectrum of anthracene **15** showed two two-proton singlets in the aromatic region (δ 8.17, 7.76) for the isolated protons of the anthracene moiety. The bridgehead protons appeared at δ 5.84, 6.08, and 6.42 with relative areas of 2:2:1, respectively. The ^{13}C spectrum showed three sp^3 carbon peaks as required at δ 45.40, 49.99 and 50.23.

Addition of benzyne to anthracene **15** gave **16** in 64% yield. Iptycene **16** was a white solid that did not melt below 470 °C. As required, its ^{1}H NMR spectrum showed four bridgehead proton peaks (δ 5.19, 5.77, 5.93, and 6.17) with relative areas 2:4:4:2. Compound **16** is one of two possible[3] iptycenes with five 9,10-anthradiyl moieties fused to the triptycene framework.

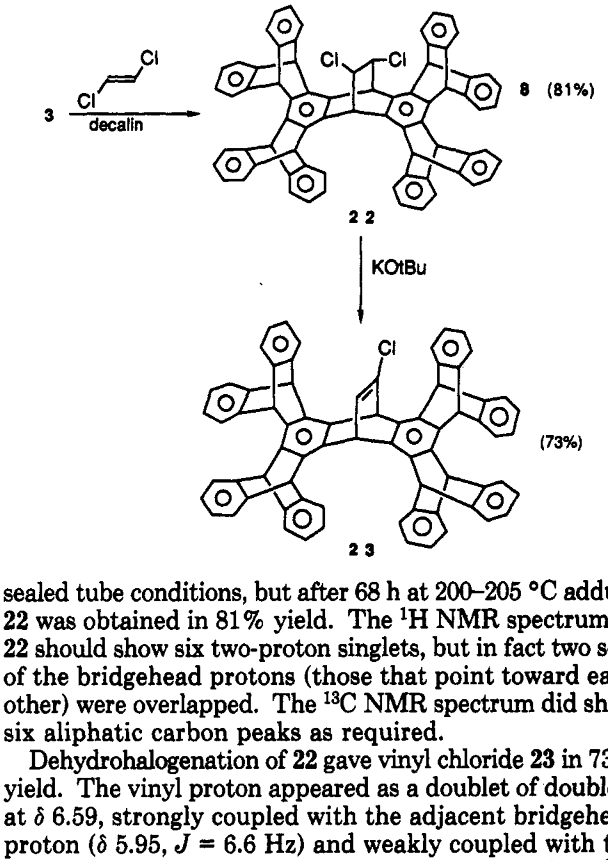
The successful synthesis of **12** and **16** showed that the central ring of anthracene **3** was accessible to dienophiles despite the heavy substitution that extends above and below the anthracene ring plane. Thus, the stage was set for an assault on supertriptycene.

Synthesis of Supertriptycene (2). First Attempt. Mechanistic studies on the "trimerization" of vinyl chloride **5** to heptiptycene **20** demonstrated that the reaction proceeds via addition of initially formed vinyllithium **17** to bicycloalkyne **18**.[2,8] Our first approach to supertriptycene used this chemistry in the following way. We reasoned that a vinyl chloride analogous to **5** but derived from anthracene **3** (e.g., **23**) would be incapable of trimerization due to steric hindrance (the "trimer" is an impossible structure). However, it might be possible to generate and trap the corresponding bicycloalkyne **21** with vinyllithium **19**, leading directly to supertriptycene as shown.





Accordingly, anthracene **3** was converted to vinyl chloride **23** via intermediate **22**. Addition of *trans*-1,2-dichloroethene to **3** proceeded very slowly and required sealed tube conditions, but after 68 h at 200–205 °C adduct **22** was obtained in 81% yield. The ^{1}H NMR spectrum of **22** should show six two-proton singlets, but in fact two sets of the bridgehead protons (those that point toward each other) were overlapped. The ^{13}C NMR spectrum did show six aliphatic carbon peaks as required.

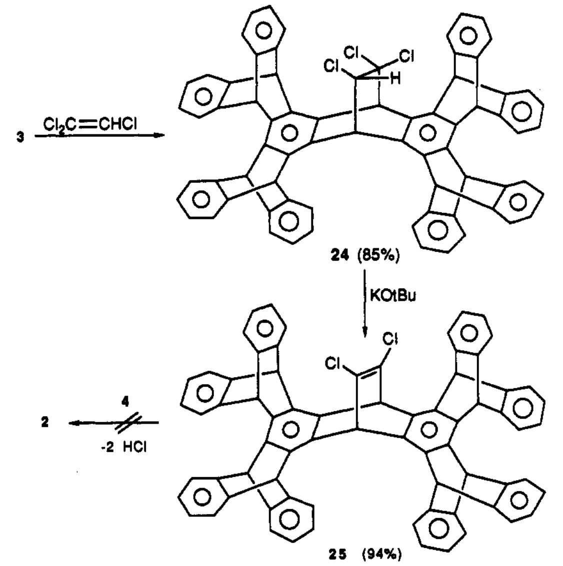


Dehydrohalogenation of **22** gave vinyl chloride **23** in 73% yield. The vinyl proton appeared as a doublet of doublets at δ 6.59, strongly coupled with the adjacent bridgehead proton (δ 5.95, J = 6.6 Hz) and weakly coupled with the allylic bridgehead proton (δ 5.83, J = 2.1 Hz). The ^{13}C spectrum showed six aliphatic carbon signals for the 10 bridgehead carbons, consistent with the presence of a σ plane.

A mixture of vinyl chlorides **5** and **23** was treated at −78 °C with sufficient butyllithium to metalate both reactants. A small amount of insoluble product, later shown to be supertriptycene (1–4%), was indeed formed. However, the major products after aqueous quench were chloro diene **6** (32%, derived from **19**), **20** (16%), and **26** (45%, from reduction of **23**). It is clear that this direct, one-step approach to supertriptycene is doomed to low yields because of competing possibilities.

Second Attempt. Part of the difficulty with the first approach might be that it involved a very short-lived dienophile, **21**. We therefore synthesized dichloroalkene **25** with the intent that cycloaddition to diene **4** might proceed with aromatization through the loss of two equivalents of HCl to give **2** directly.

Addition of trichlorethene to anthracene **3** proceeded in 85% yield, and dehydrohalogenation gave the desired **25** in 94% yield. Its structure was clear from its NMR spectra, which showed a two-proton singlet at δ 5.85 for the central bridgehead protons and two four-proton singlets at δ 5.86 and 5.88 for the "outer" bridgehead protons, consistent with the presence of two σ planes in the mole-



cule. The ^{13}C peaks for the bridgehead carbon atoms appeared at δ 51.03, 50.21, and 49.87.

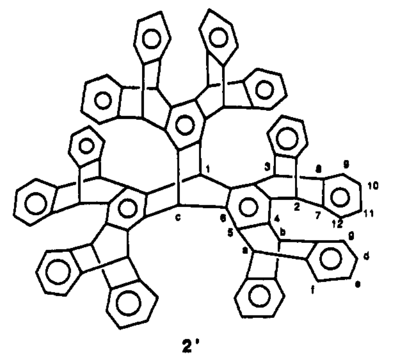
Unfortunately, heating **25** with **4** failed to give any supertriptycene; instead, extensive decomposition and polymerization gave an intractable product mixture containing a small amount of recovered starting material.

Successful Route to 2. Thinking that the failure of **25** to add to **4** might be due to steric hindrance, we decided to remove the offending chlorines (Scheme IV). Treatment of vicinal dichloride **22** with lithium in refluxing THF (72 h) effected reductive elimination to give alkene **26** in 92% yield. The ^1H NMR spectrum of **26** showed two four-proton singlets (δ 5.82, 5.87) for the peripheral bridgehead protons and a doublet of doublets for the two central bridgehead protons at δ 5.98 (J = 3.7, <1.0 Hz) coupled to each of the vinyl protons, which also appeared as a doublet of doublets at δ 6.76.

The crucial Diels–Alder step between unactivated dienophile **26** and hindered (and probably s-trans) diene **4** occurred in refluxing decalin (8 h) to give cyclohexene **27** in the remarkable yield of 89%. The NMR spectra of **27** left no doubt about its structure. The peripheral bridgehead protons appeared as six two-proton singlets (δ 4.97, 5.18, 5.66, 5.70, 5.75, 5.81) whereas the central bridgehead protons (δ 4.55) were weakly coupled with the adjacent protons of the cyclohexene ring (d, J = 1 Hz). The remaining protons of the cyclohexene ring appeared as two mutually coupled broad doublets (δ 0.88, 1.48, J = 8 Hz). The ^{13}C NMR spectrum showed eight sp^3 carbon peaks as required.

Adduct **27** has an extremely crowded structure. Nevertheless, it was possible to aromatize the cyclohexene ring in 85% yield with bromine in refluxing 1,1,2,2-tetrachloroethane (4 h).[17]

Supertriptycene **2** was obtained as a white powder that does not melt below 500 °C. The simplicity of its ^1H and ^{13}C NMR spectra left no doubt about the structure of this $C_{104}H_{62}$ hydrocarbon. The numbering is shown in structure **2′**. The proton spectrum showed only seven magnetically unique types of protons. Bridgehead protons H_a and H_b appeared as 6-proton singlets at δ 5.63 and 5.90, respectively,[18] whereas the two central bridgehead protons appeared as a singlet at δ 6.60. Aryl protons H_f and H_g appeared essentially as 12-proton doublets (J = 6 Hz) at δ 7.16 and 7.50, respectively, whereas the remaining 24 aryl protons (H_d and H_e) appeared as a narrow multiplet (looks like a quintet) at δ 6.73–6.79.



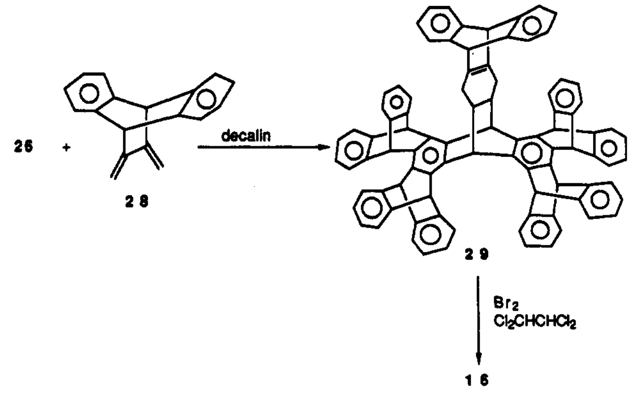
2′

The ^{13}C spectrum of **2** showed only 12 magnetically unique carbons as required. The central bridgehead carbon C_1 appeared at δ 43.46, whereas the outer bridgehead carbons C_2 and C_3 appeared at δ 52.55 and 53.01. The three unique aryl carbons of the inner aromatic rings (C_4–C_6) appeared at δ 136.74, 136.93, and 137.48. The nonprotonated carbons of the outer rings (C_7, C_8) appeared at δ 146.76 and 146.96, whereas the protonated carbons of these rings (C_9–C_{12}) appeared at δ 125.46, 126.06, 126.90, and 127.14.

Supertriptycene is soluble in hot decalin, tetrachloroethene, or benzonitrile. Unfortunately, it precipitates from these solutions as a white powder rather than crystals. Beautiful crystals can be obtained from a mixture of tetrachloroethene and ethyl acetate, but the symmetry is destroyed due to the presence of a substantial number of solvent molecules, and it has not yet been possible to solve the X-ray structure. Attempts to sublime supertriptycene have not yielded crystals suitable for X-ray study.

Weight loss on thermogravimetric analysis of supertriptycene began at 508 °C, reached 50% at 572 °C, and was complete at 622 °C. In a nitrogen atmosphere, however, weight loss did not begin until 580 °C and the sample weight only dropped to 50% of its original value (at 640 °C), after which it remained constant, suggesting the possibility of rearrangement to a more stable structure. The residue, which was colorless, was insoluble in all solvents.

Independent Synthesis of Iptycene 16. The unexpectedly facile cycloaddition between the two unlikely Diels–Alder partners **26** and **4** prompted us to try **26** as a dienophile with other dienes. Reaction with diene **28**[20]



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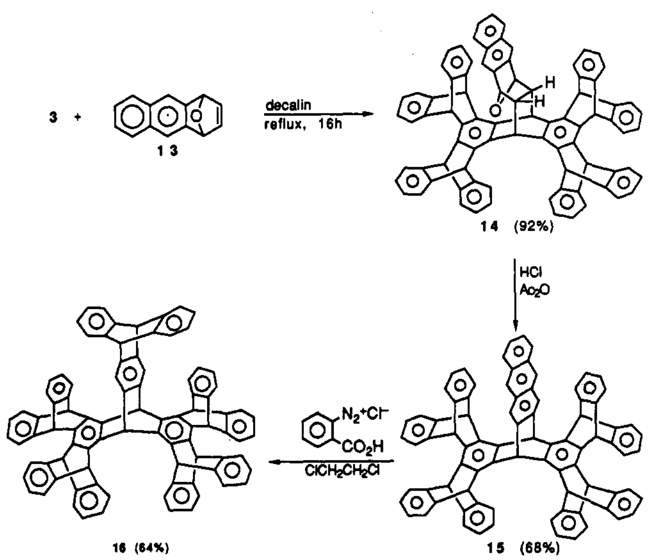
[17] An initial dehydrogenation of **27** to **2** with DDQ in refluxing 1,1,2,2-tetrachloroethane was successful and quantitative, but we were never able to reproduce this result in several subsequent attempts.

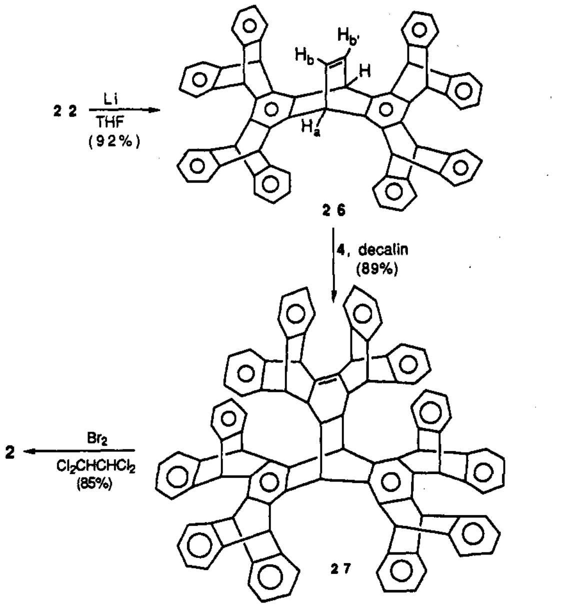
[18] The relative assignments of H_a and H_b and of the aryl protons are made by comparison with other iptycenes.

[19] We are indebted to Dr. Mary Ann Meador, National Aeronautics and Space Administration, for these studies.

Scheme III



Scheme IV



in refluxing decalin gave adduct **29** in 58% yield. The NMR spectra of **29** were consistent with its structure, which was proved by dehydrogenation with DDQ to **16** (92% yield), identical spectroscopically with material prepared as outlined in Scheme III. Thus, it seems possible that dibenzobicyclooctenes such as **26** may be useful dienophiles for other syntheses.

In summary, we describe here a six-step efficient (41–53% overall) synthesis of novel anthracene **3** from readily available vinyl chloride **5**. We then describe a one-step (58% yield) synthesis of undecaiptycene **12** from **3**, a three-step (40% overall) synthesis of tridecaiptycene **16** from **3**, and a four-step synthesis of supertriptycene **2** (65% overall) from **3**. The synthesis of supertriptycene from vinyl chloride **5** proceeds in 10 steps and 23-30% overall yield and is amenable to the preparation of gram quantities. The synthesis of supertriptycene features a remarkably effective Diels–Alder reaction between unlikely partners **26** and **4**; a similar Diels–Alder reaction between **26** and diene **28** was used to provide an independent synthesis of tridecaiptycene **16**.

Experimental Section[21]

1′,4′:7,12-Di-*o*-benzeno-1′,4′,7,12-tetrahydro-5,6-naphthotetraphene-1,4-dione (7). A solution of chlorodiene **6**[10] (4.41 g, 10 mmol) and 1,4-benzoquinone (10.8 g, 100 mmol) in xylenes (250 mL) was heated at reflux for 36 h. Solvent and most of the excess benzoquinone were removed by vacuum distillation. Chromatography of the dark brown residue over silica gel using 3:2 CH_2Cl_2/hexanes as eluent afforded 4.4 g (86%) of **7** as a bright yellow solid: mp 393 °C; ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 2 H), 6.77 (s, 2 H), 7.01 (m, 8 H), 7.41 (s, 2 H), 7.48 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 48.69, 50.27, 118.53, 123.69, 125.11, 126.22, 139.00, 143.84, 144.32, 146.06, 188.55 (2 arom overlapped); MS *m/e* (relative intensity) 512 (8), 511 (44), 427 (23), 410 (100), 178 (28). Anal. Calcd for $C_{38}H_{22}O_2$: C, 89.39; H, 4.34. Found: C, 89.23; H, 4.24.

Tetrahydroanthraquinone (8). A solution of diene **4**[11] (2.05 g, 5 mmol) and naphthoquinone **7** (2.51 g, 5 mmol) in xylenes (250 mL) was heated at reflux for 12 h. Solvent removal (rotavap) and chromatography of the residue over silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave 4.3 g (94%) of **8** as a white solid: mp 380–382 °C; ^{1}H NMR ($CDCl_3$) δ 1.85 (m, 4 H), 4.57 (s, 2 H), 5.31 (s, 2 H), 6.04 (s, 2 H), 6.63 (s, 2 H), 6.98 (m, 8 H), 7.10 (m, 4 H), 7.27 (m, 8 H), 7.44 (m, 6 H), 7.56–7.67 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 45.33, 47.88, 48.63, 49.86, 50.63, 52.90, 123.12, 123.94, 124.13, 124.22, 124.33, 124.67, 125.36, 126.21, 126.36, 126.66, 127.13, 127.24, 128.75, 128.94, 130.72, 140.20, 142.07, 143.58, 144.04, 144.64, 144.95, 145.19, 199.25; MS *m/e* (relative intensity) 918 (0.7, M + 2), 917 (2, M + 1), 916 (3, M), 738 (19), 485 (22), 427 (14), 426 (12), 178 (100). Anal. Calcd for $C_{70}H_{44}O_2$: C, 91.67; H, 4.83. Found: C, 91.63; H, 4.82.

Octahydroanthraquinone (9). A solution of diene **4** (1.63 g, 4 mmol) and 1,4-benzoquinone (0.25 g, 2.3 mmol) in xylenes (50 mL) was heated at reflux for 16 h. Workup as with **8** gave 1.33 g (72%) of **9** as a white powder: mp 405–407 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (dd, J = 3.1, 7.3 Hz, 4 H), 2.30 (ddd, J = 2.2, 3.0, 7.3 Hz, 4 H), 4.47 (d, J = 2.2 Hz, 4 H), 5.32 (s, 4 H), 7.04 (m, 8 H), 7.10 (m, 8 H), 7.23 (m, 4 H), 7.32 (m, 8 H), 7.40 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 43.67, 48.12, 48.51, 52.92, 123.27, 124.11, 124.40, 126.34, 126.49, 126.61, 126.78, 127.41, 130.48, 140.21, 141.82, 142.14, 143.53, 209.56.

Anthraquinone 10. From 8. A solution of diketone **8** (1.84 g, 2 mmol) and 2.5 g of *N*-bromosuccinimide in 300 mL of CCl_4 was heated at reflux for 12 h. Solvent removal (rotavap) and chromatography of the residue on silica gel using 1:1 methylene chloride/hexanes as eluent gave 1.78 g (97%) of **10** as a pale yellow solid: mp >450 °C; ^{1}H NMR ($CDCl_3$) δ 6.08 (s, 4 H), 7.00 (m, 16 H), 7.10 (s, 4 H), 7.45 (m, 8 H), 7.56 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 50.01, 50.70, 124.14, 125.18, 126.27, 126.37, 127.85, 143.90, 144.48, 144.93, 145.09, 188.63; a MS could not be obtained. Anal. Calcd for $C_{70}H_{40}O_2$: C, 92.08; H, 4.41. Found: C, 91.96; H, 4.39. **From 9.** A solution of **9** (0.46 g, 0.5 mmol), 0.45 g of *N*-bromosuccinimide, and a catalytic amount (5–10 mg) of benzoyl peroxide in 50 mL of CCl_4 was heated at reflux for 24 h. The suspended succinimide was filtered and washed with CCl_4. Combined CCl_4 solutions were evaporated to dryness, and the residue was chromatographed on silica gel using 3:2 CH_2Cl_2/hexanes as eluent to give 0.424 g (93%) of **10**, identical (NMR) with product from **8**.

Dihydroanthracene 11. To a suspension of $LiAlH_4$ (0.38 g, 10 mmol) in anhydrous THF (100 mL) under Ar was added 0.92 g (1 mmol) of anthraquinone **10**. The mixture was heated at reflux for 4 h then cooled to 0 °C, and anhydrous $AlCl_3$ (0.66 g, 5 mmol) was added in small portions. The mixture was heated at reflux for 2 h, after which the excess $LiAlH_4$ was hydrolyzed with water (3 mL). The organic layer was decanted, and the solvent was removed (rotavap). The residue was dissolved in CH_2Cl_2 (50 mL), washed with water and saturated NaCl solution, and dried ($MgSO_4$). The solution volume was reduced to 10 mL (rotavap), and 50 mg (excess) of TCNE was added. Absorption of the mixture on silica gel and chromatography using 1:2 CH_2Cl_2/

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(20) Meek, J. S.; Stacy, R. D. *J. Org. Chem.* **1961**, *26*, 300–302. Johnson G. C.; Bergman, R. G. *Tetrahedron Lett.* **1979**, 2093–2096, footnote 4.

(21) For general procedures, see ref 8.

hexanes as eluent gave 0.8 g (90%) of **11** as a white solid: mp >500 °C; ^{1}H NMR ($CDCl_3$) δ 4.24 (s, 4 H), 5.90 (s, 4 H), 5.94 (s, 4 H), 6.94 (m, 16 H), 7.35 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 28.71, 50.58, 50.84, 124.07, 125.63, 125.84, 128.11, 137.11, 137.25, 138.45, 145.57, 145.80. Anal. Calcd for $C_{70}H_{44}$: C, 94.99; H, 5.01. Found: C, 94.83; H, 5.17.

Anthracene 3. A solution of **11** (0.89 g, 1 mmol) and DDQ (0.3 g, 1.3 mmol) in benzene (150 mL) was heated at reflux under Ar for 16 h. The solvent was removed (rotavap), and the residue was absorbed onto 10 g of 30–60-mesh silica gel, heated at 250–300 °C under vacuum for 10 min, and then immediately chromatographed using 2:1 hexanes/CH_2Cl_2 as eluent to give 0.86 g (97%) of **3** as a yellow solid: mp >500 °C; ^{1}H NMR (CD_2Cl_2) δ 6.31 (s, 4 H), 6.42 (s, 4 H), 6.97–7.05 (m, 16 H), 7.55–7.59 (m, 8 H), 7.62–7.66 (m, 8 H), 9.26 (s, 2 H); ^{13}C NMR (CD_2Cl_2) δ 50.31, 51.24, 116.41, 123.75, 124.03, 125.33, 125.49, 125.76, 139.91, 146.04, 146.52 (one overlapped); MS *m/e* (relative intensity) 883 (15, M + 1), 882 (18, M), 207 (24), 178 (16), 149 (54), 44 (100); HRMS calcd for $C_{70}H_{42}$ 882.3224, found 882.3286.

Undecaiptycene 12. To a solution of anthracene **3** (450 mg, 0.5 mmol) and propylene oxide (1 mL) in 50 mL of 1,2-dichloroethane heated at reflux was added benzenediazonium 2-carboxylate hydrochloride[22] (460 mg, 2.5 mmol) in four equal portions over 4 h, after which the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (5 mL) and chromatographed on a silica gel preparative glass plate using 3:2 ether/hexanes as eluent. The yellowish white solid (280 mg, 58%) was recrystallized from 1:5 CH_2Cl_2/hexanes to give pure **12** as a white crystalline solid: mp >470 °C; ^{1}H NMR ($CDCl_3$) δ 5.83 (s, 4 H), 6.01 (s, 4 H), 6.29 (s, 2 H), 6.82–6.97 (m, 18 H), 7.26–7.39 (m, 10 H), 7.46–7.61 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 45.78, 49.92, 50.17, 123.21, 123.46, 123.52, 123.58. 123.76, 124.87, 125.22, 125.33, 125.49, 134.74, 134.92, 135.05, 144.60, 144.81, 145.21 (3 arom overlapped); HRMS calcd. for $C_{76}H_{46}$ 958.3599, found 958.3577.

Endoxide Cycloadduct 14. A solution of anthracene **3** (0.9 g, 1 mmol) and anthracene 1,4-endoxide **13**[23] (0.4 g, 2.1 mmol) in 100 mL of decalin was heated at reflux for 16 h. Removal of the solvent (rotavap) and chromatography of the yellow residue on silica gel using 4:1 CH_2Cl_2/hexanes gave 920 mg (92%) of **14** as a white solid: mp 460–462 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 2 H), 4.68 (s, 2 H), 5.50 (s, 2 H), 5.83 (s, 2 H), 5.89 (s, 2 H), 5.90 (s, 2 H), 6.01 (s, 2 H), 6.85–7.08 (m, 16 H), 7.32–7.68 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 38.91, 48.60, 49.97, 50.01, 50.05, 50.09, 80.93, 116.75, 122.69, 123.31, 123.52, 123.64, 124.75, 124.91, 125.00, 125.17, 125.31, 125.49, 127.90, 130.96, 132.40, 133.44, 134.92, 135.28, 135.75, 135.96, 143.99, 144.64, 145.04, 145.16, 145.44, 145.65; HRMS calcd for $C_{84}H_{52}O$ 1076.4017, found 1076.4040.

Anthracenoiptycene 15. A solution of cycloadduct **14** (540 mg, 0.5 mmol) in 20 mL of acetic anhydride containing 1 mL of concentrated HCl was heated at reflux for 8 h. The solvent was removed (rotavap), and the residue was chromatographed on a preparative silica gel glass plate using 4:1 CH_2Cl_2/hexanes as eluent. Recrystallization from methanol/acetone gave 360 mg (68%) of **15** as a white solid: mp >470 °C; ^{1}H NMR ($CDCl_3$) δ 5.84 (s, 4 H), 6.08 (s, 4 H), 6.42 (s, 2 H), 6.90 (m, 18 H), 7.31 (m, 8 H), 7.53 (m, 4 H), 7.61 (m, 4 H), 7.76 (s, 2 H), 7.84 (dd, *J* = 3.3 Hz, 2 H), 8.17 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 45.40, 49.99, 50.23, 120.90, 123.49, 123.58, 123.79, 124.78, 124.95, 125.27, 125.30, 125.39, 125.63, 127.89, 130.46, 131.52, 133.76, 135.18, 135.75, 140.75, 144.62, 144.64, 144.83, 145.12, 145.17; HRMS calcd for $C_{84}H_{50}$ 1058.3912, found 1058.3871.

Tridecaiptycene 16. From 15. To a solution of anthracene **15** (265 mg, 0.25 mmol) and 1 mL of propylene oxide in 50 mL of 1,2-dichloroethane heated at reflux was added benzenediazonium 2-carboxylate hydrochloride[22] (230 mg, 1.25 mmol) in four equal portions over 4 h. The solvent was removed (rotavap), and the residue was chromatographed on a preparative silica gel glass plate with 1:4 hexanes/CH_2Cl_2 as eluent to give 180 mg (64%) of **16** as a white solid: mp >470 °C; ^{1}H NMR ($CDCl_3$) δ 5.19 (s, 2 H), 5.77 (s, 4 H), 5.93 (s, 4 H), 6.17 (s, 2 H), 6.74–6.95 (m, 20 H), 7.22–7.36 (m, 14 H), 7.45–7.64 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 45.64, 49.86 (2), 50.16 (2), 53.80, 119.31, 123.33, 123.45, 123.76, 124.76, 124.80, 125.17, 125.25, 134.58, 134.80, 135.01, 142.25, 142.36, 144.68, 144.89, 145.04, 145.10, 145.27; HRMS calcd for $C_{90}H_{54}$ 1134.4256, found 1134.4170. **From 29.** A solution of 0.57 g (0.5 mmol) of **29** and 0.5 g (excess) of DDQ in 30 mL of benzene was heated at reflux for 15 h. Evaporation of the solvent (rotavap) and chromatography of the remaining residue on a silica gel column using 3:2 CH_2Cl_2/hexanes as eluent gave 0.52 g (92% yield) of **16** with a ^{1}H NMR spectrum identical with that described above.

Cycloadduct 22. A suspension of anthracene **3** (2.21 g, 2.5 mmol) in 80 mL of a 1:1 mixture of *trans*-1,2-dichloroethene and decalin was heated in a sealed tube at 200–205 °C for 68 h. The cooled contents were stripped of excess dichloroethene (rotavap), the remaining solvent was vacuum distilled, and the residue was chromatographed on silica gel using 2:1 CH_2Cl_2/hexanes as eluent to give 2.0 g (81%) of **22** as a white solid: mp dec >280 °C; ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 2 H), 5.33 (s, 2 H), 5.77 (s, 2 H), 5.88 (s, 4 H), 5.89 (s, 2 H), 6.77–7.08 (m, 16 H), 7.25–7.59 (m, 16 H); ^{13}C NMR (CD_2Cl_2) δ 44.91, 50.15, 50.23, 50.29, 65.88, 77.90, 123.78, 123.87, 123.96, 124.05, 124.19, 124.28, 125.35, 125.66, 125.78, 125.85, 126.01, 127.64, 129.93, 137.81, 138.04, 138.69, 144.72, 144.81, 145.10, 145.25, 145.31, 145.57; MS *m/e* (relative intensity) 983 (3), 982 (7), 981 (12), 980 (14), 979 (15), 978 (7), 882 (35), 289 (56). Anal. Calcd for $C_{72}H_{44}Cl_2$: C, 88.24; H, 4.52. Found: C, 88.17; H, 4.43.

Vinyl Chloride 23. To a suspension of 3.0 g (3 mmol) of the dichloro adduct **22** in 50 mL of dioxane was added 0.5 g (excess) of KO-t-Bu. The reaction mixture was heated at reflux for 12 h, after which the solvent was removed (rotavap) and the residue was taken up in CH_2Cl_2 (100 mL). The solution was washed with water and saturated NaCl solution and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue over silica gel using 3:2 CH_2Cl_2/hexanes as eluent gave 2.1 g (73%) of the desired product as a white powder: mp >390 °C dec; ^{1}H NMR (CD_2Cl_2) δ 5.83 (d, *J* = 2.1 Hz, 1 H), 5.87 (br s, 6 H), 5.88 (s, 2 H), 5.95 (d, *J* = 6.6 Hz, 1 H), 6.59 (dd, *J* = 6.6, 2.1 Hz, 1 H), 6.83–7.07 (m, 16 H), 7.30–7.58 (m, 16 H); ^{13}C NMR (CD_2Cl_2) δ 32.72, 43.24, 49.96, 50.28, 50.87, 51.13, 123.68, 123.82, 123.97, 125.18, 125.26, 125.61, 125.70, 125.79, 133.04, 133.15, 134.20, 134.64, 135.02, 135.21, 135.51, 135.60, 135.97, 136.76, 139.87, 144.25, 144.44, 144.65, 144.81, 144.96, 145.08, 145.20, 145.29, 145.39; HRMS calcd for $C_{72}H_{43}Cl$ 942.3053, found 942.3080.

Reaction of Vinyl Chlorides 5 and 23 with Butyllithium. To a suspension of 2.4 g (10 mmol) of **5** and 2.36 g (2.5 mmol) of **23** in 100 mL of anhydrous THF under Ar at −78 °C was added dropwise 5.5 mL (1.1 equiv) of 2.5 M *n*-butyllithium in hexanes. The reaction mixture was stirred for 30 min at the above temperature, allowed to warm to rt, stirred for an additional 2 h, and then heated at reflux for 15 min. The reaction mixture was quenched with methanol (1 mL). The solvent was removed, and the residue was chromatographed over silica gel using 1:4 CH_2Cl_2/hexanes, 3:2 CH_2Cl_2/hexanes, CH_2Cl_2, and finally 2:1 ethyl acetate/hexanes as eluent. Product analysis of the collected fractions showed the presence of the following compounds: **6** (32%), **20** (16%), **26** (vide infra, 45%), and **2** (vide infra, 1–4%) and unidentified minor products.

Cycloadduct 24. A suspension of 1.33 g (1.5 mmol) of the anthracene **3** in 30 mL of a 1:1 mixture of cycloctane and trichloroethene in a sealed tube was heated at 200–205 °C for 48 h. The tube was cooled (ice bath), and its contents were transferred to a rovatap to remove the solvents. Chromatography of the residue over silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave 1.3 g (85%) of **24**: mp 365–368 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.42 (d, *J* = 2.3 Hz, 1 H), 5.34 (d, *J* = 2.3 Hz, 1 H), 5.75 (s, 1 H), 5.82 (s, 1 H), 5.86 (br s, 6 H), 5.89 (s, 1 H), 5.97 (s, 1 H), 6.79–7.05 (m, 16 H), 7.22–7.52 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 46.17, 49.86 (3), 49.97 (5), 54.78, 70.51, 90.43, 123.45, 123.56, 123.67, 123.87, 124.01, 124.89, 125.04, 125.08, 125.24, 125.32, 125.45, 125.66, 128.32, 137.60, 137.71, 137.97, 138.00, 144.04, 144.24, 144.39, 144.45, 144.53, 144.65, 144.77, 144.78, 144.93, 145.00 (33 signals overlapped); HRMS calcd for $C_{72}H_{43}Cl_3$ 1012.2430, found 1012.2461.

Dichloroethene 25. To a solution of 1.02 g (1.0 mmol) of **24** in 50 mL of THF was added 0.25 g (excess) of KO-t-Bu. The reaction mixture was heated at reflux for 8 h. Evaporation of the solvent and chromatography of the residue over silica gel using 2:1 CH_2Cl_2/hexane as eluent gave 0.92 g (94%) of **25** as a white solid, mp >320 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.85 (s, 2 H), 5.86 (s,

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(22) Logullo, F. M., Ph.D. Thesis, Case Institute of Technology, Cleveland, OH, 1965.

(23) Rees, C. W.; Storr, R. C.; *J. Chem. Soc. C* **1969**, 765–769.

4 H), 5.88 (s, 4 H), 6.89 (m, 8 H), 7.02 (m, 8 H), 7.31 (m, 4 H), 7.41 (m, 4 H), 7.53 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 49.87, 50.21, 51.03, 111.46, 123.61, 123.81, 125.04, 125.52, 133.01, 135.13, 135.56, 136.57, 144.15, 144.49, 144.90, 145.01; HRMS calcd for $C_{72}H_{42}Cl_2$ 976.2663, found 976.2628.

Attempted Cycloaddition of 25 and 4. A solution of 0.49 g (0.5 mmol) of **25** and 0.3 g (excess) of **4** were heated at reflux for 24 h. Removal of the solvent (vacuum distillation) and chromatography of the remaining residue over silica gel using 2:1 CH_2Cl_2/hexanes as eluent gave only a small amount of the starting materials.

Alkene 26. To a solution of dichloride **22** (1.96 g, 2 mmol) in 100 mL of anhydrous THF under Ar was added 0.28 g (40 mmol) of Li wire, and the mixture was heated at reflux for 72 h. Excess Li was removed with tweezers, solvent was evaporated, and the residue was taken up in 100 mL of CH_2Cl_2, washed with water and saturated NaCl solution, and dried ($MgSO_4$). Solvent was removed, and the slightly yellow residue was triturated with 60 mL of 2:1 hexanes/ether to give 1.67 g (92%) of **26** as a white powder: mp dec >350 °C; ^{1}H NMR ($CDCl_3$) δ 5.82 (s, 4 H), 5.87 (s, 4 H), 5.98 (dd, J = 3.7, <1 Hz, 2 H), 6.76 (dd, J = 3.7, <1 Hz, 2 H), 6.80–7.01 (m, 16 H), 7.25–7.54 (m, 16 H); ^{13}C NMR (CD_2Cl_2) δ 42.77, 50.12, 50.32, 123.77, 123.93, 124.11, 125.22, 125.64, 125.69, 135.02, 135.95, 140.01, 144.89, 145.13, 145.66, 145.72; HRMS calcd for $C_{72}H_{44}$ 908.3442, found 908.3471.

Cycloadduct 27. A suspension of alkene **26** (910 mg, 1.0 mmol) and diene **4** (450 mg, 1.1 mmol) in decalin (50 mL) was heated at reflux for 8 h. The cooled mixture was diluted with 45 mL of 1:2 CH_2Cl_2/hexanes. Filtration and vacuum drying gave 1.17 g (89%) of **27** as a fine white powder: mp dec >450 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (br d, J = 8 Hz, 2 H), 1.48 (br d, J = 8 Hz, 2 H), 4.55 (d, J = 1 Hz, 2 H), 4.97 (s, 2 H), 5.18 (s, 2 H), 5.66 (s, 2 H), 5.70 (s, 2 H), 5.75 (s, 2 H), 5.81 (s, 2 H), 6.60–7.58 (m, 48 H); ^{13}C NMR ($CDCl_3$) δ 38.50, 45.02, 46.78, 48.52, 48.89, 50.43, 50.61, 50.91, 123.13, 123.44, 123.74, 124.15, 124.34, 124.64, 124.94, 125.19, 125.64, 125.84, 126.07, 126.41, 127.10, 130.57, 132.46, 134.33, 134.87, 135.73, 136.27, 137.07, 141.24, 142.27, 142.51, 143.69, 145.37, 145.62, 146.03; HRMS calcd for $C_{104}H_{66}$ 1314.5164, found 1314.5180.

Aromatization of 27. Supertriptycene (2). To a solution of cycloadduct **27** (1.0 g, 0.76 mmol) in 200 mL of 1,1,2,2-tetrachloroethane at reflux was added 3 mL of bromine, and the mixture was heated at reflux for 4 h. Removal of the solvent (rotavap) and trituration of the residue with 40 mL of 3:1 CH_2Cl_2/ethyl acetate gave, on filtration, 850 mg (85%) of **2** as a white powder: mp >500 °C; ^{1}H NMR (tetrachloroethene) δ 5.63 (s, 6 H), 5.90 (s, 6 H), 6.60 (s, 2 H), 6.73–6.79 (m, 24 H), 7.16 (m, 12 H), 7.50 (m, 12 H); ^{13}C NMR (tetrachloroethene) δ 43.46, 52.55, 53.01, 125.46, 126.06, 126.90, 127.14, 136.74, 136.93, 137.48, 146.76, 146.96; HRMS calcd for $C_{104}H_{62}$ 1311.4930 (MH^+), found 1311.4890.

Cycloadduct 29. A solution of 0.91 g (1 mmol) of **26** and 0.92 g (4 mmol) of **28** in 25 mL of decalin was heated at reflux for 24 h. Removal of the solvent (vacuum distillation) and chromatography of the residue over silica gel using 3:2 CH_2Cl_2/hexanes as eluent gave 0.66 g (58%) of **29**: mp 305–308 °C; ^{1}H NMR ($CDCl_3$) δ 1.32 (ddd, J = 14.7, 6.0, 2.1 Hz, 2 H), 1.76 (dd, J = 6.0, 5.3 Hz, 2 H), 2.41 (dd, J = 14.7, 5.3 Hz, 2 H), 4.61 (s, 2 H), 4.91 (br s, 2 H), 5.801 (s, 2 H), 5.808 (s, 2 H), 5.81 (s, 2 H), 5.82 (s, 2 H), 6.71–7.09 (m, 24 H), 7.22–7.49 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 30.91, 40.53, 40.84, 49.92 (4), 55.55, 122.21, 122.38, 123.07, 123.23, 123.31, 123.37, 123.47, 123.53, 123.64, 123.73, 123.82, 123.91, 124.07, 124.65, 124.75, 124.90, 124.99, 125.12, 125.19, 125.24, 125.45, 131.47, 134.02, 134.31, 135.48, 135.72, 136.75, 143.05, 144.77, 144.82, 145.01, 145.08, 145.19, 145.43, 145.50, 145.55, 145.90, 146.46; HRMS calcd for $C_{90}H_{58}$ 1138.4571, found 1138.4532.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds **2**, **3**, **9**, **12**, **14–16**, **23–27**, and **29** (39 pages). Ordering information is given on any current masthead page.

Synthesis of Three Helically Chiral Iptycenes

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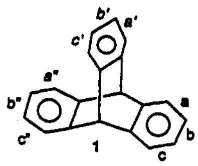
The synthesis of iptycenes **2–4**, each of which is helically chiral and has a C_2 symmetry axis, is described. Key intermediates are diene **7**, prepared in two steps and 44% yield from known ketone **5**, and anthracene **11**, prepared in four steps and 48% yield from diene **7**. A noteworthy step in the latter sequence is the aluminum chloride catalyzed, room-temperature, regio- and stereoselective cycloaddition of naphthoquinone **8** to diene **7** to give a single isomer of **9**. Anthracene **11** was converted in one step to **2** and in four steps to **3** (Scheme II). Bicycloalkene **15**, an intermediate in the latter synthesis, was converted to **4** in two steps (Scheme III). Cycloaddition of unactivated dienophile **15** to unactivated dienes **17** and **18** proceeds in good yields. Hydrocarbon **3** could be resolved on several chiral columns.

Twenty-four iptycenes[1] can be generated by fusing from zero to six 9,10-anthradiyl moieties to the benzenoid rings of triptycene **1**.[2] Of these, six are chiral, three with C_1 and three with C_2 symmetry. We describe here the first synthesis of three of these chiral iptycenes, the heptiptycene **2**, the noniptycene **3**, and the undecaiptycene **4**, the three that have C_2 symmetry. They are formally derived from triptycene by fusing 9,10-anthradiyl moieties to the ac′, ab′c″ and aca′c″ bonds, respectively.[3]



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These iptycenes are interesting for at least two reasons. First, they have cavities that might be useful for resolving nonpolar guest molecules. Second, they present a synthetic challenge that is quite different from previously synthesized iptycenes[1,2,4] in that two of the 9,10-anthradiyl moieties are angularly[5] rather than linearly fused to the central triptycene portion of the molecule.

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(1) Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427–4432.

(2) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641–1654.

0022-3263/91/1956-6912$02.50/0