Synthesis and Spectroscopic Studies of Expanded Planar Dehydrotribenzo[*n*]annulenes Containing One or Two Isolated Alkene Units

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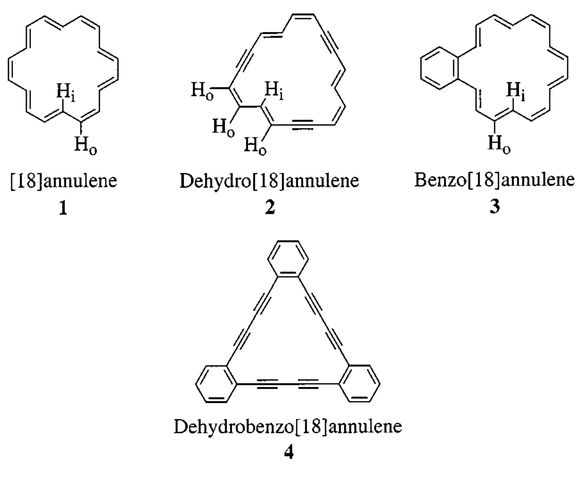
Dehydrobenzoannulene derivatives **5**–**7** containing isolated alkene linkages were synthesized by combining an in-situ Pd/Cu-mediated cross-coupling with an intramolecular cyclization strategy. ^{1}H NMR studies of these macrocycles and comparison with related systems verify that highly alkynylated dehydrobenzoannulenes possess weak induced ring currents, indicative of aromatic ($4n$+2 π-systems) and anti-aromatic ($4n$ π-systems) behavior, in spite of their large size and extensive benzannulation.

Introduction

For over a century the question, "What constitutes an aromatic molecule?" has elicited a variety of responses.[1] Whatever the answer, benzene, or [6]annulene, has long been considered the definitive aromatic compound. Larger [*n*]annulenes (e.g. **1**), however, raise further questions. Are they also aromatic? If so, how do they compare to benzene? Over the past 40 years, hundreds of annulenic structures have been synthesized and studied in an attempt to answer such questions. Some examples include larger [*n*]annulenes **1**, dehydro derivatives **2**, benzo derivatives **3**, bridged annulenes, hetero-annulenes, and hybrids of these subdivisions (Scheme 1).[2]



Scheme 1. Representative [18]annulenes

One of the best and most commonly applied qualifiers[3] for aromaticity is NMR spectroscopy. Both aromatic and anti-aromatic systems[4] have the ability to sustain induced ring currents when placed in the magnetic field of an NMR spectrometer and are classified as *diatropic*[5] and *paratropic*[6] molecules, respectively. By studying the NMR spectra of the vast family of annulenic structures encompassed by **1**−**3**, it was determined that these systems do indeed conform to accepted aromaticity trends. It was also confirmed that the magnitude of the induced ring current decreases as ring size increases to the limit of $n > 26$, at which point the conjugated macrocycles become atropic.

Many problems arise, however, in the larger members of families **1**−**3**. These large systems are quite flexible and prone to non-planar conformations, giving rise to analytical complications. Many compounds are unstable and/or susceptible to rearrangement, complicating structure determination. Inclusion of benzene rings and/or triple bonds weakens the overall diatropicity or paratropicity of the macrocycle.[7] In many cases, the overall synthetic yields are extremely low (< 1%), providing minute amounts of material for study.

The annulenes we have been investigating are hybrids of the above, known as dehydrobenzo[*n*]annulenes or DBAs **4**.[8] These macrocycles are stable, rigid, planar, highly symmetrical, structurally simple, and resistant to rearrangement, making structure determination straightforward. In addition, recent synthetic advances[9] have permitted the assembly of a wide variety of DBAs, allowing detailed study of their aromaticity.[9,10] We[9b,9c] and others[11] have shown that this class of annulenes can indeed sustain a weak induced ring current, but the only protons available in DBAs for NMR aromaticity studies are the arene protons. It is expected that the induced ring current effects on these protons will be weak because of the localized aromaticity of the benzene rings, the inclusion of triple bonds, and the size of the macrocycles.[1,6] The alternative is construction of mixed ene/yne analogues, such as [20]- and [22]DBA hybrids **5**−**7**, which incorporate alkenes into the backbone of the macrocycle (Scheme 2). These molecules, constructed by the intramolecular cyclization of a suitable α,ω-polyyne precursor, will allow "traditional" aromaticity studies to be

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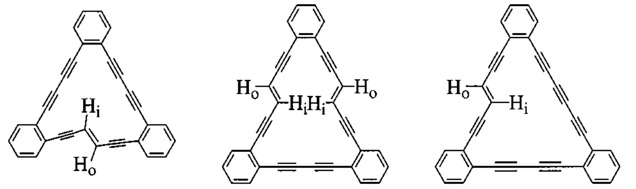
performed by analysis of the inner (H_i) and outer (H_o) alkene protons using NMR spectroscopy. Reported herein is the synthesis and study of ene/yne annulenes **5−7**.

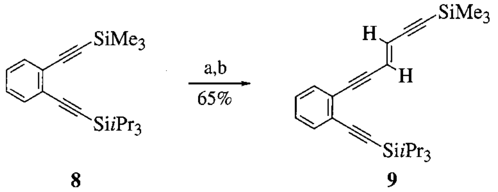


5 **6** **7**

Scheme 2. Target annulenes

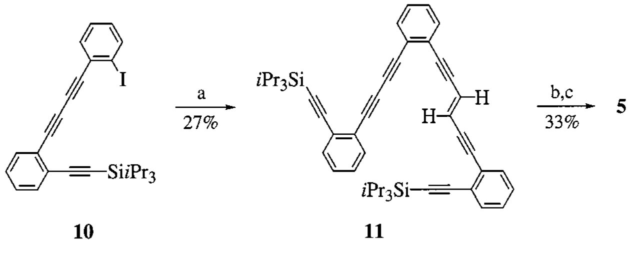
Results and Discussion

The trimethylsilyl protecting group was selectively removed from precursor **8**[9c] using methanolic K_2CO_3 (Scheme 3). The deprotected material was then coupled to [(*E*)-4-chloro-3-buten-1-ynyl]trimethylsilane[12] to give the requisite alkene building block **9**, the common intermediate necessary for the preparation of macrocycles **5−7**.



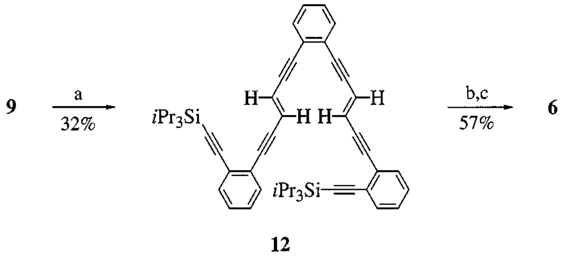
Scheme 3. Reagents: (a) K_2CO_3, Et_2O, MeOH, THF; (b) [(*E*)-4-chloro-3-buten-1-ynyl]trimethylsilane, $Pd(PPh_3)_4$, CuI, THF, Et_3N

Compound **9** (1 equiv.) was dissolved in Et_3N and added dropwise to a deoxygenated suspension of coupling catalysts, iodotriyne **10**,[9c] and a few drops of aqueous KOH.[9] In this manner the trimethylsilyl group was selectively removed to generate the reactive terminal acetylene in situ.[9] Cross-coupling with **10** occurred readily, furnishing precursor **11** in 27% yield (Scheme 4). It is interesting to note that the vinyl protons of **11** resonate as a singlet at δ = 6.39. This could be due to rapid exchange of the inner and outer protons caused by free rotation or, more likely, due to the pseudo symmetry about the alkene bond. The remaining silyl protecting groups were removed upon treatment with Bu_4NF, followed by copper-mediated intramolecular cyclization to give monoene[20]DBA **5** in 33% yield. Surprisingly, the vinyl protons of **5** also appear as a singlet at δ = 6.62.



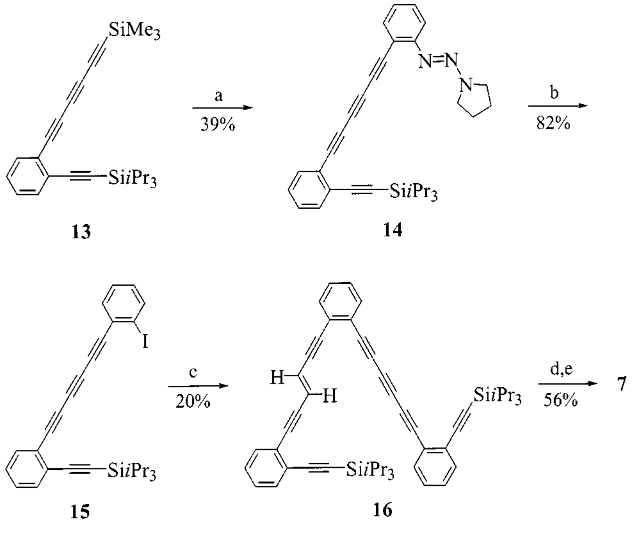
Scheme 4. Reagents: (a) **9**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, aq KOH; (b) Bu_4NF, THF, EtOH; (c) CuCl, $Cu(OAc)_2\cdot H_2O$, pyridine

Compound **9** (2 equiv.) was coupled to 1,2-diiodobenzene using the in-situ protiodesilylation/alkynylation procedure to give α,ω-polyyne **12** in 32% yield (Scheme 5). Analogous to **11**, the vinyl protons of **12** appear as a singlet at δ = 6.34. Upon closure, however, the vinyl protons of **6** resonate as two doublets at δ = 6.30 and 6.42 with *J* = 15.9 Hz, confirming the retention of the (*E*) geometry about the double bonds. Since diene[22]DBA **6** has (4*n* + 2) π-electrons in the macrocyclic circuit, these resonances are assigned to the inner and outer protons, respectively.[1]



Scheme 5. Reagents: (a) 1,2-diiodobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, aq KOH; (b) Bu_4NF, THF, EtOH; (c) CuCl, $Cu(OAc)_2\cdot H_2O$, pyridine

The preparation of **7**, which is the monoene counterpart to **6**, is shown in Scheme 6. Tetrayne **13**[9c] was coupled to 1-[(*E*)-(2-iodophenyl)azo]pyrrolidine[10c] by the in-situ coupling procedure to give triazene **14** in 39% yield. Treatment with iodomethane gave **15**, the triyne-linked counterpart to **10**, in 82% yield.[13] Cross-coupling alkene **9** with iodotetrayne **15** by the in-situ method furnished **16** in 20% yield. Like the other alkene-DBA precursors (**11** and **12**), NMR-spectroscopic data of molecule **16** shows a singlet at δ = 6.38 for the vinyl protons. Desilylation and oxidative cyclization gave monoene[22]DBA **7** in 56% yield. The vinyl protons of closed macrocycle **7** produce signals at δ = 6.28 and 6.42 (doublet, *J* = 16.1 Hz), analogous to **6**, and are assigned to H_i and H_o, respectively.



Scheme 6. Reagents: (a) 1-[(*E*)-(2-iodophenyl)azo]pyrrolidine, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, aq KOH; (b) MeI, 120 °C, (c) **9**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, aq KOH; (d) Bu_4NF, THF, EtOH; (e) CuCl, $Cu(OAc)_2\cdot H_2O$, pyridine

Unlike most other planar, purely hydrocarbon DBAs, we obtained crystals of **7** suitable for X-ray analysis. Shown in Figure 1, the structure confirms the conformation depicted in Scheme 2 as the lowest energy structure in the solid state and confirms that these molecules are virtually planar, with **7** exhibiting a mean deviation of 0.054 Å. The ring strain present in **7**, although minimal, is contained primarily in the (*E*)-enediyne side of the molecule, as the triple bonds deviate from linearity in the order of 0.6−7.5°. The distortions are considerably less (0.5−3.1°) on the diyne and triyne sides. These triple-bond angles are smaller than those found in other planar, yet slightly more strained tribenzo-DBAs.[9c,11a]

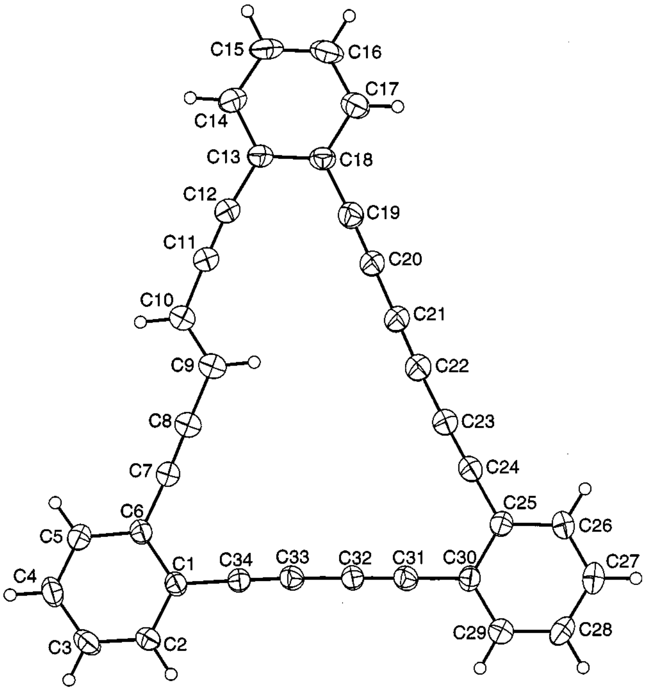
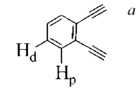
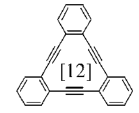
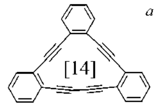
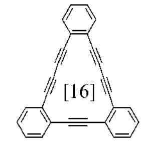
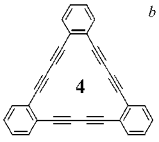
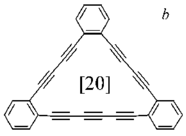
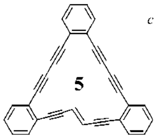
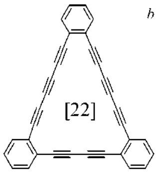
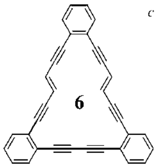
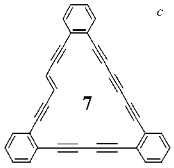


Figure 1. ORTEP diagram of annulene **7**; ellipsoids shown at the 30% probability level; CH_2Cl_2 solvent molecule omitted for clarity

Qualitative analysis of the nature of the ring currents in the planar, tribenzo-annulated DBAs was accomplished by comparing the chemical shift range of the proximal and distal protons (H_p and H_d, respectively) in the benzene rings of each DBA.[14] The presence of a diatropic ring current will manifest as an observable downfield shift of H_p and H_d signals relative to the reference signals; an upfield shift will indicate a paratropic system. Furthermore, the extent of deviation from the reference can be correlated to the strength of the induced ring current. The arene protons in *o*-diethynylbenzene serve as ideal reference standards[15] because this simple subunit is structurally similar to our DBAs, yet lacks the effects of macrocyclic delocalization and the anisotropic effects of dangling alkynes.[16]

Table 1. Chemical shift data of proximal (H_p) and distal (H_d) protons relative to *o*-diethynylbenzene

Compound	H_p	Mean deviation from reference	H_d	Mean deviation from reference
 H_d H_p [a]	7.50	N.A.	7.29	N.A.
 [12] [a]	7.34	−0.16	7.18	−0.11
 [14] [a]	7.73	+0.23	7.42	+0.13
 [16] [a]	7.40	−0.10	7.25	−0.04
 **4** [b]	7.68	+0.18	7.42	+0.13
 [20] [b]	7.49	−0.01	7.31	+0.02
 **5** [c]	7.45	−0.05	7.30	+0.01
 [22] [b]	7.64	+0.14	7.39	+0.10
 **6** [c]	7.59	+0.09	7.37	+0.08
 **7** [c]	7.56	+0.06	7.34	+0.05

[a] Ref.[11b] – [b] Ref.[9c] – [c] This work.

The data in Table 1 show that dehydrobenzo[*n*]annulenes are in accordance with the aromaticity convention displayed by their annulenic cousins. The (4*n*+2) Hückel-type systems (i.e., [14]DBA, [18]DBA, [22]DBA, **6**, and **7**) show weak but distinct downfield shifts of their arene proton signals (Δδ = 0.05−0.25) indicative of an aromatic, diatropic ring current. In general, the (4*n*) systems (i.e., [12]DBA and [16]DBA) show opposite behavior (Δδ = 0.02−0.12), suggesting paratropicity or anti-aromatic character. Furthermore, the magnitude of the induced ring current is stronger for diatropic systems than paratropic systems, and for both cases the effects diminish rapidly as the size of the macrocycle increases. The NMR-spectroscopic data for the two 20-membered rings (**5** and the parent [20]DBA) suggest that these macrocycles are atropic or very weakly paratropic, as the chemical shifts of the arene protons are virtually identical to those of the reference compounds. The vinyl protons of **5**, however, behave somewhat differently. Both the acyclic precursor **11** and the closed macrocycle **5** produce singlets in the vinyl region at $\delta = 6.39$ and $\delta = 6.62$, respectively. Utilizing the results from a monoene[12]annulene system studied by Staab et al.[17] with the alkene resonance in (*E*)-1,6-diphenyl-3-hexen-1,5-diyne as a suitable reference ($\delta = 6.33$),[18] the $\delta = 0.29$ downfield shift, which clearly indicates the presence of a weak induced current, roughly translates to H_i ($\delta \approx 6.9$) for **5**. Taken together with previous monoene-annulene examples that exhibit rapid exchange about the alkene bond in solution,[2,17] the data suggests that **5** (and thus likely [20]DBA) is marginally paratropic. Nevertheless, without an accurate assignment of H_i and H_o, we cannot make any definitive claims as to its diatropic or paratropic nature. On the other hand, the vinyl protons of **6** and **7** show virtually identical resonances at $\delta = 6.29$ (avg.) and $\delta = 6.42$, which are attributed to H_i and H_o, respectively. Both macrocycles originate from acyclic precursors that give a singlet at $\delta = 6.38$. This chemical shift behavior, especially that of H_i, corroborates the diatropic nature of these [22]DBA derivatives.

Since annulenes **6** and **7** give distinct resonances for H_i and H_o, we were able to calculate the free-energy barrier for interconversion ($\Delta G^{\ddagger}$) using variable-temperature NMR spectroscopy. The coalescence temperature (T_c) was determined in [D$_5$]pyridine, which allowed for an upper limit of 100 °C. T_c for dialkene[22]annulene **6** was found experimentally to be 94 °C. From a linear regression of the NMR-spectroscopic data, T_c for monoene **7**, which exceeds the upper limit, was estimated to be 115 °C. Using the method of Garratt and Calder,[19] $\Delta G^{\ddagger}$ for interconversion was determined to be 18.9 and 19.1 kcal·mol^{-1} for **6** and **7**, respectively. These values are slightly larger than those of related annulene and dehydroannulene structures, which are more flexible. For example, $\Delta G^{\ddagger}$ for [18]annulene (**1**) is 13.4 kcal·mol^{-1}.[20] The vinyl protons of **5** failed to resolve into discrete resonances, even when cooled to −90 °C (CD_2Cl_2). This is indicative of essentially unrestrained rotation, i.e., $\Delta G^{\ddagger}$ is extremely small.

Typical of polycyclic aromatic hydrocarbons, the molecular ion peaks in the mass spectra of DBAs **5−7** are also the base peaks. The mass spectra show strong $[M + 1]^+$ and $[M + 2]^+$ peaks characteristic of high carbon content compounds. In addition, very strong $[M - 2]^+$ (**5−7**) and $[M - 4]^+$ (**6** only) peaks were observed, which suggests facile loss of hydrogen atoms to give the fully alkynylated DBAs. Analogous to other purely hydrocarbon annulenes, molecules **5−7** exhibit essentially no fragmentation. The IR spectra of **5−7** display weak $-C\equiv C-$ stretches (ca. 2210 and 2165 cm^{-1}), which are characteristic of highly symmetrical structures. The UV/Vis spectra of DBAs **5−7** are somewhat broadened and exhibit less fine structure compared to their fully alkynylated counterparts. The general UV/Vis characteristics, however, are comparable: λ_{max} values are in the 330 (**5**) to 345 nm (**6**, **7**) region, cutoffs ca. 420 nm, and extinction coefficients in the 45,000−60,000 M^{-1}·cm^{-1} range.

Conclusions

In summary, we have assembled three new alkene-containing annulenes by an efficient intramolecular synthetic strategy. Our results strongly suggest that expanded planar, highly alkynylated dehydrobenzo[*n*]annulenes do indeed possess induced ring currents despite their large size and extensive benzannulation. By comparing the ^1H NMR spectra of a broad range of macrocycle sizes from $n = 12-22$, it is apparent that these molecules adhere to conventional notions of aromaticity. Efforts to quantify the ring currents in DBAs are currently underway.[10d]

Experimental Section

^1H and ^{13}C NMR spectra were recorded using a Varian Unity Inova 300 (^1H: 299.95 MHz, ^{13}C: 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual non-deuterated solvent as internal standard ($CDCl_3$: ^1H: $\delta = 7.26$; ^{13}C: $\delta = 77.00$). Coupling constants are expressed in Hertz. − IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. − UV/Vis spectra were recorded in CH_2Cl_2 using a Hewlett Packard 8453 spectrophotometer. − Mass spectra were recorded using a Kratos MS50 spectrometer (EI, CI, FAB) or a PerSeptive Biosystems Voyager-DE STR Biospectrometry Workstation (MALDI-TOF) with 2,5-dihydroxybenzoic acid as matrix (calibrated with C_{60} and C_{70}). − DSC analyses were performed using a TA Instruments DSC 2920 Modulated DSC. − Elemental analyses were performed by Robertson Microlit Laboratories, Inc. − Melting points were determined with a Mel-temp II apparatus and are uncorrected. − CH_2Cl_2 and Et_3N were distilled from CaH_2 under nitrogen prior to use. THF and Et_2O were distilled from Na and benzophenone under N_2 prior to use. All other chemicals were of reagent quality and used as obtained from manufacturers. Reactions were carried out in dry N_2 or Ar when necessary. − Column chromatography was performed on Whatman reagent grade silica gel (230−400 mesh). Preparative radial thin layer chromatography was performed with a Chromatotron using silica gel (60 PF$_{254}$) plates (1−4 mm). Pre-coated silica gel plates (EM Separations Technology, 60 PF$_{254}$, 200 × 50 × 0.20 mm) were used for analytical thin layer chromatography.

General in-situ Desilylation−Alkynylation Procedure A: An iodoarene (1 equiv.) was dissolved in THF/Et_3N (1:5, v:v, 25 mL per mmol). To this was added $PdCl_2(PPh_3)_2$ (0.03 equiv.), CuI (0.06 equiv.), and aqueous KOH (1 M, 10 equiv.). The reaction mixture was deoxygenated with bubbling nitrogen, or by the freeze-pump-thaw method. In a separate vessel, the trimethylsilyl-protected coupling partner (1.2 equiv.) was dissolved in a small volume of Et_3N and was degassed. The acetylene solution was added via syringe pump over 12−24 h to the iodoarene solution under N_2 at 60 °C. Upon completion, the reaction mixture was concentrated in vacuo, suspended in CH_2Cl_2, and filtered through a bed of silica gel. The filtrate was concentrated, and the crude product was purified by radial chromatography or by preparative TLC.

General Macrocyclization Procedure B: The silyl-protected macrocycle precursor (1 equiv.) was dissolved in THF (25 mL per mmol) and EtOH (10−20 drops). A solution of Bu_4NF was added (1 M in THF, 2.1 equiv.) with stirring at room temperature. The reaction was monitored by TLC. Upon completion, the mixture was diluted with Et_2O, washed three times with water, twice with brine, and dried ($MgSO_4$). After filtration through a short pad of silica gel and removal of the solvent, the resulting product was dissolved in a small volume of pyridine and was used immediately in the next step. − The deprotected precursor was added over 16−20 h via syringe pump to a suspension of CuCl (20 equiv.) and $Cu(OAc)_2{\cdot}H_2O$ (25 equiv.) in pyridine (250 mL per mmol of α,ω-polyyne) at 60 °C. Upon completion, the mixture was concentrated in vacuo and diluted with CH_2Cl_2. The organic layer was subsequently washed with dilute HCl solution and repeatedly with water. The organic layer was dried ($MgSO_4$), filtered, concentrated, and purified by column or radial chromatography.

1-(Triisopropylsilyl)ethynyl-2-[(*E*)-6-(trimethylsilyl)hex-3-ene-1,5-diynyl]benzene (9): Diacetylene **8**[9c] (2.84 g, 8.0 mmol) was dissolved in a solution of THF, Et_2O, and MeOH (6:3:1 v:v, 200 mL). Anhydrous K_2CO_3 (553 mg, 4.0 mmol) was added and the reaction mixture was stirred vigorously for 2 h. Upon completion, the mixture was diluted with water and extracted into additional Et_2O. After washing with water and then brine, the organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the desired terminal acetylene (2.25 g, ca. 100%), which was used immediately in the next step. − The deprotected material was dissolved in Et_3N (30 mL), deoxygenated, and added via syringe pump (0.6 mL/h) to a deoxygenated solution of [(*E*)-4-chloro-3-buten-1-ynyl]trimethylsilane[12] (800 mg, 5 mmol), $Pd(PPh_3)_4$ (180 mg, 0.16 mmol), and CuI (50 mg, 0.26 mmol) in Et_3N (30 mL) and THF (30 mL) while stirring at 60 °C under nitrogen. Upon completion, the reaction mixture was diluted with hexanes and washed with 10% HCl solution, several times with H_2O, dried ($MgSO_4$), and concentrated. Purification by radial chromatography (4-mm plate, 2% EtOAc in hexanes) gave **9** as an orange oil (1.31 g, 65%). − ^{1}H NMR: δ = 0.22 (s, 9 H), 1.15 (s, 21 H), 6.08 (d, *J* = 16.5 Hz, 1 H), 6.21 (d, *J* = 16.5 Hz, 1 H), 7.23−7.27 (m, 2 H), 7.40−7.50 (m, 2 H). − ^{13}C NMR: δ = −0.2, 11.3, 18.7, 91.4, 93.9, 95.4, 100.7, 103.3, 105.0, 120.8, 121.9, 125.5, 125.8, 128.0, 128.2, 132.1, 132.7. − IR (neat): ṽ = 2945, 2866, 2156, 2123, 1467 cm^{-1}. − MS (CI pos): *m/z* (%) = 404.1 (11) [M^+], 361.1 (27), 391 (14), 217 (25), 129.1 (47), 73 (100). − HRMS ($C_{26}H_{36}Si_2$): calcd. 404.2359; found 404.2356.

α,ω-Polyyne 11: Iodoarene **10**[9c] (500 mg, 1.06 mmol) was treated with alkene **9** (554 mg, 1.38 mmol) as described in General Procedure A. Purification by preparative TLC (hexanes) furnished **11** as an orange oil (195 mg, 27%). − ^{1}H NMR: δ = 1.14 (s, 21 H), 1.19 (s, 21 H), 6.39 (s, 2 H), 7.20−7.37 (m, 6 H), 7.47−7.50 (m, 6 H). − ^{13}C NMR: δ = 11.4, 18.8, 77.8, 78.2, 80.7, 81.5, 91.8, 92.7, 93.1, 94.3, 95.5, 96.2, 104.6, 105.0, 120.8, 121.7, 124.6, 124.8, 125.6, 125.9, 126.4, 127.3, 127.9, 128.0, 128.2, 128.3, 128.7, 128.8, 132.0, 132.1, 132.4, 132.6, 132.8, 133.0. − IR (neat): ṽ = 2942, 2891, 2864, 2156, 1465 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (30,200), 269 (20,800), 308 (14,350), 327 (16,800), 356 (12,500), 383 (7,500) nm. − MS (CI Pos): *m/z* (%) = 712.3 (92) [M^+], 451.3 (38), 410.3 (54).

Monoalkene[20]annulene 5: Polyyne **11** (195 mg, 0.29 mmol) was subjected to General Procedure B. Purification by radial chromatography (2-mm plate, 5% EtOAc in hexanes) followed by concentration and trituration with hexanes gave annulene **5** as a bright orange solid (39 mg, 33%). − M.p. 205 °C (dec). − ^{1}H NMR: δ = 6.62 (s, 2 H), 7.23−7.38 (m, 8 H), 7.46−7.54 (m, 4 H). − ^{13}C NMR: δ = 77.4, 78.2, 81.2, 81.7, 93.9, 94.2, 121.4, 124.4, 125.6, 126.7, 128.4, 129.0, 129.1, 130.7, 132.8, 134.8. − IR (KBr): ṽ = 2942, 2863, 2211, 2156, 1734, 1463 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 309 (34,100), 331 (60,000), 352 (7,400), 368 (4,500) nm. − MS(EI): *m/z* (%) = 398 (100) M^+) [M^+], 396 (75), 394 (38). − MS (MALDI-TOF): $C_{32}H_{14}$ (398.45): 419.91 [M^+ + Na], 398.90 [M^+].

α,ω-Polyyne 12: 1,2-Diiodobenzene (180 mg, 0.55 mmol) was treated with alkene **9** (450 mg, 1.12 mmol) as described in General Procedure A. Purification by radial chromatography (2-mm plate, 2% EtOAc in hexanes) furnished **12** as an orange oil (134 mg, 32%). − ^{1}H NMR: δ = 1.14 (s, 42 H), 6.34 (s, 4 H), 7.20−7.35 (m, 6 H), 7.41−7.58 (m, 6 H). − ^{13}C NMR: δ = 11.3, 18.7, 91.7, 92.3, 93.4, 94.2, 95.4, 105.0, 120.7, 121.4, 125.36, 125.42, 125.9, 127.9, 128.2, 128.3, 131.9, 132.1, 132.6. − IR (neat): ṽ = 2960, 2925, 2864, 2156, 1732, 1463 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 239 (30,000), 266 (19,000), 308 (8,500), 331 (7,900) nm. − MS (MALDI-TOF): $C_{52}H_{58}Si_2$ (739.19): 739.31 [M^+].

Dialkenyl[22]annulene 6: Polyyne **12** (134 mg, 0.18 mmol) was subjected to General Procedure B. Purification by flash chromatography on silica gel (CH_2Cl_2) followed by concentration and trituration with hexanes gave **6** as a bright yellow solid (44 mg, 57%). − M.p. 189 °C (dec). − ^{1}H NMR: δ = 6.30 (d, *J* = 15.9 Hz, 2 H), 6.42 (d, *J* = 15.9 Hz, 2 H), 7.24−7.40 (m, 6 H), 7.47−7.64 (m, 6 H). − ^{13}C NMR: δ = 77.1, 81.1, 92.4, 93.0, 93.7, 94.2, 121.1, 121.2, 124.2, 125.7, 125.9, 128.3, 128.4, 128.9, 131.4, 132.2, 133.3. − IR (KBr): ṽ = 2956, 2924, 2849, 2193, 1726, 1465 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 279 (22,100), 295 (28,400), 328 (40,000), 343 (50,300), 378 (12,450), 395 (7,900) nm. − MS (EI): *m/z* (%) = 424 (91) [M^+], 422 (100). − MS (MALDI-TOF): $C_{34}H_{16}$ (424.49): 446.63 [M^+ + Na], 424.56 [M^+].

Triazene 14: Tetrayne **13**[9c] (1.01 g, 2.5 mmol) was treated with 1-[(*E*)-(2-iodophenyl)azo]pyrrolidine[10c] (750 mg, 2.5 mmol) as described in General Procedure A. Purification by radial chromatography (4-mm plate, 5% EtOAc in petroleum ether) gave **14** as a dark oil (490 mg, 39%). − ^{1}H NMR: δ = 1.18 (s, 21 H), 2.07 (br. s, 4 H), 3.78 (br. s, 2 H), 3.90 (br. s, 2 H), 7.06 (t, *J* = 6.9 Hz, 1 H), 7.23−7.33 (m, 3 H), 7.41−7.54 (m, 4 H). − ^{13}C NMR: δ = 11.3, 18.7, 23.6, 24.0, 46.8, 51.2, 66.7, 68.2, 77.1, 77.9, 78.1, 78.4, 96.3, 104.4, 115.4, 117.2, 124.3, 124.6, 127.6, 128.0, 128.9, 130.3, 132.4, 133.0, 134.2, 154.9. − IR (neat): ṽ = 2943, 2864, 2191, 2171, 1404, 1315, 881, 758 cm^{-1}. − MS (FAB pos): *m/z* (%) = 504.5 [M^+ + H] (100), 391 (24), 285 (33). − HRMS: calcd. 504.2830; found 504.2835 for $C_{33}H_{37}N_3Si$ (503.75).

Iodotetrayne 15: Triazene **14** (490 mg, 0.97 mmol) was dissolved in freshly distilled iodomethane (20 mL) and heated in a sealable pressure reactor at 120 °C for 12 h. The reaction mixture was cooled, diluted with hexanes, and filtered through a pad of Celite and silica gel. Concentration and purification of the crude product by column chromatography (hexanes) provided **15** as a dark oil (427 mg, 82%). − ^{1}H NMR: δ = 1.18 (s, 21 H), 7.06 (dt, *J* = 7.4, 1.8 Hz, 1 H), 7.24−7.36 (m, 3 H), 7.47−7.56 (m, 3 H), 7.85 (d, *J* = 7.8 Hz, 1 H). − ^{13}C NMR: δ = 11.3, 18.7, 67.1, 68.2, 77.8, 78.0, 78.1, 79.9, 96.6, 101.2, 104.2, 123.9, 127.84, 127.90, 127.96, 129.2, 130.5, 132.4, 133.1, 134.3, 138.9. − IR (neat): ṽ = 2957, 2864, 2158, 1464 cm^{-1}. − MS (CI pos): *m/z* (%) = 532 (9) [M^+], 489 (13), 441 (100), 271 (15), 243 (15). − $C_{29}H_{29}ISi$ (532.53): calcd. C 65.41, H 5.49; found C 65.28, H 5.54.

α,ω-Polyyne 16: Iodotetrayne **15** (385 mg, 0.72 mmol) was coupled with alkene **9** (380 mg, 0.94 mmol) as described in General Procedure A. Purification by preparatory TLC (5% EtOAc in hexanes) gave **16** as a dark orange oil (104 mg, 20%). − ^{1}H NMR: δ = 1.16 (s, 21 H), 1.17 (s, 21 H), 6.38 (s, 2 H), 7.22−7.38 (m, 6 H), 7.43−7.60 (m, 6 H). − ^{13}C NMR: δ = 65.8, 67.2, 67.9, 77.8, 78.1, 78.3, 91.7, 92.7, 92.9, 94.4, 95.5, 96.6, 104.2, 105.0, 120.5, 121.9, 123.7, 123.9, 125.5, 125.9, 127.1, 127.8, 127.9 (2), 128.3, 128.3, 129.1, 129.2, 131.9, 132.1, 132.4, 132.6, 133.1, 133.3. − IR (neat): $\tilde{\nu}$ = 2939, 2899, 2866, 2156, 1475 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 300 (29,900), 323 (24,700), 332 (25,000), 344 (26,200), 388 (16,100) nm. − MS (MALDI-TOF): 737.34 [M$^+$]. − $C_{52}H_{56}Si_2$ (737.17): calcd. C 84.72, H 7.66; found C 84.50, H 7.65.

Monoalkene[22]annulene 7: Polyyne **16** (100 mg, 0.14 mmol) was subjected to General Procedure B. Purification by column chromatography (10% CH_2Cl_2 in petroleum ether) followed by recrystallization (petroleum ether/CH_2Cl_2) furnished **7** as yellow-orange crystals (32 mg, 56%). − M.p. 123 °C (dec). − ^{1}H NMR: δ = 6.28 (d, J = 16.1 Hz, 1 H), 6.44 (d, J = 16.1 Hz, 1 H), 7.27−7.46 (m, 6 H), 7.47−7.68 (m, 6 H). − ^{13}C NMR: δ = 67.5, 67.6, 76.7, 77.4, 77.7, 78.3, 78.8, 80.5, 81.5, 92.9, 93.4, 93.8, 94.1, 120.8, 122.4, 123.9, 124.0, 124.2, 125.8, 125.9, 127.9, 128.26, 128.33, 128.8, 129.0, 129.2, 129.4, 130.9, 132.2, 132.4, 133.47, 133.50, 133.55. − IR (KBr) $\tilde{\nu}$ = 2919, 2853, 2204, 2170, 1719, 1474 cm^{-1}. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 294 (22,450), 329 (41,700), 345 (57,000), 392 (15,700) nm. − MS (MALDI-TOF): $C_{34}H_{14}$ (422.47): 446.63 [M$^+$ − 2 H + Na], 422.24 [M$^+$], 420.28 [M$^+$ − 2 H].

Crystal Structure of 7: $C_{34}H_{14}\cdot CH_2Cl_2$, M_r = 507.42, yellow tablet, 0.08 × 0.42 × 0.43 mm, triclinic, space group $P\bar{1}$, a = 8.298(9), b = 10.755(23), c = 15.676(22) Å, α = 83.28(15), β = 89.44(12), γ = 73.65(15)°, V = 1332(1) Å^3, Z = 2, $\rho_{calcd.}$ = 1.265 g·cm^{-3}, Mo-K_α radiation (λ = 0.71073 Å), μ = 2.63 cm^{-1}, F(000) = 520, T = 22 °C, $2\theta_{max}$ = 50°, 4675 independent reflections scanned, 2849 reflections in refinement [$I \geq 1.5\sigma(I)$], 334 parameters, R = 0.063, R_w = 0.055. Data were obtained with an Enraf−Nonius CAD-4 Turbo diffractometer. Structure refinement (C atoms anisotropic, H atoms isotropic, solvate H atoms riding) was accomplished with teXsan (v. 1.7 for SGI workstations). Supplementary crystallographic data (excluding structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-158305. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ U.K. [Fax (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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