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A versatile synthetic route to dehydrobenzoannulenes via in situ generation of reactive alkynes

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Abstract—This paper outlines the development of a protocol that allows in situ generation of unstable alkynes under Pd-catalyzed cross-coupling conditions. Cu-mediated intramolecular cyclization of the resultant α,ω-polyynes provides dehydrobenzoannulenes as singular species, in very good overall yields, and in a variety of topologies that are inaccessible by traditional routes or previously available in low yield only. In addition, we will discuss the solid-state structure and reactivity of these macrocycles, as well as the ability of the planar dehydrobenzoannulenes to support weak induced ring currents. © 2001 Elsevier Science Ltd. All rights reserved.

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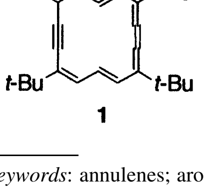
1. Introduction

The 1960s and 1970s saw the 'golden age' in the field of dehydrobenzoannulene (DBA) chemistry.[1] The groups of Nakagawa, Staab, and Sondheimer, the principal protagonists of this era, prepared an impressive array of DBA structures. Molecules **1**–**3** are representative examples from each group, respectively.[2] The main factor driving this research was the question of ring currents in the annulenic macrocycles. How diatropic, paratropic, or atropic were each of these systems? While there were and still are an infinite number of DBA topologies that could be synthesized, it eventually became apparent that there needed to be additional impetus for this research; thus, interest waned and the area languished in the 1980s.

The resurgence of DBA chemistry began in the early 1990s.[3] Two key events made this revival possible. The first was the isolation and characterization of the fullerenes.[4] Fullerene chemistry single-handedly made research on all-carbon and carbon-rich molecular and polymeric systems, of which DBAs are a prime example, in vogue once more. Many of these molecules, including DBAs, can potentially serve as precursors for a variety of technologically important materials, such as novel allotropes of carbon,[5] molecular tubes,[6] and ladder polymers.[7] Particularly attractive is the possibility of topochemical polymerization of diacetylenic and triacetylenic DBAs as a means of generating crystalline polymers containing conjugated backbones.[8] Such systems might be viable precursors to materials possessing nonlinear optical and/or other fascinating physiochemical properties.[9]



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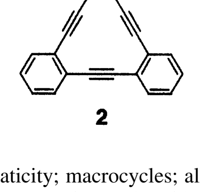

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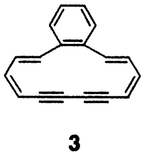

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The second factor responsible for the DBA renaissance has been the extensive development of Pd-catalyzed cross-coupling reactions using alkynes.[10] Quite simply, this method revolutionized the way in which the DBA skeleton is constructed (vide infra). Not only have new topologies become accessible, but also the number of steps to known macrocycles has been shortened and overall yields dramatically increased in some cases. For example, Staab's original synthesis of DBA **2** required six steps (8% yield) starting from *o*-tolane, itself the product of a four-step reaction sequence.[2b] Conversely, using commercially available 1-bromo-2-iodobenzene, molecule **2** can be assembled quickly in two steps (23% yield) via palladium chemistry.[11] A drawback to this and most other routes for DBA assembly is the formation of higher cyclooligomers, making isolation of pure **2** somewhat laborious.[12]

Diacetylene-containing macrocycles, such as **3**, traditionally have been synthesized either by the cyclooligomerization method or via an intramolecular cyclization strategy, the choice depending upon the symmetry of the final product.[3] In the case of C_{2v}-symmetric **3**, the intramolecular route worked adequately, furnishing the annulene in six

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Keywords: annulenes; aromaticity; macrocycles; alkynes; polyynes.

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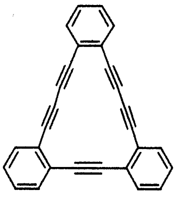

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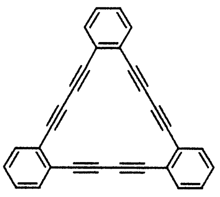

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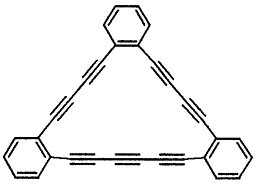

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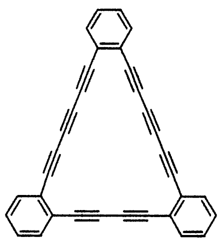

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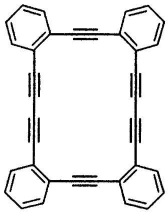

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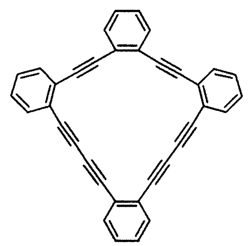

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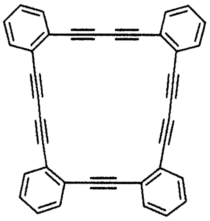

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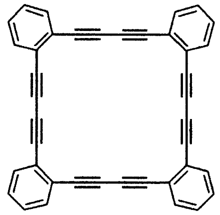

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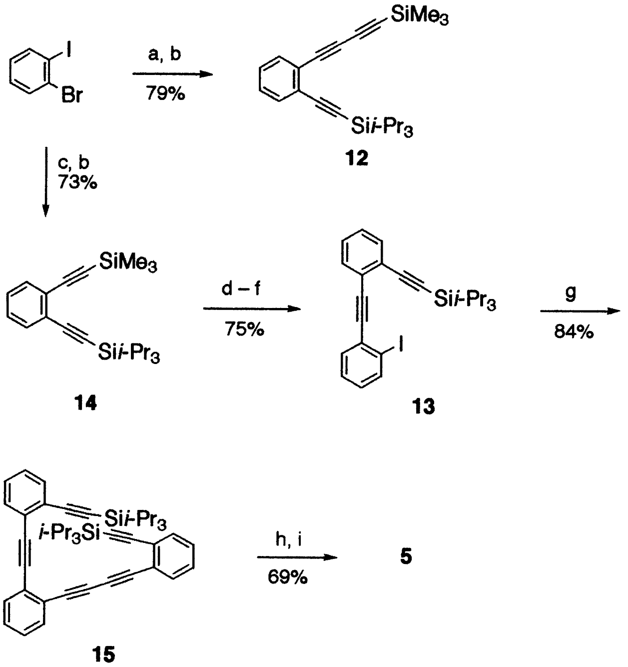
steps and 16% overall yield.[2c] In general, however, the cyclooligomerization method, which provides annulenes with D_{nh} symmetry, is preferred as it is usually a shorter pathway. For example, cyclodimerization of bis(2-ethynylphenyl)ethyne, which was prepared from 1-bromo-2-iodobenzene in three steps, afforded DBA **4**.[13] Unfortunately, compound **4** was produced in low yield (<8% for four steps), and was accompanied by formation of higher cyclooligomers. Efforts to manipulate the relative ratio of products by varying reaction conditions (i.e. temperature, concentration, solvent, catalyst, etc.) achieved limited success as a mixture of cyclooligomers was almost always obtained.[7] Owing to their similarity in structure, composition, and solubility, it is often difficult or impossible to isolate a specific macrocycle from the product mixture. Thus, we faced the following dilemma: how to synthesize diacetylenic and triacetylenic DBAs quickly and efficiently, maximizing overall yield yet minimizing the number of synthetic steps and purification shortcomings. The remedy, the subject of this report, is a simple, one-pot procedure that allows the preparation of novel α,ω-polyynes, thus leading to diyne- and triyne-linked dehydrobenzoannulenes of varying topologies either previously available only in low yield (**4**,[13] **11**[14]) or altogether inaccessible by traditional routes (**5–10**).[15] Additionally, we will discuss the induced ring currents in these systems and their solid-state structures and reactivity.

2. Results

2.1. Development of the in situ desilylation/alkynylation reaction sequence: diyne-linked DBAs

In order to ensure formation of a single DBA product, we envisaged an intramolecular cyclization of a corresponding α,ω-polyyne to prepare macrocycles **4–11**. Synthesis of each polyyne would necessitate the use of a suitably functionalized phenylbutadiyne. In the case of DBA **5**, our initial target, the requisite synthon was triyne **12** (Scheme 1). 1-Bromo-2-iodobenzene served as the cornerstone for construction of multigram quantities of both **12** and iodoarene **13** by repetitive alkynylation,[10] protiodesilylation,[16] and/or iodination[17] methods. Sequential Sonogashira cross-coupling reactions with (trimethylsilyl)-butadiyne[18] and (triisopropylsilyl)ethyne gave synthon **12** as a pale yellow oil in 79% yield. Conversely, initial use of (trimethylsilyl)ethyne instead furnished diyne **14** in 73% yield. Protiodesilylation with K_2CO_3 in MeOH, cross-coupling with *N*,*N*-diethyl-*N*′-(2-iodophenyl)triazene,[19] and triazene decomposition with iodomethane[17] at 120°C provided arene **13** in 75% yield for the three steps.

Selective desilylation of **12** with K_2CO_3 was hoped to afford



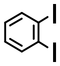
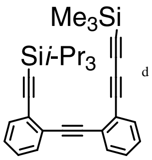
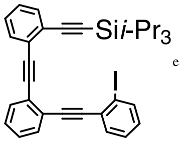
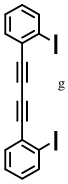
Scheme 1. (a) $HC{\equiv}CC{\equiv}CSiMe_3$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (b) $HC{\equiv}CSi\textit{i}\text{-}Pr_3$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (c) $HC{\equiv}CSiMe_3$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (d) K_2CO_3, MeOH, Et_2O; (e) *N*,*N*-diethyl-*N*′-(2-iodophenyl)triazene, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (f) MeI, 120°C; (g) **12**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, KOH, H_2O; (h) Bu_4NF, MeOH, THF; (i) CuCl, $Cu(OAc)_2{\cdot}H_2O$, pyridine.

the free phenylbutadiyne, which would be subjected to standard Pd-coupling conditions. When this was tried, concentration of the reaction mixture gave a dark brown gum instead of a free-flowing oil. In hindsight, this result was not surprising given the propensity of the parent molecule, phenyl-1,3-butadiyne, to polymerize rapidly when neat or in concentrated solution; even a dilute solution at −20°C is reported to polymerize within a few hours.[20] This extreme reactivity has limited the synthetic utility of phenylbutadiynes to date. Indeed, our attempts to use unprotected phenylbutadiynes in Pd-catalyzed alkynylation reactions typically provided intractable polymeric gums.[21] Other approaches have been developed that formally introduce a phenylbutadiyne moiety; however, these are generally multistep conversions with low overall yields.[22]

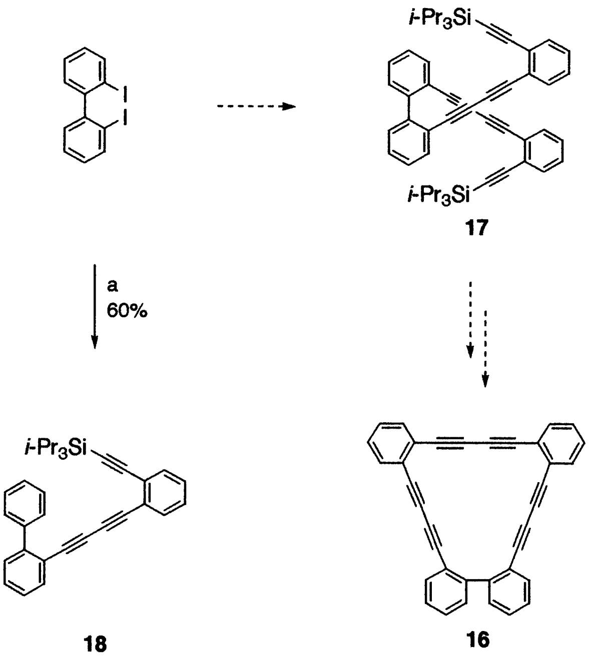
The resolution of this impasse was in situ generation of the reactive phenylbutadiyne under standard Sonogashira coupling conditions.[23,24] The question was which base to use to remove the trimethylsilyl group? The first attempt using K_2CO_3 gave back starting materials. Addition of NaOMe did furnish the desired product, but in less than 5% yield; again, mainly starting materials were recovered. The third iteration provided the answer—addition of a few milliliters of a concentrated KOH solution gave the cross-coupled product **15** in 84% yield. Thus, slow addition of **12** to a vigorously stirred, degassed solution of **13** using the deprotection/alkynylation conditions (step (g)) furnished pentayne **15** as a sticky orange gum. Extension of this reaction sequence to other iodoarenes provided a series of bis(triisopropylsilyl)-protected α,ω-polyynes in very good yields (Table 1).[25–27] Subsequent desilylation of **15** with Bu_4NF in THF/MeOH and intramolecular cyclization with $CuCl/Cu(OAc)_2$[28] under pseudo-high dilution conditions provided pale yellow needles of **5** as the sole product in 32% overall yield. In a similar manner, annulenes **4**, **6**,[25] and **9–11** were obtained in comparable overall yields (25–30%). To date, we have limited the scale-up of the desilylation/cyclization steps to the production of 500–750 mg of annulene per run, yet have observed only a minor decrease in reaction yields.

For the series of nonplanar tetrabenzoannulenes (**4**, **9–11**), we tried to prepare a third regioisomeric [20]annulene derivative (**16**) starting from 2,2′-diiodobiphenyl[29] (Scheme 2). Cross-coupling with two equivalents of **12** using the in situ deprotection/alkynylation sequence surprisingly failed to provide α,ω-polyyne **17**; instead, only compound **18** was isolated in 60% yield. Despite numerous attempts with **12** and several other alkynes, Pd-coupling

Table 1. Reactants and yields

Annulene	Iodoarene	Butadiyne synthon	Yield of polyyne[a] (%)	Yield of annulene[b] (%)
5	**13**	**12**	84	69
6		**12**	71[c]	35[c]
4	**13**	 [d]	77	55
9	 [e]	**12**	76	61
10	 [f]	**12**	60	59
11	 [g]	**12**	68	63

[a] Step (g).
[b] Combined yield of steps (h) and (i).
[c] Ref. 25.
[d] Prepared from molecule **13** and (trimethysilyl)butadiyne (see Section 5).
[e] Prepared in two steps from **13** (see Section 5).
[f] Ref. 26.
[g] Ref. 14.



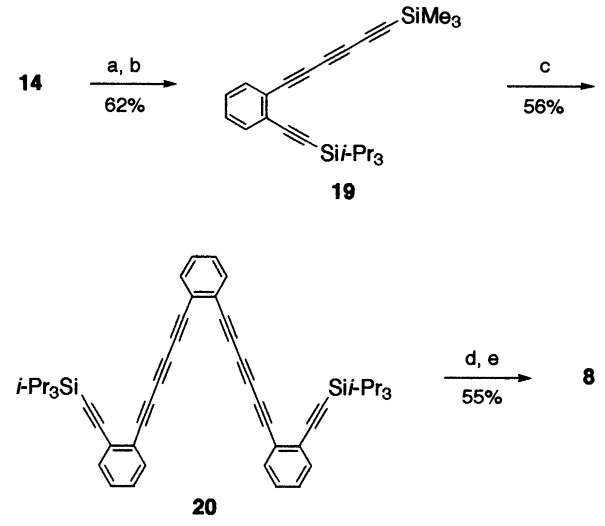
Scheme 2. (a) **12**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, KOH, H_2O.

reactions never furnished dialkynylated products. It is likely that, after attachment of the first alkyne, the resulting intermediate after the second oxidative addition is sufficiently crowded that reductive protonation occurs before transmetallation with the second alkyne. It is worth noting that formation of **18** occurred preferentially over the formation of an alkylidenefluorene, which was previously observed in Pd-catalyzed alkynylations of 2,2′-diiodobiphenyl.[30]

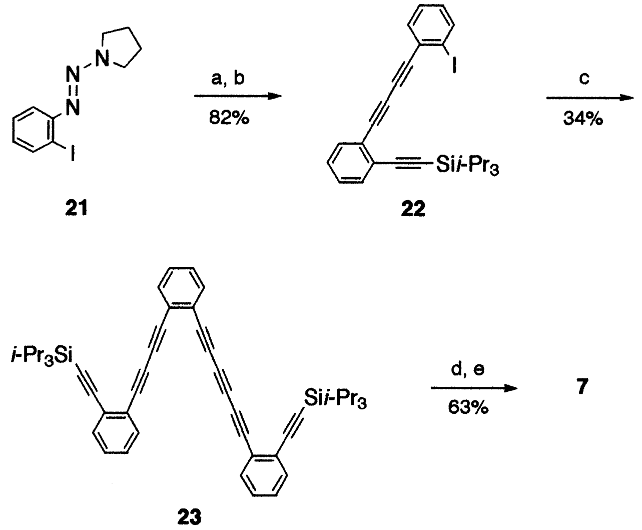
2.2. Triyne-linked DBAs

Using intermolecular methods, the synthesis of DBAs with an odd number of acetylenic linkers (e.g. **7**, **8**) is problematic as it requires two different alkyne-containing partners, further compounding product isolation from the cyclooligomeric mixtures. In contrast, the intramolecular α,ω-polyyne cyclization route is more applicable for the synthesis of triyne-linked DBAs. Accordingly, it is necessary to generate phenylhexatriyne intermediates to form the α,ω-polyynes. Given the aforementioned sensitivity of terminal diynes, it is not surprising that terminal triynes are prone to rapid decomposition. Although the synthesis of 1-phenyl-1,3,5-hexatriyne has been reported previously, identification of the extremely unstable parent molecule was limited solely to UV–Vis spectroscopy.[31] Again, the synthetic answer was in situ generation of the unstable species.

The essential intermediate for the assembly of triyne-linked DBAs was phenylhexatriyne synthon **19** (Scheme 3). Protiodesilylation of **14** and subsequent exposure to $Me_3SiC{\equiv}C{-}C{\equiv}CBr$[32] using modified Cadiot–Chodkiewicz conditions[33] gave **19** in 62% yield. In situ generation of the reactive triyne under Sonogashira coupling conditions afforded octayne **20** in 56% yield. Sequential desilylation with fluoride ion and Cu-mediated intramolecular coupling furnished [22]annulene **8** as a tan solid in 55% yield.[34]



Scheme 3. (a) K_2CO_3, MeOH, Et_2O; (b) i] BuLi, THF, ii] CuBr, iii] $Me_3SiC{\equiv}CC{\equiv}CBr$, pyridine; (c) *o*-diiodobenzene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, KOH, H_2O; (d) Bu_4NF, MeOH, THF; (e) CuCl, $Cu(OAc)_2{\cdot}H_2O$, pyridine.



Scheme 4. (a) **12**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, KOH, H_2O; (b) MeI, 120°C; (c) **19**, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, KOH, H_2O; (d) Bu_4NF, MeOH, THF; (e) CuCl, $Cu(OAc)_2{\cdot}H_2O$, pyridine.

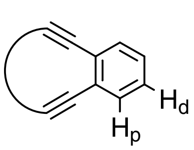
Construction of [20]annulene **7** (Scheme 4) was accomplished using the in situ deprotection/alkynylation reaction in two key steps: in step (a) diyne synthon **12** was attached to **21**, and in step (c) **19** was affixed to **22**. Cyclization of α,ω-polyyne **23** using analogous chemistry gave **7** in good overall yield.

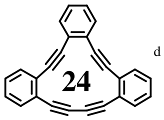
3. Discussion

3.1. Spectroscopic properties

All annulenic structures and intermediates were identified unequivocally by standard spectroscopic techniques. Particularly instructive to the present study were the ^1H NMR spectra of the completed DBAs. Although the nonplanarity of the tetrabenzo derivatives **4** and **9–11** precludes the

Table 2. Chemical shift range for the two different arene proton environments in tribenzo-annelated DBAs and related reference molecules; mean values in parentheses



Compound	H_p	H_d
ODEB[a]	7.49–7.51 (7.50)	7.28–7.30 (7.29)
12[b]	7.44–7.49 (7.47)	7.22–7.32 (7.27)
14[b]	7.45–7.49 (7.47)	7.21–7.25 (7.23)
2[c]	7.32–7.36 (7.34)	7.16–7.20 (7.18)
 **24** [d]	7.58–7.88 (7.73)	7.38–7.46 (7.42)
5[b]	7.32–7.48 (7.40)	7.19–7.30 (7.25)
6[b]	7.66–7.70 (7.68)	7.40–7.44 (7.42)
7[b]	7.44–7.53 (7.49)	7.23–7.38 (7.31)
8[b]	7.56–7.71 (7.64)	7.35–7.43 (7.39)

[a] Ref. 36d.
[b] This work.
[c] Ref. 2b.
[d] Ref. 6.

possibility of induced ring currents in the annulenic core, planar DBAs **5–8**[35] possess either $(4n+2)$ or $(4n)$ π-electron circuits, which suggest that these macrocycles might exhibit aromatic or antiaromatic character. Induced ring currents in dehydrobenzoannulenes has been the topic of considerable debate in the literature over the last 30 years.[1,36] Although fusion of arenes to the annulenic core provides rigidity and stability, this also weakens the diatropicity/paratropicity of the macrocycle significantly. Until now, the number of planar systems available for study was limited; however, with the addition of **5–8**, the series of alkyne-linked, tribenzo-annelated DBAs is complete from [12]- to [22]annulene.[2b,6,25] A qualitative determination of the nature of the ring current in these macrocycles can be made 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.[36d,37] The arene proton environments in *o*-diethynylbenzene (ODEB), **12**, and **14** are used as suitable reference standards[38] because of their structural similarity, yet these simple DBA subunits lack the effects of macrocyclic delocalization as well as lack of the anisotropic effects attributable to dangling alkynes.[39]

As can be seen in Table 2, the DBAs display alternation between diatropic and paratropic character. All three of the $(4n+2)$ Hückel-type π-systems (**24**, **6**, **8**) show small but distinct downfield shifts of their arene protons ($\Delta\delta=0.05$–0.35 ppm), while only two of the $(4n)$ systems (**2**, **5**) show opposite behavior ($\Delta\delta=0.02$–0.12 ppm). Nucleus-independent chemical shift (NICS) calculations for the series **2–6** corroborate these findings.[36d] The mean experimental chemical shifts for **7**, on the other hand, are essentially the same as ODEB, **12**, and **14**, and are virtually unchanged compared to the acyclic precursors. These data suggest that **7** is atropic. Although it is well known that ring currents lessen with increasing macrocycle size and that paratropicity diminishes faster than diatropicity,[1,36a,b] we were surprised that, based on the arene protons, the 20-membered macrocycle seemed to lack a ring current. Efforts to quantify induced ring currents in DBAs are in progress.[40]

Typical of polycyclic aromatic hydrocarbons, the molecular ion peaks in the mass spectra of DBAs **4–11** are also the base peaks. The mass spectra show strong $(M+1)^+$ and $(M+2)^+$ peaks typical of high carbon content compounds. Analogous to other purely hydrocarbon annulenes, molecules **4–11** exhibit essentially no fragmentation. The IR spectra of **4–11** display moderately weak $-C{\equiv}C-$ stretches centered around 2215 cm^{-1}, characteristic of highly symmetrical structures, and are sometimes accompanied by one or more bands around 2150 cm^{-1}.

The UV–Vis spectra of planar DBAs **5–8** (Fig. 1) represent

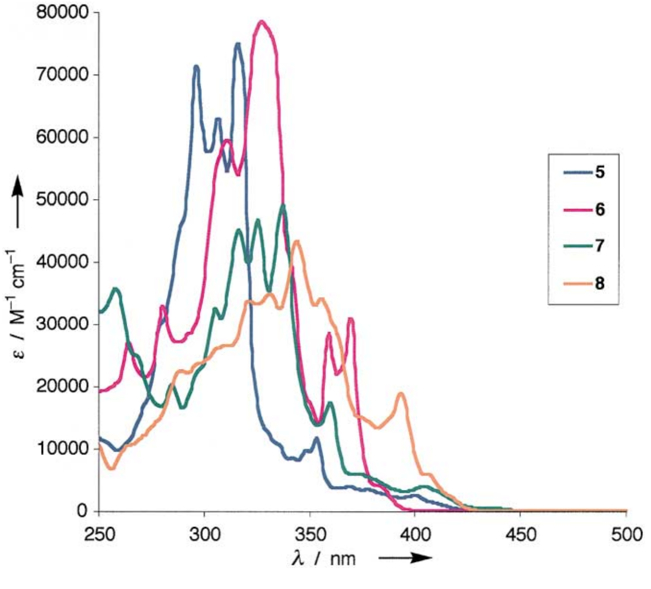


Figure 1. Electronic absorption spectra of planar annulenes **5–8**.

the combination of diphenylacetylene (ca. 280–300 nm), diphenylbutadiyne (ca. 290–330 nm), and/or diphenylhexatriyne (ca. 310–360 nm) chromophores.[41] Indeed, the (4*n*) π-systems (**5** and **7**) resemble an overlay of these respective chromophores. DBAs **5** and **7** also possess two weaker bands (ca. 355 and 400 nm) in the low energy region and end absorption points around 425 nm. The ($4n+2$) π-system **8** shows analogous behavior to **7**, though the peaks are red-shifted ca. 20–40 nm. DBA **6** has a somewhat different spectrum, including two peaks of moderate intensity in the lower energy region (359 and 369 nm). This pattern is typical of the dodecadehydro[18]annulene chromophore.[25] The absorption bands at longer wavelengths of all four DBAs are attributed to the interaction of the ^1L_a-state of the benzene nucleus with the polyacetylenic chromophore.[42] In contrast to **5–8**, the UV–Vis spectra of the nonplanar systems (**4**, **9–11**) are ill-defined, containing two strong, featureless absorptions in the 230–280 nm region, with much weaker peaks and/or shoulders in the 300–350 nm region and end absorptions around 375 nm.

3.2. Solid-state structures

Thermal analysis of DBAs **4–11** showed the molecules to have interesting reactivity. All of the macrocycles underwent an irreversible exothermic reaction (ca. 175–250°C) prior to melting as determined by differential scanning calorimetry (Table 3). [16]Annulene **5** was the notable exception, reacting around 135°C; this was most likely because of ring strain in the constricted annulenic core. The DSC exotherms were relatively sharp ($w^{1/2}\approx 5-10$°C), suggesting the occurrence of well-ordered polymerization of the materials. The resultant black thermoproducts were completely insoluble in common solvents.

In order to gain insight into the nature of the thermal transformation(s), we obtained X-ray crystal structures for DBAs **5**, **9**,[15a] and **10**; the molecular structures of **5** and **10** are shown in Fig. 2. Similar to **9**, nonplanar **10** possesses a distorted saddle shape, with the alkyne moieties showing a deviation from linearity of the order of 1.0–3.6°. This range is slightly greater than the deformation observed in DBA **4** (1–2°)[13] but less than that found in **11** (0.6–6.0°)[14] and **9** (1.5–8.1°).[15a] In contrast, the triple bonds in annulene **5** are more strained, deviating from linearity by the order of 2–12°. The molecule is essentially planar, with a mean deviation less than 0.07 Å. Semi-empirical calculations accurately reproduce the above geometrical observations.[43] Recent results from Vollhardt's group illustrate two possible pathways for dehydrobenzoannulene decomposition. In particular, spectroscopic evidence strongly suggested that highly strained, planar **24** underwent topochemical 1,4-polymerization at 120°C to give a novel polydiacetylene tube structure.[6] Alternately, nonplanar tetrabenzo molecule **4** decomposed explosively at ca. 250°C to give almost purely carbon residue that included a small amount of 'bucky tubes' and 'bucky onions'.[4,13] In contrast, isomeric **9** reacted nonviolently at 50°C lower temperature yet generated 50 kJ mol^{-1} more energy. Although this result can be attributed partly to the greater bending in the alkyne units relative to **4**, the difference in energy is likely attributable to the influence of other factors such as solid-state packing.[44] This factor appears to be of prime importance, especially for all planar DBAs. Similar to **24**[6] and most other planar, purely hydrocarbon DBAs,[7,45] the overall packing in **5** consists of columns of molecules stacked along the *a*-axis (Fig. 3). Unlike **24**, however, the closest diyne contacts do not correspond to those required for a 1,4-polymerization. The diyne polymerization parameters for **5** are $d=3.85$ Å, $\gamma=73°$, and $S_1=3.55$ Å, which are outside the observed range for such monomers ($d\approx 5$ Å, $\gamma\approx 45°$).[46] However, these parameters are close to those suggested for the potential formation of *cis*-polydiacetylene,[47] which may explain why the results obtained to date are conflicting with regards to the absence or presence of a 1,4-polymerization reaction.[48]

Table 3. DSC data for DBAs **4–11**

DBA	T_{onset} (°C)	$T_{\max}$ (°C)	$w^{1/2}$	ΔH_{rxn} (kJ mol^{-1})
4	248	265	11	385
5	135	142	4	282
6	224	232	6	314
7	134	152	12	360
8	139	147	5	420
9	197	211	8	440
10	176	193	9	495
11	177	187	6	482

Data obtained under an N_2 atmosphere.

The varying temperatures and heats of reaction in Table 3 indicate that each annulenic system behaves independently. Based on these numbers and the above results for **5** and **9**, no generalization for accurately predicting decomposition product structure based on annulene topology can be proposed at this time. It is likely that additional pathways for dehydrobenzoannulene decomposition are operational for these macrocycles. It therefore appears that systematic study of the thermoproducts of each new DBA is warranted; this goal is being pursued.

4. Conclusions

In summary, we have developed a simple and efficient method for the synthesis of novel α,ω-polyynes, which in turn can be intramolecularly cyclized to furnish dehydrobenzoannulenes. Compared with the more commonly used one-pot cyclooligomerization approach, our method provides vital reaction efficiency, product purity, ease of product separation, and complete control over DBA topology. With this synthetic advance, we were able to prepare previously inaccessible DBA structures, including the first examples of triyne-linked DBAs. ^{1}H NMR spectra of the planar annulenes showed that these large macrocycles possess very weak but discernible induced ring currents. DSC analysis revealed that annulene polymerization was a highly exothermic process; however, elucidation of thermoproduct structure(s) has been elusive. We are continuing to investigate the thermal and spectral properties of these and other DBAs; the results of these studies will be presented in due course.

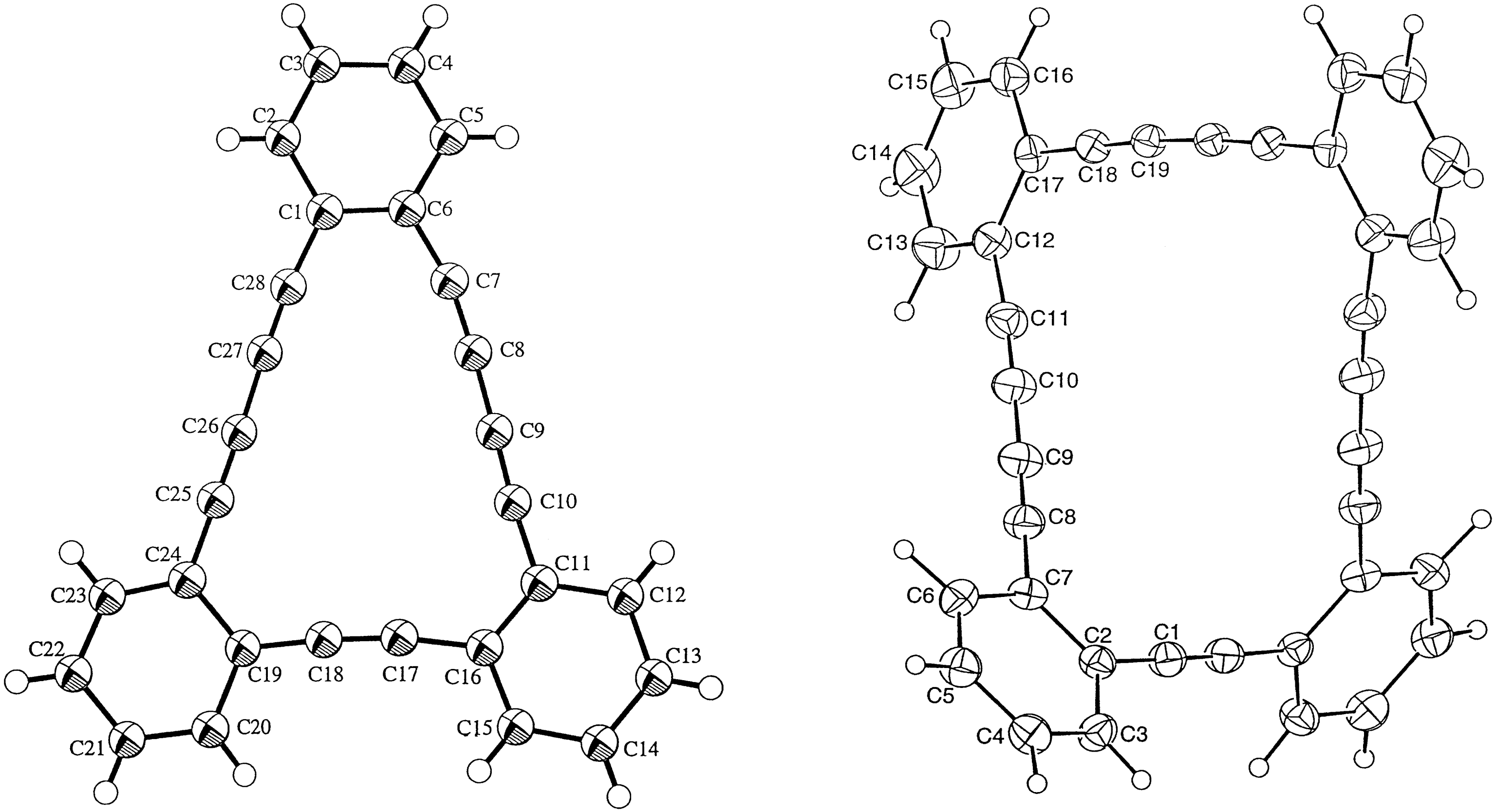


Figure 2. Molecular structures of DBAs **5** (left) and **10** (right).

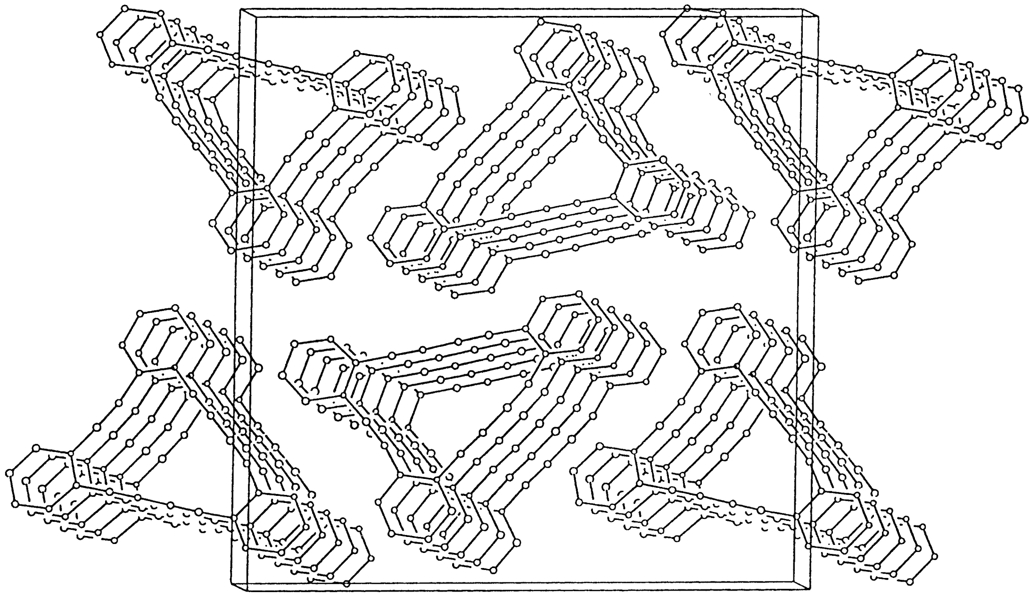


Figure 3. Packing of annulene **5**.

5. Experimental

5.1. General

^1H and ^{13}C NMR spectra were recorded in chloroform-d (unless otherwise specified) using a Varian Inova 300 NMR (^1H: 299.94 MHz; ^{13}C: 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual solvent as internal standard (chloroform-d, ^1H: 7.27 ppm; ^{13}C: 77.0 ppm; dichloromethane-d$_2$, ^1H: 5.32 ppm; ^{13}C: 54.0 ppm). Coupling constants are expressed in Hz. IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. UV–Vis spectra were recorded using a Hewlett Packard 8453 UV–Vis spectrophotometer in CH_2Cl_2. MS spectra were recorded using a Kratos MS50 spectrometer. DSC analyses were performed using a TA Instruments DSC 2920 Modulated DSC. Elemental analyses were performed by Robertson Microlit Laboratories. CH_2Cl_2, Et_3N, and pyridine were distilled from CaH_2 under an N_2 atmosphere prior to use. THF was distilled from Na and benzophenone under an N_2 atmosphere prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Column chromatography was performed on Whatman reagent grade silica gel (230–400 mesh). Rotary chromatography was performed on a Chromatotron using silica gel (60 PF_{254}) plates (1–4 mm). Baker pre-coated silica gel plates were used for analytical (200×50×0.25 mm) thin layer chromatography. Reactions were carried out in an inert atmosphere (dry nitrogen or argon) when necessary.

5.2. General acetylene coupling procedure A

A round bottom flask (for iodine cross-coupling reactions) or a sealable pressure reactor (for bromine cross-coupling reactions) was charged with haloarene (1 equiv.), $PdCl_2(PPh_3)_2$ (0.03 equiv.), CuI (0.06 equiv.), and Et_3N (0.1 M). After bubbling with N_2 for 30 min, the silyl-protected terminal acetylene (1.1–1.3 equiv.) was added by syringe under an N_2 atmosphere. The reaction mixture was stirred at 50°C (for I) or 120°C (for Br) for 2–24 h and was monitored by TLC. Upon completion, the reaction mixture was cooled and concentrated in vacuo. The dark residue was redissolved in CH_2Cl_2 and filtered through a thin cake of silica gel using CH_2Cl_2. The solution was concentrated then chromatographed on silica gel.

5.3. General in situ protiodesilylation/alkynylation procedure B

Iodoarene (1 equiv.) was dissolved in an H_2O/THF/Et_3N (0.01:1:5) solution charged with $PdCl_2(PPh_3)_2$ (0.03 equiv.), CuI (0.06 equiv.), and KOH (10 equiv. per silyl group). In a separate vessel, (trimethylsilylbutadiynyl)-arene (1.1–1.2 equiv.) was dissolved in Et_3N (1 M solution). Both solutions were degassed vigorously by either bubbling of N_2 or by three freeze–pump–thaw cycles. The silylacetylene solution was added via syringe pump to the iodoarene solution over 12–24 h under nitrogen atmosphere at 50°C. Upon completion, the mixture was concentrated in vacuo and redissolved in CH_2Cl_2. The dark residue was filtered through a thin cake of silica gel using CH_2Cl_2, concentrated, and then chromatographed on silica gel.

5.4. General macrocyclization procedure C

A 0.01 M solution of the bis(silyl)-protected α,ω-polyyne in THF/MeOH (10:1 v:v) was treated with Bu_4NF (2.5 equiv. of a 1 M THF solution) at room temperature. The reaction was monitored by TLC and was typically complete within 30 min. The reaction mixture was diluted with Et_2O, washed three times with water, twice with brine, and dried ($MgSO_4$). The solution was concentrated in vacuo and the resultant oil was redissolved in pyridine (ca. 10 mL). The pyridine solution was slowly added via syringe pump to a round bottom flask charged with 25 equiv. $Cu(OAc)_2$, 20 equiv. CuCl, and pyridine (0.005 M solution based on α,ω-polyyne) at 60°C.

The addition was done under house air over 10–20 h. Upon completion of the reaction, the mixture was concentrated in vacuo and then redissolved in CH_2Cl_2. The mixture was filtered through a thin cake of silica gel using CH_2Cl_2, concentrated, and chromatographed on silica gel.

5.5. General triazene decomposition procedure D

A 0.3 M solution of the diethyltriazene substrate in distilled iodomethane was stirred under argon at 120°C for 6–18 h in a sealable pressure reactor. Upon being cooled, the reaction mixture was diluted with hexanes, filtered, and concentrated in vacuo. The crude product was then purified by flash chromatography over silica gel.

5.5.1. 1-(Trimethylsilyl)-1,3-butadiyne. Prepared in 8–10 g amounts by the method of Brandsma.[18]

Warning. The procedure involves use of butadiyne gas, which is highly explosive. It is important not to store the ether solution of dissolved gas overnight, but rather to continue until distillation of pure (trimethylsilyl)butadiyne is complete. ^{1}H NMR δ 2.11 (s, 1H), 0.21 (s, 9H).

5.5.2. 1-(Triisopropylsilylethynyl)-2-(4-trimethylsilyl-1,3-butadiynyl)benzene (12). 1-Bromo-2-iodobenzene (5.66 g, 20 mmol) was reacted with trimethylsilylbutadiyne (3.06 g, 25 mmol) using acetylene coupling procedure A. Chromatography on silica gel (hexanes) yielded 1-bromo-2-(4-trimethylsilyl-1,3-butadiynyl)benzene (5.16 g, 93% yield) as a pale yellow oil. ^{1}H NMR δ 7.57 (dd, J=7.8, 1.5 Hz, 1H), 7.51 (dd, J=7.5, 2.0 Hz, 1H), 7.30–7.17 (m, 2H), 0.24 (s, 9H); ^{13}C NMR δ 134.63, 132.52, 130.29, 127.05, 126.27, 123.86, 92.45, 87.47, 78.28, 74.68, −0.45.

The above arene (3.33 g, 12 mmol) was reacted with triisopropylsilylethyne (2.74 g, 15 mmol) using acetylene coupling procedure A. Chromatography on silica gel (hexanes) yielded **12** (3.86 g, 85% yield) as a pale yellow oil. ^{1}H NMR δ 7.49–7.44 (m, 2H), 7.32–7.22 (m, 2H), 1.17 (s, 21H), 0.23 (s, 9H); ^{13}C NMR δ 132.62, 132.22, 128.71, 127.89, 127.62, 124.51, 104.43, 96.08, 91.44, 88.03, 77.98, 75.22, 18.69, 11.31, −0.42; IR (CH_2Cl_2) ν 3064, 2210, 2159, 2102 cm^{-1}; MS (EI, 70 eV) *m/z* 378 (12, M^+), 335 (27, $M^+-C_3H_7$), 73 (100).

5.5.3. 1-(Triisopropylsilylethynyl)-2-(trimethylsilylethynyl)benzene (14). 2-Bromo-1-(trimethylsilylethynyl)benzene[49] (3.04 g, 12 mmol) was reacted with triisopropylsilylethyne (2.74 g, 15 mmol) using acetylene coupling procedure A, substituting 1:1 Et_3N/piperidine as solvent. Chromatography on silica gel (hexanes) yielded **14** (3.49 g, 82% yield) as a pale yellow oil. ^{1}H NMR δ 7.49–7.45 (*AA*′m, 2H), 7.25–7.21 (*BB*′m, 2H), 1.16 (s, 21H), 0.25 (s, 9H); ^{13}C NMR δ 132.88, 132.84, 127.96, 127.81, 125.82, 125.50, 105.20, 103.39, 98.14, 94.84, 18.78, 11.27, −0.06; IR (KBr) ν 3062, 2866, 2158, 1475 cm^{-1}; MS (EI, 70 eV) 354 (M^+, 20), 311 (57, $M^+-C_3H_7$), 269 (100), 227 (58), 73 (91).

5.5.4. 1-(2-Iodophenylethynyl)-2-(triisopropylsilylethynyl)benzene (13). Arene **14** (2.84 g, 8.0 mmol) and anhydrous K_2CO_3 (553 mg, 4.0 mmol) were dissolved in MeOH (20 mL) and Et_2O (5 mL) and the solution was vigorously stirred for 2 h. Upon completion, the mixture was diluted with water (50 mL) and extracted into additional Et_2O (50 mL). 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%) in sufficiently pure form for further elaboration. ^{1}H NMR δ 7.51–7.46 (m, 2H), 7.32–7.22 (m, 2H), 3.26 (s, 1H), 1.15 (s, 21H); ^{13}C NMR δ 132.42, 128.30, 127.89, 126.68, 124.94, 104.79, 95.28, 82.26, 81.03, 18.69, 11.30.

The above acetylene (2.25 g, 8.0 mmol) was reacted with *N*,*N*-diethyl-*N*′-(2-iodophenyl)triazene[19] (2.12 g, 7.0 mmol) using acetylene coupling procedure A. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) yielded cross-coupled product (2.75 g, 86% yield) as an orange oil. ^{1}H NMR δ 7.57–7.47 (m, 3H), 7.43 (dd, J=8.0, 1.1 Hz, 1H), 7.31–7.19 (m, 3H), 7.07 (dt, J=7.5, 1.1 Hz, 1H), 3.81 (q, J=7.1 Hz, 4H), 1.31 (br t, J=7.1 Hz, 6H), 1.13 (s, 21H); ^{13}C NMR δ 152.35, 133.02, 132.78, 131.91, 128.89, 127.83, 127.26, 126.70, 125.55, 124.41, 118.21, 116.77, 105.56, 94.72, 92.17, 92.02, 18.70, 11.34.

The resultant diaryltriazene (2.51 g, 5.5 mmol) in iodomethane (18 mL) was subjected to triazene decomposition procedure D. Chromatography on silica gel (hexanes) yielded **13** (2.32 g, 87% yield) as a viscous orange oil. ^{1}H NMR δ 7.88 (dd, J=8.1, 1.2 Hz, 1H), 7.66–7.62 (m, 1H), 7.55–7.51 (m, 2H), 7.35–7.27 (m, 3H), 7.02 (dt, J=7.8, 1.6 Hz, 1H), 1.13 (s, 21H); ^{13}C NMR δ 138.64, 132.80, 132.62, 132.32, 129.81, 129.39, 128.16, 128.01, 127.57, 125.69, 125.47, 105.20, 101.13, 95.24, 95.05, 91.81, 18.70, 11.31; IR (CH_2Cl_2) ν 3056, 2160 cm^{-1}; MS (EI, 70 eV) *m/z* 484 (5, M^+), 441 (100, $M^+-C_3H_7$).

5.5.5. Bis-protected polyyne 15. Iodoarene **13** (242 mg, 0.50 mmol) was reacted with triyne **12** (227 mg, 0.60 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) yielded **15** (278 mg, 84% yield) as a dark orange gum. ^{1}H NMR δ 7.72–7.67 (m, 1H), 7.60–7.48 (m, 5H), 7.38–7.25 (m, 6H), 1.17 (s, 42H); ^{13}C NMR δ 132.82 (2), 132.70, 132.63, 132.34, 131.98, 128.63, 128.56, 128.04 (2), 127.96, 127.93, 127.18, 126.92, 125.73, 125.70, 124.85, 124.76, 105.34, 104.54, 96.11, 95.05, 93. 02, 91.32, 81.27, 81.15, 78.06, 77.94, 18.70, 18.67, 11.35, 11.29; MS (EI, 70 eV) *m/z* 662 (4, M^+), 619 (8, $M^+-C_3H_7$), 619 (19, $M^+-C_6H_{13}$), 73 (65), 59 (100).

5.5.6. Dehydrobenzo[16]annulene 5. α,ω-Polyyne **15** (100 mg, 0.15 mmol) was subjected to macrocyclization reaction procedure C. Chromatography on silica gel (3:1 hexanes/CH_2Cl_2) yielded DBA **5** (36 mg, 69% yield) as a bright yellow solid. ^{1}H NMR δ 7.49–7.44 (m, 2H), 7.42–7.37 (m, 2H), 7.35–7.31 (m, 2H), 7.31–7.19 (m, 6H); ^{13}C NMR δ 134.49, 133.67, 130.45, 129.07, 129.01, 128.48, 128.14, 126.93, 123.20, 93.00, 82.17, 81.59, 80.83, 77.67; IR (CH_2Cl_2) ν 3056, 3024, 2215, 2146 cm^{-1}; MS (EI, 70 eV) *m/z* 349 (36), 348 (100, M^+), 347 (19), 346 (40); UV (CH_2Cl_2) λ_{max} (ϵ) 239 (12,100), 297 (34,900), 307 (31,400), 316 (41,400), 353 (6900), 395 sh (1600) nm; Anal. Calcd for $C_{28}H_{12}$: C, 96.53; H, 3.47. Found: C, 96.46; H, 3.53.

5.5.7. Dehydrobenzo[20]annulene 4. The required butadiyne synthon was prepared from iodoarene **13** (969 mg, 2.0 mmol) and trimethylsilylbutadiyne (294 mg, 2.4 mmol) using acetylene coupling procedure A. Chromatography on silica gel (hexanes) yielded the correct product (814 mg, 85% yield) as a yellow oil. ^{1}H NMR δ 7.67–7.64 (m, 1H), 7.55–7.49 (m, 3H), 7.35–7.24 (m, 4H), 1.14 (s, 21H), 0.24 (s, 9H); ^{13}C NMR δ 132.84 (2), 132.68, 131.79, 128.73, 128.09, 127.94, 127.92, 127.34, 125.68 (2), 124.26, 105.24, 95.15, 93.09, 91.76, 91.24, 87.98, 78.07, 75.41, 18.72, 11.34, −0.37.

Iodoarene **13** (242 mg, 0.50 mmol) was reacted with the above synthon (287 mg, 0.60 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded the bis-protected polyyne (293 mg, 77% yield) as an orange gum. ^{1}H NMR δ 7.65–7.61 (m, 2H), 7.60–7.55 (m, 4H), 7.50–7.46 (m, 2H), 7.38–7.28 (m, 4H), 7.24–7.19 (m, 4H), 1.18 (s, 42H); ^{13}C NMR δ 132.87, 132.72, 132.56, 131.80, 128.65, 128.12, 127.98, 127.94, 127.13, 125.50, 125.45, 124.69, 105.39, 94.93, 93.28, 91.28, 81.38, 77.99, 18.73, 11.35.

α,ω-Polyyne (100 mg, 0.131 mmol) was subjected to macrocyclization reaction procedure C. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded DBA **4** (32 mg, 55% yield) as a yellow–orange solid. ^{1}H NMR δ 7.56–7.54 (m, 4H), 7.54–7.52 (m, 4H), 7.37–7.24 (m, 8H); ^{13}C NMR δ 133.91, 131.64, 128.68, 128.21, 126.42, 125.02, 91.58, 80.99, 78.10; IR (KCl) ν 3053, 2213, 2173 cm^{-1}; MS (70 eV) *m/z* 448 (M$^+$, 100); UV (CH$_2$Cl$_2$): $\lambda_{\max}$ (ϵ) 235 sh (32,300), 258 (57,400), 271 (59,300), 326 sh (17,900) nm; Anal. Calcd for C$_{36}$H$_{16}$: C, 96.40; H, 3.60. Found: C, 96.25; H, 3.55.

5.5.8. Dehydrobenzo[20]annulene 9. The requisite iodoarene coupling partner was prepared as follows: compound **13** (1.55 g, 3.2 mmol) was reacted with *N*,*N*-diethyl-*N′*-(2-ethynylphenyl)triazene[19] (705 mg, 3.5 mmol) using acetylene coupling procedure A. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded cross-coupled product (1.21 g, 69% yield) as a viscous orange oil. ^{1}H NMR δ 7.56–7.49 (m, 4H), 7.41 (d, J=8.1 Hz, 1H), 7.30–7.17 (m, 6H), 7.03 (t, J=7.5 Hz, 1H), 3.74 (q, J=6.9 Hz, 4H), 1.26 (t, J=6.9 Hz, 6H), 1.12 (s, 21H); ^{13}C NMR δ 152.35, 133.10, 132.63, 131.79, 131.56, 128.97, 127.92, 127.86, 127.74, 127.25, 126.86, 125.99, 125.59, 125.46, 124.56, 118.13, 116.93, 105.36, 94.91, 92.58, 92.32, 92.24, 92.08, 49.40, 41.94, 18.69, 11.31.

The resultant triaryltriazene (1.11 g, 2.0 mmol) in iodomethane (10 mL) was subjected to triazene decomposition procedure D. Chromatography on silica gel (5:1 hexanes/CH$_2$Cl$_2$) yielded the iodoarene coupling partner (1.07 g, 92% yield) as a pale orange oil. ^{1}H NMR δ 7.85 (d, J=8.1 Hz, 1H), 7.66–7.51 (m, 4H), 7.34–7.26 (m, 6H), 7.00 (t, J=7.7 Hz, 1H), 1.09 (s, 21H); ^{13}C NMR δ 138.71, 132.92, 132.74, 132.40, 132.14, 129.93, 129.40, 128.12, 128.06, 128.00, 127.99, 127.72, 125.99, 125.89, 125.73, 125.51, 105.30, 100.73, 95.30, 92.42, 91.94, 91.92, 18.73, 11.35.

The above iodoarene (584 mg, 1.0 mmol) was reacted with synthon **12** (454 mg, 1.2 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded the bis-protected polyyne (580 mg, 76% yield) as a dark orange gum. ^{1}H NMR δ 7.69–7.65 (m, 1H), 7.64–7.60 (m, 1H), 7.57–7.46 (m, 6H), 7.32–7.23 (m, 8H), 1.13 (s, 21H), 1.10 (s, 21H); ^{13}C NMR δ 132.86, 132.71, 132.48, 132.30, 131.90, 128.72, 128.60, 128.05, 127.97, 127.89, 127.17, 126.93, 125.89, 125.77, 125.73, 125.69, 124.85, 124.35, 105.34, 104.55, 96.08, 95.09, 93.05, 92.42, 91.89, 91.74, 81.31, 81.04, 78.11, 77.90, 18.69, 11.33, 11.30.

α,ω-Polyyne (100 mg, 0.131 mmol) was subjected to macrocyclization reaction procedure C. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded DBA **9** (36 mg, 61% yield) as a tan solid. ^{1}H NMR δ 7.64–7.59 (m, 2H), 7.57–7.52 (m, 4H), 7.51–7.46 (m, 2H), 7.40–7.28 (m, 8H); ^{13}C NMR δ 133.53, 133.39, 132.84, 132.06, 129.62, 129.58, 128.98, 128.87, 127.38, 126.97, 125.27, 124.47, 92.00, 90.78, 81.75, 80.88, 78.99, 77.45; IR (KCl) ν 3064, 2217 cm^{-1}; MS (EI, 70 eV) *m/z* 448 (M$^+$, 85); UV (CH$_2$Cl$_2$): $\lambda_{\max}$ (ϵ) 232 (239,000), 249 sh (205,000), 280 sh (70,500), 314 (55,000), 355 sh (15,000) nm; Anal. Calcd for C$_{36}$H$_{16}$: C, 96.40; H, 3.60. Found: C, 96.17; H, 3.63.

5.5.9. Dehydrobenzo[22]annulene 10. Bis(2-iodophenyl)-ethyne[26] (323 mg, 0.75 mmol) was reacted with triyne **12** (663 mg, 1.75 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH$_2$Cl$_2$) yielded the bis-protected polyyne (354 mg, 60% yield) as a dark orange gum. ^{1}H NMR δ 7.67–7.64 (m, 2H), 7.55–7.47 (m, 6H), 7.37–7.22 (m, 8H), 1.14 (s, 42H); ^{13}C NMR δ 132.82, 132.75, 132.63, 132.31, 128.81, 128.60, 128.16, 127.92, 127.21, 126.69, 124.90, 124.47, 104.54, 96.12, 92.32, 81.37, 81.02, 78.15, 77.98, 18.67, 11.30.

α,ω-Polyyne (100 mg, 0.127 mmol) was subjected to macrocyclization reaction procedure C. Chromatography on silica gel (3:1 hexanes/CH$_2$Cl$_2$) yielded DBA **10** (35 mg, 59% yield) as a cream-colored solid. ^{1}H NMR δ 7.62–7.56 (m, 4H), 7.55–7.49 (m, 4H), 7.44–7.32 (m, 8H); ^{13}C NMR δ 134.09, 133.35, 132.80, 132.76, 129.73, 129.70, 129.62, 129.13, 126.60 (2), 125.86, 124.72, 91.76, 81.55, 81.51, 80.60, 78.32, 78.25, 77.48; IR (CH$_2$Cl$_2$) ν 3062, 3022, 2215 cm^{-1}; MS (EI, 70 eV) *m/z* 472 (100, M$^+$); UV (CH$_2$Cl$_2$) $\lambda_{\max}$ (ϵ) 240 (123,000), 270 (103,000), 295 (25,000), 330 (28,200), 350 sh (10,300) nm; Anal. Calcd for C$_{38}$H$_{16}$: C, 96.59; H, 3.41. Found: C, 96.28; H, 3.46.

5.5.10. Dehydrobenzo[24]annulene 11. Bis(2-iodophenyl)-butadiyne[14] (301 mg, 0.70 mmol) was reacted with triyne **12** (606 mg, 1.6 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH$_2$Cl$_2$) yielded the bis-protected polyyne (386 mg, 68% yield) as an orange gum. ^{1}H NMR δ 7.60–7.45 (m, 8H), 7.36–7.20 (m, 8H), 1.17 (s, 42H); ^{13}C NMR δ 133.43, 133.31, 132.79, 132.23, 128.84, 128.69 (2), 127.92, 127.17, 125.41, 125.07, 124.73, 104.54, 96.16, 81.83, 80.97, 80.30, 78.48, 78.26, 77.79, 18.70, 11.33.

α,ω-Polyyne (100 mg, 0.123 mmol) was subjected to macrocyclization reaction procedure C. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) yielded DBA **11** (39 mg, 63% yield) as a beige solid. ^{1}H NMR δ 7.58 (AA'm, 8H), 7.38 (BB'm, 8H); ^{13}C NMR δ 134.01, 129.75, 125.51, 81.25, 78.08; IR (CH_2Cl_2) ν 3059, 3025, 2210 cm^{-1}; MS (EI, 70 eV) *m/z* 496 (100, M^+); UV (CH_2Cl_2) λ_{max} (ϵ) 241 (96,300), 259 (86,200), 292 (26,600), 328 (30,800), 352 sh (15,000) nm; Anal. Calcd for $C_{40}H_{16}$: C, 96.75; H, 3.25. Found: C, 96.36; H, 3.31.

5.5.11. 1-[4-(2-Phenylphenyl)-1,3-butadiynyl]-2-(triisopropylsilylethynyl)benzene (18). 2,2′-Diiodobiphenyl[29] (162 mg, 0.40 mmol) was reacted with triyne **12** (379 mg, 1.0 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (5:1 hexanes/CH_2Cl_2) yielded none of the bis-protected polyyne **17**; instead, compound **18** (386 mg, 60% yield) was isolated as a yellow oil. ^{1}H NMR δ 7.66–7.58 (m, 2H), 7.48–7.40 (m, 6H), 7.39–7.23 (m, 5H), 1.14 (s, 21H); ^{13}C NMR δ 144.84, 139.96, 134.46, 132.66, 132.31, 129.68, 129.29, 129.05, 128.52, 128.17, 127.90, 127.77, 127.70, 127.04, 124.89, 120.28, 104.60, 95.95, 82.00, 80.39, 77.92, 76.77, 18.66, 11.26.

5.5.12. 2-(Triisopropylsilylethynyl)-1-(6-trimethylsilyl-1,3,5-hexatriynyl)benzene (19). Arene **14** (710 mg, 2.0 mmol) was deprotected with anhydrous K_2CO_3 (138 mg, 1.0 mmol) as described above. The resultant terminal acetylene (565 mg, ca. 100%) was used without purification.

The deprotected alkyne was placed in a three-neck flask and diluted with dry THF (30 mL). Dry CuBr (717 mg, 5.0 mmol) was placed in a solid addition arm. The entire system was degassed via four freeze–pump–thaw cycles and placed under an N_2 atmosphere. The stirred solution was cooled to −78°C and BuLi (0.8 mL, 2.5 M, 2.25 mmol) was added dropwise. After stirring for 20 min at −78°C, the flask was placed in an ice bath and the pale yellow solution was allowed to warm to 0°C. The CuBr was added and the mixture stirred for 15 min at 0°C. The bath was removed and the reaction warmed to rt. During this period the mixture turned a bright yellow–orange. After 20 min, $Me_3SiC{\equiv}CC{\equiv}CBr$[32] (443 mg, 2.2 mmol) was added rapidly and the dark orange reaction stirred at rt for 2 h. After setting overnight in the freezer, the mixture was filtered through Celite and then diluted with Et_2O. The filtrate was washed once with saturated NaCl solution and three times with water. The aqueous washes were back extracted twice with Et_2O. The combined organic layers were dried ($MgSO_4$) and concentrated. Chromatography on silica gel (hexanes) yielded **19** (524 mg, 62% yield) as a red–orange oil. ^{1}H NMR δ 7.43–7.52 (m, 2H), 7.20–7.38 (m, 2H), 1.18 (s, 21H), 0.25 (s, 9H); ^{13}C NMR δ 133.27, 132.40, 129.14, 127.96, 127.86, 123.83, 104.27, 96.51, 89.18, 88.11, 77.91, 75.54, 67.77, 61.68, 18.64, 11.31, −0.52; IR (CH_2Cl_2) ν 2939, 2866, 2183, 2156, 1607 cm^{-1}; MS (EI, 70 eV) *m/z* 402 (2, M^+), 338 (21), 295 (52), 269 (45), 239 (100); UV (CH_2Cl_2) λ_{max} (ϵ) 249 (101,300), 264 (41,100), 280 (36,100), 290 (12,600), 308 (19,900), 329 (26,300), 352 (21,200) nm.

5.5.13. Bis-protected polyyne 20. 1,2-Diiodobenzene (132 mg, 0.40 mmol) was reacted with tetrayne **19** (403 mg, 1.0 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) yielded **20** (132 mg, 56% yield) as a dark orange gum. ^{1}H NMR δ 7.56–7.47 (m, 6H), 7.36–7.23 (m, 6H), 1.17 (s, 42H); ^{13}C NMR δ 133.51, 133.07, 132.39, 129.16 (2), 127.96, 127.92, 125.35, 123.92, 104.19, 96.71, 78.75, 78.07 (2), 76.31, 68.31, 67.15, 18.66, 11.31; IR (CH_2Cl_2) ν 3062, 2249, 2196, 2163, 2156 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ) 252 (56,300), 284 (25,100), 300 (21,300), 347 (12,800), 364 (12,100), 394 (11,000) nm.

5.5.14. Dehydrobenzo[22]annulene 8. α,ω-Polyyne **20** (100 mg, 0.14 mmol) was subjected to macrocyclization reaction procedure C. Purification using a Chromatotron (2 mm plate, hexanes) yielded DBA **8** (31 mg, 55% yield) as a yellow–brown solid. ^{1}H NMR δ 7.70–7.66 (m, 2H), 7.64–7.61 (m, 2H), 7.59–7.55 (AA'm, 2H), 7.45–7.36 (m, 6H); ^{13}C NMR δ 133.87, 133.33, 131.48, 129.15, 129.09, 128.78, 125.77, 124.98, 122.75, 80.70, 78.55, 77.49, 77.40, 76.61, 76.53, 67.42, 66.94; IR (CH_2Cl_2) ν 2187, 2162 cm^{-1}; MS (EI, 70 eV) *m/z* 421 (40), 420 (100, M^+); UV (CH_2Cl_2) λ_{max} (ϵ) 311 sh (26,500), 321 (32,900), 331 (33,300), 344 (45,100), 356 (34,200), 393 (18,900), 406 (6000) nm.

5.5.15. *N,N*-Tetramethylene-*N′*-(2-iodophenyl)triazene (21). 2-Iodoaniline (2.74 g, 20 mmol) was dissolved in concentrated HCl (5.6 mL) and H_2O (10 mL), then cooled to 0°C. An ice-cold solution of $NaNO_2$ (1.52 g, 22 mmol) in H_2O (4.0 mL) was added dropwise to the mixture. After stirring at 0°C for 30 min, the brown reaction mixture was poured into a solution of pyrrolidine (2.20 g, 31 mmol) and K_2CO_3 (5.11 g, 37 mmol) in H_2O (25 mL) and stirred for 30 min. The mixture was filtered and the solid was washed with H_2O (20 mL) and Et_2O (20 mL). Recrystallization of the brown solid from EtOH gave **21** (4.87 g, 81%) as yellow needles. Mp 52–53°C; ^{1}H NMR δ 7.84 (dd, J=7.8 Hz, 1.2, 1H), 7.36 (dd, J=8.2, 1.4 Hz, 1H), 7.26 (dt, J=8.2, 1.2 Hz, 1H), 6.83 (dt, J=7.8, 1.4 Hz, 1H), 3.94 (br s, 2H), 3.75 (br s, 2H), 2.05 (br s, 4H); ^{13}C NMR δ 150.47, 139.03, 128.68, 126.49, 117.45, 96.30, 50.96, 47.10, 24.01; IR (CH_2Cl_2) ν 3052, 2979, 2873, 1408, 1268 cm^{-1}; MS (EI, 70 eV) *m/z* 301 (34, M^+), 231 (50), 203 (100).

5.5.16. 1-[4-(2-Iodophenyl)-1,3-butadiynyl]-2-(triisopropylsilylethynyl)benzene (22). Iodotriazene **21** (1.05 g, 3.5 mmol) was reacted with triyne **12** (1.51 g, 4.0 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) yielded the alkynyltriazene (1.39 g, 87% yield) as a light orange oil which slowly solidified upon standing. ^{1}H NMR δ 7.53–7.46 (m, 3H), 7.42 (dd, J=8.1, 1.2 Hz, 1H), 7.32–7.22 (m, 3H), 7.07 (dt, J=7.8, 1.2 Hz, 1H), 3.94 (br s, 2H), 3.76 (br s, 2H), 2.04 (br s, 4H), 1.17 (s, 21H); ^{13}C NMR δ 154.02, 133.95, 132.66, 132.34, 129.71, 128.28, 127.88, 126.98, 125.34, 124.62, 117.19, 116.51, 104.75, 95.83, 81.47, 80.13, 78.60, 77.80, 23.89, 18.71, 11.31.

The resultant triazene (1.32 g, 2.9 mmol) in iodomethane

(10 mL) was subjected to triazene decomposition procedure D. Chromatography on silica gel (5:1 hexanes/CH_2Cl_2) yielded **22** (1.47 g, 94% yield) as a dark orange oil. ^{1}H NMR δ 7.84 (dd, J=7.8, 1.2 Hz, 1H), 7.56–7.48 (m, 3H), 7.36–7.24 (m, 3H), 7.05 (dt, J=7.8, 1.5 Hz, 1H), 1.19 (s, 21H); ^{13}C NMR δ 138.81, 133.89, 132.74, 132.35, 130.08, 128.79, 127.96, 127.80, 127.18, 124.61, 104.51, 100.62, 99.94, 96.19, 83.54, 81.78, 77.59, 18.75, 11.30; IR (CH_2Cl_2) ν 3060, 2941, 2864, 2216, 2158 cm^{-1}; MS (EI, 70 eV) *m/z* 509 (26, M^++1), 508 (14, M^+), 465 (55, $M^+-C_3H_7$).

5.5.17. Bis-protected polyyne 23. Iodoarene **22** (508 mg, 1.0 mmol) was reacted with tetrayne **19** (481 mg, 1.2 mmol) using in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (4:1 hexanes/CH_2Cl_2) followed by preparative TLC (hexanes) yielded **23** (241 mg, 34% yield) as a brown oil. ^{1}H NMR δ 7.53–7.43 (m, 6H), 7.34–7.17 (m, 6H), 1.14 (s, 21H), 1.11 (s, 21H); ^{13}C NMR δ 133.63, 133.27, 133.09, 132.78, 132.39, 132.32, 129.19, 129.13, 128.77, 128.72, 127.96, 127.92, 127.89. 127.34, 126.10, 124.71, 124.50, 123.98, 104.50, 104.23, 96.66, 96.28, 81.97, 79.96, 78.63, 78.50, 78.12, 77.96, 77.60, 76.68, 68.13, 67.41, 18.73, 18.65, 11.35, 11.29; IR (CH_2Cl_2) ν 3061, 2943, 2891, 2214, 2158 cm^{-1}; MS (EI, 70 eV) *m/z* 667 (10, $M^+-C_3H_7$), 624 (20, $M^+-2(C_3H_7)$), 581 (40, $M^+-3(C_3H_7)$), 538 (47, $M^+-4(C_3H_7)$), 495 (49, $M^+-5(C_3H_7)$); UV (CH_2Cl_2) λ_{max} (ϵ) 242 (68,300), 300 sh (21,400), 309 (23,000), 331 (21,500), 355 (15,900) nm.

5.5.18. Dehydrobenzo[20]annulene 7. α,ω-Polyyne **23** (100 mg, 0.14 mmol) was subjected to macrocyclization reaction procedure C. Purification using a Chromatotron (2 mm plate, hexanes) yielded DBA **7** (35 mg, 63% yield) as a yellow solid. ^{1}H NMR δ 7.54–7.45 (m, 4H), 7.38–7.23 (m, 8H); ^{13}C NMR (CD_2Cl_2) δ 135.06, 133.18, 131.40, 129.44, 129.07, 129.01, 128.02, 124.75, 124.33, 81.55, 81.07, 79.26, 78.74, 78.56, 78.32, 68.85. IR (CH_2Cl_2) ν 3061, 2212, 2156 cm^{-1}; MS (EI, 70 eV) *m/z* 397 (35), 396 (100, M^+); UV (CH_2Cl_2) λ_{max} (ϵ) 258 (33,900), 285 (19,300), 305 (30,800), 316 (42,800), 325 (44,300), 337 (46,500), 360 (16,400), 405 (3900) nm.

5.6. X-Ray crystal structures

Data were obtained on either a Siemens SMART diffractometer (**5**) or an Enraf–Nonius CAD-4 Turbo diffractometer (**10**). Structure refinement (C atoms anisotropic, H atoms riding) was accomplished with teXsan. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 161521 and 161522.

5.6.1. DBA 5. $C_{28}H_{12}$, M_r=348.41, yellow needle, 0.20×0.05×0.04 mm, monoclinic, space group $P2_1/c$, a=3.8508 (2), b=21.5422 (3), c=21.4937 (8) Å, β=91.860 (2)°, V=1782.06 (9) Å^3, Z=4, ρ_{calc}=1.298 g cm^{-3}, MoKα radiation (λ=0.71069 Å), μ=0.74 cm^{-1}, F(000)=720, T=−114°C, $2\theta_{max}$=45°, 2657 independent reflections scanned, 548 reflections in refinement ($I\geq3\sigma(I)$), 113 parameters, R=0.085, R_w=0.089.

5.6.2. DBA 10. $C_{38}H_{16}\cdot CH_2Cl_2$, M_r=557.47, pale yellow tablet, 0.11×0.39×0.41 mm, monoclinic, space group $P2/n$, a=10.9543 (8), b=10.8855 (9), c=12.8149 (11) Å, β=103.354 (7)°, V=1486.8 (4) Å^3, Z=2, ρ_{calc}=1.245 g cm^{-3}, MoKα radiation (λ=0.71073 Å), μ=2.42 cm^{-1}, F(000)=572, T=22°C, $2\theta_{max}$=50°, 2606 independent reflections scanned, 1938 reflections in refinement ($I\geq\sigma(I)$), 218 parameters, R=0.085, R_w=0.106.

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