Stepwise Assembly of Site Specifically Functionalized Dehydrobenzo[18]annulenes†

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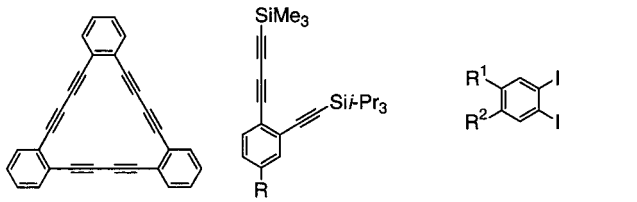
Abstract: Site specifically functionalized dehydrobenzo[18]annulenes (DBAs) with previously inaccessible topologies (C_{2v} and C_s symmetry) were prepared by utilizing an in situ protiodesilylation/alkynylation reaction. By application of a stepwise synthetic route, donor and/or acceptor functional groups were introduced to the annulenic core in a designed manner. The electronic absorption spectra of the DBAs revealed moderate to dramatic changes in the electronic structure of the [18]annulene core when subtle changes were made in substitution patterns and/or functional groups. Macrocycles containing C_{2v} symmetry exhibited progressive and predictable bathochromic shifts ranging from 20 to 80 nm along with increasing intramolecular excited state change transfer (CT) behavior. Asymmetric (C_s) molecules presented more interesting absorption behavior, such as accentuation of bands in the visible region. X-ray crystal structures of [18]DBAs **20**, **22**, **23**, and **25** showed normal bond lengths and bond angles within the planar annulenic core. A solid-state thermal study indicated ordered polymerization of the DBAs between 164 and 240 °C.

Introduction

Recent studies have shown diacetylenic dehydrobenzoannulenes (DBAs)[1] and related phenylacetylene macrocycles[2] to be useful precursors for a variety of carbon-rich polymeric systems, such as ladder polymers,[3] molecular tubes,[4] and novel allotropes of carbon.[5] In addition, these and other highly conjugated organic molecules and polymers have been actively investigated for possible application toward the next generation of electronics and photonics.[6] To exploit the technological potential of these discoveries, it is not only necessary to have ready availability to an ample supply of the desired materials (greater than milligram scale) but also to tailor and fine-tune the chemical and physical properties of the DBA precursors. The former concern has been addressed with our recent report on an intramolecular synthetic process which allowed construction of previously inaccessible DBA structures.[7] The latter concern, the subject of this study, can be achieved only through easy access to different topologies of the macrocycles as well as total control over substitution pattern specificity.

Although 40 years have elapsed since Eglinton's pioneering research on diacetylenic DBAs (e.g., **1**),[7b,8] most systems are still constructed via Cu-mediated cyclooligomerization of an *o*-diethynylbenzene.[1−5] While this intermolecular route usually



1 **2a** R=H; **2b** R=NO_2; **2c** R=NBu_2; **3a** R^1=NBu_2; R^2=NO_2; **3b** R^1=H; R^2=NBu_2, NO_2; **3c** R^1=R^2=H, alkyl, alkoxy

requires a small number of synthetic steps, the complex mixture of products, the difficulty of separating structurally related macrocycles,[3,5b] and the low isolated yield of a given DBA[5a] often outweigh the synthetic advantage. More importantly, the substitution pattern of the desired molecule is absolutely restricted by obligatory symmetry of the starting building block; thus, product symmetries other than D_{nh} ($n = 2-4$), such as C_s or even C_{2v}, are impossible to obtain.[9]

The growing interest in preparing extended π-conjugated systems containing a variety of electron donor and acceptor

† Dedicated to Professor Virgil Boekelheide on the occasion of his 80th birthday.

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(9) In theory, both higher and lower symmetries are possible; in practice, macroscopic amounts of systems other than D_{nh} ($n = 2-4$) have proven elusive via the cyclooligomerization route.

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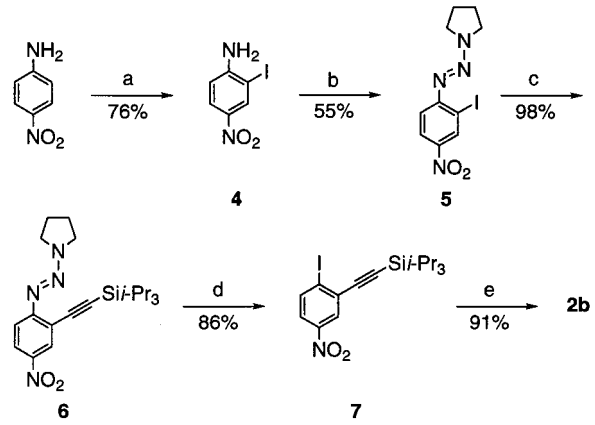
functional groups[10,11] inspired our preparation and study of substituted [18]DBAs. Discreet placement of these moieties should lead to distinct changes in the electronic characteristics and materials properties of the DBAs. Most notably, there have been extensive studies on linear π-conjugated systems containing donor−acceptor substituents.[10−12] However, due to the lack of viable preparative methods to produce functionalized macrocyclic systems, augmented studies of such classes of molecules have been difficult at best. As part of our continuing program exploring the chemistry of dehydrobenzoannulenes,[1,2,7,13] we report herein a synthetic method that allows efficient and versatile construction of site-specifically functionalized [18]-DBAs originating from simple building blocks. The characterization of the resultant donor and/or acceptor macrocycles and elucidation of their solution and solid-state physiochemical properties provide the first fundamental investigation of substituted dehydrobenzoannulenes. We describe our insights toward understanding the structure−property relationship (SPR) of these DBA derivatives through study of their electronic absorption spectra. We also examine the solid-state behavior of the novel macrocycles by X-ray crystallography and differential scanning calorimetry (DSC).

Results and Discussion

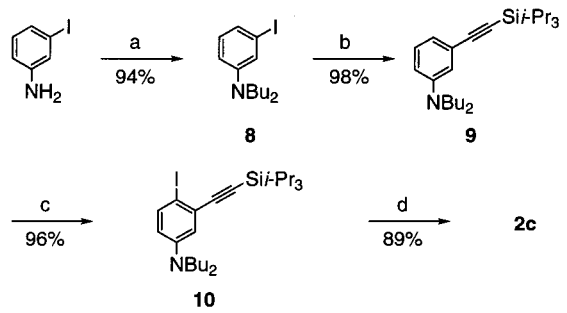
Synthesis of Building Blocks. To overcome the aforementioned synthetic difficulties in DBA assembly, we employed a stepwise construction method in which functionality is introduced from phenylbutadiyne and diiodoarene synthons (**2** and **3**, respectively) and is then carried over to the corresponding macrocycles via intramolecular cyclization of the intermediate silyl-protected α,ω-polyynes. In addition to the known triyne **2a**,[7b] we also desired phenylbutadiyne synthons substituted with acceptor (**2b**) and donor (**2c**) substituents. Unlike the parent triyne **2a**, construction of the functionalized triynes required additional synthetic transformations. Scheme 1 illustrates the preparation of nitro−triyne **2b**. Commercially available 4-nitroaniline was treated with 1 equiv of ICl to give 2-iodo-4-nitroaniline (**4**) in 76% yield.[14] Diazonium ion formation with HCl and $NaNO_2$ followed by trapping with pyrrolidine afforded *N*,*N*-tetramethylene-*N*′-(2-iodo-4-nitrophenyl)triazene (**5**).[15] Triazene **5** underwent Pd-catalyzed cross-coupling[16] with (triisopropylsilyl)acetylene smoothly to give trisubstituted phenylacetylene **6** in almost quantitative yield. Subsequent triazene decomposition[15] with iodomethane at 120 °C generated iodobenzene **7** in 86% yield. The final alkynylation with (trimethylsilyl)butadiyne[17] furnished the nitro-functionalized triyne **2b** in 32% overall yield for the five steps.

Scheme 1[a]



[a] (a) ICl, AcOH; (b) [i] $NaNO_2$, HCl, [ii] pyrrolidine, K_2CO_3; (c) *i*-$Pr_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (d) MeI, 120 °C; (e) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N.

Scheme 2[a]



[a] (a) BuBr, $NaHCO_3$, THF, DMSO; (b) *i*-$Pr_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (c) $(BnNEt_3)^+ICl_2^-$, $CaCO_3$, MeOH, CH_2Cl_2; (d) $Me_3SiC{\equiv}CC{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, Et_3N.

As shown in Scheme 2, donor synthon **2c** can be prepared readily from 3-iodoaniline. Alkylation with 1-bromobutane in a THF/DMSO solution in the presence of $NaHCO_3$ generated *N*,*N*-dibutyl-3-iodoaniline (**8**) in 94% yield. Cross-coupling of aniline **8** with (triisopropylsilyl)acetylene gave **9**. Compound **9** was conveniently iodinated by use of the mild reagent $(BnNEt_3)^+ICl_2^-$ [18] to provide the desired 4-iodoaniline **10** in near-quantitative yield. A second Sonogashira coupling with (trimethylsilyl)butadiyne furnished building block **2c** in 78% overall yield for the four steps.

Synthesis of Functionalized [18]DBAs. With triynes **2a−c** in hand, we assembled an array of functionalized [18]DBAs (Table 1). First, we applied our in situ coupling route to generate C_{2v}-substituted DBAs (**11−18** and **25**). A typical synthetic representation is illustrated in Scheme 3. Diiodoveratrole (**3c**) was treated with 2 equiv of **2b** using the in situ protiodesilylation/alkynylation reaction under pseudo-high-dilution conditions.[1,7] Thus, slow addition via syringe pump of the triyne solution to a triethylamine/THF mixture containing both palladium catalyst and aqueous potassium hydroxide afforded the tetrafunctionalized α,ω-polyyne **27**. Macrocycle precursor **27** was then desilylated with tetrabutylammonium fluoride in THF/ethanol solution. After aqueous workup, the crude material was filtered through a short plug of silica gel. Without further

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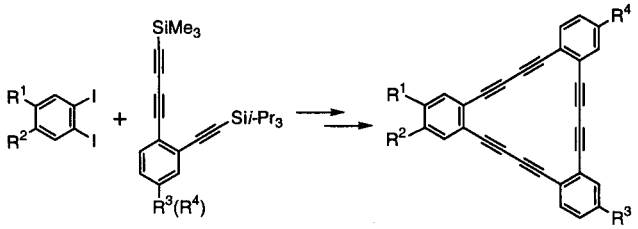
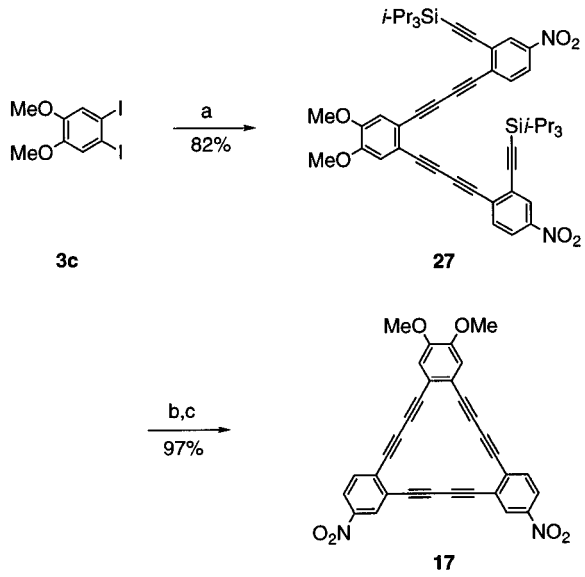
Table 1. Yields for in Situ Pd-Catalyzed Cross-Coupling Reaction and Cu-Mediated Intramolecular Cyclization



DBAs	R^1	R^2	R^3	R^4	Pd Coupling	Cyclization[b]
11	Dec	Dec	H	H	87	83
12	OMe	OMe	H	H	71	38
13	OOct	OOct	H	H	94	73
14	$-O(CH_2CH_2O)_4-$		H	H	74	93
15	H	H	NO_2	NO_2	53	–
16	Dec	Dec	NO_2	NO_2	56	96
17	OMe	OMe	NO_2	NO_2	82	97
18	OOct	OOct	NO_2	NO_2	64	46
19	NBu_2	NO_2	NBu_2	NO_2	48[a]	93
20	NBu_2	NO_2	NO_2	NBu_2	62[a]	84
21	NBu_2	NO_2	H	H	64	87
22	H	H	NO_2	NBu_2	68[a]	94
23	NO_2	H	NBu_2	H	14[a]	99
24	NBu_2	H	H	H	74	60
25	H	H	NBu_2	NBu_2	89	92
26	NO_2	OH	NBu_2	NBu_2	45	78

[a] Combined yield for sequential cross-coupling reactions. [b] Combined yield for protiodesilylation/intramolecular cyclization.

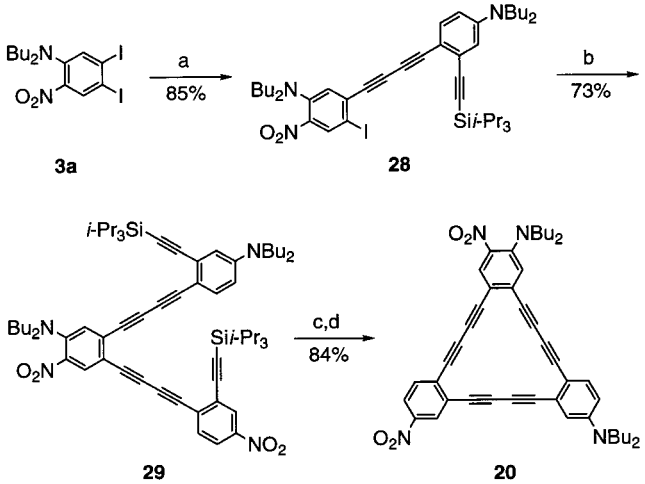
Scheme 3[a]



[a] (a) **2b**, aqueous KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (b) Bu_4NF, EtOH, THF; (c) $Cu(OAc)_2$, CuCl, pyridine.

purification, cyclization of the desilylated α,ω-polyyne was carried out via Cu-mediated intramolecular oxidative dimerization under pseudo-high-dilution conditions, generating tetra-substituted annulene **17** as bright red-orange microcrystals in 97% yield. The cyclization reactions were exceptionally efficient in most cases, providing only the desired products with no detection of higher cyclooligomers or catenanes.

Scheme 4[a]



[a] (a) **2c**, aqueous KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (b) **2b**, aqueous KOH, $PdCl_2(PPh_3)_2$, CuI, Et_3N; (c) Bu_4NF, EtOH, THF; (d) $Cu(OAc)_2$, CuCl, pyridine.

The assembly of DBAs with lower symmetry illustrates the versatility of this route and is best exemplified by the preparation of C_s macrocycle **20** (Scheme 4). Selective and sequential Sonogashira cross-coupling of **2c** and **2b** to diiodobenzene **3a**[19] using in situ desilylation/alkynylation reaction conditions furnished the asymmetrically functionalized α,ω-polyyne **29** in 62% overall yield. It is noteworthy that only dibenzotriyne **28** was isolated and that no product of double alkynylation was detected from the first cross-coupling reaction. This fact can be attributed to the greater tendency of electron-poor arenes to undergo Pd-catalyzed cross-coupling reactions much faster than the corresponding electron-rich arenes.[16] Polyyne **29** underwent the standard protiodesilylation/cyclization steps, generating tetrasubstituted annulene **20** as deep red crystals in 84% yield. Using this strategy, we were able to assemble various C_s-symmetric donor/acceptor macrocycles (Table 1, DBAs **19**−**24**).

Attempts to prepare the C_{2v}-donor/acceptor DBA **30** from 1,2-diiodo-4,5-dinitrobenzene (**31**) using analogous chemistry were unsuccessful; instead, an unusually broad triplet at 8.01 ppm in the proton NMR spectrum suggested formation of hydroxy-containing macrocycle **26** (Figure 1). The presence of the hydroxyl group in **26** was confirmed by a deuterium exchange experiment. The proton NMR spectrum of the resultant molecule showed the disappearance of the broad triplet while the remaining signals were virtually unchanged. Arene **31** is known to undergo facile substitution under certain conditions in the presence of nucleophiles (e.g., reaction of **31** with dibutylamine yields **3a**).[19] Thus, under our standard reaction conditions for coupling triyne synthons, hydroxide ion first replaces one of the nitro groups in **31** and then cross-coupling with desilylated **2c** occurs.

Upon cyclization of the gummy acyclic precursors, the product macrocycles were obtained as solids of variable solubility in common organic solvents. We circumvented low solubility problems by adjoining decyl, alkoxy, and dibutylamino groups to the annulenic core. Although incorporation of alkoxy

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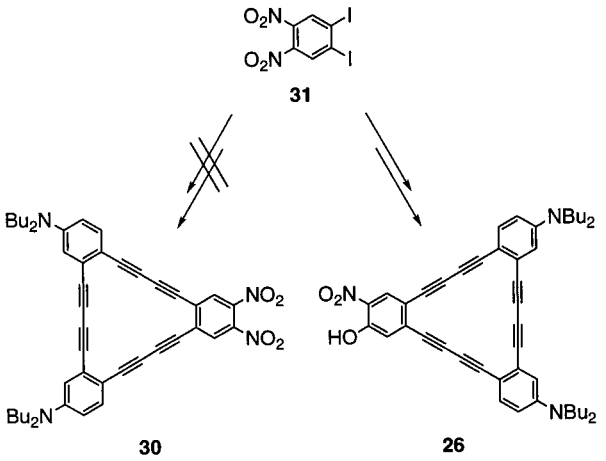

Figure 1. Unsuccessful attempt to synthesize donor−acceptor DBA **30** using the in situ protiodesilylation/alkynylation route.

groups helped reduce the solubility problem of the macrocycles, the DBA products were found to be somewhat unstable, slowly decomposing under ambient conditions over the course of a few days. Conversely, DBAs containing both alkoxy and nitro groups exhibited increased stability without any detectable decomposition after months under analogous conditions. However, incorporation of the nitro moieties significantly decreased the solubility of the final products. Inclusion of dialkylamino groups (DBAs **19**−**26**), on the other hand, dramatically increased DBA solubility.

Clearly, judicious choice of the coupling partners (triynes **2a**−**c** and diiodobenzenes **3a**−**c**) can furnish [18]DBAs with one, two, or three benzene rings bearing one or two functional groups. Depending on the viability of multisubstituted building blocks, it should be possible to produce even more complicated topologies not only of [18]annulene derivatives but also of other DBA sizes as well.[7a] The latter avenue is currently under further exploration.

Electronic Characteristics of DBAs. To design organic materials possessing desired properties, it is absolutely critical to have a systematic understanding of the structure−property relationship (SPR) of a given class of compounds. Previously, most of the efforts in the acetylenic area were focused on linear and acyclic systems.[10−12] The advent of our synthetic method to generate DBAs substituted in various positions provided us with the opportunity to conduct an inclusive study on the planar [18]annulene system for the first time.

In a previous report we discussed that the electronic absorption spectra of dodecadehydro[18]annulenes possess a characteristic pattern of four absorption bands,[7b] which are attributable primarily to $\pi \rightarrow \pi^*$ transitions.[10a,c,20] This pattern includes the trend in peak intensity of decreasing order of second, first, third, and fourth peak, as shown for **1** in Figure 2. The alkyl substituents of DBA **11** did not alter the electronic absorption spectra significantly and showed very good agreement with spectra of **1**. All four peaks only deviated within 3 or 4 nm with essentially the same molar extinction coefficient (ϵ) (Table 2) as alkyl groups are known to be only slightly electron donating. Comparison with the spectra of alkoxy containing DBAs such as **12**−**14** showed the same pattern for the [18]-annulenic core but exhibited a general bathochromic shift for the diagnostic peaks. For example, peak 4 shifted 32 nm from 370 nm for **13**. The end absorption points of **12**−**14** also displayed shifts of ca. 30 nm to lower energy. Retention of the general annulenic core pattern of the spectra suggests that most of the electron-donating ability of the alkoxy groups is localized in the benzene ring.

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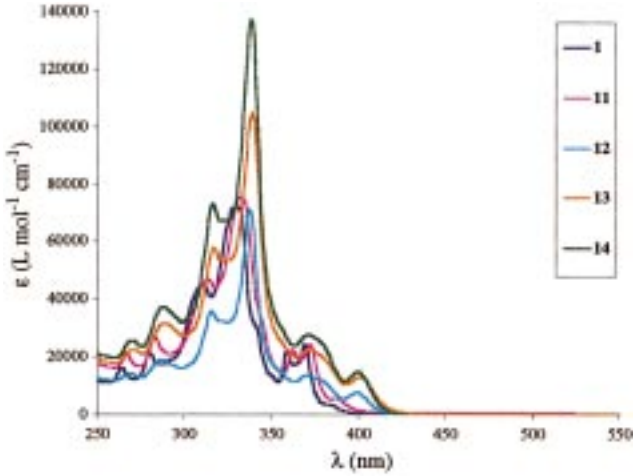

Figure 2. Electronic absorption spectra of DBA **1** and C_{2v} DBAs **11**−**14**.

Table 2. Selected λ_{max} Values (nm) and Molar Extinction Coefficients (L mol^{-1} cm^{-1}) of DBAs **1**, **11**−**14**, **16**−**18**, and **25** in CH_2Cl_2

DBA	peak 1	peak 2	peak 3	peak 4
1	312 (44 900)	331 (72 200)	359 (22 200)	370 (23 900)
11	315 (46 700)	334 (74 600)	363 (22 300)	373 (24 400)
12	316 (35 800)	338 (70 900)	372 (13 400)	401 (7300)
13	318 (57 100)	339 (104 900)	374 (21 900)	402 (12 900)
14	317 (73 100)	339 (136 500)	373 (27 600)	402 (14100)
16	310 (34 000)	349 (54 100)	364 (58 400)	414 (20 200)
17	309 (11 800)	351 (12 100)	370 (13 700)	433 (6100)
18	311 (18 200)	352 (17 200)	372 (20 400)	435 (8600)
25	311 (40 700)	351 (54 200)	387 (57 500)	437 (22 900)

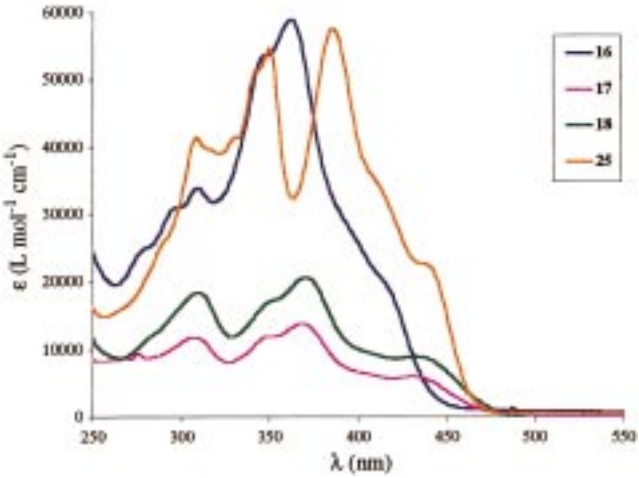

Figure 3. Electronic absorption spectra of C_{2v} DBAs **16**−**18** and **25**.

The electronic absorption spectrum of dibutylamino-containing DBA **25** presented a somewhat more interesting spectrum (Figure 3). DBA **25**, which contains two donor groups, showed a large bathochromic shift as well as lack of the characteristic pattern. The strongest absorption band appeared at 387 nm in comparison to 330 nm (for **1** and **11**) and 340 nm (for **12**−**14**). Along with significant shifting of the peaks, a general broadening of the bands was also observed, suggesting strong intramolecular excited-state charge-transfer (CT) activities. The above observations indicate that the effect of the dibutylamino groups is much more influential on the electronic circuit of [18]DBA

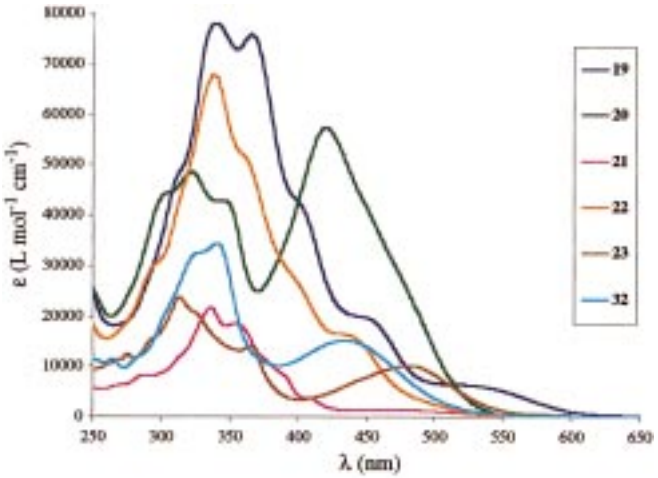

Figure 4. Electronic absorption spectra of asymmetric DBAs **19**−**23** and diyne model **32**.

Table 3. Selected λ_{max} Values (nm) and Molar Extinction Coefficients (L mol^{-1} cm^{-1}) of DBAs **19**−**23** and **32** in CH_2Cl_2

DBA	peak 1	peak 2	peak 3	peak 4
19	340 (77 900)	360 (75 600)	451 (19 400)	529 (6200)
20	308 (44 700)	324 (48 300)	348 (42 700)	422 (57 300)
21	338 (59 200)	357 (50 200)	409 (10 200)	474 (4000)
22	339 (67 900)	362 (51 400)	400 (26 700)	435 (16 500)
23	315 (24 000)	327 (20 900)	367 (14 200)	483 (10 200)
32	326 (32 500)	341 (34 200)		435 (15 200)

than that of alkoxy groups. The positioning of the functional groups also emerges as an important component in tailoring the electronic properties, as DBA **25** carries only one substituent per benzene ring and yet causes considerable CT behavior.[21]

To study the affects of nitro groups on the DBA electronic circuit, we assembled compound **15** but could not isolate pure material due to its extreme insolubility. A logical soluble alternative was didecyl derivative **16**. Due to its substitution pattern, the spectrum of **16** exhibited largely broadened CT bands (Figure 3). In comparison to its amino-substituted analogue **25**, the end absorption point extended only to 460 nm, about 15 nm short of its counterpart. When alkyl groups were replaced with alkoxy groups, as represented by DBAs **17** and **18**, the end absorption points were extended beyond 475 nm, accompanied by severe broadening of absorption bands throughout the spectra.

Up to this point, all of the macrocycles examined were symmetrically substituted systems (C_{2v}) and exhibited reasonably uncomplicated and somewhat predictable electronic absorption spectra. By introducing asymmetry to the annulenic core, we expected that more intricate and intriguing electronic behavior might transpire; this indeed proved to be the case. The UV−vis spectra of annulenes **19** and **20** displayed end absorption points extending beyond 600 and 560 nm, respectively (Figure 4). More interestingly, the spectrum of **20** exhibited a broad yet very strong CT absorption band at 422 nm with a molar extinction coefficient of 57 300 M^{-1} cm^{-1}, the strongest low-energy level absorption we have observed in an annulene derivative (Table 3).

To investigate systematically the topological origin of this phenomenon, we prepared annulenes **21**−**23** as well as linear donor−acceptor component **32**[11c] and acquired their electronic absorption spectra (Figure 4). Compounds **21**−**23** and **32** represent segments of the conjugated and cross-conjugated

(21) Anthony, J. E.; Khan, S. I.; Rubin, Y. *Tetrahedron Lett.* **1997**, *38*, 3499−3502.

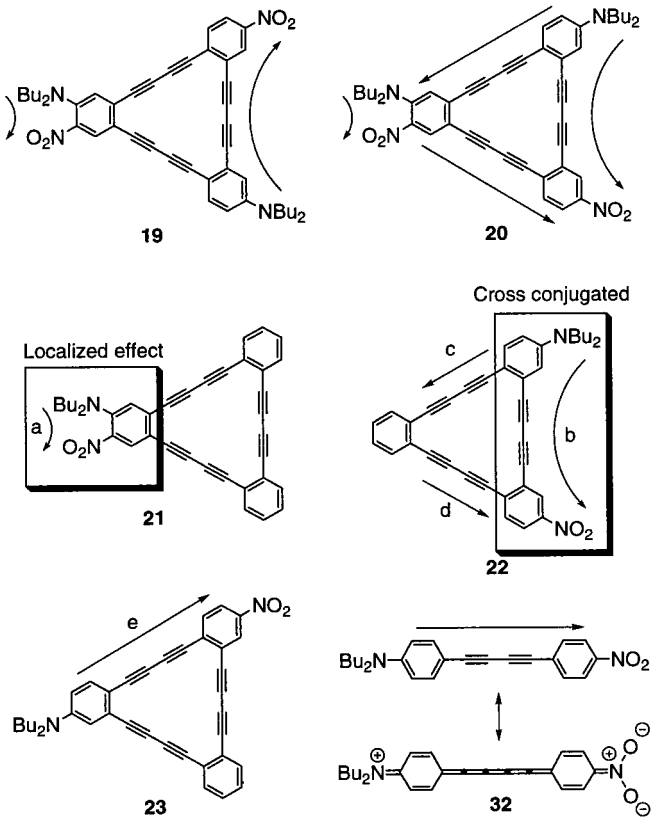

Figure 5. Electron delocalization pathways in DBAs **19**−**23** and linear component **32**. The arrows denote the possible delocalization pathways in each DBA.

electron delocalization pathways contained in DBAs **19** and **20** (Figure 5). Analysis of the spectra of nonlinearly arranged macrocycles **21** and **22** revealed that the two DBAs displayed very similar absorption patterns but with extremely distinct extinction coefficients (Table 3). Spectrum **21** was accompanied by an extremely weak CT band at 474 nm. Since both functional groups on **21** are positioned on a single benzene ring *ortho* to each other, most of the donating and accepting effects were localized in the six-membered ring (pathway a). In the case of **22**, the large increase in the degree of absorption throughout the spectrum was remarkable. The effects of the donor−acceptor groups appear to be very minor on the DBA electronic circuit through the shortest delocalization pathway (pathway b) since it is cross-conjugated, which is known to be much less efficient than a conjugated pathway.[11] However, the extreme differences between **21** and **22** may be explained by accounting for the cumulative effect of the single linear donor (c) and acceptor (d) pathways. A qualitative comparison between the spectra of **19** and **22** shows very little deviation from each other and thus is in accordance with the above interpretation.

Examination of the absorption spectra of molecules **23** and **32**, which contain linear donor−acceptor components (pathway e), exhibited moderately strong, broad CT transitions at 483 and 435 nm, respectively, with end absorptions greater than 550 nm. Comparison of DBA **23** with the parent donor−acceptor diyne **32** showed that the magnitude of the donor−acceptor conjugation, as approximated by the position of the CT bands, was strengthened when the chromophore was locked into planarity. Therefore, incorporation of the donor−acceptor unit of **32** into the DBA skeleton resulted in a significant bathochromic shift of nearly 50 nm. Although conjugation in the extended macrocycle might play a role in this shift, we feel it is minimal as (1) the parent DBA **1** displayed no absorption

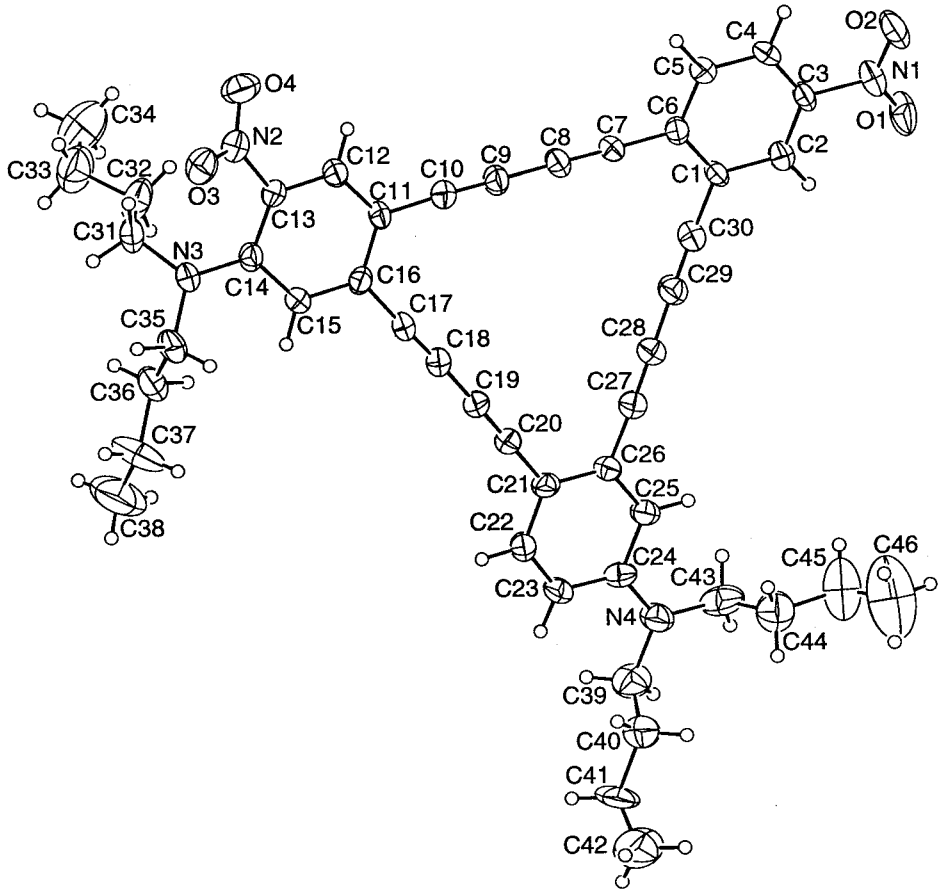

Figure 6. Molecular structure of DBA **20**; ellipsoids drawn at the 30% level.

bands above 400 nm and (2) the alternate resonance pathway in **23** is the less efficient, cross-conjugated route.

What then, is the origin for the large extinction coefficient of the CT absorption band in macrocycle **20**? Individually, the electron delocalization (resonance) pathways contained in DBAs **21**−**23** do not appear to contribute significantly, nor does a simple summation of these effects. However, it seems that a synergistic influence of the two donor−acceptor groups, when placed judiciously on the macrocycle, is likely responsible for the intriguing electronic behavior illustrated by DBA **20**.

Crystal Structures of [18]DBAs. Prior to this study, the only crystal structures reported for diacetylenic DBAs were limited to smaller macrocycles[3,4,5b,22] or nonplanar systems.[5a,7a] To gain further understanding of the structural effects of donor−acceptor functionalization on the bonding and molecular packing, we sought to perform X-ray structural analyses of the macrocycles. In our previous studies with planar DBAs, efforts to grow crystals of the parent hydrocarbons that were suitable for X-ray analysis had proven fruitless. Fortunately, inclusion of the dialkylamino groups on the [18]DBA skeleton greatly facilitated crystal formation, which was achieved by slow diffusion of hexanes into a concentrated dichloromethane solution of the appropriate DBA. Gratifyingly, we were able to obtain structural data for DBAs **20**, **22**, **23**, and **25**.

The molecular structures of the substituted [18]DBAs, for which macrocycle **20** is illustrative (Figure 6), revealed that the annulenic cores are essentially planar. For example, the mean deviation in **20** was less than 0.070 Å. The bond lengths and bond angles are typical for those found in other strain-free dehydrobenzoannulenes.[3−5,7] These results indicate that there is little or no intramolecular ground-state charge transfer, similar to what was found with acyclic donor−acceptor polyynes.[10,11,23]

Of the four structures examined, only macrocycle **22** possessed a noncentrosymmetric arrangement in the solid state (Figure 7). The organization of **22** contains a mirror plane through the planar sheet of macrocycles with no point of inversion. The unit cell of DBA **23** contains two macrocycles arranged in a centrosymmetric manner with no net dipole moment. Likewise, annulene **25** contains two molecules per centrosymmetric unit cell. A view from the top of the planar molecule shows an interesting "Star of David" arrangement.

Solid-State Behavior of DBAs. In conjunction with X-ray structural analyses, we also examined the thermal solid-state behavior of [18]DBAs. Dehydrobenzoannulenes and other phenylacetylene macrocycles potentially can be useful precursors to carbon-rich polymers. In addition, the rigid core may serve as building blocks for tubular liquid crystals and porous molecular crystals. In our study, all macrocycles exhibited sharp, irreversible exothermic transitions as determined by differential scanning calorimetry (DSC). The maximum heights for these peaks were observed between 164 and 240 °C (Table 4). The enthalpy associated with these reactions range from 389 to 740 kJ mol^{-1}, showing relatively high thermal reactivity. The half-widths of the exotherms ranged from 3 to 15 °C, suggesting the occurrence of well-ordered polymerizations. Interestingly, only macrocycles containing decyl groups (DBAs **11** and **16**) exhibited melting transitions at 135 and 93 °C, respectively.

Attempts to examine thermoproducts from the DSC experiments were severely hampered due to complete insolubility of

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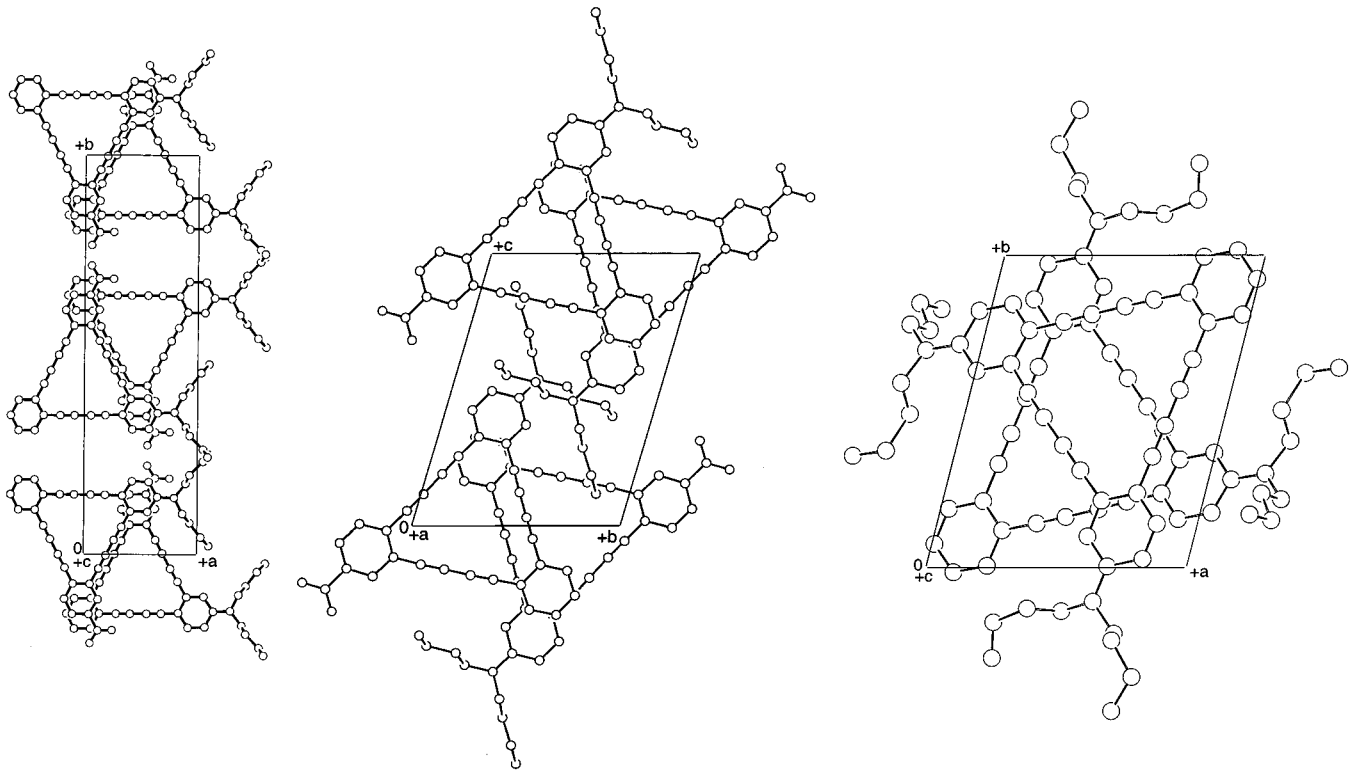

Figure 7. Crystal packing diagrams for macrocycles **22** (a, left), **23** (b, middle), and **25** (c, right).

Table 4. Selected DSC Data for Functionalized [18]DBAs

DBA	T_{max} (°C)[a]	T_{min} (°C)[b]	$w^{1/2}$	ΔH_{rxn} (kJ mol^{-1})
11	164	135	7	442
13	186		3	430
14	211		12	463
16	227	93	6	488
19	240		4	601
20	230		4	618
21	206		15	552
22	230		15	561
23	230		13	740
24	214		13	389

[a] Exotherm; thermal polymerization. [b] Endotherm; melting transition.

the shiny, black materials in common organic solvents. Therefore, the structures of these thermoproducts as well as the nature of thermal transformation remain uncertain. In-depth studies are required to determine whether the DBAs undergo topochemical solid-state polymerization to form polydiacetylenes; these studies are currently underway.

Conclusions

Herein we have described an efficient and versatile synthetic method for generating highly functionalized dehydrobenzo[18]-annulenes. The route allows placement of functionality to be determined at the building block level. With suitably functionalized building blocks, an α,ω-polyyne with a specific substitution pattern can be generated. Subsequent cyclization affords a rationally designed [18]DBA. 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 the ring substitution.

Utilizing the synthetic advances, a large series of donor−acceptor DBAs were prepared, permitting the first detailed SPR studies of these macrocycles. X-ray structure analyses of donor−acceptor DBAs exhibited the expected planarity with normal bond lengths and angles, indicating the absence of intramolecular charge-transfer behavior in the electronic ground state. The electronic absorption spectra of donor−acceptor DBAs also displayed larger bathochromic shifts as stronger donor−acceptor functionalities were incorporated. The increasingly broad and intense low-energy absorption in the spectra is attributed to the increasing polarization of the conjugated backbone from the donor to the acceptor groups in the excited state. We also observed unexpected changes in absorption spectra in the case of DBA **20** showing unusually strong CT behavior around 422 nm. The strong absorption may be the result of synergistic cooperation of the particular asymmetric substitution pattern in which the partial pattern exhibited only weak to moderate CT behavior. In conclusion, we were able to show the ability to effectively tailor the electronic structure of [18]DBAs by rational design of the substitution pattern. We are currently exploring the nonlinear optical activity of this unique class of molecules to add to the present structure−property relationship studies. We are also pursuing the study of DBA thermal products to better understand the solid-state polymerization process. These results will be presented in due course.

Experimental Section

General Considerations. ^{1}H and ^{13}C NMR spectra were recorded using a Varian Inova 300 NMR (^{1}H, 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*, ^{1}H 7.27 ppm and ^{13}C 77.0 ppm; dichloromethane-d_2, ^{1}H 5.32 ppm, ^{13}C 54.0 ppm; tetrahydrofuran-d_8, ^{1}H 3.58 ppm, ^{13}C 67.57 ppm). Coupling constants are expressed in hertz. 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. Melting points were determined on a Meltemp II apparatus. All melting points are uncorrected. 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, Inc. Dichloromethane, triethylamine, and pyridine were distilled from

calcium hydride under an atmosphere of nitrogen prior to use. Tetrahydrofuran was distilled from sodium and benzophenone under an atmosphere of nitrogen 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 precoated silica gel plates were used for analytical (200 × 50 × 0.25 mm) thin-layer chromatography. Reactions were carried out under an inert atmosphere (dry nitrogen or argon) when necessary.

General Acetylene Coupling Procedure A. A round-bottom flask was charged with iodoarene (1 equiv), bis(triphenylphosphine)palladium(II) chloride (0.03 equiv), copper(I) iodide (0.06 equiv), and triethylamine (0.1 M). After the mixture was bubbled with N_2 for 30 min, the silyl-protected terminal acetylene (1.1−1.3 equiv) was added by syringe under a nitrogen atmosphere. The reaction mixture was stirred at 50 °C for 2−12 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 the solution filtered through a thin cake of silica gel using CH_2Cl_2. The solution was concentrated and then chromatographed on silica gel.

General in Situ Protiodesilylation/Alkynylation Procedure B. Iodoarene (1 equiv) and [(trimethylsilyl)butadiynyl]arene (1.1 equiv) were dissolved in H_2O/THF/triethylamine (0.01:1:5) solutions in separate vessels. The solutions were degassed vigorously by either bubbling of nitrogen or by three freeze−pump−thaw cycles. The acetylene solution was added via syringe pump to the iodoarene solution charged with bis(triphenylphosphine)palladium(II) chloride (0.03 equiv), copper(I) iodide (0.06 equiv), and KOH (10 equiv per silyl group) over 12−24 h under a 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.

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 2.5 equiv of tetrabutylammonium fluoride (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 diethyl ether (ca. 25 mL per mmol substrate), washed three times with water and twice with brine, and dried over magnesium sulfate. 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 of $Cu(OAc)_2$, 20 equiv of CuCl, and pyridine (ca. 250 mL per mmol of α,ω-polyyne) at 60 °C. The addition was done under house air over 10−20 h. Upon completion, 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.

***N,N*-Dibutyl-4,5-diiodo-2-nitroaniline (3a).**[19] A mixture of 1,2-diiodo-4,5-dinitrobenzene (**31**;[24] 151 mg, 0.36 mmol) and dibutylamine (92 mg, 0.72 mmol) in THF (10 mL) was stirred at room temperature for 4 h. The reaction mixture was concentrated and chromatographed on silica gel (2:1 hexanes−CH_2Cl_2), furnishing **3a** (162 mg, 90% yield) as a red-orange oil. ^{1}H NMR ($CDCl_3$): δ 8.03 (s, 1H), 7.58 (s, 1H), 3.07 (t, J = 7.2 Hz, 4H), 1.62−1.40 (m, 4H), 1.32−1.20 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 144.66, 141.34, 135.19, 131.87, 113.72, 92.28, 51.58, 29.28, 19.97, 13.76. IR (neat): ν 2966, 2866, 1580, 1448, 1348 cm^{-1}. MS (EI, 70 eV): m/z 502 (M^+, 13), 485 (19), 459 (100), 443 (18), 416 (24), 402 (27).

2-Iodo-4-nitroaniline (4). 4-Nitroaniline (4.15 g, 30 mmol) was treated with ICl (4.87 g, 30 mmol) according to a literature procedure,[14] yielding **4** (6.01 g, 76% yield) as a light green powder. Mp: 157.2−159.7 °C. ^{1}H NMR ($CDCl_3$): δ 8.57 (d, J = 2.7 Hz, 1H), 8.06 (dd, J = 9.3, 2.7 Hz, 1H), 6.71 (d, J = 9.3 Hz), 4.85 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ 152.30, 135.49, 135.26, 125.71, 112.23, 80.53. IR (KBr): ν 3484, 3368, 2820, 2556, 1525 cm^{-1}. MS (EI, 70 eV): m/z 264 (M^+, 100), 234 (49), 91 (30).

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***N,N*-Tetramethylene-*N*′-(2-iodo-4-nitrophenyl)triazene (5).** Aniline **4** (5.28 g, 20 mmol) was dissolved in concentrated HCl (5.6 mL) and H_2O (10 mL) and 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 it was stirred 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 ether (20 mL). Product **5** was air-dried to give a yellow solid (3.81 g, 55% yield). Mp: 180.8−181.6 °C. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, J = 2.7 Hz, 1H), 8.11 (dd, J = 9.0, 2.7 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H), 4.01 (t, J = 6.3 Hz, 2H), 3.79 (t, J = 6.6 Hz, 2H), 2.24−2.02 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 155.37, 144.36, 134.79, 124.15, 116.09, 94.77, 51.66, 47.98, 23.91, 23.32. IR (KBr): ν 3091, 2972, 2873, 1501, 1375, 1295 cm^{-1}. MS (EI, 70 eV): m/z 346 (M^+, 42), 276 (76), 248 (100).

***N,N*-Tetramethylene-*N*′-[4-nitro-2-((triisopropylsilyl)ethynyl)-phenyl]triazene (6).** Triazene **5** (621 mg, 1.7 mmol) was treated with (triisopropylsilyl)acetylene (650 mg, 3.6 mmol) using acetylene coupling procedure A. Chromatography on silica gel (9:1 hexanes:CH_2Cl_2) afforded **6** (667 mg, 98% yield) as a yellow solid. Mp: 111.5−113.7 °C. ^{1}H NMR ($CDCl_3$): δ 8.34 (d, J = 9.0 Hz, 1H), 8.07 (dd, J = 9.0, 2.4 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 4.01 (t, J = 5.7 Hz, 2H), 3.75 (t, J = 5.7 Hz, 2H), 2.18−2.01 (m, 4H), 1.15 (s, 21H). ^{13}C NMR ($CDCl_3$): δ 157.43, 143.71, 129.53, 124.04, 118.62, 116.74, 102.91, 96.94, 51.60, 47.46, 23.89, 23.41, 18.71, 11.26. IR (KBr): ν 2939, 2873, 2164, 1507 cm^{-1}. MS (FAB): m/z 401 (M^+ + H, 100), 330 (36).

2-Iodo-4-nitro-1-[(triisopropylsilyl)ethynyl]benzene (7). Compound **6** (341 mg, 0.85 mmol) was dissolved in freshly distilled iodomethane (26 mL) and was heated in a pressure tube at 120 °C for 48 h. The cooled reaction mixture was then filtered through a cake of silica gel using a 1:1 hexanes−CH_2Cl_2 mixture. Chromatography on silica gel (3:2 hexanes−CH_2Cl_2) gave arene **7** (313 mg, 86% yield) as a reddish solid. Mp: 123.2−124.5 °C. ^{1}H NMR ($CDCl_3$): δ 8.26 (d, J = 2.4 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.81 (dd, J = 8.7, 2.4 Hz, 1H), 1.18 (s, 21H). ^{13}C NMR ($CDCl_3$): δ 147.61, 139.72, 131.74, 127.09, 123.20, 109.18, 105.82, 99.17, 18.63, 11.18. IR (KBr): ν 2943, 2865, 2164 cm^{-1}. MS (FAB): m/z 386 (M^+ − C_3H_7, 84), 358 (35), 340 (83), 300 (22).

4-Nitro-2-[(triisopropylsilyl)ethynyl]-1-[4-(trimethylsilyl)-1,3-butadiynyl]benzene (2b). Ethynylbenzene **7** (301 mg, 0.70 mmol) was reacted with (trimethylsilyl)butadiyne[17] (171 mg, 1.4 mmol) using acetylene coupling procedure A. Chromatography on silica gel (3:1 hexanes−CH_2Cl_2) yielded **2b** (270 mg, 91% yield) as a yellow gum. ^{1}H NMR ($CDCl_3$): δ 8.30 (d, J = 2.4 Hz, 1H), 8.01 (dd, J = 8.7, 2.4 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 1.18 (s, 21H), 0.25 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.00, 133.35, 130.91, 128.91, 126.96, 122.50, 102.19, 99.83, 95.13, 87.16, 82.74, 73.22, 18.63, 11.21, −0.57. IR (KBr): ν 2953, 2866, 2104 cm^{-1}. Anal. Calcd for $C_{24}H_{33}NO_2Si_2$: C, 68.03; H, 7.85; N, 3.31. Found: C 67.81; H, 7.83; N, 3.25.

***N,N*-Dibutyl-3-iodoaniline (8).** A mixture of 3-iodoaniline (1.97 g, 9.0 mmol), $NaHCO_3$ (2.27 g, 27 mmol), and 1-bromobutane (12.3 g, 90 mmol) in a 5:1 THF−DMF solution (60 mL) was stirred at reflux for 7 days. The cooled reaction mixture was washed with H_2O (3 × 50 mL) and extracted with ether (50 mL). The organic layer was dried over $MgSO_4$ and concentrated. Chromatography on silica gel (9:1 hexanes−CH_2Cl_2) gave *N,N*-dibutyl-3-iodoaniline (2.79 g, 94% yield) as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 6.97−6.70 (m, 3H), 6.62−6.51 (m, 1H), 3.22 (t, J = 7.5 Hz, 4H), 1.62−1.46 (m, 4H), 1.43−1.23 (m, 4H), 0.96 (t, J = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 149.30, 130.48, 123.86, 120.28, 110.81, 95.78, 50.61, 29.20, 20.29, 13.97. IR (neat): ν 2952, 2872, 1586 cm^{-1}. MS (EI, 70 eV): m/z 331 (M^+, 9), 288 (100), 246 (57).

***N,N*-Dibutyl-3-[(triisopropylsilyl)ethynyl]aniline (9).** *N,N*-Dibutyl-3-iodoaniline (1.69 g, 5.1 mmol) was reacted with (triisopropylsilyl)-acetylene (1.40 g, 7.7 mmol) using acetylene coupling procedure A. Chromatography on silica gel (2:1 hexanes−CH_2Cl_2) afforded compound **9** (1.93 g, 98% yield) as a light brown oil. ^{1}H NMR ($CDCl_3$): δ 7.17 (t, J = 8.4 Hz, 1H), 6.94−6.78 (m, 2H), 6.66 (dd, J = 8.4, 2.4 Hz, 1H), 3.31 (t, J = 7.6 Hz, 4H), 1.70−1.53 (m, 4H), 1.51−1.31 (m, 4H), 1.21 (s, 21H), 1.05 (t, J = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 147.84, 128.95, 124.03, 118.98, 115.07, 112.15, 108.57, 88.66, 50.63,

29.28, 20.30, 18.67, 13.96, 11.37. IR (neat): ν 2946, 2873, 2150 cm^{-1}. Anal. Calcd for $C_{25}H_{43}NSi$: C, 77.85; H, 11.24; N, 3.63. Found: C, 77.92; H, 11.34; N, 3.58.

***N,N*-Dibutyl-4-iodo-3-[(triisopropylsilyl)ethynyl]aniline (10).** Compound **9** (540 mg, 1.4 mmol) was treated with $(BnNEt_3)^+ICl_2^-$ [18] (462 mg, 1.4 mmol) and $CaCO_3$ (200 mg, 2.0 mmol) in 5:1 CH_2Cl_2−MeOH solution (30 mL). The reaction mixture was stirred for 2 h and then filtered. The filtrate was concentrated and washed with 5% $NaHSO_3$ solution (30 mL), which was back-extracted with ether (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Chromatography on silica gel (2:1 hexanes−CH_2Cl_2) gave aniline **10** (687 mg, 96% yield) as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.53 (d, J = 9.0 Hz, 1H), 6.78 (d, J = 3.0 Hz, 1H), 6.34 (d, J = 9.0, 3.0 Hz, 1H), 3.23 (t, J = 7.2 Hz, 4H), 1.58−1.47 (m, 4H), 1.40−1.28 (m, 4H), 1.18 (s, 21H), 0.96 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 147.60, 138.68, 129.95, 116.61, 114.10, 109.00, 93.22, 81.77, 50.57, 29.09, 20.22, 18.71, 13.91, 11.35. IR (neat): ν 2953, 2866, 2157 cm^{-1}. HRMS (FAB): calcd for $C_{25}H_{42}INSi$ 511.2133, found 511.2131.

***N,N*-Dibutyl-3-[(triisopropylsilyl)ethynyl]-4-[4-(trimethylsilyl)-1,3-butadiynyl]aniline (2c).** Iodoaniline **10** (333 mg, 0.65 mmol) was reacted with (trimethylsilyl)butadiyne[17] (119 mg, 0.97 mmol) using acetylene coupling procedure A. Chromatography on silica gel (2:1 hexanes−CH_2Cl_2) yielded triyne **2c** (276 mg, 89% yield) as a light brown oil. ^{1}H NMR ($CDCl_3$): δ 7.28 (d, J = 8.7 Hz, 1H), 6.67 (d, J = 2.4 Hz, 1H), 6.49 (dd, J = 8.7, 2.4 Hz, 1H), 3.27 (t, J = 7.2 Hz, 4H), 1.61−1.48 (m, 4H), 1.45−1.30 (m, 4H), 1.19 (s, 21H), 0.97 (t, J = 7.2 Hz, 6H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.95, 133.98, 128.60, 114.54, 111.39, 109.76, 105.60, 93.97, 89.47, 89.15, 77.23, 75.64, 50.49, 29.21, 20.19, 18.69, 13.88, 11.34, −0.29. IR (neat): ν 2953, 2866, 2197, 2157, 2091 cm^{-1}. Anal. Calcd for $C_{32}H_{51}NSi_2$: C, 75.97; H, 10.16; N, 2.77. Found: C, 75.60; H, 10.32; N, 2.59.

Dehydrobenzo[18]annulene 11. The corresponding α,ω-polyyne (100 mg, 0.10 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (54 mg, 83% yield) was isolated as a bright yellow microcrystalline solid after chromatography on silica gel (3:1 hexanes−CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.72−7.63 (m, 4H), 7.46 (s, 2H), 7.44−7.37 (m, 4H), 2.62 (t, J = 8.1 Hz, 4H), 1.59 (bt, J = 8.1 Hz, 4H), 1.44−1.01 (m, 28H), 0.90 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 143.70, 133.85, 133.37, 133.24, 129.65, 129.49, 125.70, 125.43, 122.65, 81.95, 81.34, 80.79, 78.50, 78.16, 77.16, 33.08, 32.49, 31.31, 30.26, 30.15, 30.03 (2), 29.91, 23.26, 14.45. IR (KBr): ν 2926, 2866, 2215, 2198 cm^{-1}. HRMS (FAB): calcd for $C_{50}H_{52}$ 652.4069, found 652.4073.

Dehydrobenzo[18]annulene 12. The corresponding α,ω-polyyne (175 mg, 0.23 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (38 mg, 38% yield) was isolated as a bright yellow microcrystalline solid after chromatography on silica gel (9:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 7.74−7.68 (m, 4H), 7.51−7.44 (m, 4H), 7.14 (s, 2H), 3.91 (s, 6H). ^{13}C NMR (CD_2Cl_2): δ 150.88, 133.36, 133.13, 129.61, 129.43, 125.62, 125.29, 118.79, 115.11, 81.82, 81.32, 80.96, 78.46, 78.14, 76.97, 56.64. IR (KBr): ν 2966, 2913, 2853, 2213, 2197 cm^{-1}. HRMS (FAB): calcd for $C_{32}H_{16}O_2$ 432.1150, found 432.1154.

Dehydrobenzo[18]annulene 13. The corresponding α,ω-polyyne (250 mg, 0.31 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (143 mg, 73% yield) was isolated as a bright yellow solid after chromatography on silica gel (4:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 7.72−7.63 (AA′ m, 4H), 7.45−7.37 (BB′ m, 4H), 7.10 (s, 2H), 4.03 (t, J = 6.6 Hz, 4H), 1.80−1.68 (m, 4H), 1.57−1.32 (m, 20H), 0.91 (t, J = 6.6 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 149.87, 132.67, 132.44, 128.71, 128.49, 125.39, 125.00, 118.32, 115.91, 81.41, 80.74, 80.30, 78.48, 78.10, 76.73, 69.18, 31.80, 29.25, 28.95, 25.92, 22.65, 17.67, 14.09. IR (KBr): ν 2957, 2927, 2856, 2213, 2197 cm^{-1}. HRMS (FAB): calcd for $C_{46}H_{44}O_2$ 628.3341, found 628.3347.

Dehydrobenzo[18]annulene 14. The corresponding α,ω-polyyne (100 mg, 0.12 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (63 mg, 93% yield) was isolated as a bright yellow solid after chromatography on silica gel (4:1 hexanes−THF). ^{1}H NMR (CD_2Cl_2): δ 7.70−7.63 (m, 4H), 7.41−7.38 (m, 4H), 7.09 (s, 2H), 4.18 (bs, 4H), 3.94 (bs, 4H), 3.77 (bs, 8H). ^{13}C NMR (CD_2Cl_2): δ 149.62, 132.66, 132.47, 128.73, 128.57, 125.27, 124.99, 118.81, 116.17, 81.01, 80.69, 80.42, 78.30, 78.04, 77.16, 70.98, 70.12, 68.95, 68.65. IR (KBr): ν 2920, 2865, 2215, 2196, 2147 cm^{-1}. HRMS (FAB): calcd for $C_{38}H_{26}O_5$ 562.1780, found 562.1781.

Dehydrobenzo[18]annulene 15. The corresponding α,ω-polyyne (90 mg, 0.12 mmol) was subjected to macrocyclization reaction procedure C. Although observation of the reaction mixture under UV light indicated formation of the product DBA, the material proved to be insoluble in a variety of organic solvents and thus could not be isolated in pure form.

Dehydrobenzo[18]annulene 16. The corresponding α,ω-polyyne (37 mg, 0.035 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (25 mg, 96% yield) was isolated as a bright yellow solid after chromatography on silica gel (3:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.50 (d, J = 2.4 Hz, 2H), 8.23 (dd, J = 8.4, 2.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.48 (s, 2H), 2.64 (bt, J = 7.8 Hz, 4H), 1.68−1.49 (m, 4H), 1.46−1.24 (m, 28H), 0.90 (bt, J = 6.0 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 146.67, 143.54, 133.54, 133.35, 131.55, 127.72, 125.94, 123.55, 122.12, 84.12, 83.54, 79.68, 79.54, 78.52, 76.79, 32.59, 31.91, 30.62, 29.64 (2), 29.56, 29.48, 29.34, 22.69, 14.12. IR (KBr): ν 2955, 2926, 2853, 2210, 2197 cm^{-1}. HRMS (FAB): calcd for $C_{50}H_{50}N_2O_4$ 742.3771, found 742.3780.

α,ω-Polyyne 27. Triyne **2c** (113 mg, 0.28 mmol) was reacted with *o*-diiodoveratrole (44 mg, 0.11 mmol) via in situ protiodesilylation/alkynylation reaction procedure B. Chromatography on silica gel (1:1 hexanes−CH_2Cl_2) gave polyyne **27** (72 mg, 82% yield) as a red gum. ^{1}H NMR ($CDCl_3$): δ 8.33 (d, J = 2.4 Hz, 2H), 8.11 (dd, J = 8.7, 2.4 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 6.98 (s, 2H), 3.93 (s, 6H), 1.17 (s, 42H). ^{13}C NMR ($CDCl_3$): δ 150.19, 146.93, 133.31, 131.11, 128.48, 127.13, 122.54, 117.98, 115.12, 102.32, 99.78, 83.28, 82.78, 79.62, 76.57, 56.13, 18.67, 11.21. IR (neat): ν 2946, 2873, 2197 cm^{-1}. HRMS (FAB): calcd for $C_{50}H_{56}N_2O_6Si_2$ 836.3677, found 836.3679.

Dehydrobenzo[18]annulene 17. α,ω-Polyyne **27** (60 mg, 0.075 mmol) was subjected to the standard macrocyclization reaction procedure C. The product DBA (38 mg, 97% yield) was isolated as a bright red-orange microcrystalline solid after chromatography on silica gel (1:1 hexanes−CH_2Cl_2). Once purified, the product exhibited very poor solubility, thus precluding complete characterization. ^{1}H NMR ($CDCl_3$): δ 8.58 (s, 2H), 8.23 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.17 (s, 2H), 3.98 (s, 6H). IR (KBr): ν 2960, 2926, 2853, 2190, 2158 cm^{-1}.

Dehydrobenzo[18]annulene 18. The corresponding α,ω-polyyne (40 mg, 0.039 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (13 mg, 46% yield) was isolated as a bright red-orange microcrystalline solid after chromatography on silica gel (1:1 hexanes−CH_2Cl_2). Once purified, the product exhibited very poor solubility, thus precluding complete characterization. ^{1}H NMR (THF-d_8): δ 8.64 (d, J = 2.1 Hz, 2H), 8.36 (dd, J = 8.4, 2.1 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.30 (s, 2H), 4.10 (t, J = 6.3 Hz, 4H), 1.98−1.27 (m, 28H), 0.91 (bt, J = 6.9 Hz, 6H). IR (KBr): ν 2956, 2922, 2853, 2196, 2160 cm^{-1}. HRMS (FAB): calcd for $C_{46}H_{42}N_2O_6$ 718.3043, found 718.3046.

Dehydrobenzo[18]annulene 19. The corresponding α,ω-polyyne (50 mg, 0.044 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (29 mg, 93% yield) was isolated as a dark red solid after chromatography on silica gel (4:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.47 (d, J = 2.1 Hz, 1H), 8.20 (dd, J = 8.7, 2.1 Hz, 1H), 7.93 (s, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 8.7 Hz, 1H), 7.34 (s, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.7, 2.4 Hz, 1H), 3.32 (t, J = 7.2 Hz, 4H), 3.17 (t, J = 7.2 Hz, 4H), 1.65−1.48 (m, 8H), 1.46−1.23 (m, 8H), 0.98 (t, J = 7.2 Hz, 6H), 0.90 (t, J = 7.2 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 148.78, 147.68, 144.58, 141.00, 134.50, 134.38, 131.09, 130.86, 128.22, 127.99, 127.28, 125.88, 125.37, 123.73, 115.43, 115.08, 113,50, 110.70, 84.23, 83.46, 82.86, 82.34, 80.85, 80.41, 79.08, 79.00, 78.94, 78.29, 76.21, 75.99, 52.26, 51.25, 29.96, 29.67, 20.79, 20.63, 14.27, 14.11. IR (KBr): ν 2959, 2926, 2866, 2203, 2144 cm^{-1}. Anal. Calcd for $C_{46}H_{44}N_4O_4$: C, 77.07; H, 6.19; N, 7.82. Found: C, 76.47; H, 6.17; N, 7.69.

Dibenzotriyne 28. Triyne **2c** (128 mg, 0.25 mmol) was reacted with diiodoarene **3a** (115 mg, 0.23 mmol) via in situ desilylation/alkynylation

reaction procedure B. Chromatography on silica gel (5:1 hexanes−CH_2Cl_2) gave compound **28** (158 mg, 85% yield) as a reddish oil. ^{1}H NMR ($CDCl_3$): δ 8.10 (s, 1H), 7.35 (d, J = 9.0 Hz, 1H), 7.20 (s, 1H), 6.69 (d, J = 2.4 Hz, 1H), 6.53 (dd, J = 9.0, 2.4 Hz, 1H), 3.30 (t, J = 7.2 Hz, 4H), 3.08 (t, J = 7.2 Hz, 4H), 1.64−1.18 (m, 16H), 1.19 (s, 21H), 0.97 (t, J = 7.2 Hz, 6H), 0.89 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 148.32, 144.50, 141.26, 135.56, 134.26, 133.70, 128.49, 126.26, 114.74, 111.48, 109.30, 105.56, 94.31, 86.03, 84.79, 81.63, 81.50, 74.86, 51.87, 50.53, 29.21, 20.19, 20.06, 18.78, 13.88, 13.79, 11.35. IR (neat): ν 2953, 2873, 2197, 2150 cm^{-1}. HRMS (FAB): calcd for $C_{43}H_{62}IN_3O_2Si$ 807.3656, found 807.3651.

α,ω-Polyyne 29. Triyne **2b** (109 mg, 0.22 mmol) was reacted with compound **28** (136 mg, 0.20 mmol) via in situ desilylation/alkynylation reaction procedure B. Chromatography on silica gel (5:1 hexanes−CH_2Cl_2) gave polyyne **29** (151 mg, 73% yield) as a red gum. ^{1}H NMR ($CDCl_3$): δ 8.32 (d, J = 2.4 Hz, 1H), 8.10 (dd, J = 9.0, 2.4 Hz, 1H), 7.88 (s, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.15 (s, 1H), 6.69 (d, J = 2.4 Hz, 1H), 6.52 (dd, J = 8.4, 2.4 Hz, 1H), 3.30 (t, J = 7.5 Hz, 4H), 3.18 (t, J = 7.5 Hz, 4H), 1.63−1.51 (m, 8H), 1.44−1.25 (m, 8H), 1.19 (s, 21H), 1.17 (s, 21H), 0.97 (t, J = 7.2 Hz, 6H), 0.91 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 148.31, 146.80, 144.88, 139.21, 134.19, 133.41, 132.04, 131.30, 130.32, 128.53, 128.38, 127.01, 124.63, 122.43, 114.72, 112.57, 111.44, 109.30, 105.54, 102.27, 99.90, 94.23, 89.08, 83.10, 82.45, 82.21, 79.54, 78.14, 76.60, 75.16, 51.67, 50.51, 29.45, 29.20, 20.18, 20.03, 18.71, 18.63, 13.87, 13.75, 11.33, 11.21. IR (neat): ν 2958, 2937, 2864, 2204, 2155 cm^{-1}. Anal. Calcd for $C_{64}H_{86}N_4O_4Si_2$: C, 74.52; H, 8.40; N, 5.43. Found: C, 74.88; H, 8.46; N, 5.06.

Dehydrobenzo[18]annulene 20. α,ω-Polyyne **29** (134 mg, 0.13 mmol) was subjected to macrocyclization reaction procedure C. The residual solid was purified by chromatography on silica gel (4:1 to 1:1 hexanes−CH_2Cl_2 gradient). Macrocycle **20** (78 mg, 84% yield) was isolated as a bright red microcrystalline solid. ^{1}H NMR (CD_2Cl_2): δ 8.42 (d, J = 2.4 Hz, 1H), 8.15 (dd, J = 8.4, 2.4 Hz, 1H), 7.97 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.7 Hz, 1H), 7.28 (s, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.67 (dd, J = 8.7, 2.4 Hz, 1H), 3.32 (t, J = 6.9 Hz, 4H), 3.19 (t, J = 6.9 Hz, 4H), 1.66−1.50 (m, 8H), 1.46−1.22 (m, 8H), 0.99 (t, J = 6.9 Hz, 6H), 0.91 (t, J = 6.9 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 149.10, 147.15, 145.66, 139.48, 134.88, 133.89, 132.21, 131.77, 130.60, 127.94, 126.59, 126.54, 124.00, 123.76, 115.49, 113.38, 112.22, 109.99, 85.47, 83.66, 83.59, 81.98, 80.41, 79.64 (3), 78.69, 76.94, 76.35, 76.05, 52.26, 51.28, 29.98, 29.67, 20.79, 20.60, 14.29, 14.11. IR (KBr): ν 2957, 2928, 2869, 2204, 2189 cm^{-1}. Anal. Calcd for $C_{46}H_{44}N_4O_4$: C, 77.07; H, 6.19; N, 7.82. Found: C, 76.87; H, 6.36; N, 7.64.

Dehydrobenzo[18]annulene 21. The corresponding α,ω-polyyne (175 mg, 0.20 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (95 mg, 87% yield) was isolated as a bright red solid after chromatography on silica gel (4:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.00 (s, 1H), 7.71−7.64 (m, 4H), 7.49−7.41 (m, 4H), 7.34 (s, 1H), 3.19 (t, J = 7.2 Hz, 4H), 1.60−1.52 (m, 4H), 1.35−1.24 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 145.20, 140.34, 133.55, 133.44, 133.36, 133.17, 131.70, 130.05, 129.74, 129.67, 129.50, 129.46, 125.88, 125.71, 125.28, 125.15, 124.97, 113.66, 82.54, 81.52, 81.21, 81.09, 80.29, 80.19, 80.03, 78.49, 78.46, 78.10, 77.78, 77.53, 52.28, 30.00, 20.60, 14.11. IR (KBr): ν 2955, 2929, 2871, 2853, 2213, 2194, 2156, 2142 cm^{-1}. Anal. Calcd for $C_{38}H_{28}N_2O_2$: C, 83.80; H, 5.18; N, 5.14. Found: C, 83.60; H, 5.37; N, 4.98.

Dehydrobenzo[18]annulene 22. The corresponding α,ω-polyyne (60 mg, 0.070 mmol) was subjected to the standard macrocyclization reaction procedure C. The product DBA (36 mg, 94% yield) was isolated as a bright red solid after chromatography on silica gel (4:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.49 (d, J = 2.4 Hz, 1H), 8.21 (dd, J = 8.7, 2.4 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.68−7.62 (m, 2H), 7.49 (d, J = 8.7 Hz, 1H), 7.47−7.7.37 (m, 2H), 6.86 (d, J = 2.7 Hz, 1H), 6.67 (dd, J = 8.7, 2.7 Hz, 1H), 3.32 (t, J = 7.2 Hz, 4H), 1.65−1.54 (m, 4H), 1.44−1.33 (m, 4H), 1.00 (t, J = 7.2 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 148.90, 147.43, 134.68, 134.19, 133.59, 132.83, 131.54, 130.17, 138.94, 127.98, 126.88, 126.66, 126.12, 124.25, 123.77, 115.44, 113.53, 110.50, 84.30, 83.98, 83.75, 83.03, 80.56, 80.33 (2), 79.77, 79.45, 78.45, 77.41, 76.07, 51.26, 29.67, 20.79, 14.27. IR (KBr): ν 2954, 2928, 2870, 2206, 2191, 2142 cm^{-1}. Anal. Calcd for $C_{38}H_{28}N_2O_2$: C, 83.80; H, 5.18; N, 5.14. Found: C, 83.88; H, 5.30; N, 5.04.

Dehydrobenzo[18]annulene 23. The corresponding α,ω-polyyne (10 mg, 0.012 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (6.5 mg, 99% yield) was isolated as a bright yellow solid after chromatography on silica gel (2:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.49 (d, J = 2.4 Hz, 1H), 8.20 (dd, J = 8.7, 2.4 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.74−7.67 (m, 2H), 7.53−7.44 (m, 3H), 6.89 (d, J = 2.7 Hz, 1H), 6.70 (dd, J = 9.0, 2.7 Hz, 1H), 3.34 (t, J = 7.2 Hz, 4H), 1.63−1.51 (m, 4H), 1.42−1.34 (m, 4H), 0.98 (t, J = 7.2 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 148.47, 147.14, 134.51, 132.98, 132.72, 132.66, 132.10, 129.16, 128.80, 127.52, 126.84, 125.69, 125.50, 124.82, 123.18, 114.75, 112.36, 109.69, 86.74, 85.04, 81.93, 81.82, 80.11, 80.00, 78.83, 78.74, 78.40, 77.21, 76.75, 75.80, 50.79, 29.21, 20.27, 13.97. IR (KBr): ν 2959, 2926, 2860, 2190 cm^{-1}. HRMS (FAB): calcd for $C_{38}H_{28}N_2O_2$ 544.2151, found 544.2155.

Dehydrobenzo[18]annulene 24. The corresponding α,ω-polyyne (100 mg, 0.14 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (42 mg, 60% yield) was isolated as a bright yellow-green solid after chromatography on silica gel (4:1 hexanes−THF). ^{1}H NMR (CD_2Cl_2): δ 7.73−7.66 (m, 4H), 7.52−7.40 (m, 5H), 6.88 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.7, 2.4 Hz, 1H), 3.32 (t, J = 7.5 Hz, 4H), 1.66−1.54 (m, 4H), 1.46−1.33 (m, 4H), 0.98 (t, J = 6.9 Hz, 6H). ^{13}C NMR (CD_2Cl_2): δ 148.86, 134.63, 133.35, 133.28, 132.76, 129.61, 129.61, 129.55, 129.51, 128.87, 126.58, 126.30, 125.59, 125.53, 124.84, 115.27, 113.20, 110.41, 83.71, 82.60, 81.63, 81.19, 80.65, 80.45, 79.51, 78.42, 78.29, 77.96, 76.61, 75.97, 51.26, 29.70, 20.80, 14.29. IR (KBr): ν 2957, 2929, 2872, 2861, 2210, 2190, 2135 cm^{-1}. HRMS (FAB): calcd for $C_{38}H_{29}N$ 499.2300, found 499.2296.

Dehydrobenzo[18]annulene 25. The corresponding α,ω-polyyne (60 mg, 0.064 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (37 mg, 92% yield) was isolated as a bright yellow solid after chromatography on silica gel (2:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 7.63 (AA′ m, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.38 (BB′ m, 2H), 6.86 (d, J = 3.0 Hz, 2H), 6.69 (dd, J = 9.0, 3.0 Hz, 2H), 3.32 (t, J = 7.5 Hz, 8H), 1.65−1.37 (m, 8H), 1.40−1.28 (m, 8H), 0.98 (t, J = 7.5 Hz, 12H). ^{13}C NMR (CD_2Cl_2): δ 148.80, 134.62, 132.68, 128.83, 126.63, 125.62, 115.19, 113.10, 110.46, 83.50, 81.94, 80.71, 79.15, 76.77, 75.95, 51.26, 29.70, 20.80, 14.29. IR (KBr): ν 2953, 2926, 2864, 2193, 2141, 1590 cm^{-1}. HRMS (FAB): calcd for $C_{46}H_{46}N_2$ 626.3661, found 626.3665.

Dehydrobenzo[18]annulene 26. The corresponding α,ω-polyyne (80 mg, 0.095 mmol) was subjected to macrocyclization reaction procedure C. The product DBA (101 mg, 45% yield) was isolated as a dark red solid after chromatography on silica gel (2:1 hexanes−CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ 8.41 (s, 1H), 8.07 (t, J = 5.1 Hz, 1H), 7.46 (d, J = 9.0 Hz, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.08 (s, 1H), 6.85−6.81 (m, 2H), 6.68 (d, J = 2.1 Hz, 1H), 6.65 (d, J = 1.8 Hz, 1H), 3.42−3.22 (m, 8H), 1.65−1.52 (m, 8H), 1.43−1.31 (m, 8H), 0.98 (t, J = 7.2 Hz, 12H). ^{13}C NMR (CD_2Cl_2): δ 149.18, 148.65, 144.92, 135.01, 134.40, 132.55, 131.40, 131.28, 127.19, 126.32, 117.72, 115.31, 115.17, 113.20, 113.01, 111.55, 110.78, 109.76, 86.16, 82.78, 82.56, 82.22, 81.62, 79.99, 79.51, 77.15, 77.05, 76.59, 76.05, 75.89, 51.25, 29.71, 20.79, 14.27. IR (KBr): ν 3370, 2959, 2926, 2866, 2190, 2137 cm^{-1}. MS (FAB): m/z 687 (M^+, 57), 671 (22).

***N,N*-Dibutyl-4-[4-(4-nitrophenyl)-1,3-butadiynyl]aniline (32).** *N,N*-Dibutyl-4-iodoaniline (50 mg, 0.15 mmol), prepared in a manner analogous to that for **8**, was reacted with 1-[4-(trimethylsilyl)-1,3-butadiynyl]-4-nitrobenzene (44 mg, 0.18 mmol) via in situ protiodesilylation/alkynylation reaction procedure B. Chromatography on silica gel (3:1 hexanes−CH_2Cl_2) gave butadiyne **32** (47 mg, 84%) as a light orange solid. ^{1}H NMR ($CDCl_3$): δ 8.20 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 9.0 Hz, 2H), 7.39 (d, J = 9.0 Hz, 2H), 6.56 (d, J = 9.0 Hz, 2H), 3.30 (t, J = 7.8 Hz, 4H), 1.62−1.51 (m, 4H), 1.40−1.31 (m, 4H), 0.97 (t, J = 7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 148.90, 134.25, 133.18, 132.79, 132.63, 128.54, 123.63, 111.09, 87.31, 80.49, 78.72, 71.57, 50.67, 29.26, 20.26, 13.96. IR (KBr): ν 2958, 2931, 2874, 2855, 2210, 2186 cm^{-1}.

Table 5. Crystallographic Data for DBAs **20**, **22**, **23**, and **25**

	20	**22**	**23**	**25**
empirical formula	$C_{46}H_{44}N_4O_4 \cdot CH_2Cl_2$	$C_{38}H_{28}N_2O_2$	$C_{38}H_{28}N_2O_2$	$C_{46}H_{46}N_2$
fw	801.81	544.65	544.65	626.89
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	*Ia*	$P\bar{1}$	$P\bar{1}$
a (Å)	10.0234(11)	9.7761(10)	10.769(2)	9.420(3)
b (Å)	13.9218(16)	31.232(4)	11.449(3)	12.022(4)
c (Å)	16.5767(19)	10.954(3)	14.308(2)	18.224(3)
α (deg)	74.555(9)	90	70.55(2)	73.26(2)
β (deg)	86.062(9)	114.464(14)	78.93(1)	82.47(2)
γ (deg)	79.957(10)	90	64.78(2)	74.29(3)
V (Å^3)	2192.5(9)	3044.2(9)	1502(1)	1899(1)
Z	2	4	2	2
T (K)	294	294	295	295
GOF	1.69	1.35	1.37	3.15
R(*F*)	0.101	0.053	0.147	0.095
$R_w(F)$	0.053	0.045	0.067	0.093

X-ray Structure Determinations. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). Pertinent crystallographic data and refinement parameters are given in Table 5. Structure refinements (C atoms anisotropic, H atoms riding) were accomplished with the TEXSAN program suite (version 5.0). Further details are contained in the Supporting Information. All crystals were weakly diffracting and exhibited disorder in the butyl groups.

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Supporting Information Available: Figures giving X-ray crystal structures and tables of atomic coordinates, thermal parameters, bond lengths, and bond angles of **20**, **22**, **23**, and **25** and crystallographic files, in CIF format, for these compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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