

Diatropicity of 3,4,7,8,9,10,13,14-Octadehydro[14]annulenes: A Combined Experimental and Theoretical Investigation

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Received July 11, 2002

The synthesis and study of a series of octadehydro[14]annulenes is described. The aromaticity of these annulenes was investigated through examination of experimental data from arene-fused systems as well as calculated nucleus-independent chemical shifts (NICS) and bond lengths. Benzene ring fusion to the parent system results in a stepwise loss in aromaticity as the number of fused rings is increased from one to two to three. This decrease in annulenic ring current is manifested in the alkene proton chemical shifts (0–2 benzenes) as well as the NICS (0–3 benzenes). Comparison of isomeric thiophene-fused annulenes shows further evidence of ring current competition as these allow for observation of intermittent degrees of delocalization throughout the annulenic core. A consistent relationship between the magnitude of the NICS values and the degree of benzannelation is also observed.

Introduction

An intensely investigated and debated area of dehydroannulene (DA) and dehydrobenzoannulene (DBA) chemistry involves the study of induced ring currents in these macrocycles.¹ With increased benzannelation and higher degrees of unsaturation (i.e., triple versus double bonds), many systems become suspect as to whether they can accurately be considered aromatic or antiaromatic. This issue has been addressed on two fronts. Classically, experimental observations, based mainly on proton NMR data,² provide strong evidence for the existence of ring currents in most DAs and DBAs. More recently, theoretical work, specifically nucleus-independent chemical shifts (NICS),³ has improved our ability to understand this fundamental yet elusive property of these macrocycles.

We have shown qualitatively through experiment that DBAs possess an induced ring current despite their large size, extensive benzannelation, and high degree of unsaturation.⁴ Unfortunately, as shown in the preceding paper in this issue, efforts to quantify the ring current of DAs and DBAs fused to dimethyldihydropyrene (DDP), Mitchell's elegant NMR probe for aromaticity, afforded

mixed results.⁵ Vollhardt,⁶ Sundholm,⁷ and Elguero⁸ have each used NICS to study DBAs, though not without some disparity of their results. In considering all of these studies, two facts become evident: (1) conclusions based solely on experimental observations can sometimes be overly optimistic, and (2) computational approaches are complicated by varying levels of theory, asymmetry of the study molecule, contributions from anisotropic regions of the macrocycle, and the size of the conjugated backbone.

Bunz's group recently reported interesting comparative aromaticity studies on arene-fused annulenes.⁹ An important assumption in their argument was the ability of the 3,4,7,8,9,10,13,14-octadehydro[14]annulene skeleton (**1**) to undergo ring current competition. This sparked our initial interest in trying to understand the extent to which **1** could be considered aromatic.¹⁰ Although it is generally accepted that certain [14]annulenes¹¹ and [18]-

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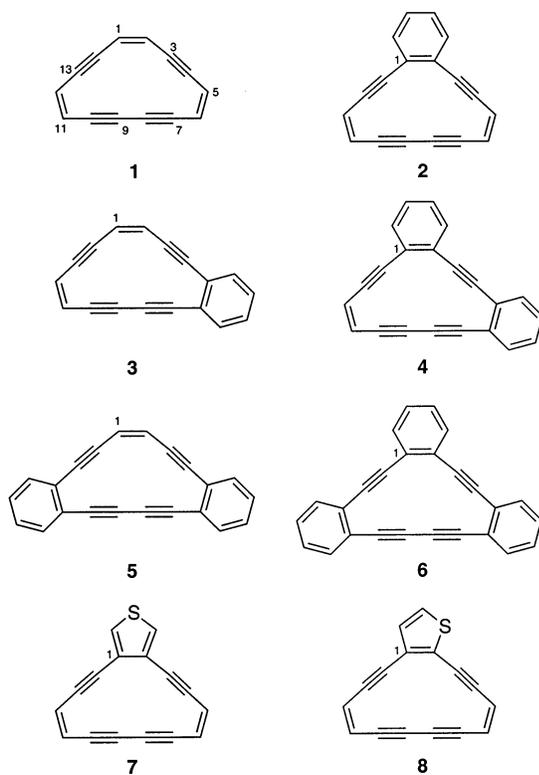


FIGURE 1. Octadehydro[14]annulene **1** and arene-fused analogues **2–8**. For comparison purposes, the top left sp^2 carbon is position 1 and the remaining carbons of the 14-membered ring are numbered in a clockwise manner.

annulenes¹² are in fact aromatic, increased unsaturation and ring strain are known to reduce delocalization,¹ thus, this gives rise to skepticism about the aromaticity of **1**. With the specific criteria for aromaticity, and even a universal definition, still being an issue of debate,¹³ we felt it was pragmatic to probe a specific system using both experimental and theoretical tools. To strengthen our arguments for the existence of aromaticity in octadehydro[14]annulenes, we report herein a comprehensive study of the ring current in **1** and arene-fused analogues **2–8** (Figure 1). This investigation involves (1) stepwise reduction in the macrocyclic ring current as a result of successive benzannelation, (2) examination of the sensitivity of the annulenic core to changes in the degree of conjugation allowed by regioisomeric thieno fusion, and (3) theoretical evidence of aromaticity and a relative quantification using NICS.

Results and Discussion

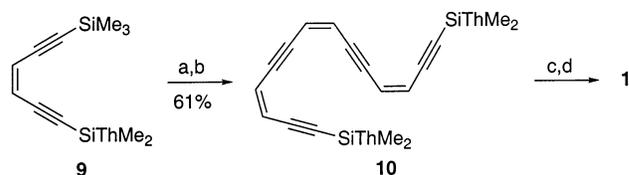
Decrease of Aromaticity by Benzannelation. Although a few derivatives have been reported, surprisingly the parent octadehydro[14]annulene (**1**) was an unknown molecule. The straightforward synthesis of this macrocycle is described in Scheme 1. Selective deprotection of enediyne **9**¹⁴ followed by Pd-catalyzed cross-coupling with (*Z*)-1,2-dichloroethene furnished α,ω -polykyne **10** in 61%

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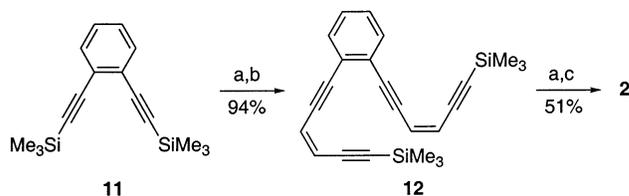
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SCHEME 1^a



^a Reagents and conditions: (a) K_2CO_3 , MeOH, THF; (b) (*Z*)-1,2-dichloroethene, $Pd(PPh_3)_4$, CuI, $PrNH_2$, THF; (c) Bu_4NF , THF, MeOH; (d) $Cu(OAc)_2$, MeCN, 100 °C. Th = thexyl = 1,1,2-trimethylpropyl.

SCHEME 2^a



^a Reagents and conditions: (a) $K_2CO_3(aq)$, MeOH, THF; (b) (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane, $Pd(PPh_3)_4$, CuI, $PrNH_2$, THF; (c) $Cu(OAc)_2$, MeCN, 100 °C.

yield. Deprotection with Bu_4NF and cyclization under Vögtle's conditions¹⁵ produced macrocycle **1**, which was stable only in dilute solutions.

Symmetric monobenzannelated annulene **2**¹⁶ was prepared from 1,2-bis(trimethylsilylethynyl)benzene¹⁷ (**11**) and (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane¹⁸ (Scheme 2). Deprotection of the aryldiynes using methanolic K_2CO_3 , followed by cross-coupling to the chloroalkene, furnished terminally protected polykyne **12** in 94% yield for the two steps. Stepwise deprotection and cyclization provided the desired macrocycle, which polymerized to form an insoluble black film upon concentration.

The synthesis of asymmetric monobenzannelated **3** (Scheme 3) made use of monoprotected phenyldiynes **13**,^{4b,19} which was cross-coupled to (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane to provide **14** in 87% yield. Deprotection and repeated cross-coupling gave polykyne **15** in 83% yield. Protodesilylation with Bu_4NF and MeOH followed by cyclization furnished unstable benzocyclyne **3**.

The synthesis of **4** is shown in Scheme 4. Starting from known iodoarene **16**,^{4b,19} an in situ deprotection/alkynylation procedure^{4b,19} was employed to give polykyne **17** in 75% yield. Deprotection and cyclization as before furnished **4**, which was stable only in dilute solutions.

With dibenzoannulene **5**²⁰ and tribenzoannulene **6**²¹ already known, we proceeded to compare proton chemical shifts to determine whether a stepwise decrease in aromaticity resulted as the number of fused rings in-

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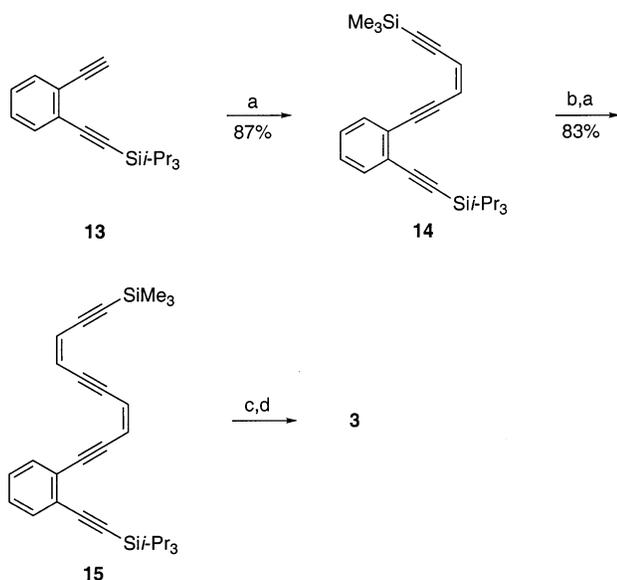
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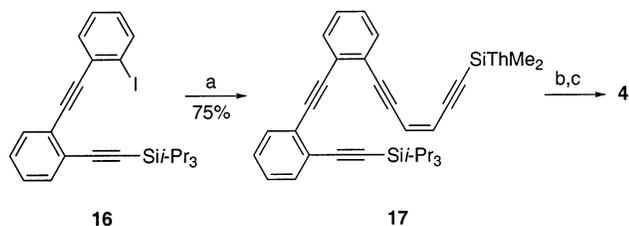
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SCHEME 3^a

^a Reagents and conditions: (a) (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane, Pd(PPh₃)₄, CuI, PrNH₂, THF; (b) NaH, MeOH, THF; (c) Bu₄NF, THF, MeOH; (d) Cu(OAc)₂·H₂O, MeCN, 100 °C.

SCHEME 4^a

^a Reagents and conditions: (a) **9**, K₂CO₃, MeOH, PdCl₂(PPh₃)₂, CuI, Et₃N; (b) Bu₄NF, THF, MeOH; (c) Cu(OAc)₂, MeCN, 100 °C.

TABLE 1. Alkene Proton Chemical Shifts (ppm) of Precyclized Compounds^a

proton ^b	10	12	15	17	pre-5 ^c	21	23
H1	6.05		6.11		6.11		
H11	5.90	5.94	5.91	5.95		5.91	5.90
H12	6.07	6.17	6.11	6.15		6.07	6.11

^a In CD₂Cl₂. ^b Proton numbering in the precyclized compounds is analogous to that shown in Figure 1, minus the C8–C9 diacetylene single bond. ^c Reference 20.

creased. First it was necessary to establish whether the simple inclusion of a benzene ring into the conjugated backbone had an effect on the overall deshielding of the alkene protons. Table 1 shows the chemical shifts of similar protons in each system. It is clear that prior to cyclization the alkene protons give little acknowledgment of the aryl moiety.

Upon cyclization, however, there is a distinct loss in aromaticity of the 14-membered macrocycle when the number of benzene rings is increased from zero to one, as illustrated by the upfield shift of the alkene protons (Table 2). In this case, the change in resonance ($\Delta\delta$) of the alkene protons is, on average, an upfield shift of 0.67 ppm (Table 3). Fusion of a second benzene ring results in an additional average $\Delta\delta$ of 0.38 ppm. The mean $\Delta\delta$ values are consistent with the notion that benzannelation reduces aromaticity in an annulene circuit by about

TABLE 2. Alkene Proton Chemical Shifts (ppm) of Cyclized Compounds^a

proton	1	2	3	4	5
H1	7.77		7.03		6.72
H2	7.77		7.16		6.72
H11	7.39	6.73	6.74	6.37	
H12	7.92	7.41	7.24	7.01	

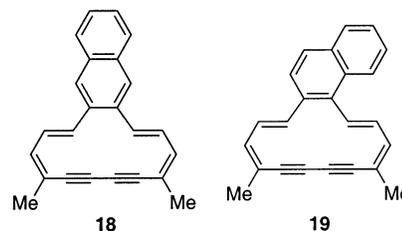
^a In CD₂Cl₂.

TABLE 3. Chemical Shift Difference (ppm) of Alkene Protons upon Successive Benzannelation

proton	1 → 3	1 → 2	3 → 4	3 → 5	2 → 4
H1	-0.74			-0.31	
H2	-0.61			-0.44	
H11	-0.65	-0.66	-0.37		-0.36
H12	-0.68	-0.51	-0.23		-0.40

half.^{2a,22} It is worth noting that the specific site of ring fusion has little effect between regioisomers (compare **2** to **3**), with the exception of an alkene proton γ to a bridging carbon. For this case, ca. 0.15 ppm must be added to the $\Delta\delta$ value (e.g., H12 in **1** → **2** vs **1** → **3**). This adjustment is attributed to the steric deshielding effect of the nearby arene proton.

Intermittent Degrees of Delocalization. Encouraged by the results presented above, we became curious about the effects of allowing intermittent degrees of delocalization. This could be achieved by fusing a thiophene ring to the annulene backbone in two different regioisomeric fashions. This was inspired by Sondheimer's observation that fusing an annulene moiety across the 2–3 bond of naphthalene (**18**) resulted in less aromatic character in the [14]annulene moiety than when fusion was done across the 1–2 bond (**19**).²³ The change



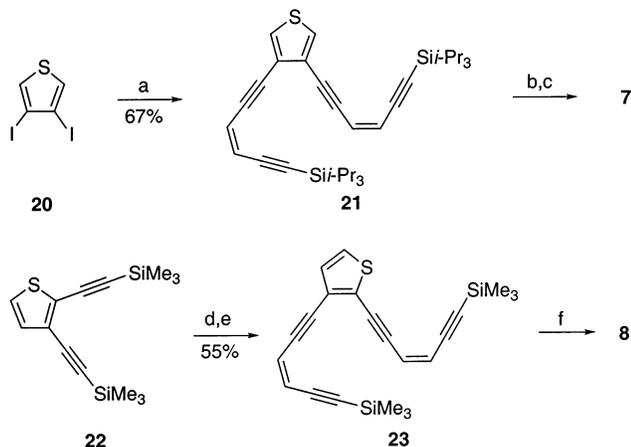
in ring current was manifested in the chemical shifts of the alkene and methyl protons about the macrocycle, and is attributable to less double bond character in the 2–3 bond than in the 1–2 bond in naphthalene. Similar to the naphthalene case, thiophene also exhibits bond alternation, with the 3–4 bond in a thiophene ring known to possess less double bond character than the 2–3 bond.²⁴ The effects of such “bond localization” have been observed in the properties of other thieno-fused dehydroannulenes,²⁵ and should be rather pronounced for **7** and **8**.

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SCHEME 5^a

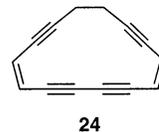
^a Reagents and conditions: (a) 1-(triisopropylsilyl)-6-(trimethylsilyl)-3-hexen-1,5-diyne, K_2CO_3 , MeOH, $\text{Pd}(\text{PPh}_3)_4$, CuI, $i\text{-Pr}_2\text{NEt}$, THF, 100 °C; (b) Bu_4NF , THF, MeOH; (c) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, MeCN, 100 °C; (d) K_2CO_3 , MeOH, THF; (e) (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane, $\text{Pd}(\text{PPh}_3)_4$, CuI, PrNH_2 , THF; (f) K_2CO_3 , MeOH, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, MeCN, 100 °C.

The synthesis of thienoannulenes **7** and **8** is shown in Scheme 5. In situ deprotection/alkynylation involving 3,4-diiodothiophene (**20**) and 1-(triisopropylsilyl)-6-(trimethylsilyl)-3-hexen-1,5-diyne²⁶ gave the requisite synthon **21** in 67% yield. Varying the solvent, reaction time, reaction temperature, and base only resulted in much lower yields. The combination of Hünig's base and THF at 100 °C gave the only yield above 25%. Deprotection and cyclization gave the symmetric annulene, which polymerized even in dilute solutions at -20 °C. The same strategy was applied to the synthesis of asymmetric **8**, but with unsatisfying results. Cross-coupling under the same conditions that produced **21** only resulted in modest amounts of monocoupled product. The site of alkynylation was not determined, nor was it of interest. Instead, known diethynylthiophene **22**²⁷ was prepared in nearly quantitative yield utilizing Hünig's base and THF at 100 °C. Deprotection and cross-coupling furnished **23** in 55% yield. Although no deprotected diethynylthiophene was found, attempts to increase the yield were unsuccessful. Use of an in situ deprotection/cyclization procedure, modified from Vögtle's conditions,¹⁵ gave cleanly the desired macrocycle, but with the usual instability upon concentration.

Gratifyingly, the thieno[14]annulenes provided the desired results. Proton NMR spectroscopy confirmed that the thiophene ring in the symmetrical system retained more of its ring current upon cyclization than did the thiophene ring in the asymmetric macrocycle. This is evident from the arene proton chemical shifts of each thiophene nucleus in the two macrocycles (8.01 ppm in **7**, 7.81 and 7.69 ppm in **8**). In **8**, the increased double bond character at the site of fusion results in an obvious increase in delocalization in the [14]annulenic circuit in comparison with that in **7**. Each of the alkene protons of **8** (7.60, 7.58, 7.02, and 6.97 ppm) appear further downfield than those of the less aromatic **7** (6.93 and 6.32

ppm). The electronic absorption spectra also support the more aromatic character of **8**. In **7** the λ_{max} is 304 nm, whereas in **8** the λ_{max} exhibits a small but distinguishable bathochromic shift to 318 nm.

We next compared the extent of delocalization in our parent, fully conjugated system to that in the 1,2-dihydro analogue **24** reported by Schreiber's group.²⁸ By breaking



the conjugation, we can compare two systems with nearly identical degrees of unsaturation, but with one being nonaromatic and the other having a classically aromatic structure. The alkene protons of **24** have chemical shifts of 6.19 and 5.79 ppm. In comparison with those of **1** (7.92 and 7.39 ppm), it is clear that a diatropic ring current is present when the system is fully conjugated. Such a difference in chemical shifts cannot be ascribed to the anisotropy of the 1–2 double bond in **1**.

Computational Studies. To provide further insight into the effects of benzannulation upon the aromaticity of the octadehydro[14]annulene (ODA) nucleus, we undertook a computational investigation similar to that used in the accompanying paper.⁵ Geometries were optimized using the B3LYP/6-31G* method as implemented in Jaguar 4.0²⁹ and were confirmed to be minima through their calculated energy second derivatives. Nucleus-independent chemical shifts^{3,30} were calculated using the Hartree–Fock (HF) gauge-invariant atomic orbital (GIAO) method on the B3LYP/6-31G*-optimized geometries (GIAO-HF/6-31G*/B3LYP/6-31G*) with the Gaussian 98 suite of programs.³¹

Comparison of calculated and experimental bond lengths for compounds **5** and **6** (Supporting Information Table S1) and of calculated and experimental NMR chemical shifts for compounds **1–8** and **24** (¹H, Supporting Information Tables S2 and S3; ¹³C, Supporting Information Tables S4 and S5) reveals a reassuringly close agreement between theory and experiment, verifying the appropriateness of the level of theory used for this study.

Schleyer and co-workers demonstrated that NICS is an effective tool for the detection of aromaticity, equating negative NICS values with the existence of aromaticity in the ring system under investigation.^{3,32} Recently, through the use of NICS, we showed not only that it

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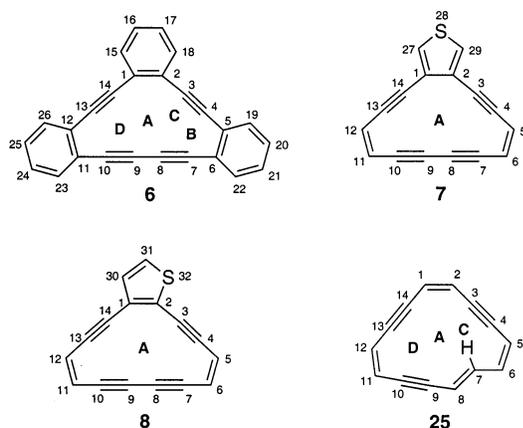


FIGURE 2. Numbering scheme and location of the NICS points for **6–8** and **25**. NICS points: A, center of C1–14; B, center of C2–8; C, center of C14 and C1–7; D, center of C1 and C14–8. The corresponding numbering scheme and location of the NICS points for **1–5** and **24** is accomplished by deleting the appropriate fused arenes.

is possible to detect aromaticity, but also that the magnitude of the NICS correlates with the experimental degree of aromaticity in a wide range of dimethyldihydropyrenes.³³ We calculated NICS at four locations in the ODA ring (points A–D in Figure 2) and also at 0.25 Å increments along the normal to the ODA ring plane from each of these points (Table 4, Supporting Information Table S6).

It is immediately apparent from the inflated NICS values associated with points B–D (especially for compound **24**, which is not aromatic due to the interrupted conjugation) that local anisotropies are adversely affecting the NICS at these points. The NICS at point A (A(0)) and along the normal emanating from this point (A(0.25)–A(2.00)) show almost identical ordering of aromaticity for the ODA nucleus of compounds **1–8** and the related species **24** and **25** (Table 4). The only difference in progressing from A(0) to A(2.00) is a reversal in the order of the essentially indistinguishable aromaticities of **4** and **5** in going from points A(0)–A(0.50) to points A(0.75)–A(2.00). We therefore, as in the preceding paper,⁵ chose to define the NICS relative aromaticity (RA_{NICS}) of the octadehydro[14]annulene (ODA) nucleus in terms of the NICS determined at A(0). For both the experimental relative aromaticity (RA_{exptl}) and the RA_{NICS} we used the nonaromatic model **24** and the fully aromatic parent (**1**) as reference compounds (eqs 1 and 2).

$$RA_{\text{exptl}} = \frac{\delta(\mathbf{24}) - \delta(\mathbf{n})}{\delta(\mathbf{24}) - \delta(\mathbf{1})} \times 100 \quad (1)$$

$$RA_{\text{NICS}} = \frac{\text{NICS}(\mathbf{24}) - \text{NICS}(\mathbf{n})}{\text{NICS}(\mathbf{24}) - \text{NICS}(\mathbf{1})} \times 100 \quad (2)$$

RA_{exptl} = experimental relative aromaticity of ODA **n** (compared to **1**),

$\delta(\mathbf{24})$ = experimental ¹H chemical shift of H11 or H12 on **24** (5.6 and 6.0 ppm, respectively),

$\delta(\mathbf{n})$ = experimental ¹H chemical shift of H11 or H12 on ODA **n**,

$\delta(\mathbf{1})$ = experimental ¹H chemical shift of H11 or H12 on **1** (7.39 and 7.92 ppm, respectively),

RA_{NICS} = NICS relative aromaticity of ODA **n** (compared to **1**),

NICS (**24**) = NICS value at point A(0) for **24** (0.88),

NICS(**n**) = NICS value at NICS point A(0) for ODA **n**, and

NICS(**1**) = NICS value at NICS point A(0) for **1** (–8.12).

In the preceding paper,⁵ we determined that the ODA nucleus is indeed aromatic, albeit weakly so. Additional support for this conclusion is provided by comparing the properties of the parent ODA (**1**) with Sondheimer’s “dihydro” derivative **25**. Hexadehydro[14]annulene (**25**) is indisputably diatropic as affirmed by the substantial difference in the observed ¹H chemical shifts of the inner proton (H7, δ –4.96 ppm) and the outer protons (H1,2,5,6,8,11,12, δ 9.47–8.08 ppm).³⁴ The protons on **1** (δ 7.77–7.92 ppm) resonate at only slightly higher field than the outer protons of **25**, a clear indication of a diatropic ring current in **1**. The NICS values at point A(0) for **1** and **25** (Figure 2) are also of very similar magnitude, –8.12 and –8.72, respectively, again indicating that the more unsaturated **1** is only slightly less aromatic than **25**.

It is well-known that benzannulation of an annulene causes bond localization with a concomitant reduction in the diatropicity of the annulene.³⁵ We thus expected benzene fusion to ODA to result in a reduction in diatropicity of the ODA nucleus. The ¹H NMR chemical shifts observed for **1–5** indicate an approximate 50% reduction in aromaticity of the ODA nucleus for each benzene fusion (vide supra). Our NICS results, principally focusing on points A (Table 4), are in complete agreement with this experimental ordering of aromaticity and, in addition, demonstrate that the degree of aromaticity of the ODA nucleus in **6** is about 50% of that in **5**. We previously found that RAs furnish a reliable ordering of aromaticity, but that their absolute magnitude is not of particular significance.^{5,33} Examination of both the experimental and calculated RAs in Table 5 shows that the order of aromaticity of the ODA nuclei in **1–6** is



As we observed previously,^{5,33} calculated RAs indicate a greater reduction in diatropicity of the annulene upon annelation than do the experimental RAs.

Vollhardt and Matzger reported the NICS (GIAO-B3LYP/6-31G*//B3LYP/6-31G*) for **6** at point A(0) to be –1.79 (compare with the corresponding NICS, –0.04, in Table 4).⁶ The discrepancy between these NICS values is accounted for by the fact that Vollhardt and Matzger used the GIAO-B3LYP/6-31G* method while in this study we used the GIAO-HF/6-31G* method to calculate NICS. We concur with their conclusion that **6** is very weakly diatropic ($RA_{\text{NICS}} = 10.2\%$, Table 5).

(33) Williams, R. V.; Armantrout, J. R.; Twamley, B.; Mitchell, R. H.; Ward, T. R.; Bandyopadhyay, S. *J. Am. Chem. Soc.* **2002**, *124*, 13495–13505.

(34) Mayer, J.; Sondheimer, F. *J. Am. Chem. Soc.* **1966**, *88*, 602–603.

(35) See Vol. II, Chapter 7, in ref 1a.

TABLE 4. NICS Values for Compounds 1–8, 24, and 25^a

	1	2	3	4	5	6	7	8	24	25
A(0)	-8.12	-3.64	-3.60	-1.28	-1.30	-0.04	-1.10	-6.16	0.88	-8.72
A(0.25)	-8.05	-3.61	-3.57	-1.27	-1.29	-0.04	-1.09	-6.10	0.88	-8.62
A(0.50)	-7.85	-3.52	-3.48	-1.23	-1.24	-0.02	-1.05	-5.94	0.87	-8.34
A(0.75)	-7.53	-3.38	-3.33	-1.18	-1.18	-0.02	-1.01	-5.69	0.85	-7.96
A(1.00)	-7.10	-3.20	-3.15	-1.12	-1.12	-0.02	-0.97	-5.35	0.81	-7.51
A(1.25)	-6.59	-2.99	-2.93	-1.08	-1.05	-0.05	-0.92	-4.96	0.75	-7.02
A(1.50)	-6.04	-2.77	-2.70	-1.04	-0.99	-0.10	-0.88	-4.55	0.67	-6.48
A(1.75)	-5.46	-2.55	-2.47	-1.00	-0.94	-0.15	-0.84	-4.12	0.59	-5.92
A(2.00)	-4.89	-2.33	-2.24	-0.96	-0.88	-0.20	-0.80	-3.71	0.51	-5.35

^a For the complete table including NICS points B–D, please see Table S6 in the Supporting Information.

TABLE 5. Relative Aromaticity (%) of the ODA Nucleus of 2–8

	RA _{exptl} (H11)	RA _{exptl} (H12)	RA _{NICS} ^a
2	63.1	73.4	50.2
3	63.1	64.6	49.8
4	43.0	52.6	24.0
5			24.2
6			10.2
7	40.2	48.4	22.0
8	79.3	88.0	78.2

^a Relative aromaticity (%) calculated using NICS point A(0).

Consistent with the reductions in aromaticity upon benzannelation of **1**, reported above, this annelation also causes the expected bond localization in compounds **2–6** (Table S1). The calculated (and experimental) “single” bond lengths (2–3, 4–5, 6–7, 8–9, 10–11, 12–13, and 14–1) are longer, while the “triple” bond lengths (3–4, 7–8, 9–10, and 13–14) are shorter than those in **1**. The “double” bonds of **2–5**, which are not benzannelated, show a similar shortening, while the “double” bonds at the sites of annelation are elongated compared with those in **1**. In general for **2–6**, the more benzene rings fused to the ODA nucleus the greater the observed lengthening/shortening of the ODA bonds.

As already noted from the experimental ¹H NMR chemical shifts, thiophene fusion to the ODA attenuates the diatropicity of this nucleus, with the ODA of **7** being significantly less aromatic than that of **8**. Our calculated data similarly demonstrate for the ODA nucleus of **8** a relatively high degree of aromaticity (reasonably large negative NICS, deshielded peripheral protons, and significant bond equalization) while **7** has properties more typical of dibenzannelated ODAs **4** and **5** (Tables 4 and S2–S5). The more efficient delocalization in the ODA nucleus of **8** than **7** is due to the increased double bond character of the thiophene 2–3 bond over the 3–4 bond, or alternatively, the difference in character between **7** and **8** can also be explained by viewing **7** as a zero-bridged dehydrothia[17]annulene in which 18 π electrons are delocalized over the whole periphery while **8** is a thieno-annelated ODA. Following the usual trend, the larger annulene **7** is less aromatic than the effectively smaller annulene **8**.¹

Conclusions

The synthesis and comparative aromaticity study of a family of octadehydro[14]annulenes has been accomplished. Experimentally, proton NMR analysis allows for a qualitative comparison of aromaticity which has disclosed evidence for a weak induced ring current too subtle

to be accurately studied using the dimethyldihydropyrene probe.⁵ Although the magnitude of ring current present in these ODAs is below the advisory limits for use of a DDP hybrid to quantify the aromaticity, the combination of sensitive alkene proton chemical shifts with consistent calculated data has allowed for a strong understanding of the relative amounts of induced ring current in these systems. Mean $\Delta\delta$ values upon successive benzannelation provide insight into the relative amount of ring current present after fusion. NICS calculations provide data in excellent agreement with the experimentally observed trends.

Experimental Section

Materials and Methods. ¹H and ¹³C NMR spectra were recorded on a 300 MHz (¹H, 299.94 MHz; ¹³C, 75.43 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane using the residual solvent as an internal standard (CDCl₃, ¹H 7.26, ¹³C 77.00; CD₂Cl₂, ¹H 5.32, ¹³C 54.00). Coupling constants are expressed in hertz. Et₃N and PrNH₂ were distilled from CaH₂ under a N₂ atmosphere prior to use. THF and Et₂O were distilled from Na and benzophenone under a N₂ atmosphere prior to use. All other chemicals were of reagent quality and used as obtained from the manufacturers. Column chromatography was performed on reagent grade silica gel (230–400 mesh). Preparative radial thin-layer chromatography was performed using silica gel (60 PF₂₅₄) plates (1–4 mm). Precoated silica gel plates (200 × 50 × 0.25 mm) were used for analytical thin-layer chromatography. Reactions were carried out in an inert atmosphere (dry N₂) when necessary.

α,ω -Polyne 10. Eneidyne **9**¹⁴ (347 mg, 1.19 mmol) was dissolved in MeOH/THF (50 mL, 1:1 v/v), and K₂CO₃ (332 mg, 2.40 mmol) was added. The mixture was stirred for 2–3 h and monitored by TLC. Upon completion, the reaction was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the monoprotected eneidyne in sufficiently pure form and nearly quantitative yield.

The above eneidyne was dissolved in THF (30 mL) and PrNH₂ (0.20 mL, 2.40 mmol) and the mixture degassed by N₂ bubbling for 30 min. To this were added (*Z*)-1,2-dichloroethene (47 mg, 0.48 mmol), Pd(PPh₃)₄ (33 mg, 0.03 mmol), and CuI (91 mg, 0.48 mmol). After being stirred overnight, the reaction mixture was filtered through a thin pad of silica, eluting with Et₂O, and then concentrated. Purification by column chromatography on silica (0.1% Et₃N in hexanes) provided **10** (134 mg, 61%) as an orange oil: ¹H NMR (CD₂Cl₂) δ 6.07 (d, *J* = 10.7, 2H), 6.05 (s, 2H), 5.90 (d, *J* = 10.7, 2H), 1.70 (septet, *J* = 7.2, 2H), 0.94 (s, 12H), 0.93 (d, *J* = 7.2, 12H), 0.20 (s, 12H); ¹³C NMR (CD₂Cl₂) δ 120.97, 120.57, 120.01, 104.68, 103.43, 95.72, 94.89, 35.13, 23.93, 20.99, 19.02, -2.34; IR (neat) ν 3042, 3026, 1673, 1584 cm⁻¹; UV–vis (CH₂Cl₂) λ_{\max} (ϵ) 244 (10650), 285 (11750), 296 (13100), 382 (13200), 354 (19350) nm; MS (ES⁺) *m/z* (rel intens) 478.3 (100, M⁺ + H₂O).

3,4,7,8,9,10,13,14-Octadehydro[14]annulene (1). α,ω -Polyne **10** (40 mg, 0.09 mmol) was dissolved in THF (25 mL),

and three drops of MeOH was added. To this solution was added Bu₄NF (1.0 M in THF, 0.22 mL) in one portion, and the reaction was stirred for 3 h. Upon completion, the mixture was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the deprotected tetrayne in sufficiently pure form and nearly quantitative yield.

The above tetrayne was dissolved in MeCN (200 mL), and Cu(OAc)₂ (359 mg, 1.80 mmol) was added. The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et₂O, washed with H₂O, dried (MgSO₄), filtered, and concentrated. The annulene polymerized rapidly upon concentration to give a thick purple oil (dilute solutions of **1** can be stored at -20 °C): ¹H NMR (CD₂Cl₂) δ 7.92 (d, *J* = 10.2, 2H), 7.77 (br s, 2H), 7.39 (d, *J* = 10.2, 2H); ¹³C NMR (CD₂Cl₂) δ 125.37, 117.88, 117.37, 100.80, 100.34, 92.21, 86.88; IR (CH₂Cl₂) ν 3155, 3052, 2253, 1468, 1380 cm⁻¹; UV-vis (CH₂Cl₂, qualitative) λ_{max} 228, 296, 339, 347 nm; MS (ES⁺) *m/z* (rel intens) 175.1 (14, M⁺ + H), 126.9 (40, C₁₀H₆).

α,ω-Polyyne 12. 1,2-Bis(trimethylsilylethynyl)benzene¹⁷ (125 mg, 0.46 mmol) was dissolved in MeOH/THF (50 mL, 1:1 v/v), and K₂CO₃ (319 mg, 2.31 mmol) was added. The mixture was stirred for 2–3 h and monitored by TLC. Upon completion, the reaction was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the free diethynylbenzene in sufficiently pure form and nearly quantitative yield.

The resulting 1,2-diethynylbenzene was dissolved in THF (25 mL) and PrNH₂ (0.19 mL, 2.31 mmol) and the mixture degassed by N₂ bubbling for 30 min. To this were added (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane¹⁸ (154 mg, 0.97 mmol), Pd(PPh₃)₄ (43 mg, 0.04 mmol), and CuI (88 mg, 0.46 mmol). After being stirred overnight, the reaction mixture was filtered through a thin pad of silica, eluting with Et₂O, and then concentrated. Purification on silica by radial chromatography (0.1% Et₃N in hexanes) provided **12** (161 mg, 94%) as a yellow oil: ¹H NMR (CD₂Cl₂) δ 7.52–7.49 (AA'm, 2H), 7.34–7.31 (BB'm, 2H), 6.17 (d, *J* = 10.9, 2H), 5.94 (d, *J* = 10.9, 2H), 0.22 (s, 18H); ¹³C NMR (CD₂Cl₂) δ 132.98, 129.07, 125.86, 120.96, 120.39, 104.25, 102.59, 96.31, 91.54, 0.11; IR (neat) ν 3057, 3028, 2191, 2143, 1478, 1443 cm⁻¹; UV-vis (CH₂Cl₂) λ_{max} (ε) 267 (9800), 300 (16800), 337 (14400) nm; MS (ES⁺) *m/z* (rel intens) 388.2 (55, M⁺ + H₂O), 371.2 (25, M⁺ + H), 279.1 (100).

Dehydrobenzo[14]annulene 2. α,ω-Polyyne **12** (47 mg, 0.13 mmol) was dissolved in MeOH/THF (25 mL, 1:1 v/v), and saturated K₂CO₃ solution (2 mL) was added. The mixture was stirred for 2–3 h and monitored by TLC. Upon completion, the reaction was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the free tetrayne in sufficiently pure form and nearly quantitative yield.

The resulting tetrayne was dissolved in MeCN (40 mL), and Cu(OAc)₂ (346 mg, 1.90 mmol) was added. The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et₂O, washed with H₂O, dried (MgSO₄), filtered, and concentrated. The annulene quickly polymerized in neat form to furnish an insoluble black film (14.8 mg, 51%) (dilute solutions of **2** can be stored for several weeks at rt): ¹H NMR (CD₂Cl₂) δ 8.29–8.26 (AA'm, 2H), 7.74–7.70 (BB'm, 2H), 7.41 (d, *J* = 10.0, 2H), 6.73 (d, *J* = 10.0, 2H); ¹³C NMR (CD₂Cl₂) δ 136.28, 128.84, 126.72, 122.91, 116.91, 100.01, 93.82, 90.38, 84.84; IR (CH₂Cl₂) ν 3189, 3053, 2117, 1470 cm⁻¹; UV-vis (CH₂Cl₂, qualitative) λ_{max} 234, 299, 308, 387 nm; MS (ES⁺) *m/z* (rel intens) 242.3 (100, M⁺ + H₂O).

Enetriyne 14. Phenylidyne **13**^{4b} (90 mg, 0.32 mmol) was dissolved in THF (50 mL) and PrNH₂ (0.05 mL, 0.64 mmol) and the mixture degassed by N₂ bubbling for 60 min. To this were added (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane (101 mg, 0.64 mmol), Pd(PPh₃)₄ (18 mg, 0.02 mmol), and CuI (61 mg, 0.32 mmol). After being stirred overnight, the reaction mixture was concentrated and redissolved in hexanes. The slurry was filtered through silica (hexanes) to give enetriyne

14 (112 mg, 87%) as a light orange oil: ¹H NMR (CD₂Cl₂) δ 7.51–7.48 (m, 2H), 7.32–7.29 (m, 2H), 6.06 (d, *J* = 10.9, 1H), 5.91 (d, *J* = 10.9, 1H), 1.15 (s, 21H), 0.23 (s, 9H); ¹³C NMR (CD₂Cl₂) δ 132.97, 132.86, 128.97, 128.68, 126.41, 126.25, 121.12, 120.32, 105.58, 104.16, 102.69, 96.75, 96.03, 91.22, 19.02, 12.37, 0.13; IR (neat) ν 3061, 3027, 2157, 2144 cm⁻¹; UV-vis (CH₂Cl₂) λ_{max} (ε) 255 (16150), 260 (16050), 269 (21850), 318 (22100), 341 (20250) nm; MS (APCI) *m/z* (rel intens) 405.2 (8, M⁺), 145.1 (100).

α,ω-Polyyne 15. Enetriyne **14** (112 mg, 0.28 mmol) was dissolved in MeOH/THF (40 mL, 1:1 v/v), and NaH (33 mg, 1.38 mmol) was added. After being stirred for 30 min, the solution was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the free enetriyne in sufficiently pure form and nearly quantitative yield.

The deprotected material was dissolved in THF (40 mL) and PrNH₂ (0.05 mL, 0.56 mmol) and the mixture degassed by N₂ bubbling for 40 min. To this were added (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane (89 mg, 0.56 mmol), Pd(PPh₃)₄ (16 mg, 0.01 mmol), and CuI (53 mg, 0.28 mmol). After being stirred overnight, the reaction mixture was filtered through a thin pad of silica, eluting with Et₂O, and then concentrated. Purification by column chromatography (0.1% Et₃N, 10% CH₂Cl₂ in hexanes) provided **15** (106 mg, 83%) as a light orange oil: ¹H NMR (CD₂Cl₂) δ 7.51–7.48 (m, 2H), 7.31–7.28 (m, 2H), 6.11 (d, *J* = 11.0, 1H), 6.10 (s, 2H), 5.91 (d, *J* = 11.0, 1H), 1.15 (s, 21H), 0.15 (s, 9H); ¹³C NMR (CD₂Cl₂) δ 133.26, 132.90, 128.96, 128.69, 126.38, 126.21, 120.77, 120.67, 120.57, 119.79, 105.56, 104.74, 102.53, 97.26, 96.07, 95.33, 95.25, 91.30, 19.01, 11.88, -0.02; IR (neat) ν 3060, 3043, 3028, 2157, 2141 cm⁻¹; UV-vis (CH₂Cl₂) λ_{max} (ε) 252 (22600), 262 (22050), 291 (12850), 349 (21900) nm; MS (ES⁺) *m/z* (rel intens) 455.2 (100, M⁺).

Dehydrobenzo[14]annulene 3. α,ω-Polyyne **15** (34 mg, 0.07 mmol) was dissolved in THF (20 mL), and two drops of MeOH was added. To this solution was added Bu₄NF (1.0 M in THF, 0.19 mL) in one portion, and the reaction was monitored by TLC. Upon completion, the mixture was diluted with Et₂O, washed successively with saturated NH₄Cl solution, brine, and H₂O, dried (MgSO₄), and filtered. Concentration of the product gave the deprotected tetrayne in sufficiently pure form and nearly quantitative yield.

The resultant tetrayne was dissolved in MeCN (150 mL), and Cu(OAc)₂·H₂O (279 mg, 1.40 mmol) was added. The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et₂O, washed with H₂O, dried (MgSO₄), filtered, and concentrated. The annulene polymerized upon concentration to give an insoluble brown solid (dilute solutions of **3** can be stored for several weeks at -20 °C): ¹H NMR (CD₂Cl₂) δ 8.23 (dd, *J* = 7.1, 2.0, 1H), 8.01 (dd, *J* = 6.9, 2.1, 1H), 7.79–7.69 (m, 2H), 7.24 (dd, *J* = 10.2, 3.3, 1H), 7.16 (d, *J* = 11.7, 1H), 7.03 (dd, *J* = 11.7, 3.3, 1H), 6.73 (d, *J* = 10.2, 1H); ¹³C NMR (CD₂Cl₂) δ 133.81, 130.14, 129.31, 129.00, 128.63, 126.04, 122.98, 118.65, 116.91, 99.37, 98.21, 98.14, 93.08, 88.98, 87.53, 85.52, 81.00; IR (CH₂Cl₂) ν 3054, 2306, 2253, 1469, 1422 cm⁻¹; UV-vis (CH₂Cl₂, qualitative) λ_{max} 229, 294, 302, 312, 359, 385 nm; MS (ES⁺) *m/z* (rel intens) 242.3 (100, M⁺ + H₂O).

α,ω-Polyyne 17. Iodoarene **16**^{4b} (200 mg, 0.41 mmol) was dissolved in MeOH (55 mL) and Et₃N (55 mL), and K₂CO₃ (57 mg, 0.41 mmol) was added. The reaction mixture was degassed by N₂ bubbling for 90 min. To this solution were added enediene **9** (131 mg, 0.45 mmol), PdCl₂(PPh₃)₂ (9 mg, 0.01 mmol), and CuI (23 mg, 0.12 mmol), and the reaction was stirred at 50 °C for 48 h. After cooling, the mixture was concentrated, redissolved in Et₂O, filtered through a thin pad of silica, and concentrated again. Purification by column chromatography on silica (5% CH₂Cl₂ in hexanes) provided **17** (193 mg, 75%) as a dark orange oil: ¹H NMR (CD₂Cl₂) δ 7.57–7.52 (m, 4H), 7.35–7.30 (m, 4H), 6.15 (d, *J* = 10.8, 1H), 5.95 (d, *J* = 10.8, 1H), 1.68 (sept, *J* = 7.0, 1H), 1.14 (s, 21H), 0.90 (s, 6H), 0.87 (d, *J* = 7.0, 6H), 0.19 (s, 6H); ¹³C NMR (CD₂Cl₂)

δ 133.29, 132.63, 132.46, 128.85, 128.75, 128.69, 126.28, 126.16, 120.65, 120.47, 105.84, 104.17, 103.53, 96.32, 95.81, 93.12, 92.30, 91.51, 35.13, 21.07, 19.09, 19.02, 11.96, -2.13; IR (neat) ν 3067, 3020, 2154, 2144, 1489, 1463, 1446 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (ϵ) 238 (38200), 263 (32300), 297 (26000), 321 (22250), 327 (22250) nm; MS (ES^+) m/z (rel intens) 525.1 (7, $\text{M}^+ + \text{H}$), 205.2 (100).

Dehydrobenzo[14]annulene 4. Tetrayne **17** (87 mg, 0.15 mmol) was dissolved in THF (20 mL), and three drops of MeOH was added. To this solution was added Bu_4NF (1.0 M in THF, 0.38 mL) in one portion, and the reaction was stirred for 3 h. Upon completion, the mixture was diluted with Et_2O , washed successively with saturated NH_4Cl solution, brine, and H_2O , dried (MgSO_4), and filtered. Concentration of the product gave the deprotected tetrayne in sufficiently pure form and nearly quantitative yield.

The tetrayne was dissolved in MeCN (150 mL), and $\text{Cu}(\text{OAc})_2$ (545 mg, 3.00 mmol) was added. The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et_2O , washed with H_2O , dried (MgSO_4), filtered, and concentrated. The annulene polymerized upon concentration to give an insoluble brown solid (dilute solutions of **4** can be stored for several weeks at rt): ^1H NMR (CD_2Cl_2) δ 8.12 (dd, $J = 7.0, 1.8, 1\text{H}$), 8.09 (dd, $J = 6.6, 1.8, 1\text{H}$), 7.99 (dd, $J = 7.1, 1.8, 1\text{H}$), 7.76 (dd, $J = 7.5, 1.5, 1\text{H}$), 7.64–7.53 (m, 4H), 7.01 (d, $J = 10.3, 1\text{H}$), 6.37 (d, $J = 10.3, 1\text{H}$); ^{13}C NMR (CD_2Cl_2) δ 136.64, 136.27, 133.98, 129.80, 129.51, 129.40, 129.04, 128.73, 128.69, 127.00, 123.86, 122.84, 122.39, 117.42, 99.33, 98.62, 94.25, 93.88, 92.93, 87.37, 84.37, 80.34; IR (CH_2Cl_2) ν 3053, 2302, 2196, 1492 cm^{-1} ; UV-vis (CH_2Cl_2 , qualitative) λ_{max} 230, 255, 271, 295, 306, 313, 355, 383 nm; MS (ES^+) m/z (rel intens) 292 (7, $\text{M}^+ + \text{H}_2\text{O}$), 186.3 (100).

α,ω -Polyynes 21. 3,4-Diiodothiophene (69 mg, 0.21 mmol), K_2CO_3 (232 mg, 1.68 mmol), MeOH (4 mL), *i*-Pr₂NEt (0.22 mL, 1.26 mmol), and THF (10 mL) were added to a glass pressure tube. After the mixture was degassed by N_2 bubbling for 30 min, 1-(triisopropylsilyl)-6-(trimethylsilyl)-1,5-hexadiyn-3-ene²⁶ (384 mg, 1.26 mmol), Pd(PPh_3)₄ (24 mg, 0.02 mmol), and CuI (8 mg, 0.04 mmol) were added. The tube was sealed and the reaction stirred at 100 °C for 24 h. After cooling, the mixture was diluted with hexanes and washed successively with 10% HCl solution, brine, and H_2O . The organic layer was dried (MgSO_4), filtered through a thin pad of silica (hexanes), and concentrated. Purification of the crude oil by column chromatography on silica (0.1% Et₃N in hexanes) gave **21** (77 mg, 67%) as an orange oil: ^1H NMR (CDCl_3) δ 7.34 (s, 2H), 6.07 (d, $J = 10.9, 2\text{H}$), 5.91 (d, $J = 10.9, 2\text{H}$), 1.10 (s, 42H); ^{13}C NMR (CDCl_3) δ 128.63, 124.64, 120.19, 119.72, 103.95, 99.97, 90.54, 89.09, 18.65, 11.24; IR (neat) ν 3112, 3053, 2942, 2865, 2201, 2142, 1463, 1434 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (ϵ) 291 (21900), 311 (24150), 333 (22450) nm; MS (ES^+) m/z (rel intens) 562.3 (100, $\text{M}^+ + \text{H}_2\text{O}$), 545.3 (38, $\text{M}^+ + \text{H}$).

Dehydrothieno[14]annulene 7. α,ω -Polyynes **21** (65 mg, 0.12 mmol) was dissolved in THF (30 mL), and two drops of MeOH was added. To this was added Bu_4NF (1.0 M in THF, 0.19 mL) in one portion, and the reaction was stirred for 2.5 h. Upon completion, the mixture was diluted with Et_2O , washed successively with saturated NH_4Cl solution, brine, and H_2O , dried (MgSO_4), and filtered. Concentration of the product gave the deprotected tetrayne in sufficiently pure form and nearly quantitative yield.

The above tetrayne was dissolved in MeCN (120 mL), and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (479 mg, 2.40 mmol) was added. The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et_2O , washed with H_2O , dried (MgSO_4), filtered, and concentrated. The annulene polymerized upon concentration to give an insoluble brown solid (dilute solutions of **7** can be stored for 2–3 weeks at -20 °C): ^1H NMR (CDCl_3) δ 8.01 (s, 2H) 6.93 (d, $J = 10.2, 2\text{H}$), 6.32 (d, $J = 10.2, 2\text{H}$); ^{13}C NMR (CDCl_3) δ 131.61, 126.13, 122.59, 116.42, 93.44, 90.85, 88.43, 83.96; IR (CH_2Cl_2) ν 3007, 2257, 2244 cm^{-1} ; UV-

vis (CH_2Cl_2 , qualitative) λ_{max} 229, 295 sh, 304, 383 nm; MS (ES^+) m/z (rel intens) 269.0 (50, $\text{M} + \text{K}^+$), 231.1 (22, M^+), 150 (21, $\text{M} - \text{C}_4\text{H}_2\text{S}$).

α,ω -Polyynes 23. 2,3-Bis(trimethylsilylethynyl)thiophene²⁷ (184 mg, 0.67 mmol) was dissolved in MeOH/THF (50 mL, 1:1 v/v), and K_2CO_3 (460 mg, 3.33 mmol) was added. The deprotection was monitored by TLC. Upon completion, the reaction mixture was diluted with Et_2O , washed successively with saturated NH_4Cl solution, brine, and H_2O , dried (MgSO_4), and filtered. Concentration of the product gave the free diethynylthiophene in sufficiently pure form and nearly quantitative yield.

The deprotected diyne was dissolved in THF (50 mL) and PrNH₂ (0.27 mL, 3.33 mmol), and the mixture was degassed by N_2 bubbling for 60 min. To this were added (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane (528 mg, 3.33 mmol), Pd(PPh_3)₄ (77 mg, 0.07 mmol), and CuI (128 mg, 0.67 mmol). After being stirred overnight, the reaction mixture was filtered through a thin pad of silica (10% CH_2Cl_2 in hexanes) and concentrated. Purification by column chromatography on silica (0.1% Et₃N, 10% CH_2Cl_2 in hexanes) provided **23** (139 mg, 55%) as a light orange oil: ^1H NMR (CDCl_3) δ 7.22 (d, $J = 5.3, 1\text{H}$), 7.02 (d, $J = 5.3, 1\text{H}$), 6.12 (d, $J = 10.8, 1\text{H}$), 6.10 (d, $J = 10.8, 1\text{H}$), 5.90 (d, $J = 10.8, 1\text{H}$), 5.89 (d, $J = 10.8, 1\text{H}$), 0.24 (s, 9H), 0.23 (s, 9H); ^{13}C NMR (CDCl_3) δ 130.07, 127.05, 126.40, 120.48, 120.19, 119.66, 119.48, 104.27, 103.72, 102.09, 101.99, 95.46, 91.56, 90.97, 89.45, -0.11; IR (neat) ν 3109, 3043, 2958, 2198, 2144, 1404 cm^{-1} ; UV-vis (CH_2Cl_2) λ_{max} (ϵ) 256 (14700), 279 (13450), 308 (18000), 361 (18700) nm; MS (ES^+) m/z (rel intens) 377.1 (90, M^+), 263.1 (100).

Dehydrothieno[14]annulene 8. A mixture of tetrayne **23** (15 mg, 0.04 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (160 mg, 0.80 mmol), and K_2CO_3 (28 mg, 0.20 mmol) was dissolved in MeOH/MeCN (50 mL, 1:1 v/v). The blue-green slurry was stirred at reflux for 24 h. After cooling, the reaction mixture was diluted with Et_2O , washed with H_2O , dried (MgSO_4), filtered, and concentrated. The annulene polymerized upon concentration to give an insoluble brown solid (dilute solutions of **8** can be stored for 2–3 weeks at -20 °C): ^1H NMR (CDCl_3) δ 7.81 (d, $J = 5.4, 1\text{H}$), 7.69 (d, $J = 5.4, 1\text{H}$), 7.60 (d, $J = 9.9, 1\text{H}$), 7.58 (d, $J = 9.9, 1\text{H}$), 7.02 (d, $J = 10.2, 1\text{H}$), 6.97 (d, $J = 10.2, 1\text{H}$); ^{13}C NMR (CDCl_3) δ 131.97, 127.96, 124.92, 124.60, 124.22, 116.50, 115.81, 99.25, 95.62, 94.05, 93.41, 90.07, 89.90, 85.63, 85.11; IR (neat) ν 3055, 2987, 2305, 2253, 1422 cm^{-1} ; UV-vis (CH_2Cl_2 , qualitative) λ_{max} 302 sh, 318, 357 nm; MS (ES^+) m/z (rel intens) 269.0 (63, $\text{M} + \text{K}^+$), 187.0 (60), 105.1 (100).

Acknowledgment. We thank the Petroleum Research Fund (M.M.H.), administered by the American Chemical Society, the University of Idaho for a Seed Grant (R.V.W.), and The Camille and Henry Dreyfus Foundation (Teacher-Scholar Award 1998–2003 to M.M.H.) for financial support.

Supporting Information Available: Calculated and experimental bond lengths for **1–8** and **24** (Table S1), ^1H NMR experimental and calculated (using the GIAO-HF/6-31G**/B3LYP/6-31G* method) chemical shifts of **1–8** and **24** (Tables S2 and S3), ^{13}C NMR experimental and calculated (using the GIAO-B3LYP/6-31G**/B3LYP/6-31G* method and scaled using the method of Forsyth and Sebag³⁶) chemical shifts of **1–8** and **24** (Tables S4–S5), NICS values for compounds **1–8**, **24**, and **25** (Table S6), Cartesian coordinates of **2–8** and **25** (coordinates for **1** and **24** are part of the Supporting Information for the accompanying paper⁵) optimized using the B3LYP/6-31G* method, and ^{13}C NMR spectra for compounds **1–4**, **7–8**, **10**, **12**, **14–15**, **17**, **21**, and **23**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO020463I

(36) Forsyth, D. A.; Sebag, A. B. *J. Am. Chem. Soc.* **1997**, *119*, 9483–9494.